PHOTOCHEMISTRY OF NITROGEN-CONTAINING CARBONYL AND THIOCARBONYL COMPOUNDS

1986

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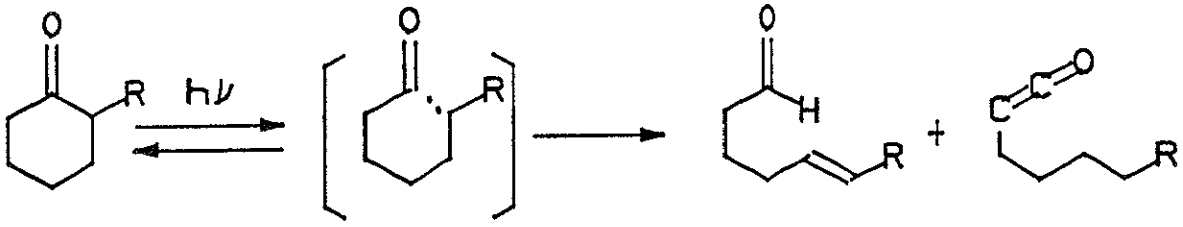
CONTENTS

I. INTRODUCTION

During the last three decades the photochemistry of organic molecules has grown into an important and pervasive branch of organic chemistry. Photochemical reactions differ from thermal reactions in several important respects. The initiating activation of a photoreaction is mainly provided by the absorption of light; activation of a thermal reaction is mainly provided by heat. The electronic distribution and nuclear configuration of a photochemically activated molecule generally differ substantially from those of a thermally activated molecule so that the excited molecule is really an electronic isomer of the corresponding ground state molecule. The thermodynamically favorable products accessible to a photoexcited molecule are far greater than those accessible to a ground state molecule, since the excited molecule possesses an excess energy content as a result of photon absorption. The fact that light absorption, rather than heat, activates a photoreaction allows for selectivity of activation (since only light-absorbing molecules are excited) and also allows for the ability to initiate reactions even at very low temperatures in all three phases. In fact, certain photoreactions are known to occur even at temperature near 0 K. A number of photochemical reactions provide the synthetic method of high strained molecules.

Most commonly photochemical processes of carbonyl compounds are classified to cleavage reactions, hydrogen abstractions, and

cycloadditions. Ketones (and aldehydes) undergo facile photolysis to acyl-alkyl radical pair.[1] Cycloalkanones necessarily lead to acyl-alkyl diradicals, as exemplified by cyclohexanone (Scheme 1).



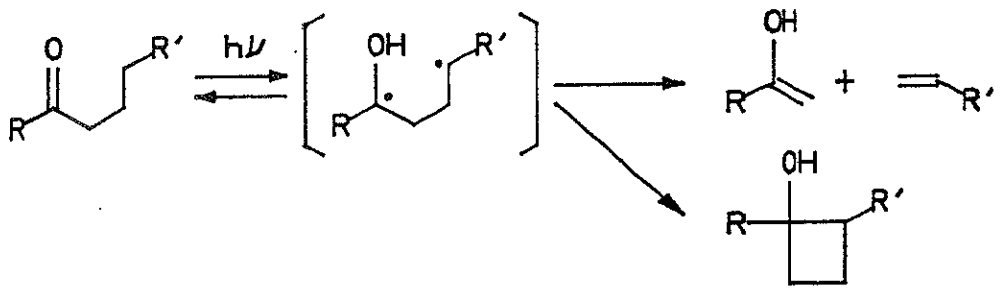
Scheme 1

The actual overall rearrangement results from disproportionation of the biradical to give unsaturated aldehyde and ketene. The competition between these two disproportionation modes and reclosure (which can result in epimerization of the α-carbon) varies markedly with structure.

Photoexcited ketones and aldehydes undergo characteristic internal hydrogen transfers to yield hydroxy biradicals. These biradicals cyclize to cycloalkanols and revert to starting materials. They can also undergo typical monoradical rearrangements before doing either. Acid derivatives also undergo excited state hydrogen transfer, but, perhaps because of high energies involved, cyclizations are rare.

The most common mode of internal hydrogen transfer is 1,5 and is equivalent to a γ-hydrogen abstraction by the carbonyl oxygen. The resulting 1,4-biradical can cleave to olefin and

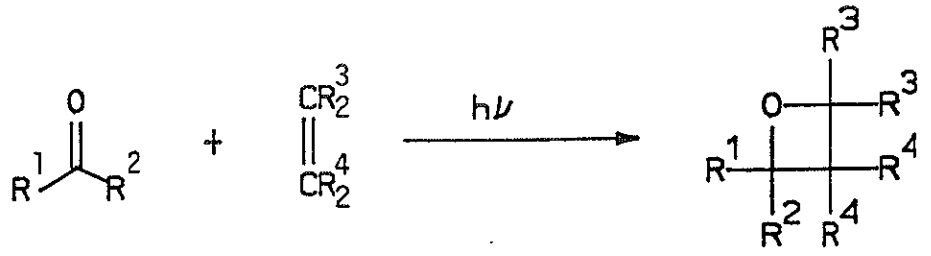
enol, the famous Norrish Type II reaction,[2] discovered 30 years before the concomitant cyclization rearrangement[3] (Scheme 2).



Scheme 2

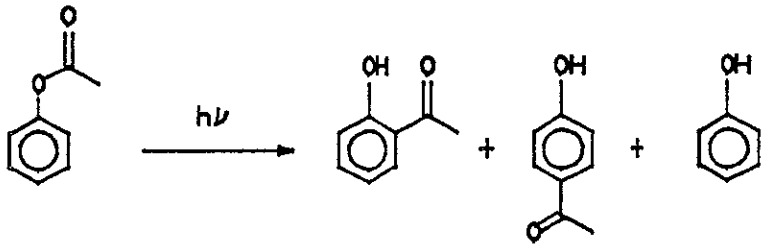
The cyclization of the biradical provides one of the best route to cyclobutanols. Hydrogen abstraction from positions other than a γ-carbon are less common, but examples of β, δ, ε and even more remote abstractions are known.

Most cycloaddition reactions are characterized by the formation of two new sigma bonds. [2+2] Photocycloaddition of carbonyl compounds to ethylenes which yield oxetanes are reactions which are well-known.[4] With mechanistic and synthetic studies continuing unabated over the last decade, the photoaddition of carbonyl compounds has taken an important place among the best known and most reliable organic photochemical transformations. A variety of alternative classical synthetic procedures for oxetane ring closure are known,[5] including dehydration of 1,3-diols or dehydrohalogenation of halohydrins. Although new techniques of this sort involving internal displacement continue to appear,[6),7] the Paterno-Büchi photocycloaddition remains the method of choice in oxetane synthesis (Scheme 3).



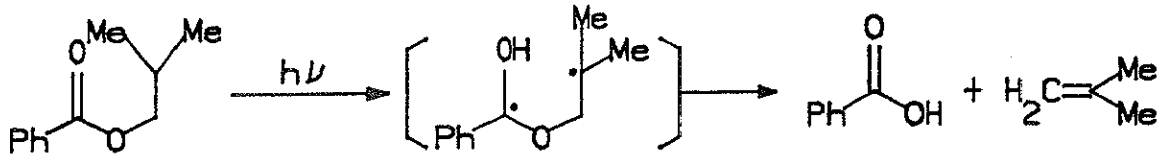
Scheme 3

The photochemistry of acid derivatives is of interest of its own right.[8] Esters and lactones can undergo α-cleavage of the (O=)C-O bond or the C-C(=O) bond on irradiation, or alternatively β-cleavage of the O-C bond (which often leads to decarbonylation). The balance between α- and β-fission depends on a number of factors related to the relative bond strengths, and stabilization of a particular radical can have a major influence. The most characteristic photoreaction of phenyl esters is the photo-Fries rearrangement, in which o- and p-acylphenols are formed together with some of parent phenol[9),10] (Scheme 4).



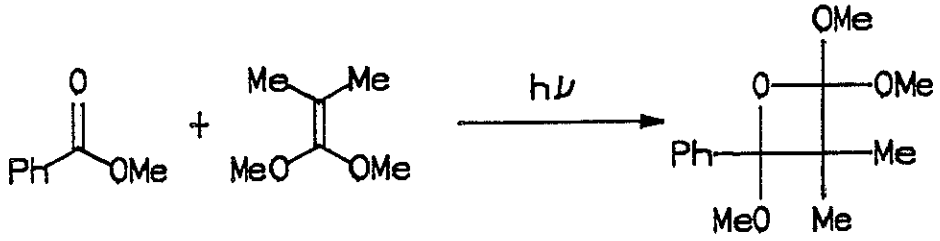
Scheme 4

Most acid derivatives do not photocyclize. The photoelimination reactions of esters have been more widely investigated. Benzoate esters and other similar aromatic esters undergo a Norrish Type II photoelimination to give the aromatic acid and an alkene[11)-13] (Scheme 5).



Scheme 5

Many of the oxetane formation reactions from esters are also reported[14),15)] (Scheme 6).

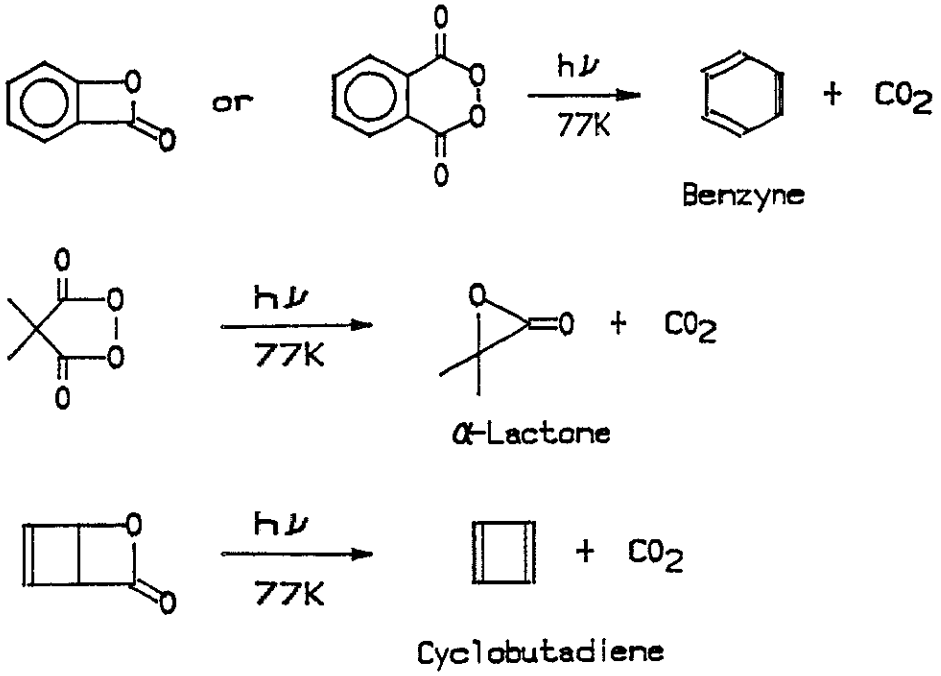


Scheme 6

In addition to the typical photochemical process of carbonyl compounds such as cleavage reactions, hydrogen abstractions, and cycloadditions, photofragmentation reactions provides the syntheses of highly strained molecules. A number of photoreactions are initiated by the cleavage of a sigma bond and result in net rearrangement, fragmentation, or elimination of a small molecule. A common feature of these reactions is cleavage of a relating weak σ-bond followed by secondary thermal reactions such as loss of molecules (CO, CO_2, N_2) to generate a highly energetic diradical, zwitterion, or fully bonded, but, strained molecules. Often these species may be generated and matrix isolated at very low

temperature.

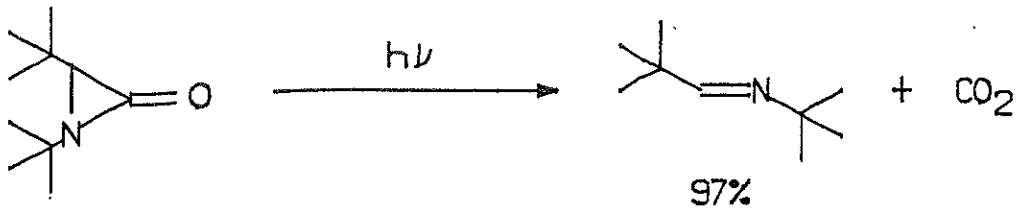
For example, benzyne,[16] α-lactones,[17] and cyclobutadiene[18] have been generated and matrix isolated by irradiation of cyclic esters at 77 K. The loss of the small, stable molecule CO_2 provides a driving force for these reactions (Scheme 7).



Scheme 7

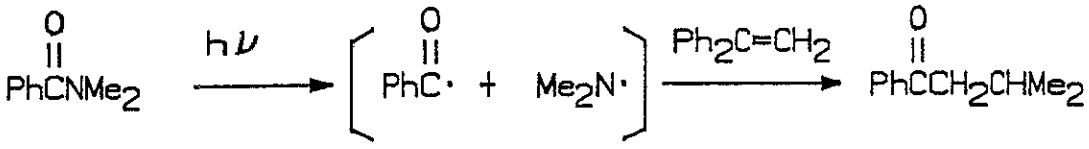
As described above, the photochemistry of ketones and esters have been extensively studied. However, those of nitrogen-containing carbonyl compounds, amides or imides, are little known except for cyclic imides.

Amides generally inert toward photolysis, though a few inefficient reactions have been reported. Saturated acyclic or cyclic amides or imides give radical-derived products. Decarbonylation occurs for α-lactams[19)-21] (Scheme 8).



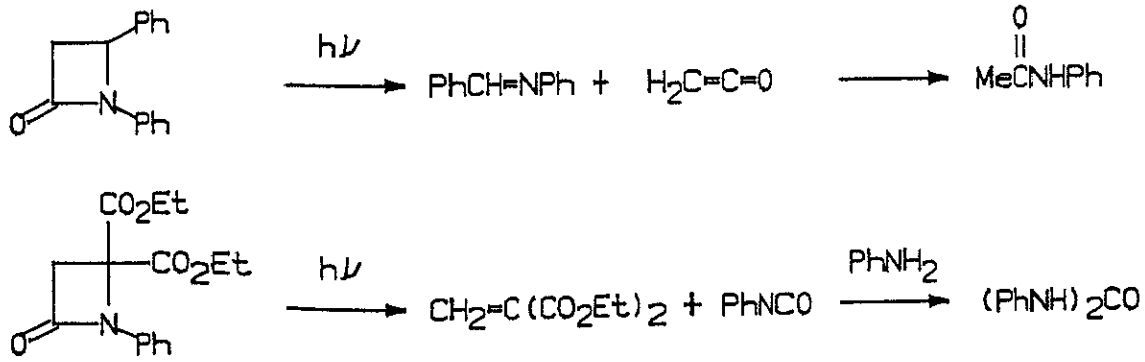
Scheme 8

(O=)C-N cleavage takes place when N,N-dimethylbenzamide is irradiated in the presence of 1,1-diphenylethylene,[22] and the isolated adduct is derived from the benzoyl radical (Scheme 9).



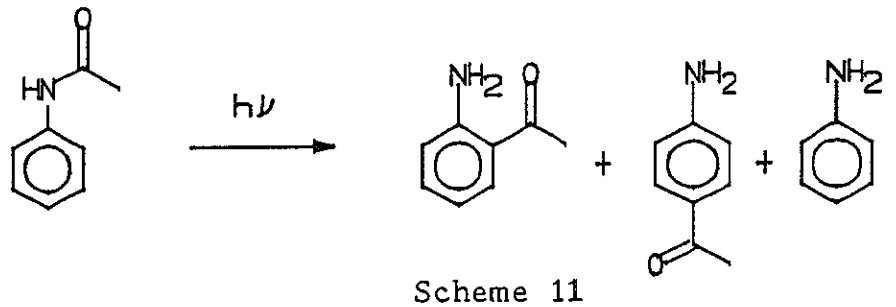
Scheme 9

β-Lactams provide an example of the balance between the two modes of α-cleavage in amides,[23] since some β-lactams give imine and ketene by photocleavage and some give alkene and isocyanate (Scheme 10). The reaction seems to proceed by way of a singlet excited state, although thermal cleavage can also give rise to alkene and isocyanate.



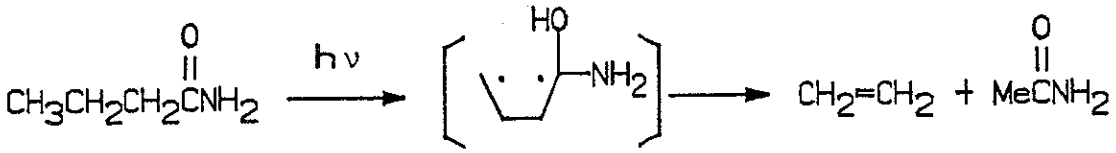
Scheme 10

N-Acylanilines undergo a photochemical rearrangement which parallels the photo-Fries rearrangement of phenyl esters, and typically acetanilide gives o- and p-acetylaniline and aniline itself. The reaction is thought to occur, like the photo-Fries reaction, by a cage-radical-pair mechanism[24] (Scheme 11).



Scheme 11

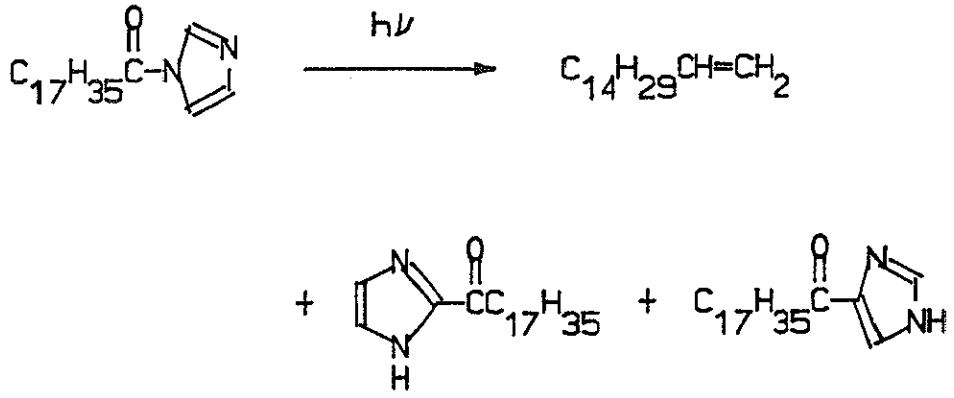
Simple aliphatic amides are either not photochemically active or else reaction involves α-cleavage of the (O=)C-N bond. There is very little products formation which might be attributed to a Norrish Type II photoelimination process. Although Type II photoelimination of butylamide have been reported,[25),26)] the efficiency of the photoreaction is very low (Scheme 12).



Scheme 12

However, N-stearoylimidazoles and similar amides do undergo a Type II photoelimination with the hydrogen abstracted from the acid chain.[27)] The other major products of this reaction arise

from initial α-cleavage of the amide bond followed by recombination of the radicals (Scheme 13).



Scheme 13

In all cases, efficiency of the photoreaction of amides is very low.

Recently, there has been a great deal of interest in the photochemistry of compounds possessing the imide moiety. The imides have shown great photochemical reactivity and versatility, undergoing most of the known reactions of other carbonyl systems and several unprecedented reactions.[28)]

The photochemistry of the imide moiety -C(=O)-N-C(=O)- is best compared to that of the related amides and ketones. Investigations on the photochemistry of simple aliphatic amides led to the surprising conclusion that the major process involved was the α-cleavage process via either C(=O)-N or C-C(=O) cleavage.[29)] The Type II cleavage process in amides is at best a minor process although it is the dominant one in the corresponding straight chain ketones[30)] and esters.[31)] These reactivity differences

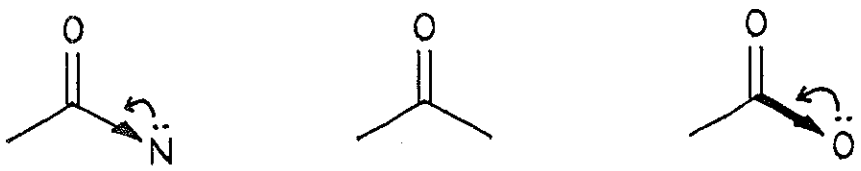


Figure 1

were best rationalized in view of the well known relationship[30] that Type II process occurs most efficiently when the reactive carbonyl n,π^* state is electrophilic. The ether oxygen in esters has two effects; it withdraws electron density through the σ-bond framework making the carbonyl oxygen electron deficient and it is a π electron donor which would tend to make the carbonyl oxygen electron rich. Since σ withdrawal is more efficient than donation for oxygen, the net result is an electrophilic n,π^* state and reactivity in the Type II process. The situation with amides is exactly the opposite, π donation from nitrogen is more efficient than σ withdrawal and the amides are predicted to have nucleophilic $n\pi^*$ states and to be nonreactive in Type II processes. These conclusions are confirmed by molecular orbital calculations.[32] Simple resonance theory suggests that the addition of a second carbonyl group on nitrogen should distribute the nitrogen pair making the imide carbonyls less nucleophilic and more reactive in Type II processes as is observed for aliphatic and aromatic imides.

The photochemistry of a series of aliphatic imides has been

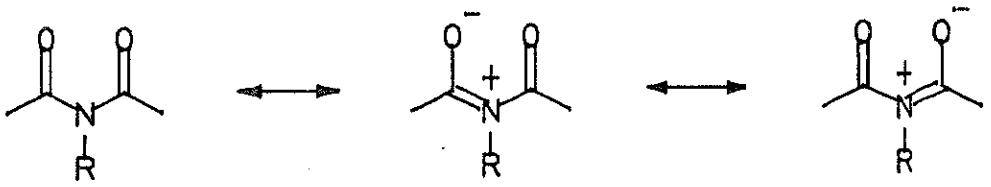
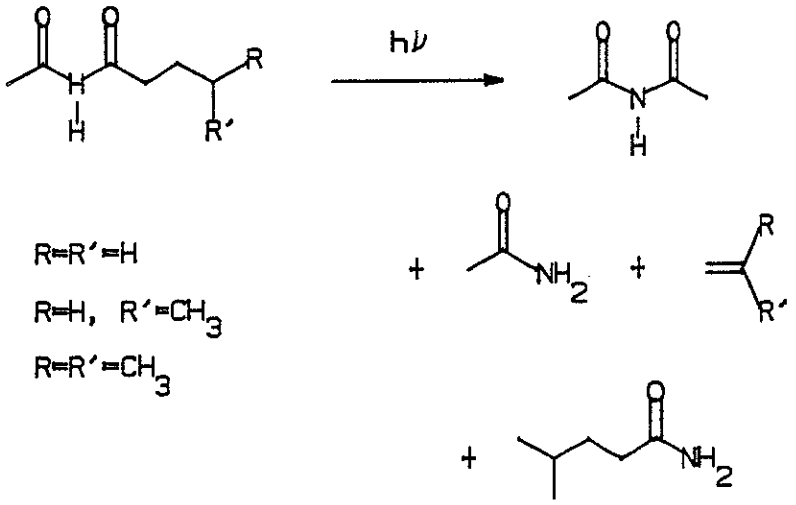


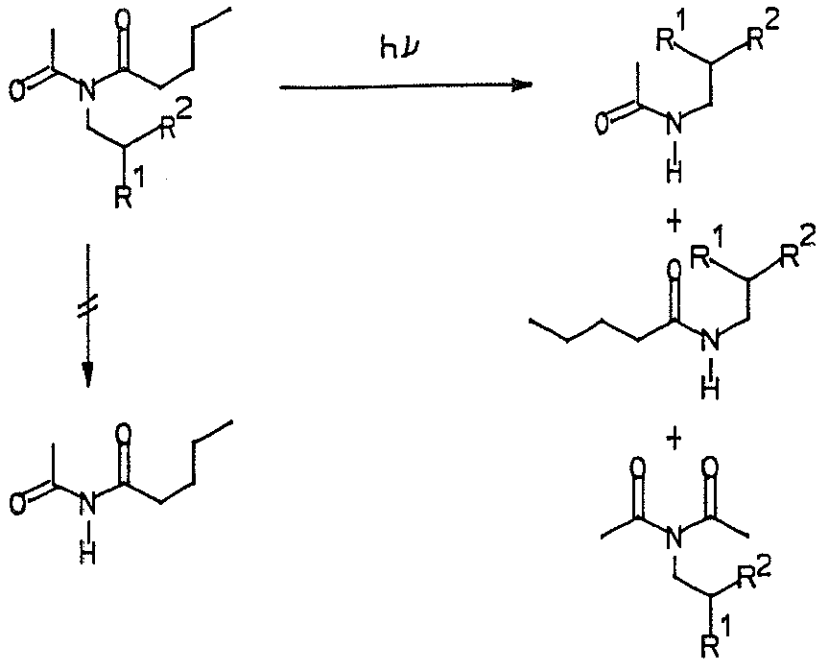
Figure 2

studied in dioxane and alcohol solvents and in all cases the amides (the presumed α-cleavage products) and diacetamide (from the Type II cleavage) were observed[33] (Scheme 14).



Scheme 14

The corresponding N-alkyl imides show a similar reaction profile except that α-cleavage products dominate the Type II process as expected since the stability of the incident radical has increased due to the alkylsubstitution. No Type II process is observed from the N-alkyl substitutent even when the abstractable hydrogen is tertiary. This is not the results of N-alkylation somehow deactivating the carbonyl group to Type II

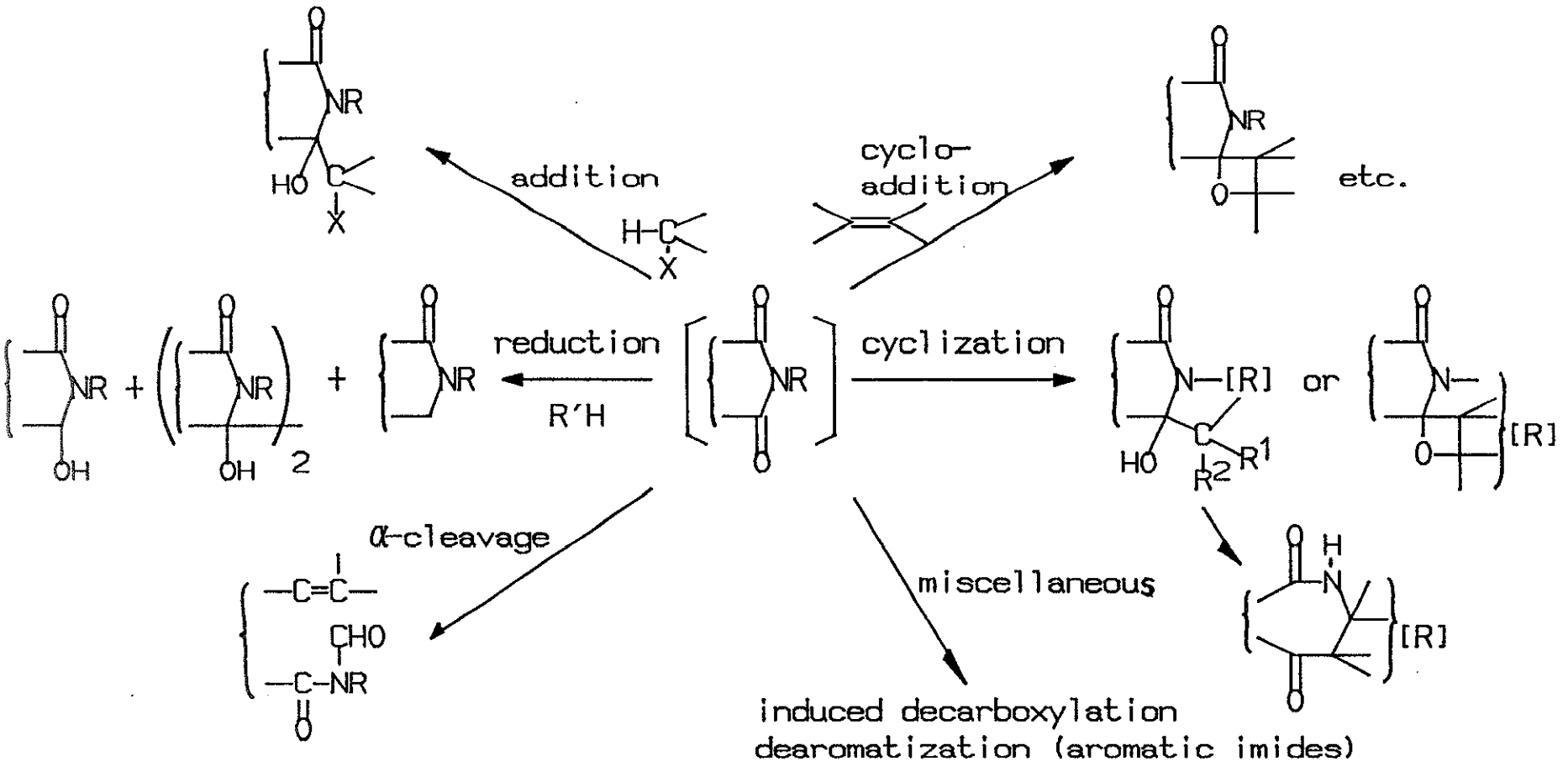


Scheme 15

abstraction, since this process still occurs on the C alkyl chain when the abstractable hydrogen is 2° or 3°. Apparently, the efficiency of the competing Type II and α-cleavage process dominates the Type II process on the N-alkyl group (Scheme 15).

It is interesting to compare the photochemistry of the cyclic and open chain aliphatic imides. The cyclic imides undergo virtualy all of the major photochemical reactions known for the simple carbonyl system, and several unique reactions as well as shown in Scheme 16.[34] The reactions characteristic of ketones include reduction, addition, cycloaddition, and Norrish Type I and Type II reactions.

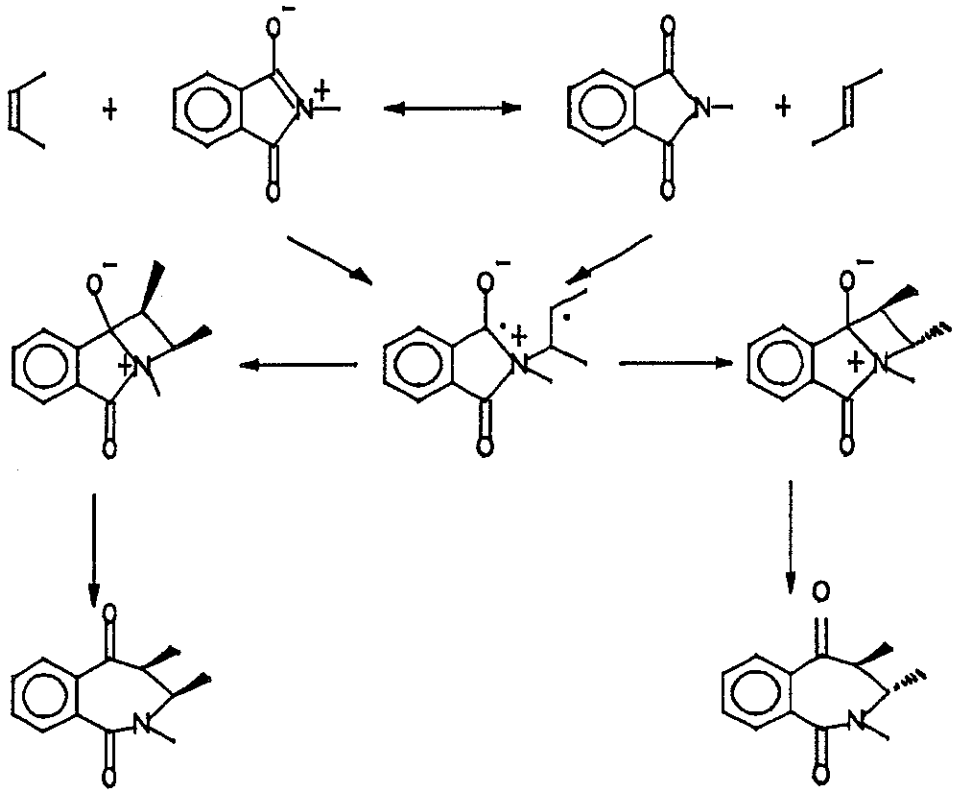
In addition to some special reactions induced by the imide group, such as dearomatization of the benzene moiety of phthal-


addition
cyclo-
addition
etc.
reduction
R'H
cyclization
or
[R]
α-cleavage
miscellaneous
induced decarboxylation
dearomatization (aromatic imides)

Scheme 16

imides, the presence of certain functional groups in their N-substituents of phthalimides leads to unique, extended Type II and other related cyclizations giving rise to a variety of new heterocycles.

Moreover, N-alkyl phthalimides undergo [2+2] cycloaddition to a C(O)-N bond with alkenes on irradiation[28),34)] (Scheme 17).



Scheme 17

As noted above, cyclic imides undergo various photochemical reactions, such as α-cleavage, hydrogen abstraction, and [2+2] cycloadditions. However, most simple amides do not undergo photochemical reactions except for α-cleavage reaction. The author investigated the photochemistry of some types of nitrogen-

containing carbonyl compounds which possess functional group (photochemically active) to amide moiety and discovered these photochemical reactions provide useful methods for the synthesis of aziridine-2,3-diones, azetidin-2-ones, azetidine-2,4-diones, and other nitrogen-containing heterocycles. The photochemical reactions described in this dissertations are below.

(1) Photochemical reactions of maleilimide ozonides: photochemical generation of aziridine-2,3-diones.

(2) Photochemical reactions of α-ketoamides.

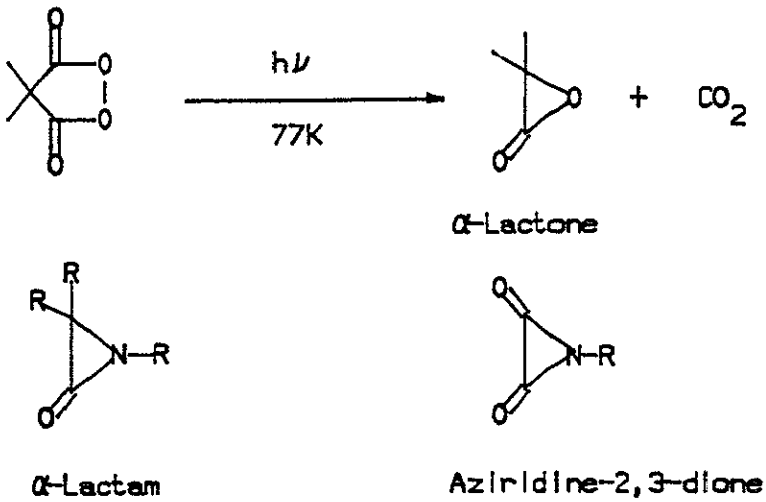
(3) Photochemical reactions of α-ketoimides.

(4) Photochemical reactions of thioimides.

II. RESULTS AND DISCUSSION

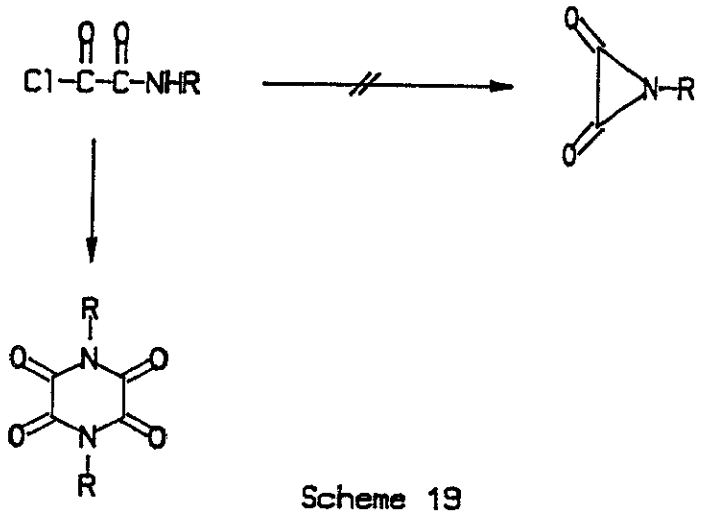
II-1. AZIRIDINE-2,3-DIONES

The study of strained molecules allows chemists to explore the limits of stability in organic chemistry, and permits calibration of theory and experiments in extreme cases.[35] Three-membered rings possessing carbonyl groups are usually unstable and quite reactive because of the large strain energies. α-Lactones have been generated at very low temperatures and observed spectroscopically,[17] and α-lactams are also unstable unless they possess bulky substituents.[36] As yet non substituted α-lactams and fused bicyclic α-lactams have not been synthesized. Introduction of one more carbonyl group to these three-membered rings should further increase the strain energies of the rings. Thus, three-membered rings bearing two carbonyl groups are hitherto unknown (Scheme 18).



Scheme 18

In view of these facts, aziridine-2,3-diones are experimentally as well as theoretically intriguing and challenging molecules. Treatment of oxanilic acid with thionyl chloride does not give N-phenylaziridine-2,3-dione but leads instead to a dimeric product, 2,3,5,6-tetraoxo-1,4-diphenylpiperazine[37] (Scheme 19).

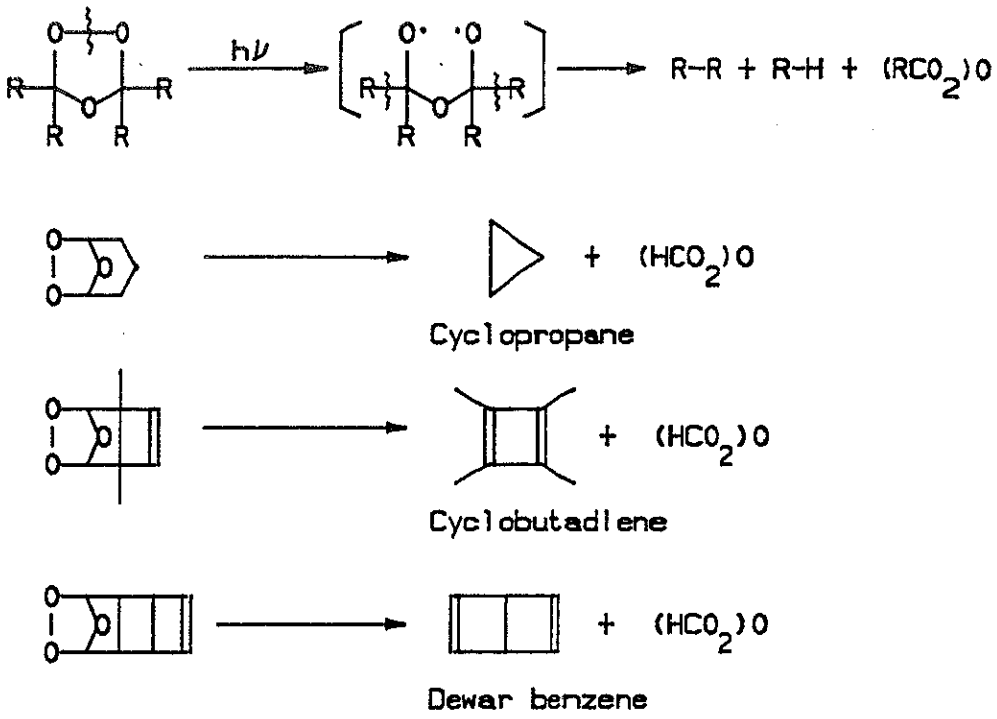


Scheme 19

The author investigated the synthesis of these unstable compounds in the low-temperature photolysis of ozonides of diphenylmaleylimides.

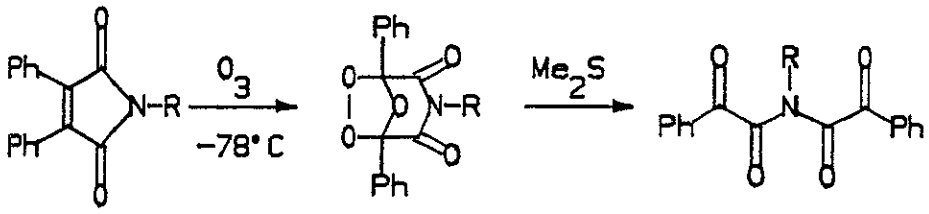
An ozonide usually undergoes homolysis of the oxygen-oxygen bond followed by a double β scission on irradiation to give an acid anhydride and a radical pair (or a biradical). Photolysis of ozonides has been utilized for the synthesis of three-membered ring such as cyclopropanes[38),39)] and for the generation of unstable compounds such as cyclobutadienes[40)-42)] and Dewar benzenes[43),44)] (Scheme 20). Therefore, photolysis of ozonides of maleylimides is quite promising method for the generation of aziridine-2,3-diones.

Ozonides of diphenylmaleylimides (1-5) were obtained as



Scheme 20

stable crystalline compounds by ozonolysis of the corresponding imides in acetone at -78°C. The structures of the ozonides were confirmed by elemental analyses, spectral data, and the fact that reduction of the ozonides with dimethyl sulfide gives the corresponding bisphenylglyoxalylimides (6-10) quantitatively (Scheme 21).

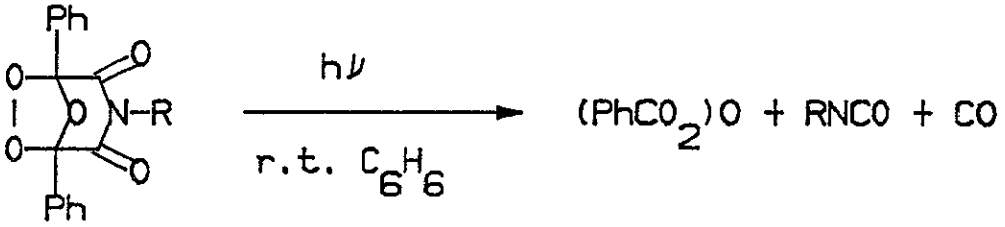


1	R=H	6	R=H
2	R=Me	7	R=Me
3	R=Pr^{i}	8	R=Pr^{i}
4	R=CH_2CH_2Ph	9	R=CH_2CH_2Ph
5	R=Ph	10	R=Ph

Scheme 21

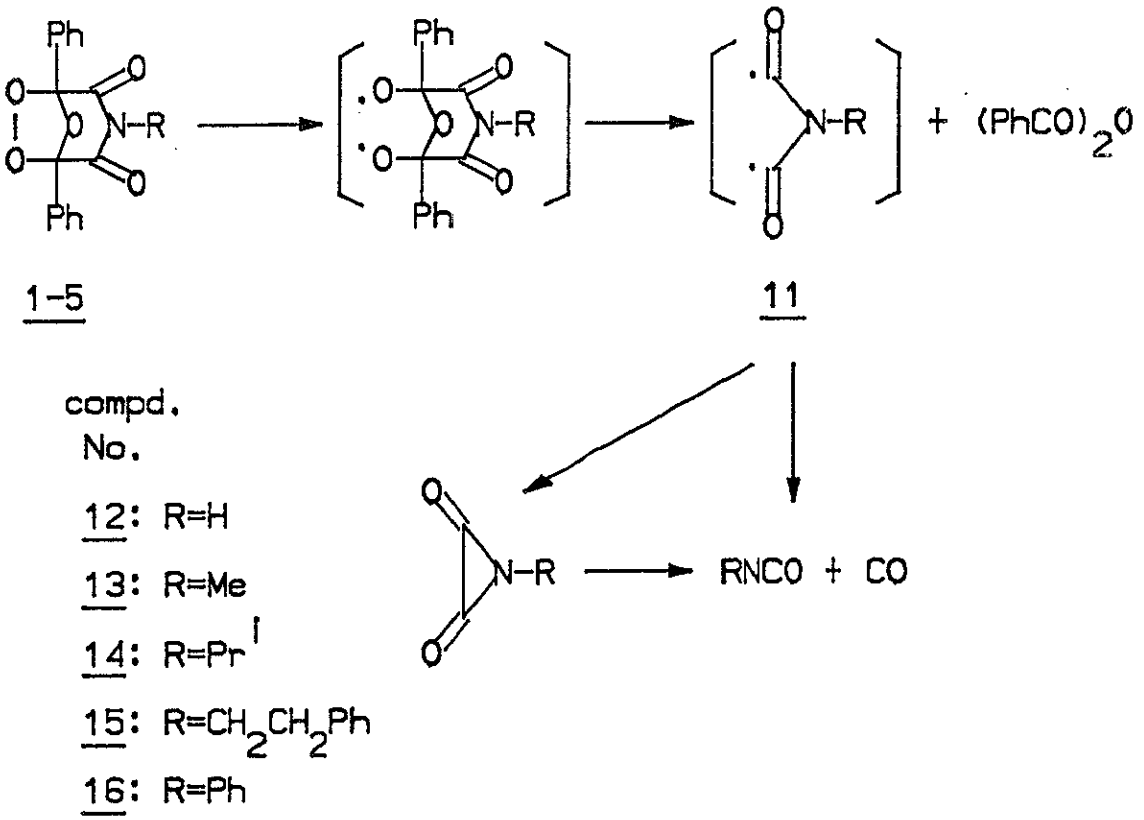
When 2 in benzene was irradiated with a high pressure mercury lamp at room temperature, benzoic anhydride and methyl isocyanate were obtained almost quantitatively. The formation of carbon monoxide was also confirmed by both hemoglobin and palladium chloride tests,[45] though the yield was not determined. Photolysis of other ozonides gave similar results (Table 1).

Table 1: Photolysis of Ozonides at Room Temperature



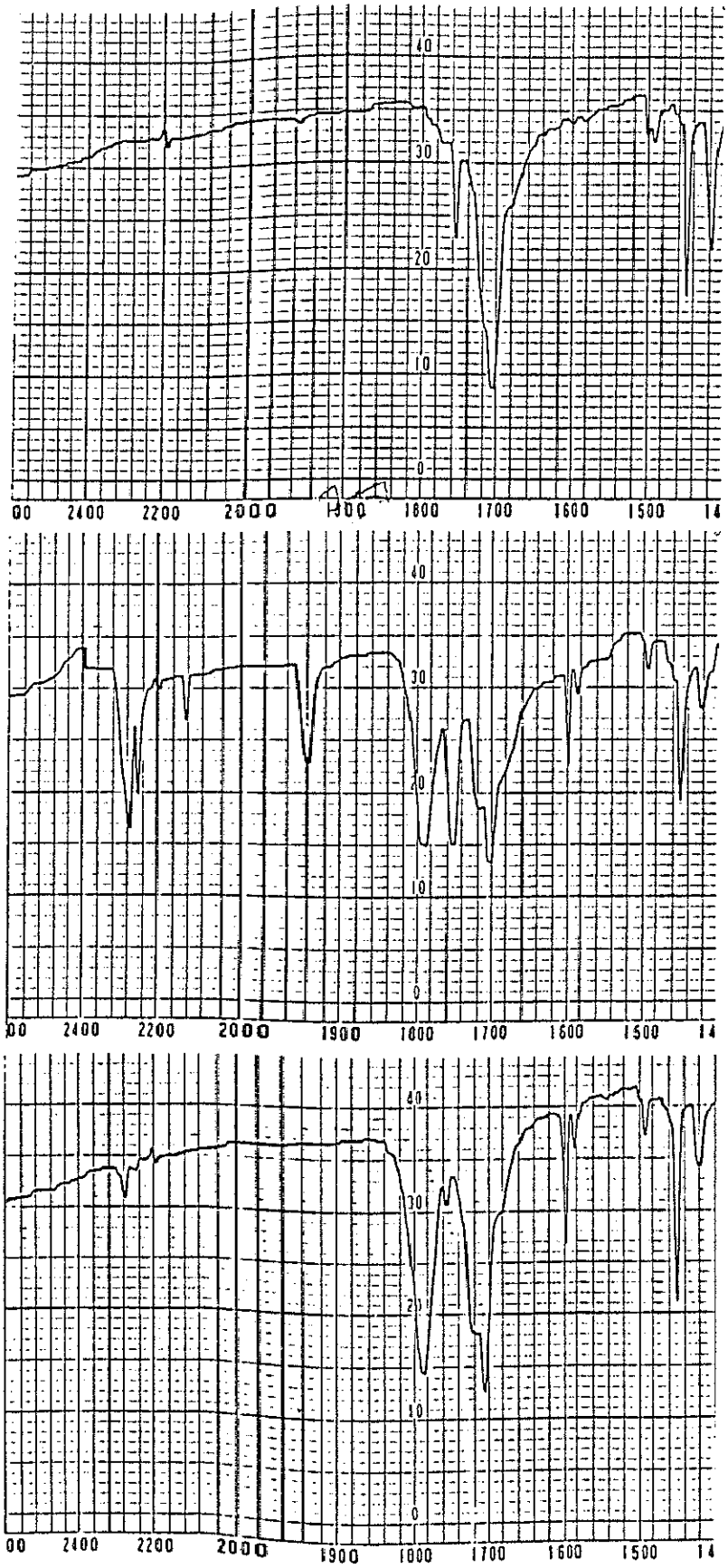
reactant No.	Yield (%)	
	$(PhCO_2)O$	RNCO
1	87	—
2	67	70
3	95	>99
4	98	96
5	>99	97

The fact that benzoic anhydride is formed efficiently in the photolysis clearly shows that these ozonide undergo the expected reaction to give 1,3-diradicals (11). The isocyanates and carbon monoxide formed in these reaction conditions are presumed to be produced by decomposition of aziridine-2,3-diones (12-16) and/or cleavage of the biradicals (11) (Scheme 22).



Scheme 22

Next, the low-temperature photolysis of 12-16 was carried out in order to examine the intermediacy of 12-16. The ozonide (2) in a KBr pellet was photolyzed at 77 K for 1 h, and the reaction was followed by IR spectroscopy. The spectrum showed two strong absorptions at 1940 and 1750 cm^{-1}, in addition to the absorptions of methyl isocyanate (2270 and 2245 cm^{-1}), carbon monoxide (2130 cm^{-1}), and benzoic anhydride (1785 and 1720 cm^{-1}). The spectrum did not change when the photolysate in KBr was allowed to stand for 1 h at 77 K after irradiation. However, shortly after liquid nitrogen had been evaporated, the two



2 (KBr)

hν
1hr
77 K

warm up

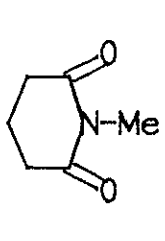
Figure 3

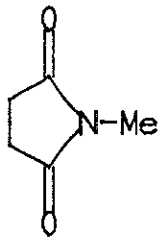
absorptions rapidly decreased, with increase of the absorptions of methyl isocyanate and carbon monoxide, while that of benzoic anhydride remained unchanged (Figure 3). This fact shows that the elusive species decomposes to these two compounds, and strongly indicates that it is N-methylaziridine-2,3-dione (13). Thermal decarbonylation of three-membered ring carbonyl compounds is not exceptional. Diaziridinones undergo decarbonylation spontaneously at room temperature.[46]

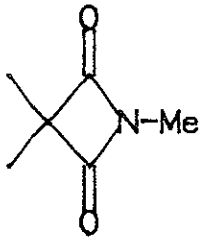
Imides show two carbonyl absorptions (symmetric and antisymmetric modes).[47] The positions of $\nu_{C=O}$ at 1940 and 1750 cm^{-1} are quite reasonable for the structure of 13 in comparison with those of other cyclic imides: a N-methylmalonimide derivative (1820 and 1710 cm^{-1} in KBr),[48] N-methylsuccinimide (1760 and 1690 cm^{-1} in KBr),[49] N-methylglutarimide (1718 and 1670 cm^{-1} in KBr).[49] The ring size effects in the carbonyl absorptions of these cyclic imides (3-6-membered rings) are quite analogous to those of other cyclic carbonyl compounds such as lactams and lactones.[17] The large splitting of the two carbonyl absorptions of 13 (190 cm^{-1}) is also reasonable for the structure, because the two carbonyls are directly bonded and should be completely coplanar[47] (Table 2).

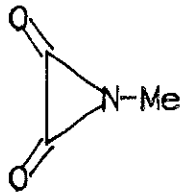
The low-temperature photolysis of other ozonides gave similar results (Table 3). In the case of 1, the absorption of aziridine-2,3-dione (12) was weak, and the lower carbonyl absorption was not clear. It is presumably hidden in the strong absorptions of benzoic anhydride. The isocyanates and carbon

Table 2: IR Spectra of Cyclic Imides









IR(KBr)	1760(s)	1690(s)	1710(s)	1750(s)
cm^{-1}	1718(w)	1770(w)	1822(w)	1940(m)

Table 3: IR Spectra of Products in the Photolysis of Ozonides (1-5)

compd. No.	aziridine-2,3-diones Product No.	*a*	iso-cyanates *a*
1	12	1954	2260
2	13	1750 1940	2245 2270
3	14	1753 1930	2260
4	15	1742 1933	2265
5	16	*b*	2260

a: Units, cm^{-1} in KBr at 77K *b*: Not detected

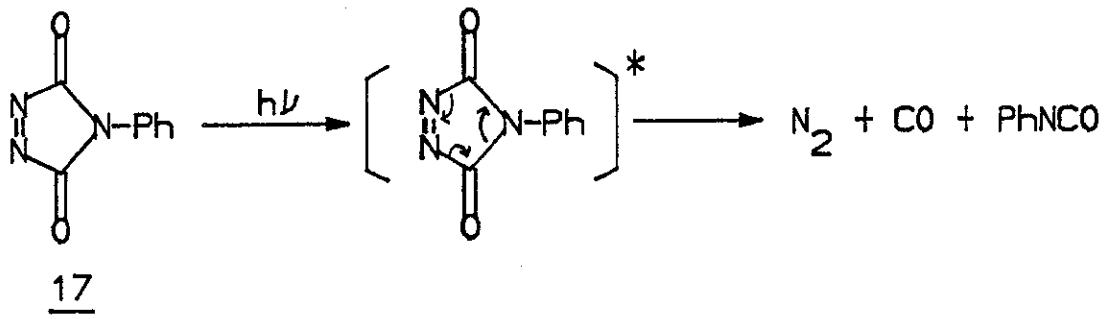
Carbon monoxide (2130cm^{-1})
Benzoic anhydride (1720 and 1785cm^{-1})

monoxide formed in the low-temperature photolysis are presumed to be produced by cleavage of the biradical (11) rather than decomposition of 12-16, because (a) the absorptions of 12-15, isocyanates, carbon monoxide, and benzoic anhydride increase in parallel during irradiation, and (b) the aziridine-2,3-diones (12-15) are stable at 77 K. Since the aziridine-2,3-diones (12-16) were not detected when the ozonides (1-5) in KBr pellets were photolyzed at -78°C, they are presumed to decompose rapidly at that temperature.

An attempt to trap 13 with ethanol at low temperature was unsuccessful. The ozonide in ethanol-ether-toluene glass (2:1:1) was photolyzed at 77 K, and the resulting reaction mixture was allowed to melt (-130 to -120°C) and eventually warmed up to room temperature gradually. Examination of the mixture by GLC indicated the absence of N-methyloxamic acid ethyl ester which would be formed by addition of ethanol to 13.

One type of photoextrusion process can be viewed as a formed ring contraction with the formation of the new bond, often a carbon-carbon bond. This method provides a synthetic entry to strained, small ring hydrocarbons. Photoextrusion reactions have been exploited for this purpose in a number of instances with varing success. The photoextrusion of nitrogen from pyrazolines has been the most extensively examined reaction.[50)-53)] Most of the pyrazolines and bicyclic derivatives in which the azo group is situated in a five-membered ring undergo extremely efficient photochemical loss of nitrogen upon excitation. Wamhoff and K. Wald reported that the photolysis of 4-aryl-1,2,4-triazoline-3,5-

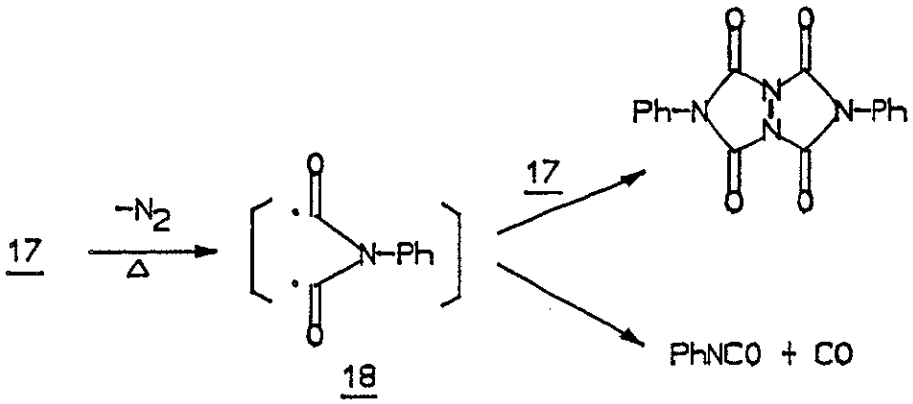
diones (17) produce nitrogen, carbon monoxide, and aryliso-cyanates at room temperature and assumed the presence of 1,3-biradicals (18) as the intermediates[54] (Scheme 23).



17

Scheme 23

Furthermore, they tried the direct observation of 1,3-biradical (18) produced by pyrolysis by ESR spectroscopy, but the attempts was unsuccessful (Scheme 24).

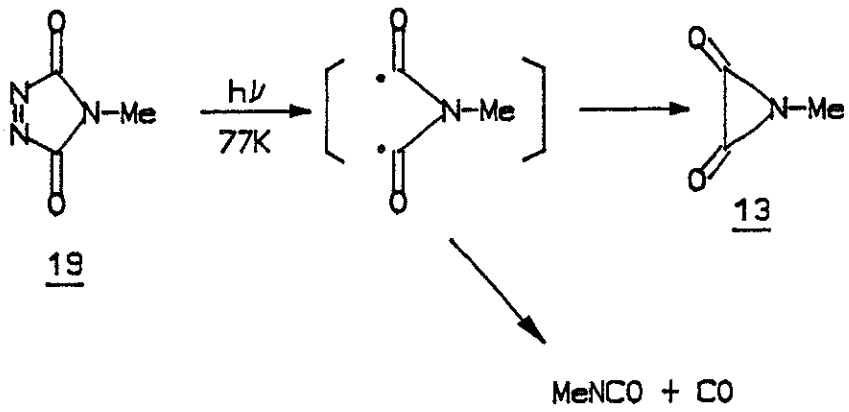


18

Scheme 24

If the 1,3-biradical (18) is formed in this reaction, it is expected that the low-temperature photolysis of 1,2,4-triazoline-3,5-diones gives aziridine-2,3-diones as in the case of maleylimide ozonides (1-4). 4-Methyl-1,2,4-triazolin-3,5-dione (19) in a KBr pellet was photolyzed at 77 K, and the reaction was followed by IR spectroscopy. The spectrum showed the absorption

at 1940 cm^{-1}, in addition to the absorptions of methyl isocyanate and carbon monoxide as expected. However, the absorption was very weak compared with that of methy isocyanate. The lower absorption (1750 cm^{-1}) was not apparent since it was hidden in the absorptions of other photoproducts. The absorption at 1940 cm^{-1} rapidly disappeared shortly after the evaporation of liquid nitrogen (Scheme 25). This fact indicated that the 1,3-diradical (20) was also generated by the photolysis of 1,2,4-triazoline-3,5-diones but the efficiency of the generation of aziridine-2,3-dione (13) was lower than that in the case of maleylimide ozonides (1-4). These facts showed that the 1,3-diradical intermediate is involved in the photolysis of 1,2,4-triazoline-3,5-dione. However, contribution of the concerted process can not be excluded because the yield of 13 was quite low.



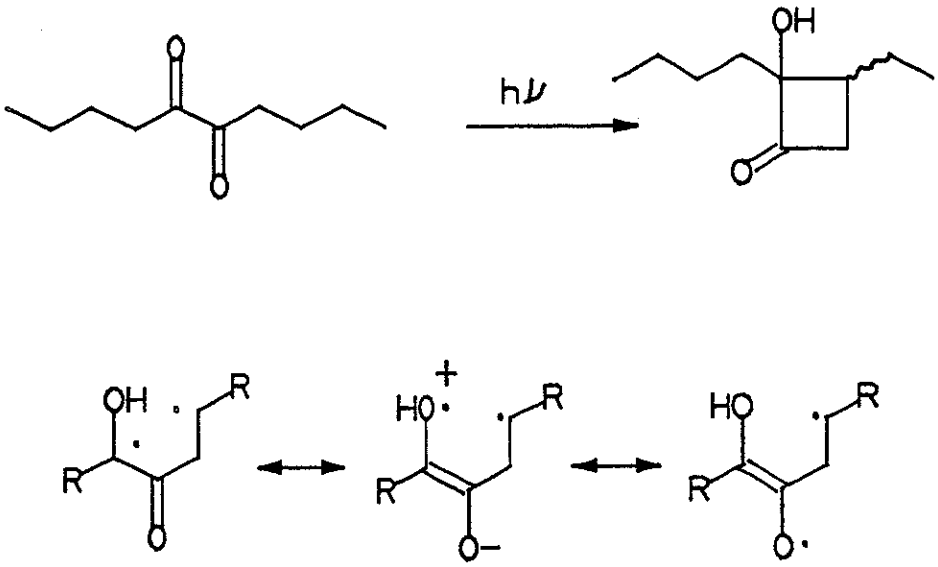
Scheme 25

In summary, the ozonides of diphenylmaleylimides (1-5) photolyzed according to Scheme 22 in which oxygen-oxygen bond homolysis is followed by double β scission, as in the case of most ozonides, to produce benzoic anhydride and the 1,3-diradical

(11). The IR spectra of the photolysates at 77 K revealed the presence of unstable compounds which decompose to carbon monoxide and the isocyanates. The spectral characteristics of the compounds are in full accord with those expected for three-membered cyclic imides. These results permit the assignment of the structure, aziridine-2,3-diones (12-15), to the elusive species.

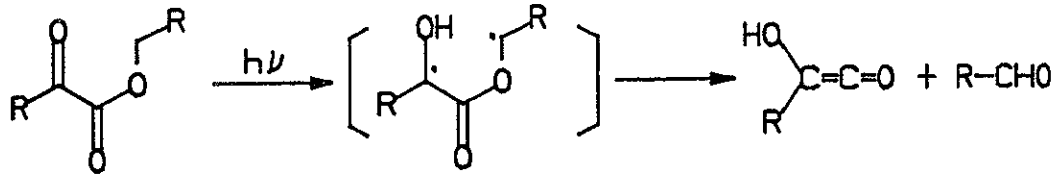
II-2. Photochemical Reactions of α-Ketoamides: Norrish Type II Reactions via Zwitterionic Intermediates

Photochemical reactions of α-dicarbonyl compounds such as α-diketones and α-ketoesters have been studied extensively. α-Diketones undergo intramolecular photoreactions unique in three respects: (a) hydroxycyclobutanones are the only products of γ-hydrogen abstraction; (b) γ-hydrogen abstraction is regiospecific to the C-H bonds β to the second carbonyl; and (c) photoenolization is sometimes competitive. All reactions are exclusively triplet-derived.[55] The exclusive cyclization of the biradicals is connected with the regiospecificity of hydrogen abstraction. The keto group in the biradical allows allylic and donor-acceptor conjugation across one radical site and holds the α,β C-C bond perpendicular to that π system (Scheme 26).



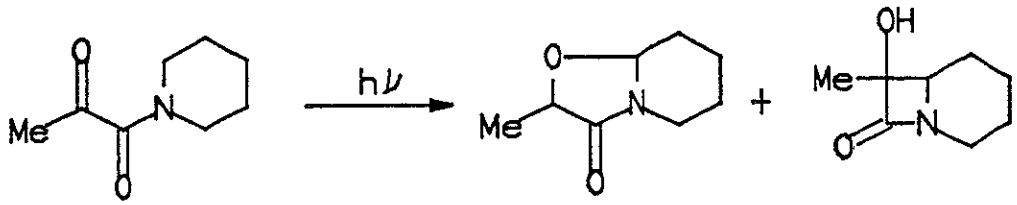
Scheme 26

Photolysis of α-ketoester such as primary and secondary alkyl esters of phenylglyoxalic acid undergo Type II cleavage in which hydroxy ketene is produced[56)-60)] (Scheme 27).



Scheme 27

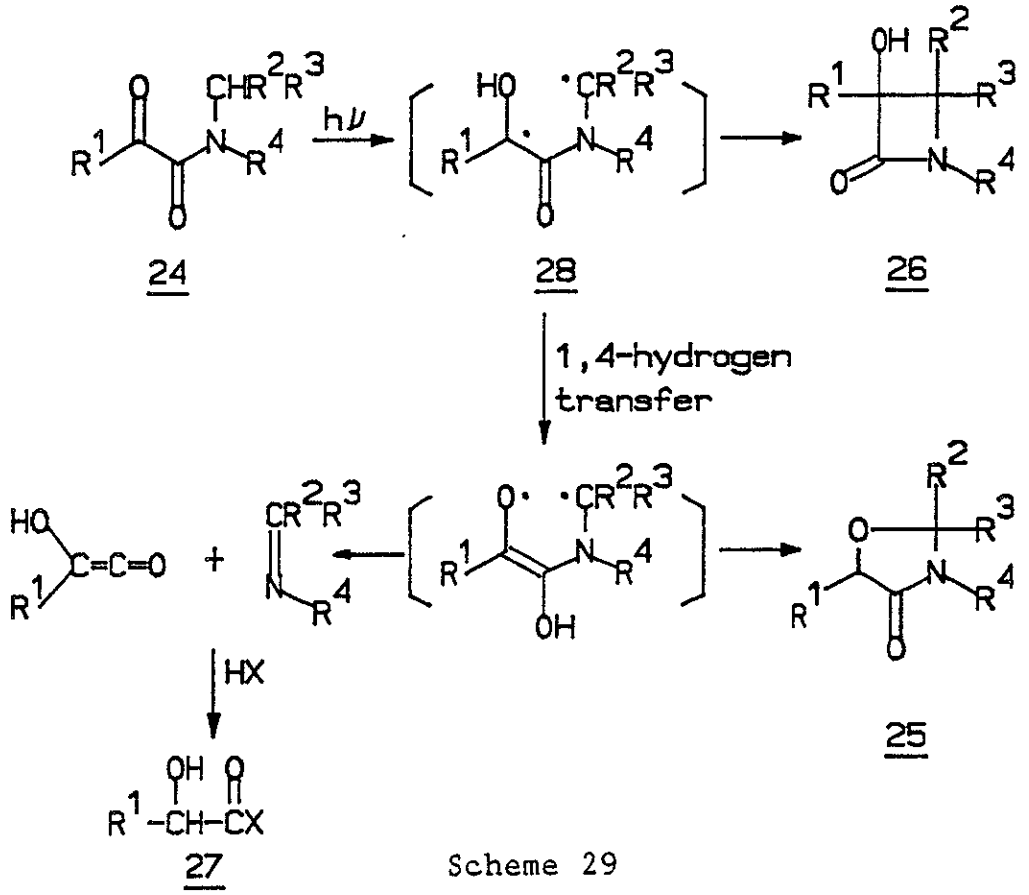
Those of α-ketoamides have received little attention. Åkermark and Johanson investigated the photochemical reaction of an α-ketoamides and some related cyclic α-ketoamides in relation to their studies on penicillin chemistry, and reported that irradiation of 21 yielded an oxazolidin-4-one (22) as a minor product accompanied by a small amount of a β-lactam (23).[61),62)] Their studies were limitted to these cyclic amides, and the mechanism for the formation of the unexpected product (22) has not been clear (Scheme 28).



21 22 23

Scheme 28

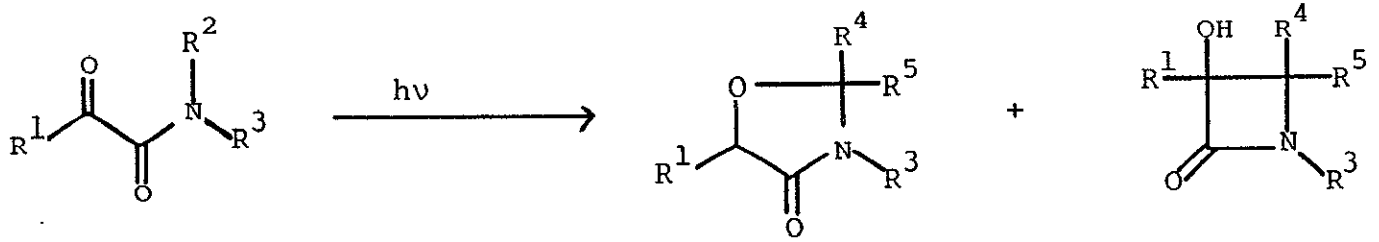
Aoyama et al. reported that photolysis of N,N-disubstituted α-oxoamides (24) gave three types of products, β-lactams (26), oxazolidin-4-ones (25), and hydroxyketene-derived products, mandelic acid derivatives (27). The formation of these products has been explained in terms of 1,4-diradical intermediates formed by γ-hydrogen abstraction (Type II process)[63)-65)] (Scheme 29).



24 28 26 25 27

Scheme 29

However, the photoreactions show remarkable solvent effects which are not easily explained by the radical mechanism. The author has investigated the mechanism of the photoreactions and clarified that the intermediate are zwitterions. Intermediacy of 1,4-diradicals in usual Type II reactions is well established.[66)-69)] The photochemical reactions of α-ketoamides provides the first example of Type II reactions which involve zwitterionic intermediates.



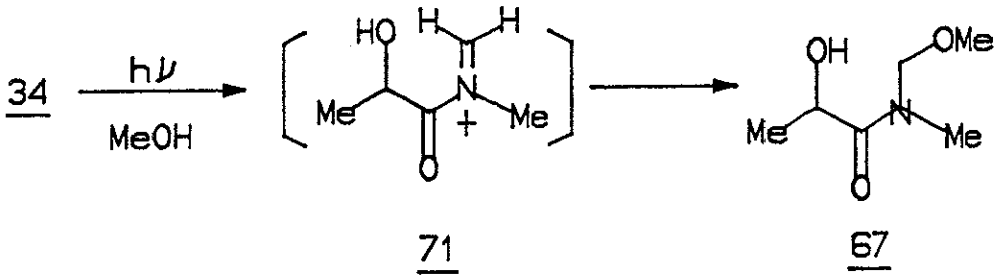
No.	R^1	R^2	R^3	No.	R^4	R^5	No.	R^4	R^5
34	Me	Me	Me	--			--		
35	Me	Et	Et	45	H	Me	--		
36	Me	Pr^i	Pr^i	46	Me	Me	--		
37	Me	$PhCH_2$	$PhCH_2$	47	H	Ph	55	H	Ph
38	Me	p-$CNC_6H_4CH_2$	p-$CNC_6H_4CH_2$	48	H	p-CNC_6H_4	56	H	p-CNC_6H_4
39	Me	p-$MeOC_6H_4CH_2$	p-$MeOC_6H_4CH_2$	49	H	p-$MeOC_6H_4$	57	H	p-$MeOC_6H_4$
40	Me	Me	1-Adamanthyl	50	H	H	--		
41	Ph	Pr^i	Pr^i	51	Me	Me	58	Me	Me
42	Ph	$PhCH_2$	$PhCH_2$	52	H	Ph	59	H	Ph
43	Ph	Ph	Ph	53	H	Me	60	H	Me
44	Ph	Ph	Pr^i	54	Me	Me	61	Me	Me

Figure 4

α-Ketoamides, oxazolidinones, and β-lactams chosen in this mechanistic study are shown in Figure 4. Since photoreactions of some α-ketoamides in aprotic solvents are sensitive to moisture and the reproducibilities of these reactions are not always good, the present study is mainly concerted with the photoreactions in protic solvents.

Intermediacy of Iminium Ions in the Formation of Oxazolidin-4-ones (33)

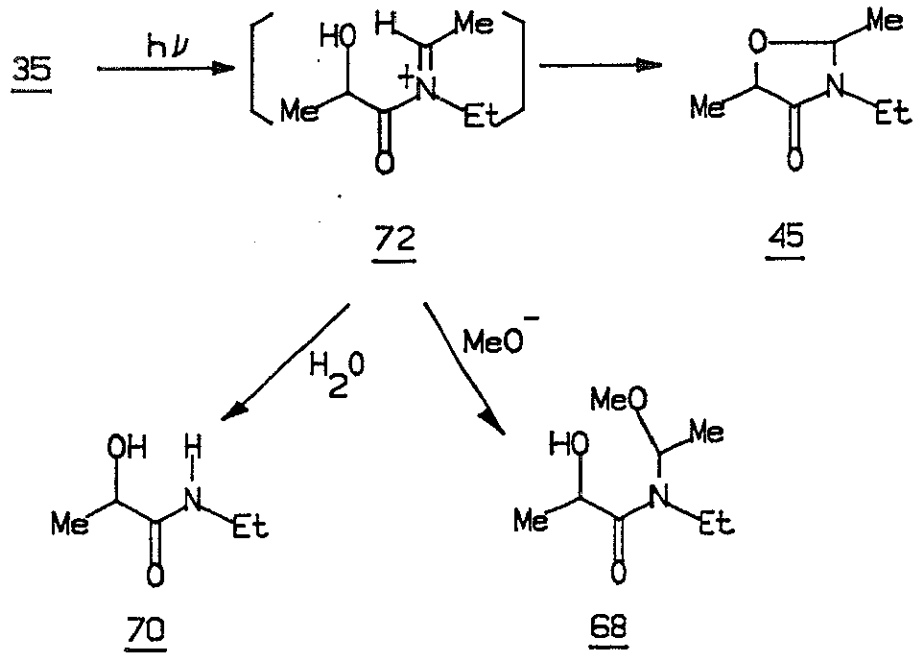
Shima et al. reported that irradiation of N,N-dimethylpyruvamide (34) in methanol gave a methanol adduct (67), and an iminium ion (71) was presumed to be an intermediate (Scheme 30).[70] A similar cyclization of an iminium ion produced by electrolysis of a carbamate bearing a hydroxy group was reported.[71]



71 67

Scheme 30

In order to examine the intermediacy of the iminium ion (72), the author tried trapping the ion with strong nucleophiles. Photolysis of N,N-diethylpyruvamide (35) in methanol does not give a methanol adduct (68) but affords an oxazolidinone (45) quantitatively.[63] However, irradiation of 35 in methanol



Scheme 31

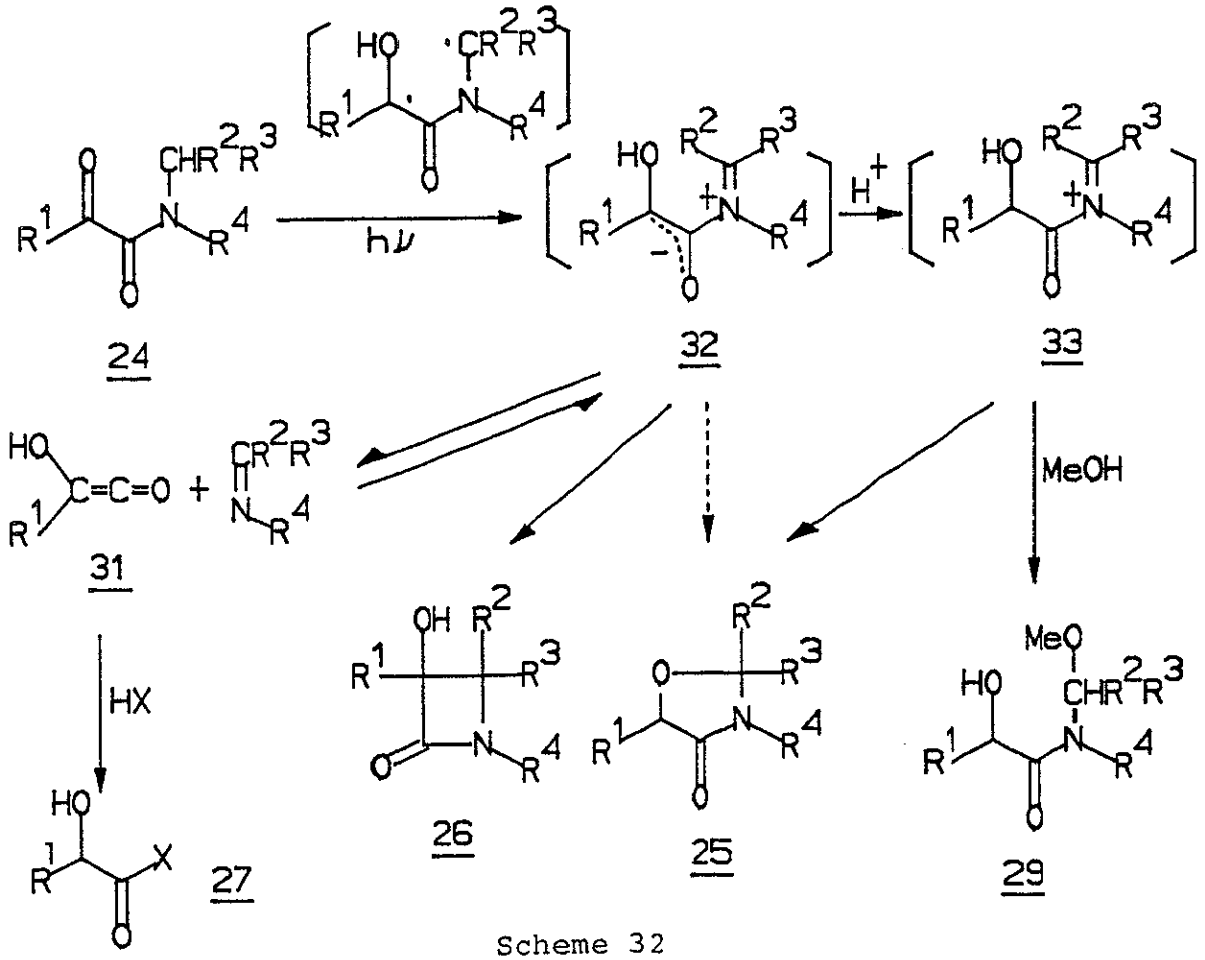
containing sodium methoxide yielded the methanol adduct (68) as a main product accompanied by 45 (Scheme 31). The ratio of the two products was dependent on the concentration of sodium methoxide (Table 4). The formation of the adduct strongly indicates that the iminium ion (72) is the intermediate of the reaction. When 35 was photolyzed in aqueous methanol, N-ethylacetamide (70) was obtained in addition to 45. The formation of 70 is also consistent with the mechanism since hydrolysis of 72 would give 70. The observation that 45 is stable in these reaction conditions rules out the possibility that 68 and 70 are formed from 45 as secondary products. On the basis of these facts, it can be concluded that the iminium ion (72) is the intermediate in the formation of the oxazolidinone (45).

It is quite difficult to explain the formation of the iminium ion (33) in terms of the diradical mechanism, whereas the

Table 4:Photolysis of 35 in the Presence of Nucleophiles

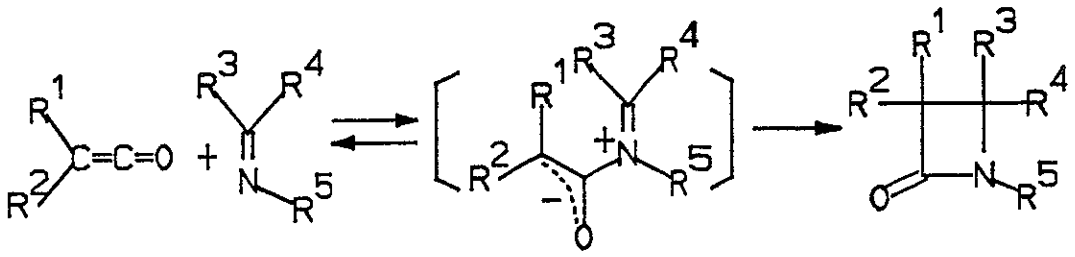
	Yield (%)[a]		
reaction medium	No. 45	68	70
MeOH	100	*b*	*b*
MeOH–MeONa (0.01M)	47	50	*b*
MeOH–MeONa (0.02M)	52	46	*b*
MeOH–H_2O (5%)	100	*b*	*b*
MeOH–H_2O (50%)	78	*b*	18

a:Determined by NMR spectroscopy.
b:Not detected.



Scheme 32

formation is reasonably explained by protonation of a zwitterion (32) (Scheme 32) (for the relation between zwitterions and diradicals, see the following section). Furthermore, the formation of other products (26 and 27) in the photoreaction of α-ketoamides (24) can be rationalized by the mechanism involving the zwitterionic intermediate (Scheme 32). It is known that β-lactams are formed from zwitterions produced by addition of ketenes with imines (Scheme 33).[72)-75)] Cleavage of the zwitterions to ketenes and imines is also known.[76)-78)]



Scheme 33

Effects of Acids and Bases

According to the mechanism shown in Scheme 32, the oxazolidinone (25) is formed from the iminium ion (33) which is produced by protonation of the zwitterion (32), while the β-lactam is formed directly from 32. If the mechanism is correct, the concentration of acids should play a crucial role in the photoreaction in which the oxazolidinone and the β-lactam are formed competitively. Accordingly, photolyses of α-oxoamides (37 and 42) in the presence of acids or bases were carried out and the results are summarized in Table 5. The presence of acids in

the reaction media apparently enhances the formation of 47, and the β-lactam (55 and 59) becomes favored in basic or aprotic media. In particular, N,N-dibenzylbenzoylformamide (42) which gives only a β-lactam (59) in both protic and aprotic solvents yields an oxazolidinone (52) as a main product on irradiation in a highly acidic medium. These results strongly support the mechanism involving the zwitterion and are inconsistent with the diradical mechanism since it is quite unlikely that diradical reactions are affected by acids and bases so remarkably.

Table 5: Photolysis of 37 and 42 in the Presence of Acids or Bases

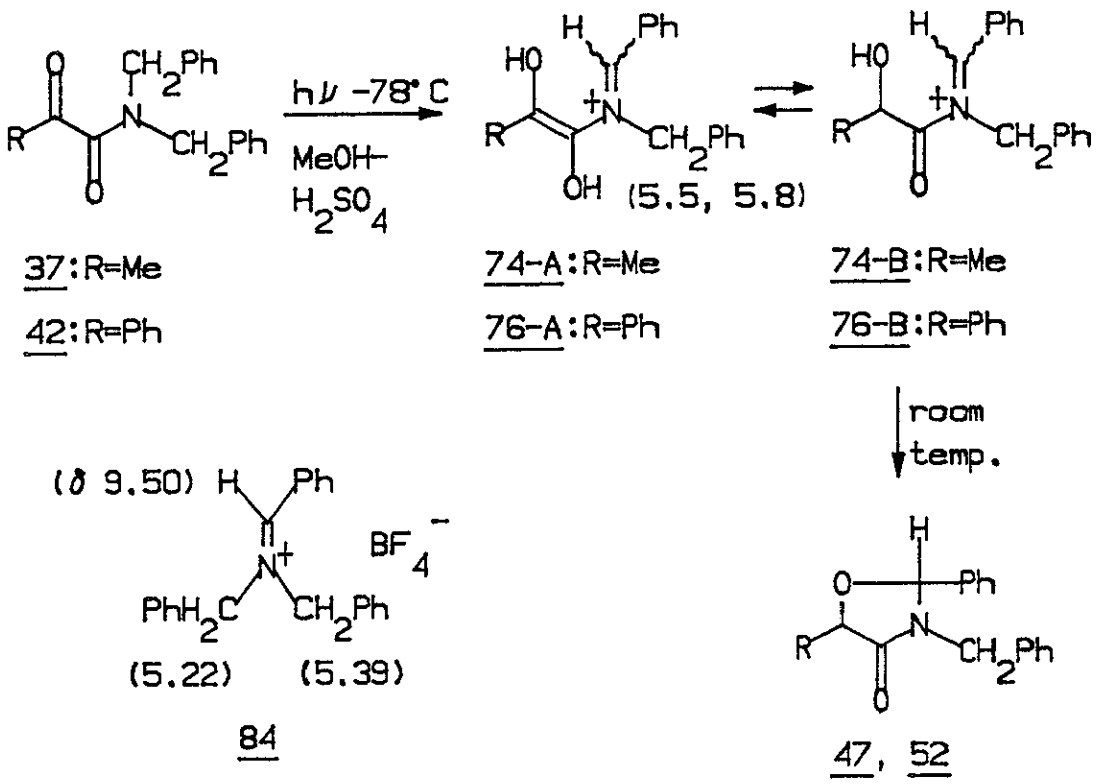
reactant No.	reaction medium	Yield(%)	
		47	55
37	C_6H_6	*a*	94
	MeOH	43	54
	MeOH-AcOH (5%)	84	*b*
	MeOH-MeONa (0.1M)	*a*	87
		52	60
42	C_6H_6	*a*	100
	MeOH	*a*	86
	MeOH-H_2SO_4 (10%)	51	24

a: Not detected. *b*: Trace.

Detection of Iminium Ions

Attempts to detect the zwitterions (32) by use of low-temperature NMR spectroscopy met with failure.[79] This is presumably due to instability of the intermediates. It is conceivable that the iminium ions produced by protonation of the zwitterions are more stable. Thus, detection of the iminium ions (33) was examined. When the oxoamide (42) in methanol containing sulfuric acis (5%) was irradiated at -78°C, the solution turned reddish brown (Scheme 34). On warming to -10°C, the solution rapidly became colorless again. This indicates the formation of an unstable intermediate. Similar phenomena occurred in the case of other acids, but were not observed when acids were absent. When a weak acid, acetic acid, was used, decoloration of the irradiated solution took place at a lower temperature (-50°C). From these facts, it is evident that the unstable compound is a protonated species. The visible spectrum of the cold reaction mixture exhibited a maximum absorption at 440 nm, which disappeared rapidly on warming. The NMR spectrum of the mixture was measured at -50°C. The spectrum showed signals at δ 9.6, 5.5, and 5.8 as broad singlets[80] in addition to those of the original amide. The three signals disappeared when the spectrum was measured after the mixture warmed to room temperature, and the signals of the oxazolidinone (52) appeared instead. These results clearly show that the unstable protonated species is converted into 52 on warming. This fact and the comparison of the chemical shifts of the three signals with those of a known iminium ion (84)[81] (Scheme 34) strongly indicate that the intermediate is an iminium ion (76). Since the ion showed an

absorption at a long wavelength region, it is presumed to exist predominantly in the enol form (76-A) rather than keto form (76-B) in these conditions.



Scheme 34

A similar phenomenon was observed when the pyruvamide (37) was irradiated under the same conditions. However, the NMR spectrum of the intermediate of this reaction could not be measured because its lifetime was short even at the low temperature. The visible spectrum of the reaction mixture showed a maximum absorption at 416 nm. This value is considerably smaller than that in the case of 42. This difference is also compatible with the enol structure (76-A) in which the phenyl group of 75 or

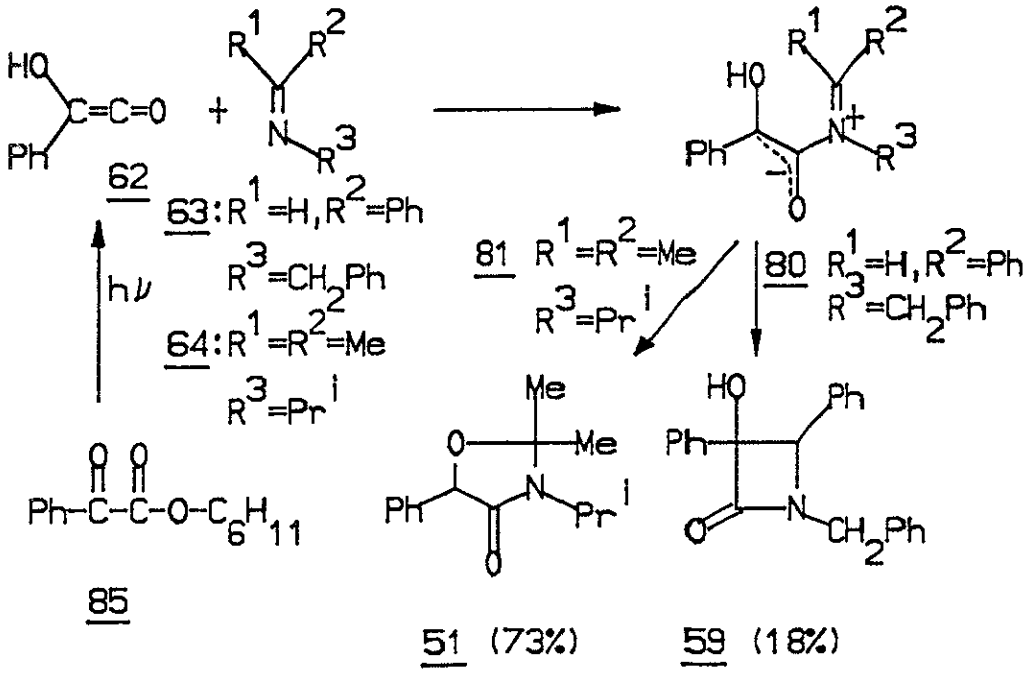
the methyl group of 74 is directly bonded to the conjugated system. Meanwhile, in spite of the preponderant presence of the enol form (74-A and 76-A) in the cold reaction mixtures, the cyclization of the iminium ion (74 and 76) to oxazolidinone (47 and 52) is presumed to occure from the keto form (74-B and 76-B) (Scheme 34) as detailed in the following section.

On the basis of these results, the author can safely concluded that the unstable intermediates are iminium ions (74 and 76), and they undergo cyclization to yield the oxazolidinones, (47) and (52), respectively. On the other hand, when α-ketoamides (35, 36, and 41) were irradiated under the same conditions, no intermediates were detected. The iminium ions from these amides presumably undergo cyclization rapidly to give the corresponding oxazolidinones even at the low temperature.

Independent Generation of the Zwitterions by the Reaction of Hydroxyphenylketene with Imines

It is well-known that the reaction of ketenes with imines yields zwitterions (Scheme 33). Therefore, the reaction of hydroxyketenes with imines should give the zwitterions which are identical with those formed in the photolysis of α-ketoamides. Hydroxyketenes do not exist as stable compounds because they readily ketonize to α-ketoaldehydes. However, it is known that hydroxyphenylketene (62) is formed in the photolysis of benzoylformic acid esters and it can be trapped by nucleophiles such as alcohols.[58] Thus the photolysis of cyclohexyl benzoylformate (85) in the presence of imines was carried out (Scheme 34). When a 1:1 mixture of 85 and N-benzylidenebenzylamine in dry benzene

was photolyzed, the β-lactam (60) was obtained in a good yield as expected. Furthermore, an oxazolidinone (51) was obtained in the case of N-isopropylideneisopropylamine (64). These products and the substituent effects fully correspond with those in the photolysis of the α-ketoamides (41 and 42): irradiation of 41 in benzene gives 51 quantitatively and that of 42 affords 59 as a main product.[63] From these results it is apparent that the photoproducts (51 and 59) arise from the zwitterions (80 and 81).



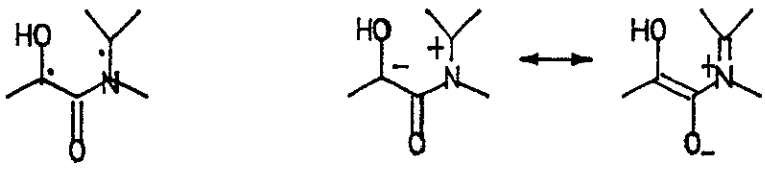
Scheme 35

It may be conceivable that the ketene (31) and the imine (30) are formed initially in the photolysis of 24 by a usual Type II cleavage of 24 and the oxazolidinone (25) and the β-lactam (26) are produced from the ketene-imine pair via the zwitterion

as secondary products. However, this mechanism is improbable because the amides (36 and 42) gave 46 and 59, respectively, almost quantitatively on irradiation in n-butylamine which is a stronger nucleophile than imines. These facts lead to the conclusion that the intermediates in the photoreaction of α-ketoamides are zwitterions (32) as shown in Scheme 32.

Diradicals and Zwitterions

The problems of diradicals and zwitterions have already been discussed extensively by Salem, Turro, and Dauben.[82)-84)] In the case of nonsymmetric structures (e.g. those shown in Figure 6) are resonance forms. Namely, the states of these diradicals or zwitterions can be represented by linear combinations of diradical (covalent) terms and zwitterionic terms. The relative weights of the contributing structures are determined by the substituents, geometries, and environmental effects. Thus, the terms "singlet diradical" and "zwitterion" are only simplifications of the real situation.[82)] Nevertheless, when contribution of the diradical structures is much larger than that of the zwitterionic ones, we can regard the species as diradicals as in the case of diradicals produced in singlet Type II reactions, whereas the species can be regarded as zwitterions in the reverse



diradical Zwitterion

Figure 6

case (e.g., intermediates in the thermal [2+2] cycloaddition of electron-rich olefins with electron-poor olefins).[85] When the lowest singlet state of a species is a diradical state, the second singlet state (the lowest excited state) is a zwitterionic state, and vice versa.[82] On the other hand, it is worth emphasizing that triplet diradicals can not have zwitterionic characters.[82,84] The states of triplet diradicals are represented only by covalent terms.

Usually, the triplet and singlet diradical states lie below the zwitterionic state. However, when the zwitterionic state is strongly stabilized by appropriate substitution, it falls below the two diradical states and becomes the ground state of the system. In the present case, the zwitterion (32) is undoubtedly the ground state of the system because it can be produced by the ground-state reaction of the ketene and imine. The cationic center of 32 is conjugated with the nitrogen and the anionic center is conjugated with the adjacent carbonyl group (Figure 6). The zwitterionic state is thus stabilized by the conjugation and becomes the ground state. The most stable geometry of the zwitterion (32) should be planar because of the conjugation.[86]

The energies of zwitterionic and diradical states are dependent on the geometry of the system.[82)-84] Figure 7 shows the qualitative potential energy surfaces for geometrical changes of the system, and three typical geometries are shown in it. The ground state of the planar conformer I is zwitterionic as described above. In the case of the partially twisted geometry II, conjugation of the cationic center with the nitrogen is

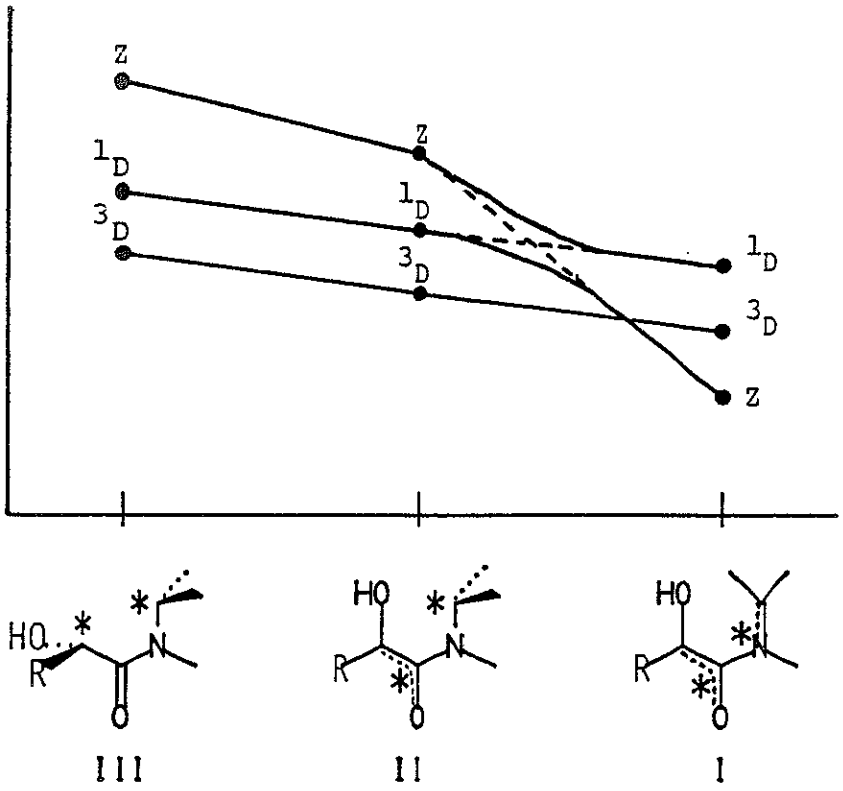
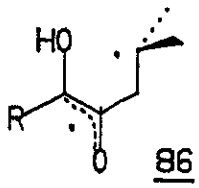


Figure 7. Qualitative potential energy diagram for geometrical changes. (*,*=+,- or •,•).



86

Figure 8

completely forbidden. Therefore, the zwitterionic state is strongly destabilized and the diradical state is presumed to become the ground state of this conformer. This diradical is closely similar to the diradical (86) formed in the Type II reaction of α-diketones (Figure 8).[56]

The ground state of the fully twisted conformer III is undoubtedly the diradical state because stabilization of the zwitterionic state is not expected in this geometry. From this diradical, the β-lactam can be smoothly formed. However, the geometry of the transition state in the formation of the β-lactam is not this geometry because the bond formation and the bond rotation should occur simultaneously in the cyclization.[87] Nevertheless, the transition state should have a partial diradical character, as in the case of butadiene-cyclobutene electrocyclization,[88] because the geometry of the transition state should be severely distorted from the planar structure.

Multiplicities of the Reactive Excited States and the Intermediates

The photochemical reactions of α-ketoamides are sensitizable but unquenchable.[63] The failure to quench the reactions makes it impossible to achieve the usual kinetic studies and difficult to determine the multiplicities of the reactive excited states in the direct photolysis because both singlet and rapid trilpet reactions are possible from the available data. In the case of sensitized reactions, triplet diradicals should be formed initially since triplet states cannot be zwitterionic as described above. The potential energy surface of the triplet diradical is presumed to lie below that of the singlet diradical (Figure 7) as in the case of usual diradicals. The triplet surface should cross the singlet surface in the region where the lowest singlet state begins to have a zwitterionic character and is strongly stabilized. The triplet diradical must undergo intersystem

crossing to the singlet state before it undergo further reactions, and the efficient intersystem crossing is expected to occure in the crossing region (Figure 7).

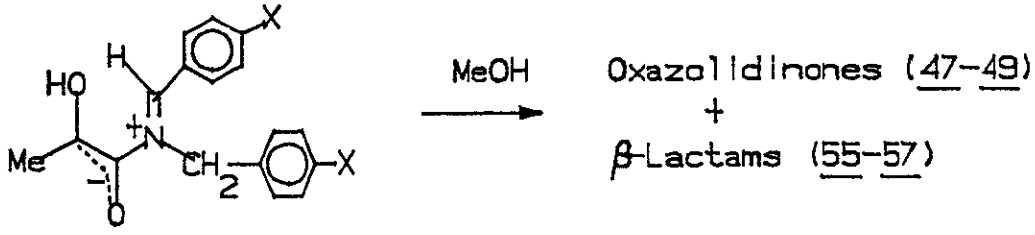
Xanthone-sensitized photolysis[89)-91)] of 35 in methanol and 37 in methanol containing acetic acid (5%) gave 45 (∿100%) and 47 (86%), respectively. The yields are almost the same as those in the direct photolysis. This indicates that the triplet diradicals formed in the sensitized reactions are eventually converted to the zwitterions exclusively, since it is sure that the oxazolidinones (25) are produced from the zwitterions (32). In particular, the fact that the formation of the β-lactam from 37 was completely supressed by the addition of acetic acid even in the sensitized reaction indicates that the direct formation of the β-lactam from the triplet diradical[92)] is negligible at least in the case of 37. On the basis of these results, the triplet diradicals formed in the sensitized photoreactions of α-ketoamides are presumed to undergo rapid intersystem crossing and to be converted to the zwitterions (32). Meanwhile, 32 might be formed directly from the singlet excited state of 24 in the case of the direct photolysis, since the singlet diradical from 24 may not represent energy minima in the potential energy surface (Figure 7) even if it is produced in the photolysis.

Substituents Effects

Photochemical reactions of α-ketoamides show substantial substituent effects.[63)] They are now reasonably explained in terms of the mechanism described in the preceding sections.

1. β-Lactams vs. Oxazolidinones

Radical-stabilizing substituents apparently enhance the formation of β-lactams: N,N-dibenzylbenzoylformamide (42) gives the β-lactams (59) as a sole product both in protic and aprotic solvents, and N,N-dialkylpyruvamides (35 and 36) afford only oxazolidinones (45 and 46), respectively, whereas 37 and 41 yield both β-lactams (55 and 58) and oxazolidinenes (47 and 51).[63] Similar substituent effects are known. With few exceptions, the formation of β-lactams from ketenes and imines has been limitted to imines which have aromatic groups at the imino carbons (Scheme 36, R^2 and/or R^3 is aryl).[75] The radical-stabilizing phenyl groups at the radical (or ionic) center of 77-79 should lower the potential energies of the transition states in the formation of β-lactams because the transition states have partial diradical characters as described in the preceding section. Thus, the stabilization of the transition states make the cyclization efficient.



77: X=H

78: X=CN

79: X=OMe

Scheme 36

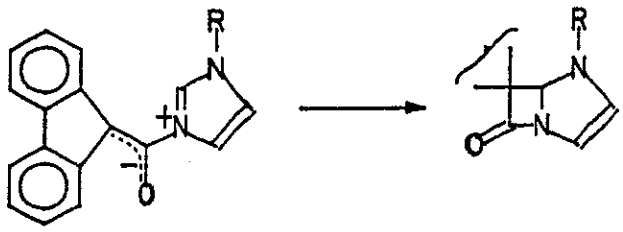
The activation energy of the cyclization is dependent not only on the potential energy of the transition state but also on that of the zwitterion (32). Therefore, it is presumed that

Table 6: Photolysis of N,N-Dibenzylpyruvamide Derivatives in Methanol

reactant No.	Oxazolidinone		β-Lactam	
	No.	Yield(%)	No.	Yield(%)
37	47	43	55	54
38	48	*a* (0)	56	86 (92)
39	49	67 (0)	57	21 (96)

Numbers in parentheses are the yields of the photolysis in benzene. *a*:Trace.

stabilization or destabilization of 32 shows substantial effects on the photoreaction (24). In confirmation of this, photolysis of N,N-dibenzylpyruvamide derivatives was examined (Scheme 36 and Table 6). As expected, introduction of cyano groups to the phenyl groups increased the yield of the β-lactam (56) and that of methoxy groups decreased the yield 57. The electron-withdrawing group at the cationic center should destabilize 78. Raising the potential energiy of the zwitterion makes the activation energy small and thus enhances the formation of the β-lactam. The reverse is true for the electron-donating methoxy group since the stabilization of the zwitterion by the methoxy group should make the activation energy large. Quite analogous substituent effects were recently reported.[79] The rate cyclization of a zwitterion (87) to a β-lactam (88) becomes fast when electron-withdrawing groups are introduced at the 1-position of the imidazole ring (Scheme 37). These facts are also consistent with the above explanation.



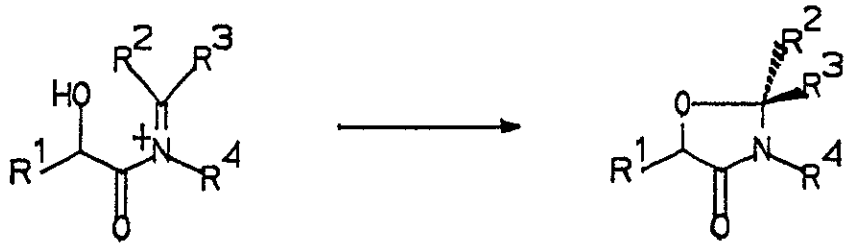
87 88

Scheme 37

2. Oxazolidinones vs. Methanol Adducts

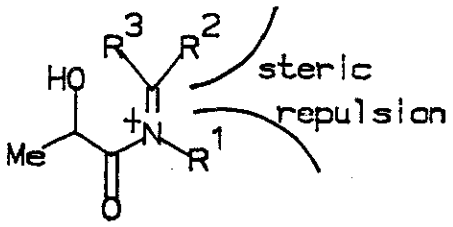
The oxazolidinone (26) and the methanol adduct (29) are formed from the iminium ion (33) competitively as shown in Scheme 31. Among pyruvamides, only the N,N-dimethylamide (34) affords the methanol adduct (67) on irradiation in methanol[70] (Scheme 30). The N,N-diethylamide (35) gives the adduct (68) only when sodium methoxide is present (vide supra). Meanwhile, the N,N-diisipropylamide (36) did not yield an adduct even in the presence of sodium methoxide. Therefore, the reactivity toward the attack of methanol or methoxide ion is reduced in the series 34>35>36. This order is in accord with that of the reactivity of the corresponding iminium ions (33) toward nucleophiles because the electron-donating methyl groups at the imino carbon should reduce the reactivity. However, the selective intermolecular reaction (methanol addition) of 71 cannot be attributed to the high reactivity because the imino group of 71 should be high reactive toward not only intermolecular but also intramolecular nucleophilic attacks (Figure 9). The efficient formation of the adduct from 34 can be rationalized in terms of steric effects as

detailed below. The intramolecular cyclization of the iminium ion (33) requires the rotation of the C=N bond (Scheme 38). The bulky substituents of 71 and 72 are presumed to destabilize the planar structure of the imino group and make the group slightly twisted (Figure 9). The twist should enhance the intramolecular reaction (oxazolidinone formation).



Scheme 38

In the case of 71 which has no bulky substituents at the imino carbon, the intramolecular reaction is less favorable process because the imino group is planar, and the intermolecular reaction with methanol takes place selectively. In confirmation of this, photolysis of N-(1-adamantyl)-N-methylpyruvamide (40) was carried out. Irradiation of 40 in methanol gave only an oxazolidinone (50; ~100%), and that of 40 in methanol containing sodium methoxide (0.1 M) yielded both 50 (47%) and a methanol adduct (69; 48%). The less efficient formation of the adduct from 40 than that from 34 is consistent with the above explanation that the steric effects are more important, since the reactivity of 75 toward the intermolecular attack by methanol should be almost the same as that of 71 and the bulky adamantyl group should destabilize the planar structure of the imino group of 75.



No.

71: R^1=Me, R^2=R^3=H

72: R^1=Et, R^2=Me, R^3=H

73: R^1=Pr^i, R^2=R^3=Me

75: R^1=adamantyl, R^2=R^3=H

Figure 9

Photoeliminations

None of the pyruvamides chosen in this investigation undergo photoeliminations. Among benzoylformamides, only N,N-diisopropylamide (41) and anilides (43 and 44) gave the elimination products, mandelic acid derivatives (89-91) (Table 7).

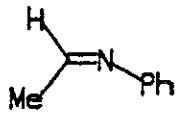
Table 7: Photolysis of 37, 43, and 44 in Methanol[a]

reactant No.	Oxazolidinone No.	Yield (%)	β-Lactam No.	Yield (%)	mandelic acid derivative No.	Yield (%)
37	47	58	55	22	89	16[b]
43	53	11	60	5	90	36[b]
44	54	16 (14)	61	13 (26)	90	69[b] (19)[c]

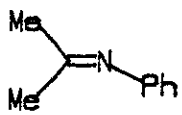
a: Numbers in parentheses are yields of the photolysis in benzene. b: Methyl mandelate. c: Mandelanilide.

The formation of the oxazolidinone (51) from hydroxyphenylketene (62) and imine (64) (Scheme 35) clearly shows that the elimination of the zwitterion (32) is reversible[76)-78)] (Scheme 32). The formation of the elimination product in the photolysis of 41 is not unreasonable since the steric congestion due to the bulky

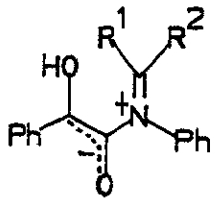
substituents should enhance the elimination. In the case of the anilides, the stabilization of the anils (65 and 66) due to the conjugation of the C=N bond with the phenyl group may be responsible for the efficient elimination; this conjugation is presumed to be stronger than that in the zwitterion (82 and 83) because the steric congestion in 65 or 66 must be smaller than that in 82 or 83 (Figure 10). Thus, the anilide (44) which possess a bulky alkyl group gave the elimination product, methyl mandelate, in a high yield on irradiation in methanol.



65



66



82: R^1=H, R^2=Me
83: R^1=R^2=Me

Figure 10

Solvent Effects.

The effects of acids and protic solvents on the photoreactions of α-ketoamides were already described in the preceding section in relation to the mechanism for the reactions. Although protic solvents enhance the formation of the oxazolidinones (25), some α-ketoamides (e.g. most of dialkylpyruvamides and 41) yield the corresponding oxazolidinones even aprotic solvents.[63] Therefore, the direct formation of 25 from the zwitterion (32) is presumed to occure in these conditions. However, most of these reactions in aprotic solvents are not clean and the yields of 25

are low. Furthermore, addition of small amount of protic substances such as alcohols or water to the aprotic solvents significantly increase the yields of 25.[63] These facts and the efficient formation of 25 in acidic media (vide supra) indicate that the direct formation of 25 from 32 is not a favorable process and the formation of 25 in protic solvents proceeds mainly from the iminium ion (32) as shown in Scheme 32.

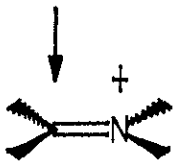


Figure 11

The more efficient cyclization of the iminium ions than that of the zwitterions can be rationalized in terms of stereoelectronic requirements for the nucleophilic attacks to imino groups. The effective attacks of nucleophiles to the imino carbon of iminium ions should be those from the directions nearly orthogonal to the imino plane (Figure 11) as in the case of nucleophilic attacks to carbonyl groups.[93] The hydroxy group of the zwitterion (32) or the enol form of the iminium ions (74-A and 76-A) (Scheme 34) cannot undergo such attacks without distorting the planar structure of the imino group or the enol moiety, whereas the geometry of the keto form of the iminium ions (74-B and 76-B) is much more suitable for the intramolecular attack because of the tetrahedral structure of the carbon bearing the hydroxy group. Therefore, the formation of 46 and 51 from the iminium ion is presumed to occure preferably from the keto forms (74-B

and 76-B) (Scheme 34).

In contrast the remarkable effects of protic substances, solvent polarities showed little effects of the photoreaction of 37 as shown in Table 8.

Table 8: Photolysis of 37 in Various Solvents

	Yield (%)	
solvents	47	55
C_6H_6	*a*	94
THF	*a*	93
MeCN	*a*	96
MeOH	43	54
Pr^iOH	22	63

a: Not detected.

Conclusion

Photochemical reactions of α-ketoamides (24) were proved to proceed via zwitterionic intermediates (32). The remarkable substituent and solvent effects can be rationalized on the basis of the mechanism involving 32. The photocyclization of 24 which yields the β-lactam (26) and the photoelimination which affords the hydroxyketene (31) and imine (30) can be regarded as Norrish Type II reactions, because the former involves γ-hydrogen abstraction by the excited carbonyl group followed by cyclization to give the four-membered cyclic compound (26), and the latter involves the hydrogen abstraction and subsequent cleavage of the β-bond. Therefore, these reactions provide the first example of

Type II reactions involving zwitterionic intermediates.

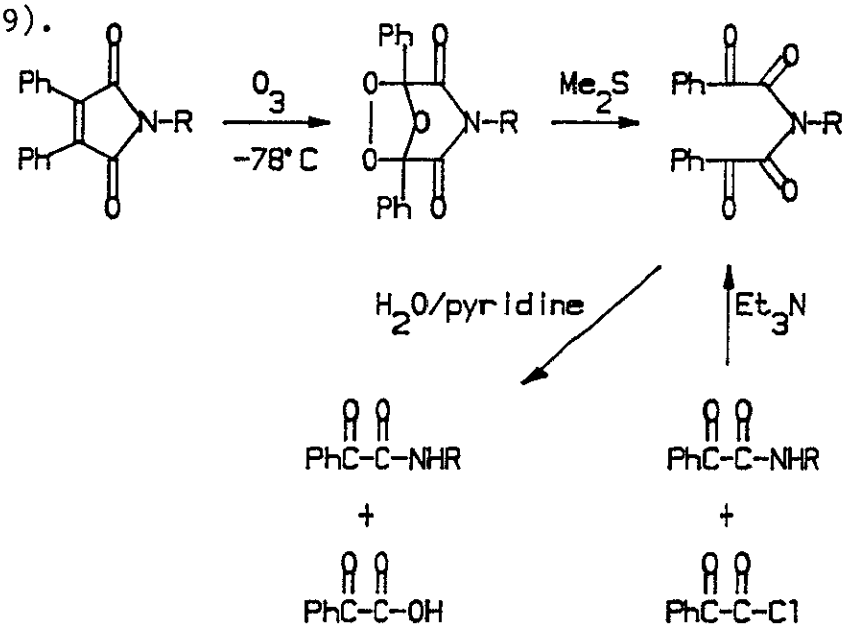
Zwitterions analogous to 32 were first reported by Huisgen et al. as intermediates in the reaction of ketenes with imines.[72] Recently, Moor et al. reported the formation of the zwitterionic intermediates in the thermolysis or photolysis of 4-azido-2-pyrrolinones.[76)-78] Therefore, the present reaction affords a novel entry to the structurally interesting and synthetically important zwitterions.

II-3. PHOTOCHEMICAL REACTIONS OF α-KETOIMIDES

Cyclic imides undergo various photochemical reactions, such as, α-cleavage, hydrogen abstractions, and [2+2] cycloadditions. On the contrary, only a few photochemical reactions of acyclic imides have been examined. In relation to the studies on photochemistry of α-ketoamides, the author studied the photochemical reaction of various kinds of α-ketoacid imides. Furtheremore, the author examined the photochemical reaction of N-acyl ureas which have two carbonyl groups and two nitrogen atoms. Amides are photochemicaly unreactive in comparison with ketones and esters and they usually do not undergo hydrogen abstraction, whereas imides which two carbonyl groups and one nitrogen atom exhibited photochemical reactivities similar to those of ketones. This has been explained in terms of the π-electron donating effects of nitrogenes of amides and those of imides. Therefore, it is of interest to investigate the photochemical reaction of N-acyl ureas which possess two carbonyl groups and two nitrogen atoms.

II-3-1. Photochemical Reactions of α-Ketoimides

Bisphenylglyoxalylimides were obtained quantitatively by the reduction of corresponding ozonides of diphenylmaleimide with dimethyl sulfide (Chepter II-1). The structure of 91 was determined by an unequivocal synthesis from phenylglyoxalyl chloride and N-benzylphenylglyoxalyamide in the presence of triethylamine (Scheme 39).

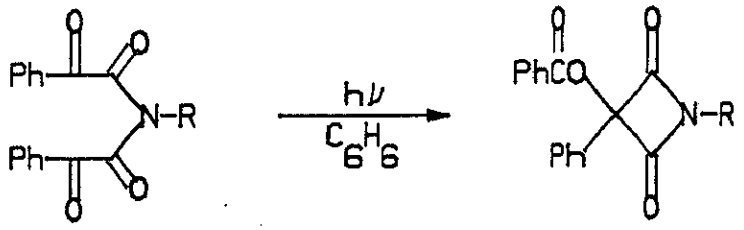


Scheme 39

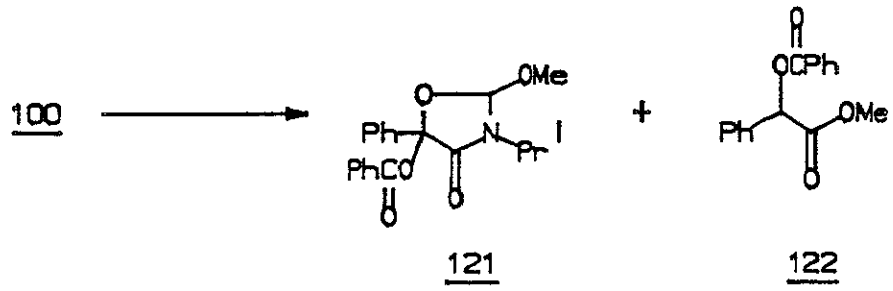
When bisphenylglyoxalyl-N-methylimide (7) in benzene was irradiated with a high pressure mercury lamp under argon, 3-benzoyloxy-1-methyl-3-phenylazetidine-2,4-dione (99) was obtained in 61% yield. Irradiation of other N-alkyl imides (8, 9, and 91-92) under the same conditions also gave the corresponding four-membered cyclic imides (100-103) in good yields (Table 9).

The structure was supported by the fact that irradiation of 100 in methanol with a low pressure mercury lamp under argon gave oxazolidine-4-one (121) and O-benzoyl manderic acid methyl ester

Table 9:Photolysis of Bisphenylglyoxalylimides

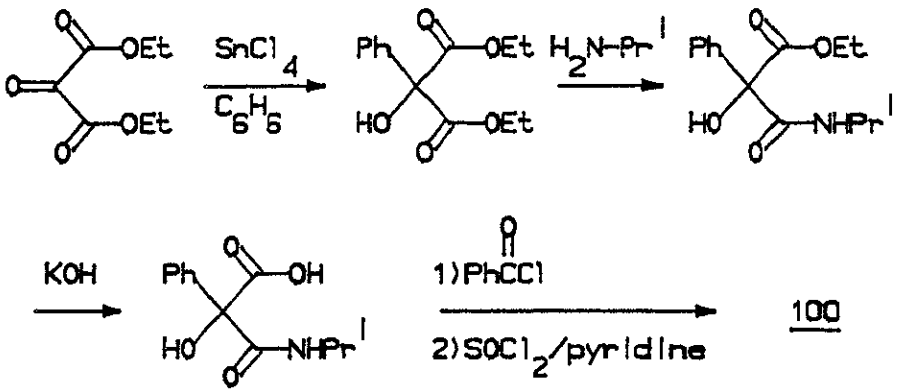


reactant No.	R	product No.	Yield (%)
7	Me	99	61
8	Pr^i	100	63
91	CH_2Ph	101	52
9	CH_2CH_2Ph	102	63
92	C_6H_{11}	103	52



121 122

Scheme 40



Scheme 41

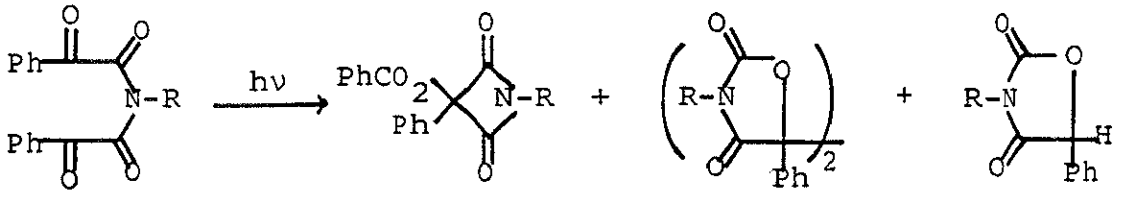
(122)[95] (Scheme 40). The structure was confirmed by an unequivocal synthesis as shown in Scheme 41, whereas those of other photoproducts were determined on the basis of elemental analyses and spectral data.

On the other hand, photolysis of bisphenylglyoxalyl-N-phenylimide (10) yielded bis-5,5'-(3,5-diphenyloxazolidine-2,4-dione) (112) as a major product accompanied by small amount of azetidine-2,4-dione (105) and 3,5-diphenyloxazolidine-2,4-dione (118). Other para-substituted imides (93-95) showed the similar reactivities irrespective of the substituents. In the case of N-o-tolylimide (96) possessing one methyl group on the ortho position of the phenyl group on the nitrogen atom, comparable amount of an azetidine-2,4-dione (108) and an oxazolidine-2,4-dione dimer (116) were obtained. Photolysis of N-(2,6-dimethylphenyl)imide (97) and N-(2,6-dichlorophenyl)imide (98) possessing two substituents on the ortho positions gave four-membered cyclic azetidine-2,4-diones (109, 110) in high yields, and dimers were not obtained (Table 10).

The structure of 18 was confirmed by the direct comparison with authentic sample[96] obtained by the reaction of α-chlorophenylacety chloride and N-phenylcarbamic acid methyl ester. Furtheremore, oxazolidine-2,4-dione dimer (112) was synthesized independently by oxidation of 118 with nickel peroxide (Scheme 42).[97] Whereas, the structures of other photoproducts were determined on the basis of elemental analyses and spectral data.

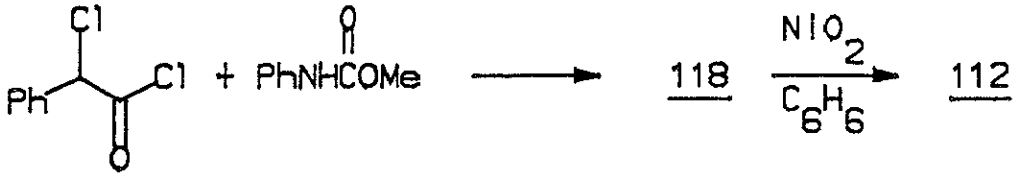
Photolysis of bispyruvyl-N-isopropylimide (123) under the same conditions gave 3-acetoxy-3-methyl-1-isopropylazetidine-2,4-

Table 10: Photolysis of Bisphenylglyoxalylimides.



reactant No.	R	product No.	Yield	No.	Yield	No.	Yield
6	H	104	34	111	32	117	b
10	Ph	105	10	112	40	118	5
93	p-MeC_6H_4	106	6	113	42	119	b
94	p-$MeOC_6H_4$		a	114	41		a
95	p-ClC_6H_6	107	11	115	59		a
96	o-MeC_6H_6	108	29	116	24	120	b
97	2,6-$Me_2C_6H_3$	109	82		a		a
98	2,6-$Cl_2C_6H_3$	110	99		a		a

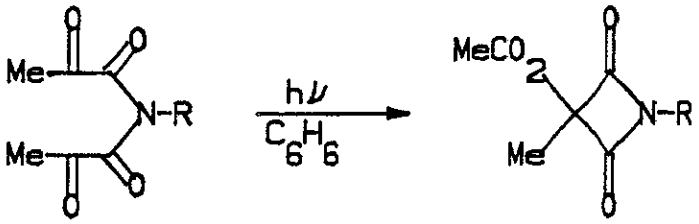
a:Not detected. b:Trace.



Scheme 42

dione (130) in high yield. In the case of the photoreactions of other bispyruvylimides (124 and 125), the corresponding azetidine-2,4-diones (131 and 132) were obtained irrespective of the substiuents on the nitrogen atom. Oxazolidine-2,4-dione dimers were not detected in the photoreaction of 123-125 (Table 11).

Table 11: Photolysis of Bispyruvylimides

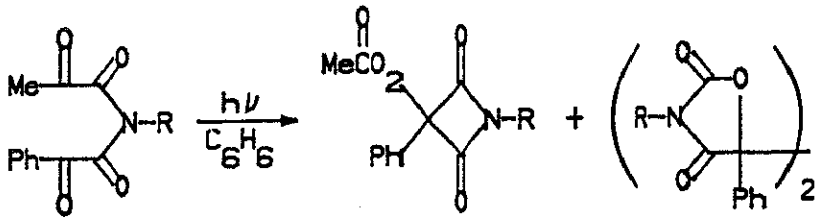


reactant No.	R	product No.	Yield (%)
123	Pr^i	130	96
124	CH_2Ph	131	92
125	Ph	132	73

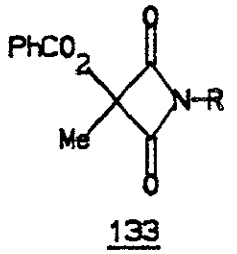
When N-isopropyl-N-pyruvylphenylglyoxalylimide (126) was irradiated in the same conditions, 3-benzoyl-3-methyl-1-isopropylazetidine-2,4-dione (133) was not obtained and 3-acetoxy-3-phenyl-1-isopropylazetidine-2,4-dione (134) which was produced by migration of acetyl group of 126 was obtained specifically. Irradiation of other unsymmetrical imide 127-129 gave the similar results. In the case of the photoreaction of 128, an oxazolidine-2,4-dione dimer (112) which was formed via elimination of an acetyl group.

Quantum yield of the reaction of 7 was 0.53 (for the formation of 99 and that of 10 was 0.15 (for the formation of

Table 12: Photolysis of Imides (126-129)



reactant No.	R	No.	Yield (%)	No.	Yield (%)
126	Pr^i	134	81		a
127	CH_2Ph	135	73		a
128	Ph	136	33	112	49
129	$2,6\text{-di}Me_2C_6H_4$	137	92		a

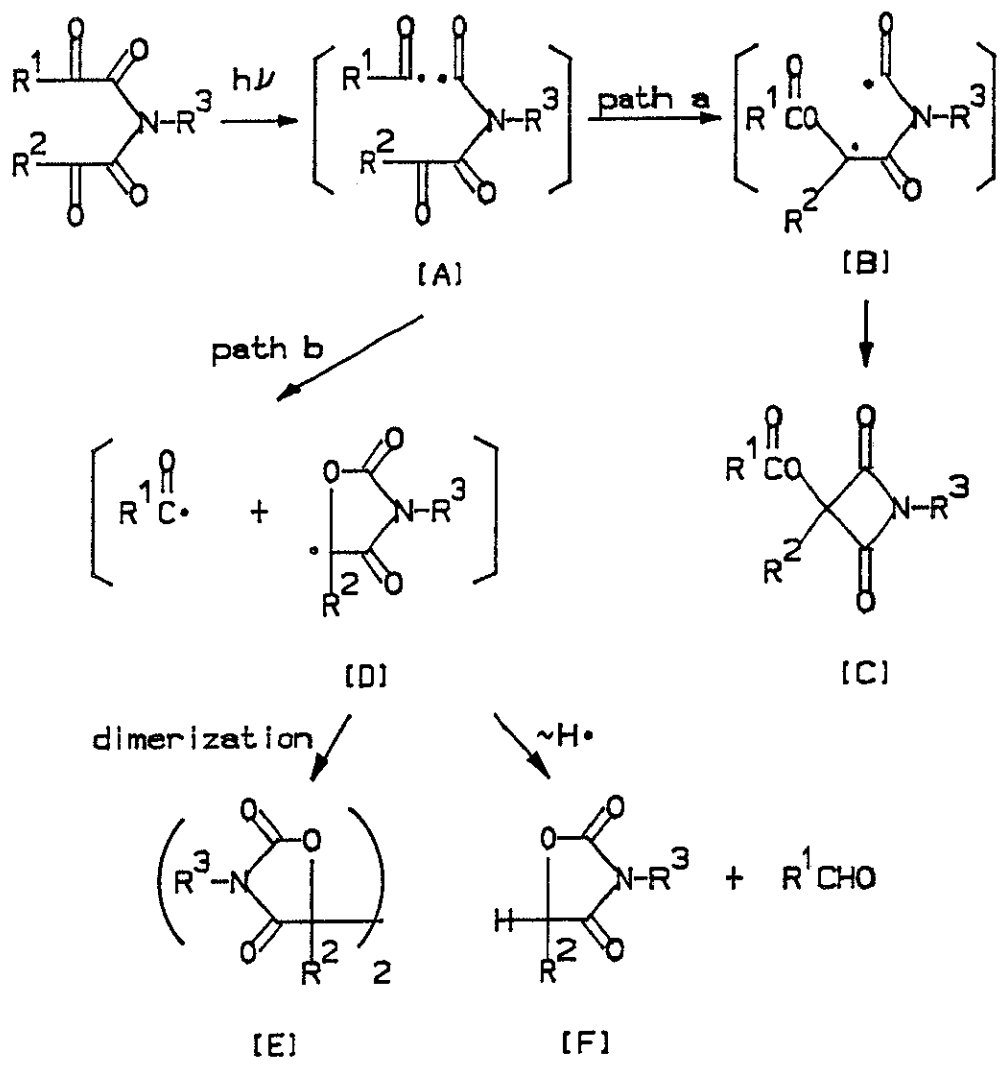


133

a:Not detected

benzaldehyde in the presence of n-dodecan thiol).[98),99)] The bisphenylglyoxalylimides show $n\pi^*$ bands at long wave length regions [7:$\lambda_{max.}$ (benzene) 373 nm] as in the case of phenylglyoxalic acid [$\lambda_{max.}$ (benzene) 376 nm; E_T=63 kcal/mol].[100),101)] When the imides were irradiated at the $n\pi^*$ bands selectively, the photochemical reactions also proceeded efficiently. The cyclization of N-alkylimides was sensitized by 4-methoxyacetophenone (E_T=72 kcal/mol), but not by Michler's ketone (E_T=62 kcal/mol).[90)] Meanwhile, quenching of the reactions by 1,3-pentadiene or stilbene was quite inefficient. N-Phenylimide (10) showed the behavior similar to those of N-alkylimides. Therefore, the photochemical reaction of bisphenylglyoxalylimides in the direct irradiation presumably involves triplet reaction[102)] faster than bimolecular quenching, though singlet reactions are not necessarily eliminated from the available data.

Though a concerted shift or a mechanism with zwitterionic intermediate is also possible, the mechanism for the photo-



Scheme 43

chemical reaction of α-ketoacid imides may involve α-cleavage reaction as shown in Scheme 43. A radical pair [A] is formed by α-cleavage, and the acyl radical transfers to oxygen atom to give a biradical [B]. Cyclization of [B] affords azetidine-2,4-dione [C] (path a). Cyclization of [A] gives a more stable radical [D] (path b), and coupling or hydrogen abstraction of [D] yiels [E] or [F] (Scheme 43).

Intermediacy of the radical [D] was supported by the fact that the yield of 118 increased at the expence of the yield of 112 when photolysis of 10 was carried out in the presence of dodecan thiol (a good hydrogen donor) (Table 13). The formation of a large amount of benzaldehyde (50% determined by GLC) in this experiment is also compatible with the intermediacy of [E]. The formation of acyl radical in the case of 7 was also suported by the fact that benzaldehyde (∿10%) was detected by GLC and NMR spectroscopy when 7 was photolyzed in the presence of decyl mercaptane.

The yields of azetidine-2,4-diones are expected to increase if the radical pair can not escape from the solvent cage, since azetidine-2,4-diones are in cage products and oxazolidine-2,4-dione dimers are out of cage products. When N-phenyl imide (10) was irradiated in frozen solution of benzene, the yield of azetidine-2,4-dione (105) and oxazolidine-2,4-dione (118) increased and dimer (112) was not detected as expected (Table 13). This fact also supported the mechanism involving α-cleavage reaction as shown in Scheme 43.

Table 13: Photolysis of 10 in Various Conditions

reaction condition	Yield (%)		
	105	112	118
C_6H_6	10	40	5
C_6H_6 + Dodecan thiol	13	23	25
C_6H_6 (-78°C) frozen solution	45	0	11

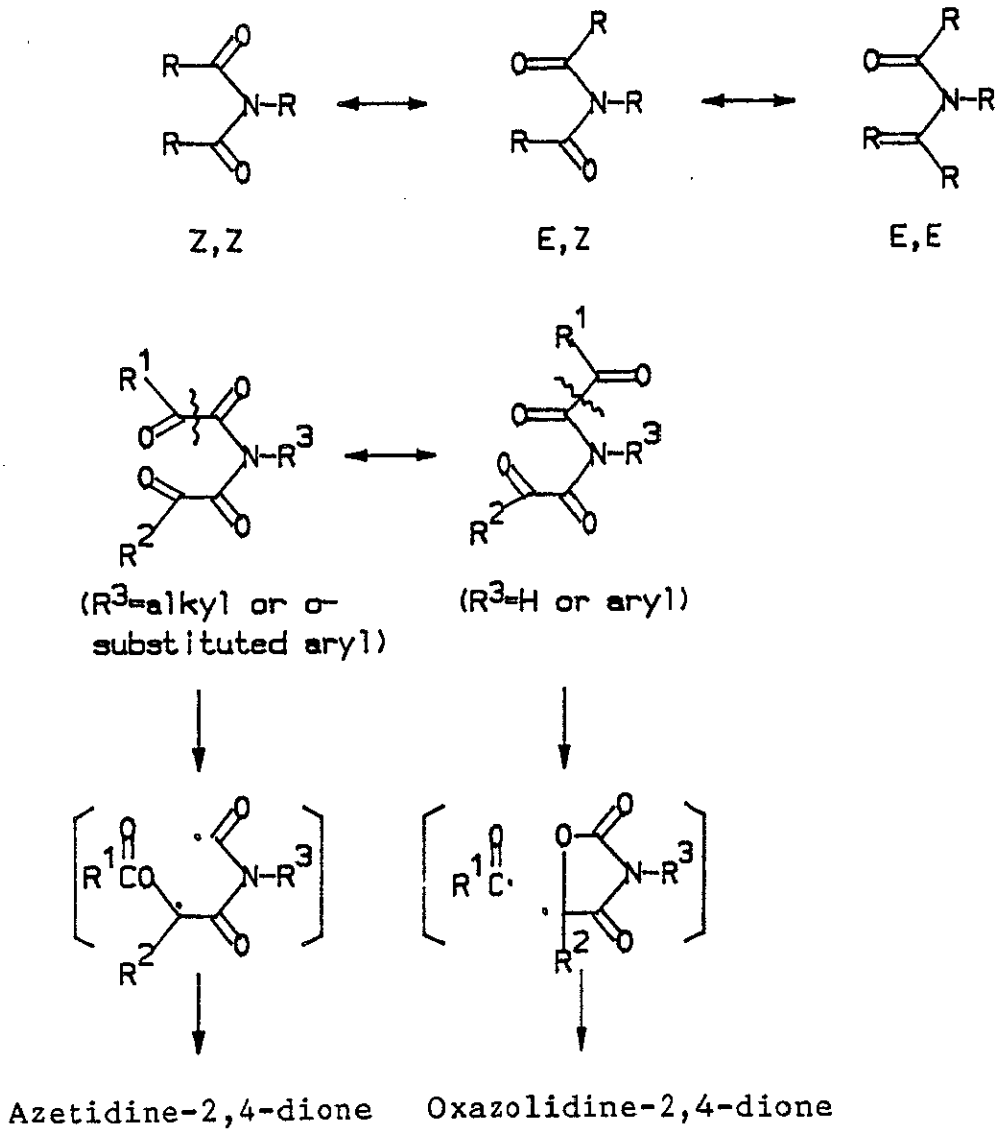


Figure 12

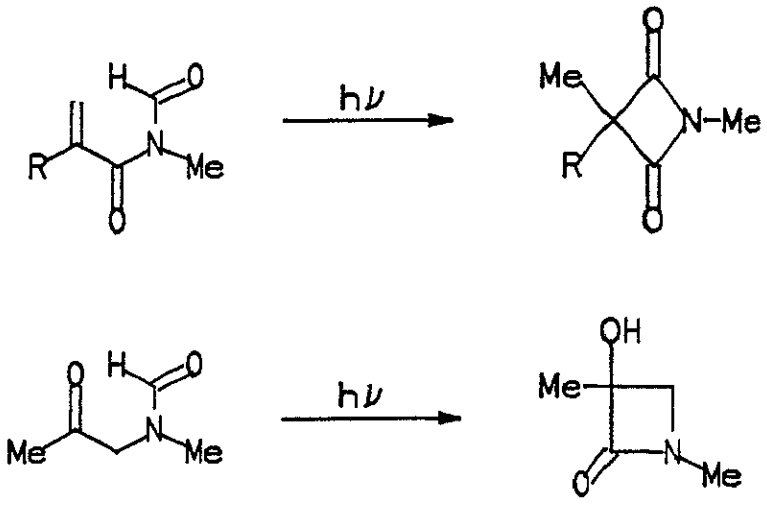
The conformations of the imides may be one of the important factors which control the reactions of the imides. The conformations of ketones have been shown to play important to their Type II processes, and conformational factors are also expected to be important in the photochemistry of imides. The conformations of imides have been studied and can be conveniently described in

terms of forms Z,Z, E,Z, and E,E (Figure 12).[103] The conformer distribution is, to a large extent, defined by the steric demands of the substituents and dipole-dipole interactions.[28), 103] When R^3 is less hindered as in the case of hydrogen, phenyl, and p-substituted phenyl groups (aryl group on the nitrogen atom is perpendicular to the imide plane), type B conformer is more stable than type A. On the contrary, bulky substituents (R^3=alkyl or 2,6-didubstituted phenyl group) on the nitrogen atom make type A conformer more stable. Formation of azetidine-2,4-diones from type A conformer is easier than from type B. On the contrary, type B conformer prefers to produce oxazolidine-2,4-diones. This difference in stable conformations reflects upon the product distribution (Figure 12).

It is well known that azetidine-2,4-diones are pharmacologically highly active.[104)-106] The present reaction provides a useful synthesis of azetidine-2,4-diones bearing an oxygen atom at the 3-position; the yields of the previously reported syntheses are generally low.[104)-106] Although photocyclization via 1,2-acyl shift (oxy-di-π-methane rearrangement) is well known, that via a 1,5-acyl shift was hitherto unknown.

II-3-2. Photochemical Reactions of N-Formyl-α-ketoamides

It is well-known that azetidine-2,4-diones, four membered cyclic imides, are pharmacollogically highly active. However, the yields of the previously reported syntheses were generally poor. In the previous chapter the author described the new synthesis of azetidine-2,4-diones involving photochemical reactions of bisphenylglyoxalylimides. It is expected that azetidine-2,4-diones are formed effectively if diradical intermediates similar to [B] (Scheme 43) can be generated. Recently, photocyclization involving abstraction of formyl-hydrogens has received considerable attention. Formamide derivatives underwent photocyclization reaction involving intramolecular formyl-hydrogen abstraction to give four-membered imides[104)-106)] and amide[107)] (Scheme 44).

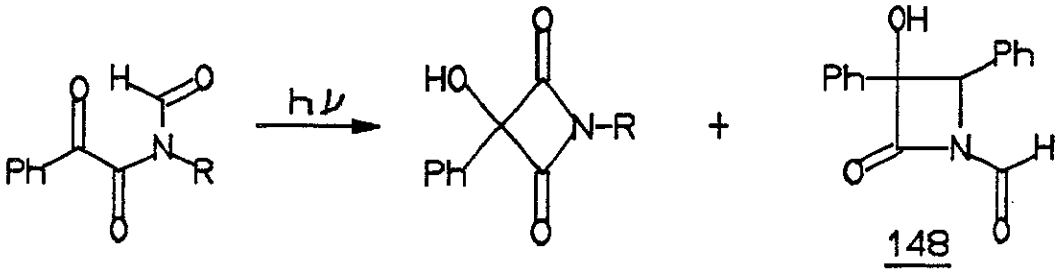


Scheme 44

In relation to the studies on photocyclization of α-ketoamides and α-ketoimides, the author investigated the photochemical synthesis of 3-hydroxyazetidine-2,4-diones involving photocyclization of N-formyl-α-ketoamides.

Irradiation of a benzene solution of N-formyl-N-methylbenzoylformamide (138) with a high pressure mercury lamp under argon gave a cyclization product, 3-hydroxy-1-methyl-3-phenylazetidine-2,4-dione (143) in 32% yield. When other N-formyl-α-ketoamides (139-142) were irradiated under the same conditions, the corresponding cyclic imides (144-147) were obtained. (Table 14) In the case of N-benzyl-N-formyl-α-ketoamide (141), an N-formyl-β-lactam (148) was obtained in 16% yield in addition to the azetidine-2,4-dione (146).

Table 14: Photolysis of N-Formyl-α-ketoamides



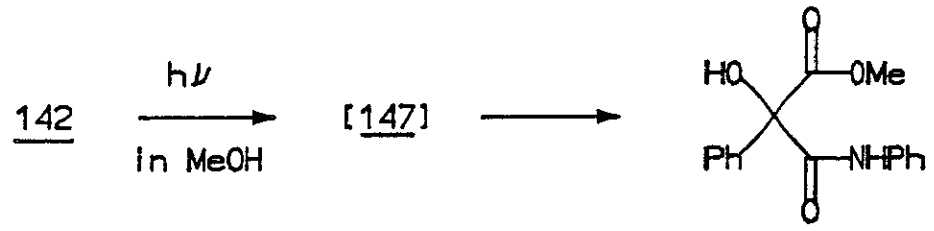
148

reactant No.	R	product No.	Yield (%) Benzene	t-Butanol
138	Me	143	32	63
139	Et	144	24	50
140	Pr^i	145	34	57
141	CH_2Ph	146	44 (16)[a]	56 (17)[a]
142	Ph	147	47	87

a: Yield of the β-lactam (148).

The structure of 145 was confirmed by the fact that benzoylation of 145 gave 3-benzoyloxy-1-isopropyl-3-phenylazetidine-2,4-dione (100) which was obtained by the photochemical reaction of 44. The structures of other photoproducts were determined by means of the spectral data and elemental analyses.

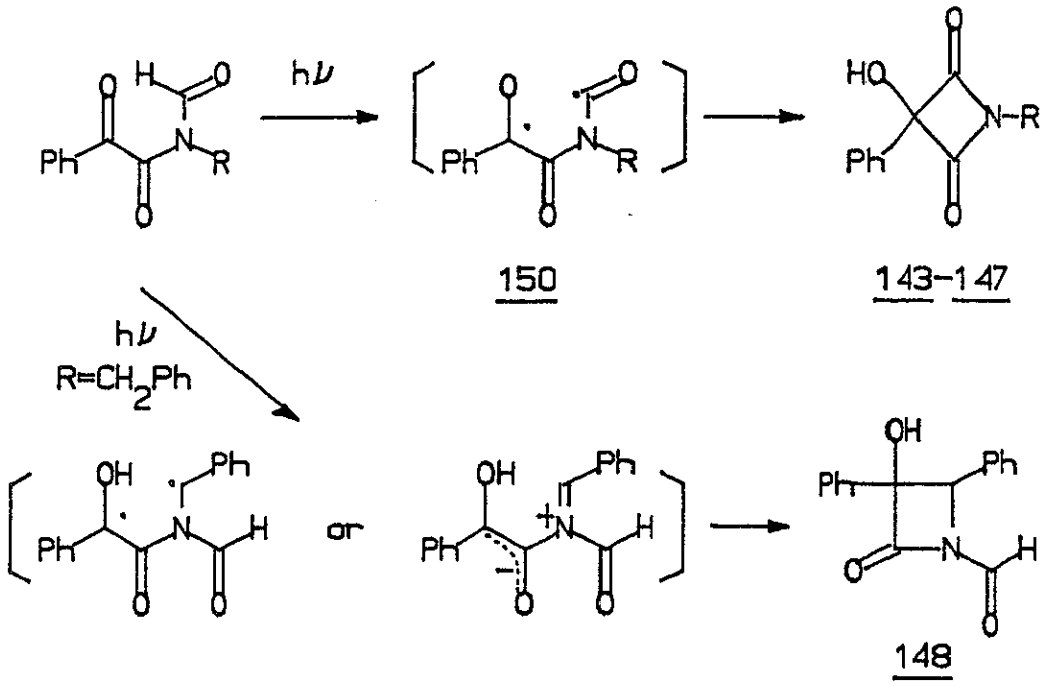
The use of tert-butyl alcohol as a solvent resulted in a significant increase of the yields of 143-147 as shown in Table 14, while photolysis of 142 in methyl alcohol gave the ring opening products (149) formed by methanolysis of 147 (Scheme 45).



149

Scheme 45

The formation of 3-hydroxyazetidine-2,4-diones is rationalized in terms of hydrogen abstraction by the ketone carbonyl from the formyl group and subsequent cyclization of the resulting 1,4-diradical (150), whereas the β-lactam is apparently formed via a diradical or zwitterion produced by benzylic hydrogen abstraction (Scheme 46). The photocyclization reaction of 141 was sensitized by 3-methoxyacetophenone (E_T=73 kcal/mol) but not by Michler's ketone (E_T=62 kcal/mol).[90] The quenching of the reaction by stilbene was inefficient. These results suggest that the cyclization involves a rapid triplet-state reaction, although a singlet-state reaction can not be excluded from the available data.

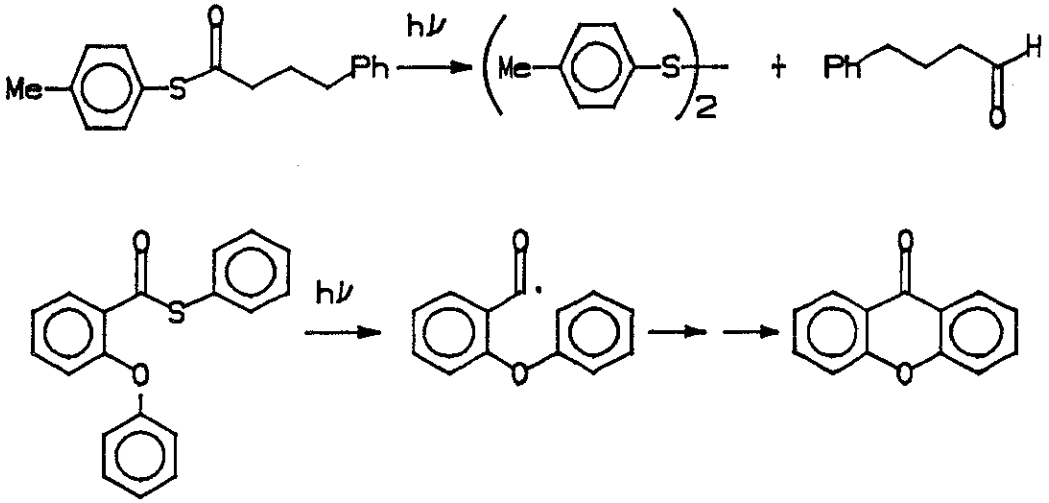


Scheme 46

In conclusion, photocyclization of N-formylbenzoylformamides gave 3-hydroxyazetidine-2,4-diones in good yields irrespective of the substituents on the nitrogen atom. The starting materials (138-142) can be easily obtained from N-substituted formamides and phenylglyoxalyl chloride. Further, the hydroxy group of 143-147 is easily acylated by a usual method as described above. Therefore, the present reaction provides a useful synthesis of azetidine-2,4-diones bearing various oxygen functions at the 3-position.

II-3-3. Photochemical Reactions of N-Phenylglyoxalyl-N-(phenylthiocarbonyl)amides.

It is well-known that many oxazolidine-2,4-dione derivatives are an important class as several members possess analgesic[108] and anti-epileptic[109] properties. On the other hand, thiol esters undergo cleavage of the C(=O)-S bonds on irradiation to produce acyl-thiyl radical pairs (Scheme 47). Similar photochemical reaction of phenol esters was also reported.[11)-13)]



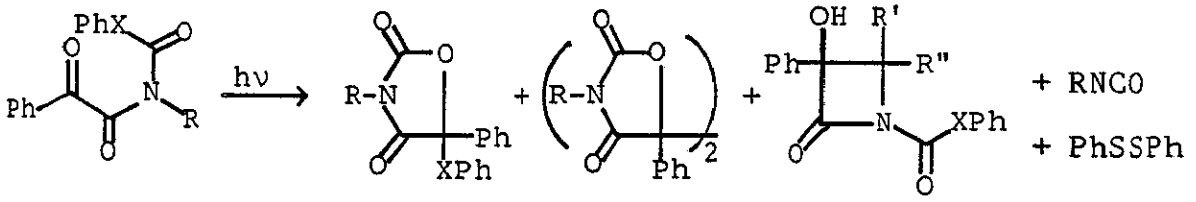
Scheme 47

It is expected that oxazolidine-2,4-diones are yielded if the radical [A] or [D] (Scheme 43) can be generated. The author investigated the photochemical reactions of N-phenylglyoxalyl-N-(phenylthiocabonyl)amides (152-156).

When N-phenylglyoxalyl-N-(phenylthiocarbonyl)anilide (152) in benzene was irradiated with a high pressure mercury lamp under argon, 3,5-diphenyl-5-phenylthiooxazolidine-2,4-dione (157) and phenylisocyanate were obtained in 53% and 40% respectively. The

structure of 157 was determined on the basis of elemental analysis and spectral data, in particular the close similarity of the IR spectrum to that of 3,5-diphenyloxazolidine-2,4-dione (118). Irradiation of 153 under the same conditions gave 158 accompanied by bis-5,5'-(3,5-diphenyloxazolidine-2,4-dione) (113) and p-tolyl isocyanate. In the case of N-alkyl compounds (154 and 155), β-lactams (163 and 164) (Type II cyclization products) were obtained in addition to oxazolidine-2,4-diones and isocyanates. In all cases described above, diphenyl disulfide was detected. Photolysis of a urethane (156) also afforded the cyclization products (161 and 112) (Table 15).

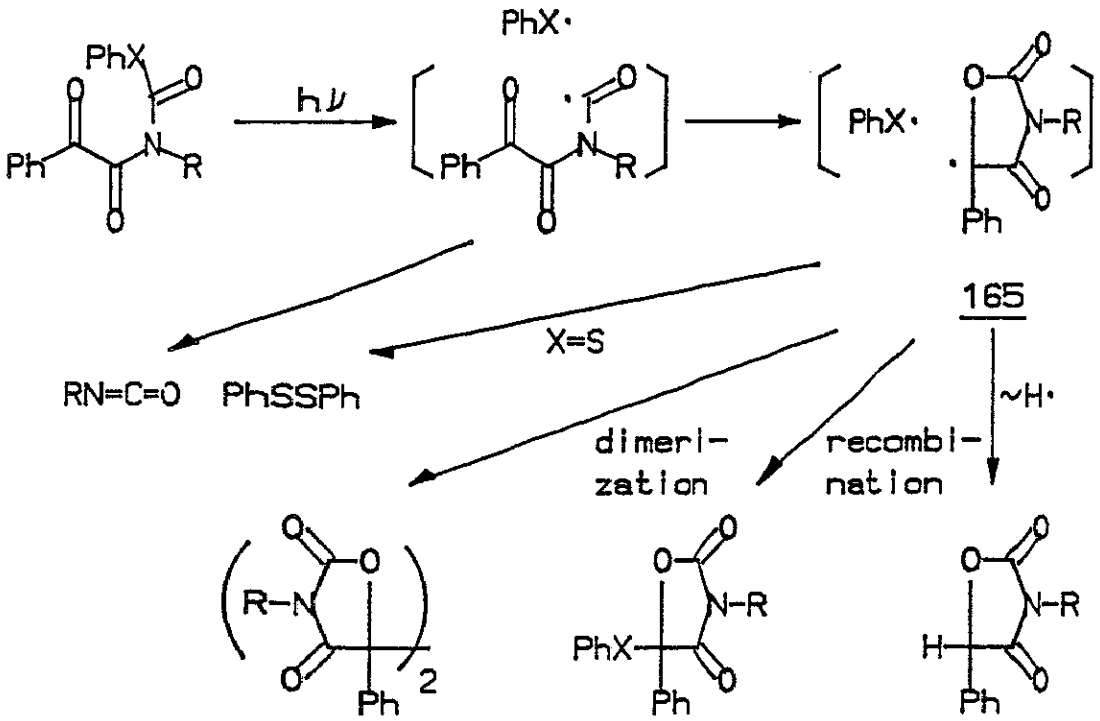
Table 15: Photolysis of 152-156



reactant			product								
No.	X	R	No.	Yield	No.	Yield	No.	R'	R''	Yield	RNCO[c]
152	S	Ph	157	53		a				--	40
153	S	p-MeC_6H_6	158	61	113	15				--	22
154	S	Pr^i	159	36	162	6	163	Me	Me	18	b
155	S	CH_2Ph	160	3		a	164	H	Ph	27	5
156	O	Ph	161	20	112	20				--	b

a:Not detected. b:Trace. c:Determined by GLC.

The formation of 157-160 is reasonably explained in terms of the cleavage of the C(=O)-S bond followed by cyclization of the acyl radical and recombination of the resulting cyclic radical (165) with the thiyl radical (Scheme 48). The formation of the dimeric products (112, 113, and 162) and the disulfide is consistent with the mechanism. Furthermore, when 153 was irradiated in benzene containg t-butyl mercaptan (a good hydrogen donor), 5-phenyl-3-(p-tolyl)oxazolidine-2,4-dione (119) was obtained in 15%. This fact strongly supported the intermediacy of the cyclic radical (165).



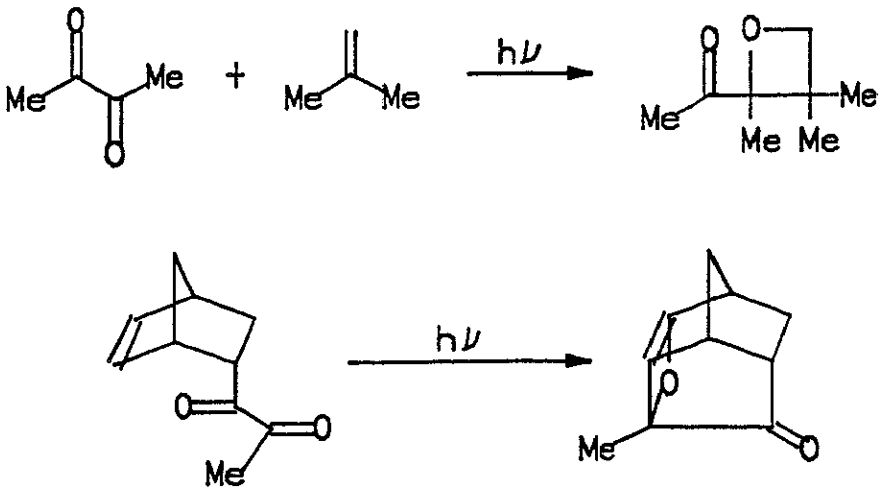
Scheme 48

Photocyclization involving 1,4-shift of phenylthio or phenoxy group is quite rare.[110)-112)] Furthermore, many oxazolidine-2,4-diones are pharmacollogically highly active, and the synthesis of these compounds has been extensively investi-

gated.[96] However, oxazolidine-2,4-diones possessing sulfur functions at 5-position are hitherto unknown to my best knowledge. Since the starting materials (152-156) can be easily prepared by benzoylformylation of the corresponding S-phenylthiocarbamates and O-phenylcarbamates, this photoreaction provides a useful synthetic method of some oxazolidine-2,4-diones.

II-3-4. Photochemical Reactions of N-Phenylglyoxalyl-α,β-unsaturated Amides

[2+2]Photocycloaddition of carbonyl compounds to olefins which give oxetanes are well-known as the Paterno-Büchi reaction, and these reactions are important synthetic methods for carbon-carbon bond formation. This process has been extensively studied from both a theoretical and an experimental points of view.[82),83)] In relation to the studies of the photochemistry of α-ketoamides and α-ketoimides, the author investigated intramolecular oxetane formation[114)-119)] of N-phenylglyoxalyl-α,β-unsaturated amide. The Paterno-Büchi reactions of α-diketones with electron rich olefins have been reported[120)-124)] (Scheme 49).

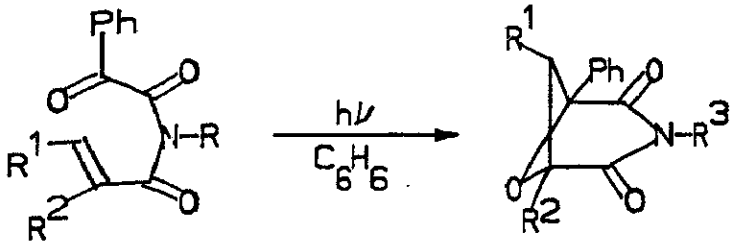


Scheme 49

Furtheremore, it is known that α-diketones do not undergo intermolecular [2+2] cycloaddition with electron deficient olefins.[125] This reaction is the first example of Paterno-Büchi reaction of α-dicarbonyl compounds with electron withdrawing olefins.

When N-benzoylformyl-N-methylmethacrylamide (166) was irradiated with a high pressure mercury lamp under argon, 3,5-dimethyl-1-phenyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (176) was obtained in 94% yield as a sole product. The structure of 176 was determined on the basis of elemental analysis and spectral data. The ^{13}C-NMR spectrum exhibited two singlet signals at 82.5 (s) and 84.5 (s) ppm assigned to C-5 and C-1. Especially, IR spectrum showed a characteristic absorptions at 1695 (s) and 1750 (m) cm^{-1} derived from six membered cyclic imides. IR spectra of six-membered imides containing two typical carbonyl streching bands at 1695-1710 (s) cm^{-1} and 1750-1775 (m) cm^{-1}, whereas in the five-membered imides both bands are 1715-1720 (s) cm^{-1} and 1775-1780 (m) cm^{-1}, respectively.[49] Therefore, the other possible structure, oxetane-fused five membered cyclic imide, could be excluded. Photolysis of other N-benzoylformylmethacrylamides (167-171) under the same conditions gave corresponding bicyclic imides (177-181) in excellent yields. Photolysis of crotonyl- and cinnamoyl derivatives (172 and 174) gave similar results and corresponding bicyclic imides (182 and 183) were obtained as mixtures of two stereoisomers (about 2:1) (Table 16). However, the imides (173 and 175) were inert to photolysis.

Table 16:Photolysis of 166-175



reactant No.	R^1	R^2	R^3	product No.	Yield (%)
166	H	Me	Me	176	94
167	H	Me	Et	177	89
168	H	Me	Pr^i	178	96
169	H	Me	CH_2Ph	179	>99
170	H	Me	p-MeC_6H_4	180	50
171	H	Me	2,6-$Me_2C_6H_3$	181	>99
172	Me	H	Pr^i	182	48
173	Me	H	p-MeC_6H_4		*a*
174	Ph	H	Pr^i	183	44
175	Ph	H	p-MeC_6H_4		*a*

a:Recovered.

Quantum yield measurement, sensitization and quenching experiments were carried out. N-Benzoylformyl-N-benzyl-methacrylamide (169) showed a UV spectrum at 214 nm (ε=15200), 257 nm (ε=12200), and 360 nm (ε=30). When the imide 169 was irradiated at the $n\pi^*$ band (>366 nm) selectively, the photo-reaction proceeded efficiently. The photoreaction of 169 to 179 was sensitized by benzophenone (E_T=69 kcal/mol). The addition of

trans-stilbene or piperylene did not lead to a significant quenching of the production of 179. These results suggest that the photocycloaddition proceeds from the $n\pi^*$ triplet state in the direct photolysis, although a fast singlet state reaction can not be excluded completely from the available data.

Quantum yields of 169, 170, and 171 (for the formation of 179, 180, and 181) were 0.56, 0.04, and 0.10, respectively. As in the case of the photoreactions of bisphenylglyoxalylimides, the difference of the conformations of imides may be one of the important factors controling the reactions of imides. When R^3 is less bulky as in the case of p-methylphenyl (aryl group on the nitrogen atom is perpendicular to the imide plane), Type B conformer is more stable than type A. On the contrary, bulky substituents (R^3=alkyl or 2,6-dimethylphenyl) on the nitrogen atom make Type A conformer more stable. Oxetane formation from Type A is more easier than from Type B (Figure 13). This difference of conformations reflects upon the differences on both chemical yields and quantum yields. Inertness of the photoreaction of 173 and 175 is also explainable in terms of the unfavorable conformation.

Two paths, path A and path B, for the formation of 176-183 are possible (Scheme 50). Path A is more reasonable than path B from the following reason. In the case of photolysis of 172 and 174, the corresponding bicyclic oxetanes (182 and 183) were obtained as mixtures of stereoisomers. Formation of the two stereoisomers via path B requires cis-trans isomerization of the starting material (172 and 174). However, this isomerization was found to be impossible as detailed below. The amide (172) was

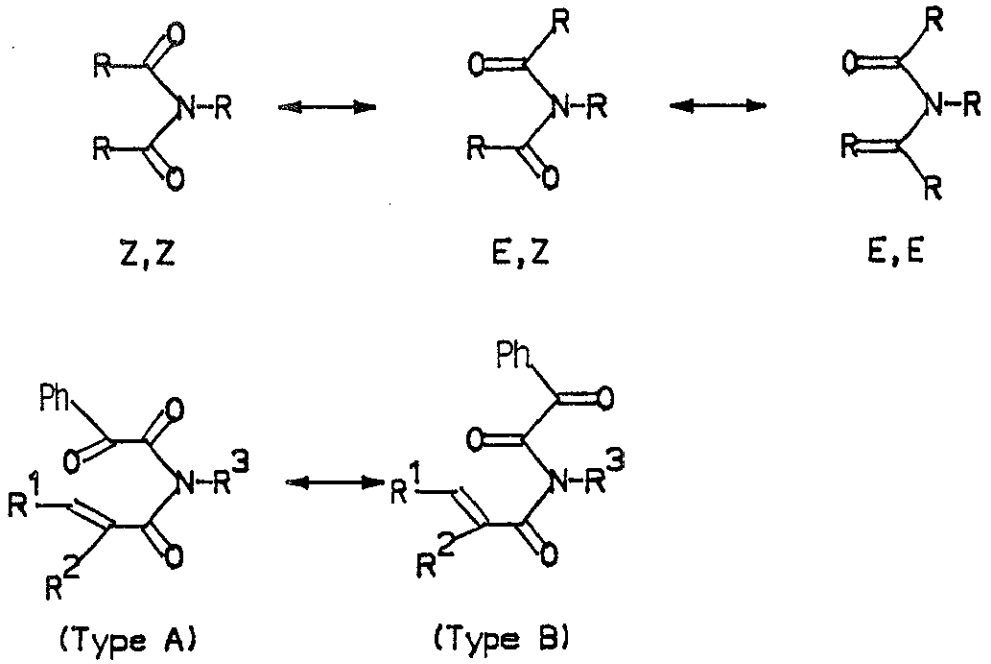
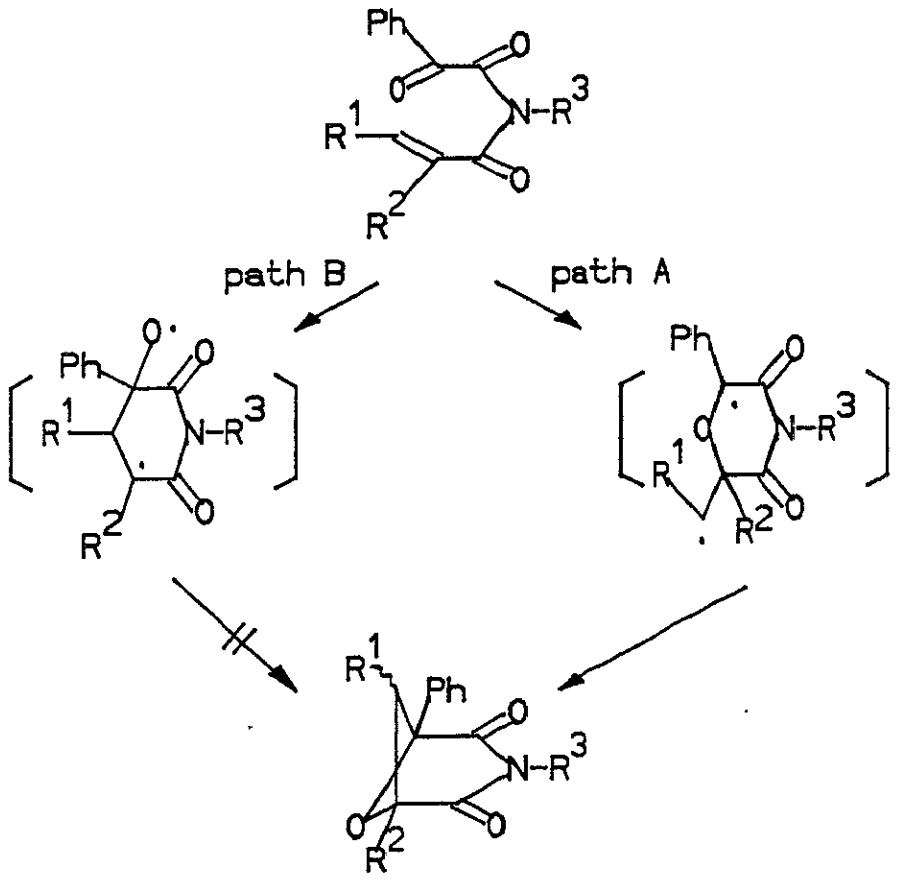


Figure 13



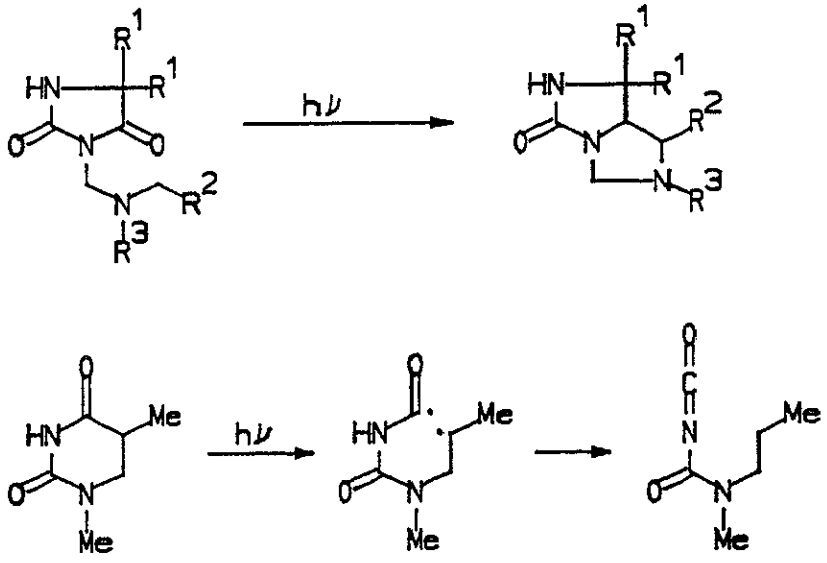
Scheme 50

irradiated in benzene to 50% conversion and ^{1}H-NMR of the reaction mixture was measured. There was no signals assignable to the cis isomer of 172. This fact supported the mechanism of path A because from path B 182 and 183 could not be obtained as mixtures of stereoisomers.

Electron deficient olefins, such as dimethyl maleate (fumarate), acrylonitrile, and other nitrile derivatives, gave oxetanes with ketones.[113] However, there is no example of the Paterno-Büchi reactions of methacrylic acid derivatives to our best knowledge. It is interesting that in the present reaction methacryl-, croton-, and cinnamamide moieties react efficiently with α-dicarbonyl moiety. Furthermore, this photochemical reaction provides the first example of Paterno-Büchi reactions of α-dicarbonyl compounds with electron poor olefins.

II-3-5. Photochemical Reactions of N',N'-Dialkyl-N-aroylureas

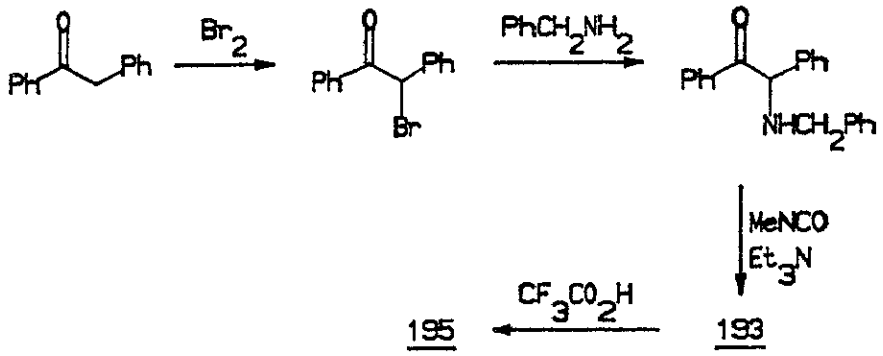
Amides are photochemically unreactive in comparison with ketones and esters and they usually do not undergo hydrogen abstraction,[126] whereas imides which have two carbonyl groups and one nitrogen atom exhibit photochemical reactivities similar to those of ketones.[28),34),104),127] This has been explained in terms of the difference between the π-electron donating effects on nitrogens of amides and those for imides.[104),127] Therefore, it is of interest to investigate the photochemical reactions of acyl or aroylureas which have two carbonyl groups and two nitrogen atoms. Although the photochemistry of these ureas has been scarcely studied, it was recently reported that five-membered cyclic acylureas (hydantoins) underwent intramolecular hydrogen abstraction when the reaction was facilitated by substituents (Scheme 51).[128)-130]



Scheme 51

The author investigated the photocyclization of acyclic aroylureas via intramolecular hydrogen abstraction by the aroyl carbonyl group.

N,N',N'-Trimethyl-N-benzoylurea (184) was unreactive toward photolysis, and irradiation of N',N'-diethyl-N-benzoyl-N-methylurea (185) gave an intractable mixture. On the other hand, when an N',N'-diisopropylurea (186) was irradiated in acetonitrile with a low pressure mercury lamp, 3,5,5-trimethyl-4-hydroxy-1-isopropyl-4-phenylimidazolidin-2-one (192) was obtained in 38% yield. The structure of 192 was determined on the basis of elemental analysis and spectral data. In the case of an N',N'-dibenzyl derivative (187), the product (193) was a mixture of two stereoisomers but they could not be completely purified because they underwent spontaneous dehydration gradually even at room temperature to give 4,5-diphenyl-1-benzyl-3-methyl-2-imidazolone (195) almost quantitatively. The structure of 195 was confirmed by the independent synthesis (Scheme 52).[131]

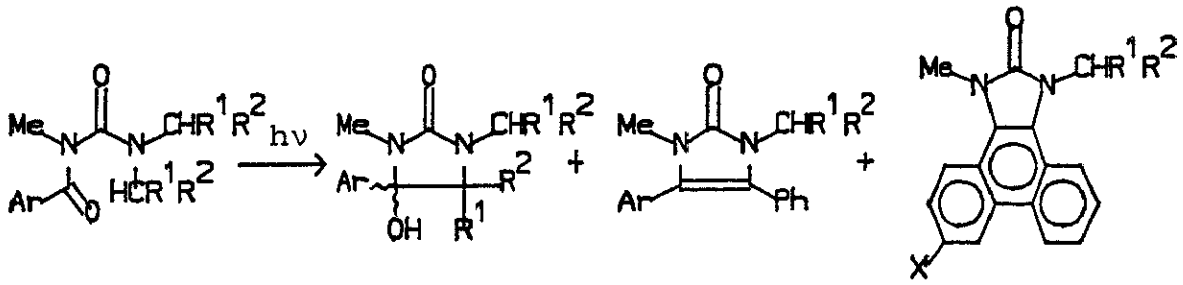


Scheme 52

Photolysis of N',N'-dibenzyl-N-(4-cyanobenzyl)-N-methylurea (188) gave a similar result. In the case of 4-methoxybenzyl and 4-chlorobenzyl derivatives (189 and 190), the dehydration took

place during irradiation, and the imidazolone (197 and 198) and phenanthrene derivatives (199 and 200) were obtained (Table 17). Meanwhile, a 2-naphthoyl derivative (191) was inert toward photolysis.

Table 17: Photolysis of N-Aroylureas

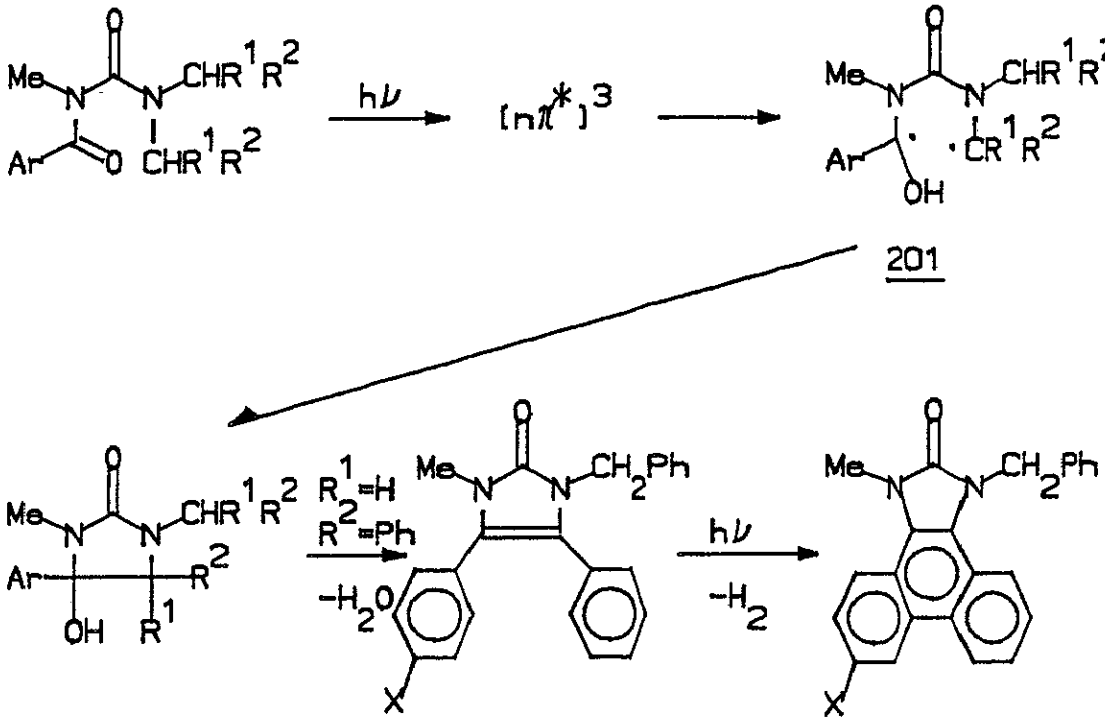


No.	Ar	R^1	R^2	No.	Yield	No.	Yield	No.	Yield
184	Ph	H	H		a		—		—
185	Ph	H	Me		a		—		—
186	Ph	Me	Me	192	38		—		—
187	Ph	H	Ph	193	77	195	0		0
188	4-ClPh	H	Ph	194	35	196	0		0
189	4-MeOPh	H	Ph		0	197	55	199	13
190	4-ClPh	H	Ph		0	198	57	200	10
191	2-Naphtyl	H	Ph		a		—		—

a:Recovered

The formation of the imidazolidinone (192-194) is easily explained in terms of δ-hydrogen abstraction by the aroyl carbonyl group via seven-membered cyclic transition states followed by cyclization of the resulting 1,5-diradical (201).

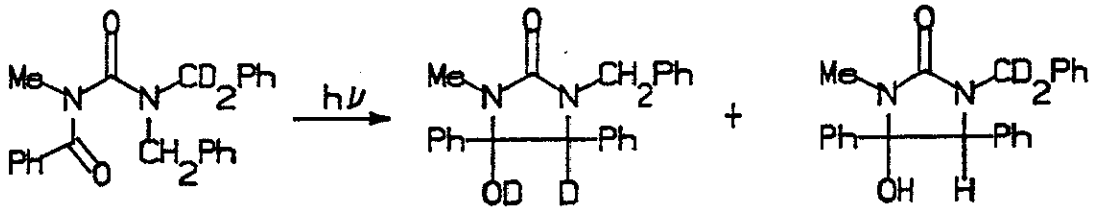
The phenanthrene derivatives (199-200) are apparently formed by dehydrocyclizations of 197 and 198 as in the case of the photochemical conversion of stilbenes to phenanthrenes.[132] This was confirmed by the fact that 199 was produced on irradiation of 197 (Scheme 53).



Scheme 53

It may be conceivable that the formation of 186-188 from 192-194 involves sequential electron-proton transfer rather than one-step hydrogen transfer since it is known that imides bearing nitrogen-containing substituents undergo electron transfer on irradiation.[34] However, this mechanism is improbable because of the following reasons. The photoreaction of 187 was effectively quenched by 1,3-pentadiene, while intramolecular photoreactions via electron transfer are usually unquenchable.[133] The deuterium isotope effects (Φ_H/Φ_D=4.3) measured by using 187-d_2 were also inconsistent with the electron transfer mechanism

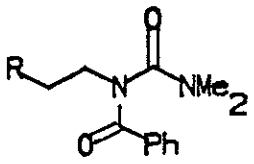
because the isotope effects in photoreactions via electron-proton transfer are usually quite small (<2)[135),136)] (Scheme 54).



187-d_2 193-d_2 193-d_2'

Scheme 54

Thus, the photoreaction of 186-190 is most reasonably explained in terms of usual hydrogen abstraction from the $n\pi^*$ triplet states. The inertness of the naphthoyl derivative (191) is also consistent with the hydrogen transfer mechanism.[83),137),138)] The nonreactivity of 184 is explainable by the strong bond-strength of the methyl C-H bonds.[137),138)]



202 R=Ph
203 R=OMe

Figure 14

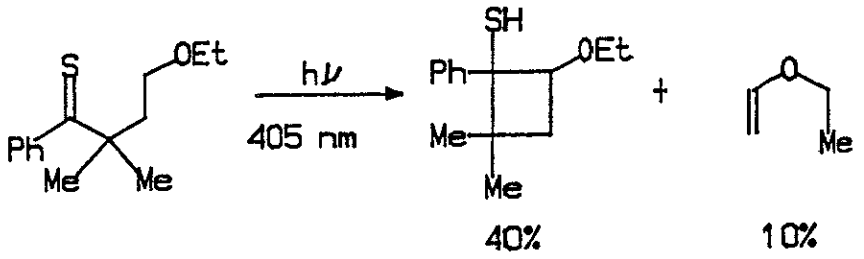
Finally, photolysis of N',N'-dimethyl-N-benzoyl-N-(2-phenylethyl)urea (202) and N-methoxyethylurea (203) was examined. these ureas were expected to undergo γ-hydrogen abstraction by the benzoyl group (Type II photoprocess) since γ-hydrogen abstraction is sterically more favorable than δ-hydrogen abstraction. Contrary to the explanation, the photoreactions of 202 and 203

was sluggish, and the prolonged irradiation resulted in the formation of an intractable mixture. The lower reactivity of 202-203 might be attributable to the fact that the activation of the γ-hydrogens by phenyl or methoxy group is significantly weaker than that of δ-hydrogens of 186-190, where the δ-hydrogens are activated toward abstraction by both the phenyl group and amide nitrogen.

The results of photoreactions of these acyclic aroylureas together with those of five-membered cyclic acylureas lead to the conclusion that these ureas undergo photochemical hydrogen abstraction as imides but their reactivities are much lower than those of imides.

II-4. PHOTOCHEMICAL REACTIONS OF THIOIMIDES

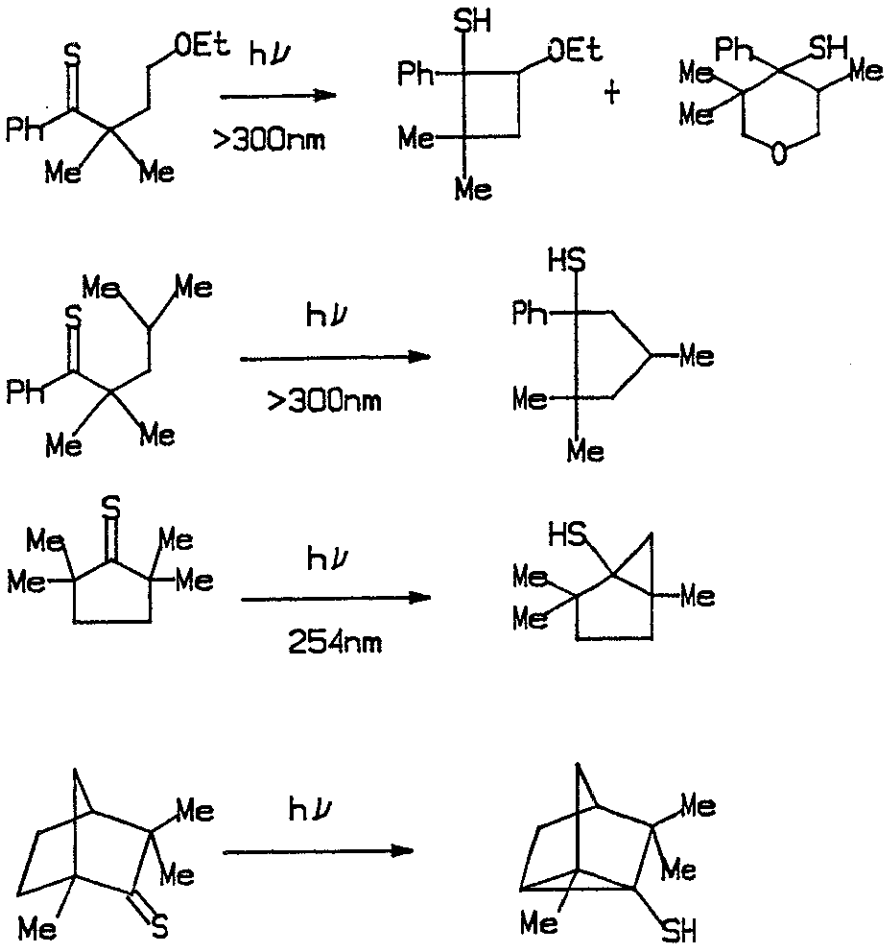
Thioketones undergo photoreactions analogous to ketones, e.g., hydrogen abstraction, cycloaddition.[139] These compounds undergo photoreactions from two distinct excited states. t-Alkylphenylthiones undergo intramolecular hydrogen abstractions following excitation. Irradiation in the visible region produces the lowest, $n\pi^*$ triplet, which reacts only with activated C-H bonds.[140),141] In particular, γ-hydrogen abstraction leads to cyclobutanethiols (Scheme 55).



Scheme 55

When the same alkoxythione is irradiated in the ultraviolet region into its second excited singlet, an additional product corresponds to ε-hydrogen abstraction; both products apparently are formed from the same long-lived, high energy π,π^* singlet. Aralkylthio ketones without heteroatoms in their alkyl chain undergo primary δ-hydrogen abstraction when irradiated into their second singlet[140),141] and provide useful syntheses of cyclopentanethiols.[142] δ-Hydrogen abstraction is preferred over γ-hydrogen abstraction, even when the γC-H bonds are far weaker. It has been proposed that conformational preferences vary from that displayed by n,π^* states because the unpaired-electron density is entirely in the π system above the carbonyl.[140),141]

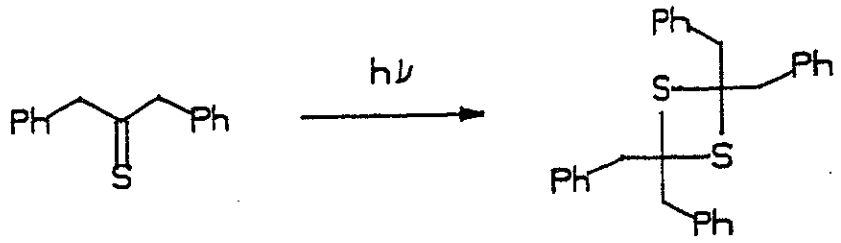
Cyclizations from excited thiocarbonyl groups are known which may give three-, four-, five-, or six-membered rings[139] (Scheme 56).



Scheme 56

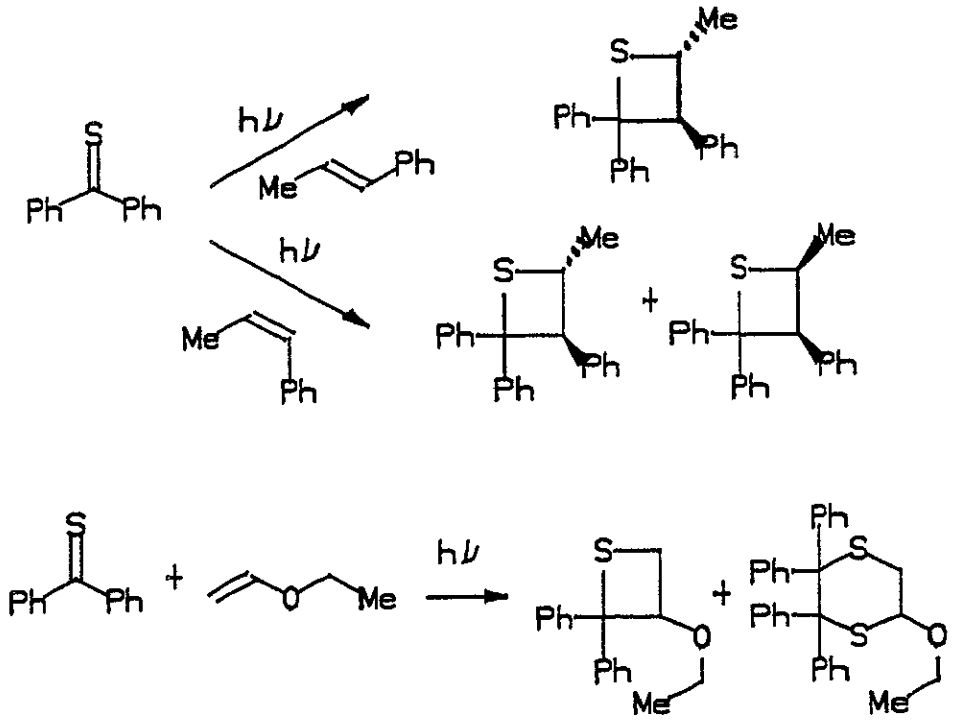
There is a rich variety of photochemical cycloaddition involving a thiocarbonyl compound and an added with a multiple bond, and because a greater range of sulfur than of oxygen four-membered heterocycles are stable, the scope of the reaction is wider for thiocarbonyl than for carbonyl substrates. Some thioketones undergo photodimerization when irradiated alone, to give 1,3-diphenylpropane-2-thione (Scheme 57).[143)-145)]

Thiobenzophenone (and other aromatic thiones) reacts readily with electron-rich alkanes (those carrying alkyl, aryl, alkoxy or



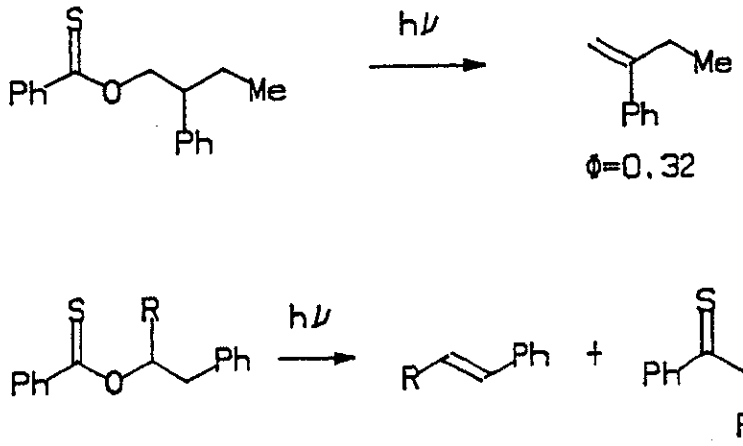
Scheme 57

alkylthio substituents) on long-wavelength irradiation to give thietanes and/or 1,4-dithianes. The reaction with 1-phenylpropane shows the regioselective but nonstereoselective nature of the process,[146] and that with ethyl vinyl ether shows the formation of dithiane product as well as the orientational preference.[147] The divergence of pathways between thietane and 1,4-dithiane arises because the intermediate biradical can be trapped by a molecule of ground-state thioketone (Scheme 58).



Scheme 58

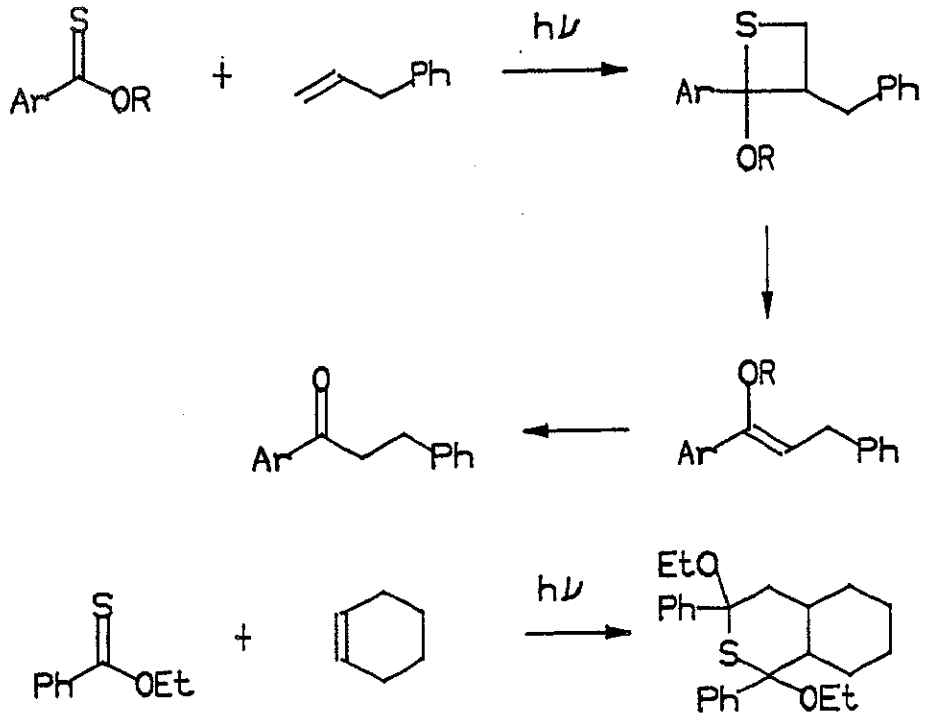
Reactions analogous to the Norrish Type II photoelimination of alkyl benzoates are observed with O-alkyl thiobenzoates.[148] This can provides a useful route for the dehydration of homo-allylic alcohols to give dienes under mild conditions, including steroidal compounds such as cholesterol.[149] Simpler O-alkyl thiobenzoates give reasonable yields of alkenes in many cases, and the quantum yields can be high.[150] With some substituent patterns a competing process becomes important, that leads by way of a ring-closed oxetane-2-thiol to a β-hydroxythio-ketone (Scheme 59).[151),152]



Scheme 59

Among the derivatives of thiocarboxylic acids, O-alkylthio-esters can give 2-alkoxythietanes or 2,4-dialkyldithianes, but often the alkoxythietane undergoes (sensitized) cleavage under the reaction conditions to give an enol ether that provides a ketone on work-up (Scheme 60).[153)-156]

Thioketones and thioesters exhibit a various photochemistry that is in some respects analogous to that of their oxygen analogues, but which also shows significant differences. It is known that thioparabanate and thioamide undergo [2+2] thietane

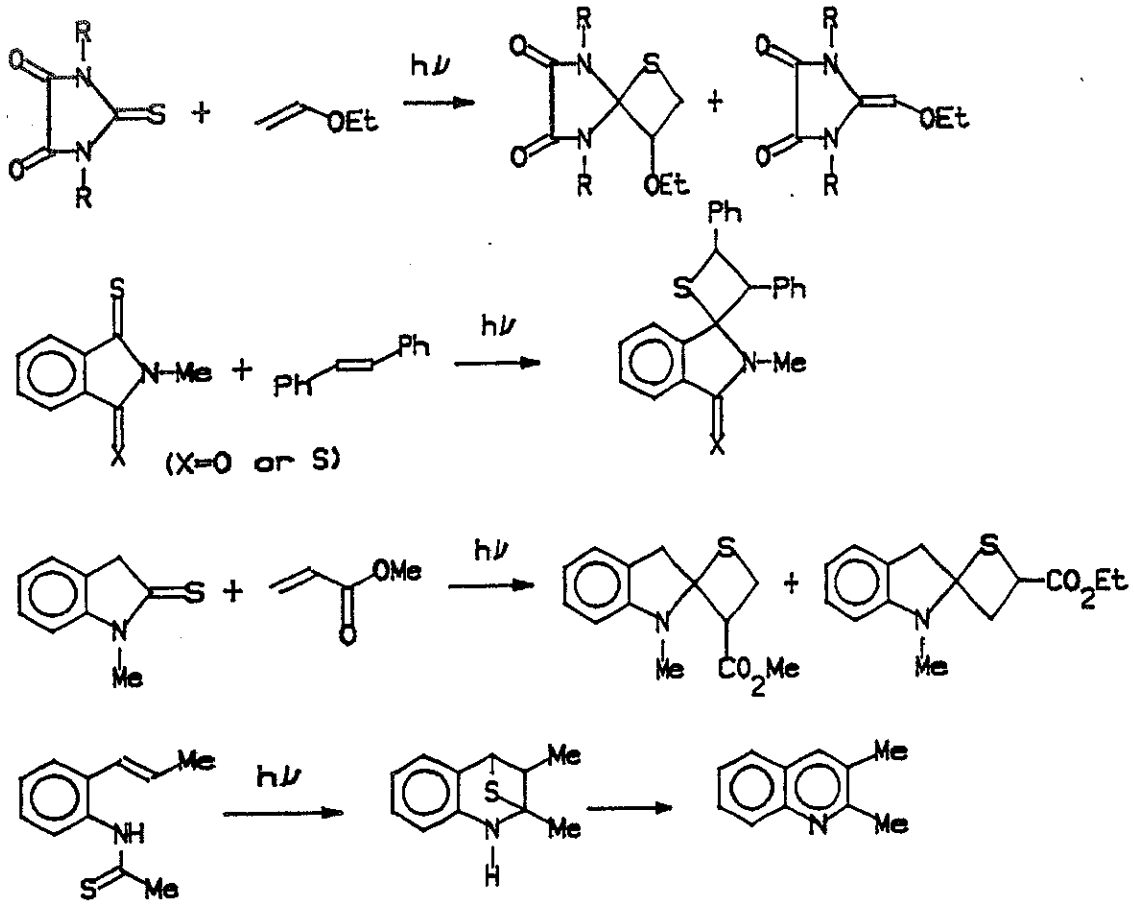


Scheme 60

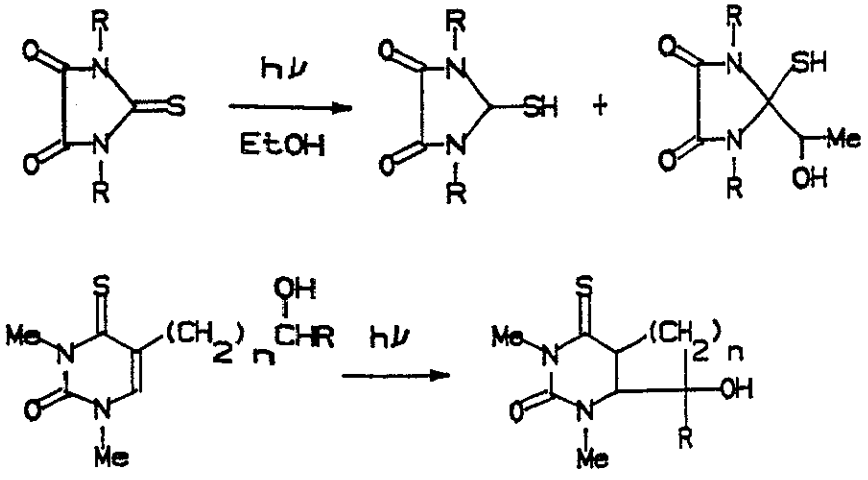
formation reaction.[157)-162)] Kanaoka et al. reported that various aliphatic and aromatic di- and monocyclic thioimides underwent intermolecularly efficient photocycloaddition with olefins to afford the imide-thietanes (Scheme 61).[163-167)]

Hydrogen abstraction reaction of thiocarbonyl-nitrogen systems are little known except for thioparabanate[168)] and thiouracil derivatives[169)] to my best knowledge (Scheme 62).

All of the studies of thioimides dealt with cyclic thioimide systems, and there is no report for the photochemical reactions of acyclic or semicyclic thioimide systems. The author found that the photochemical reactions of acyclic thioimides and semicyclic thioimides provides the useful synthetic methods of β-lactams and other lactams. Acyclic imides show different photochemical behavior to that of cyclic imides. It is interesting to



Scheme 61

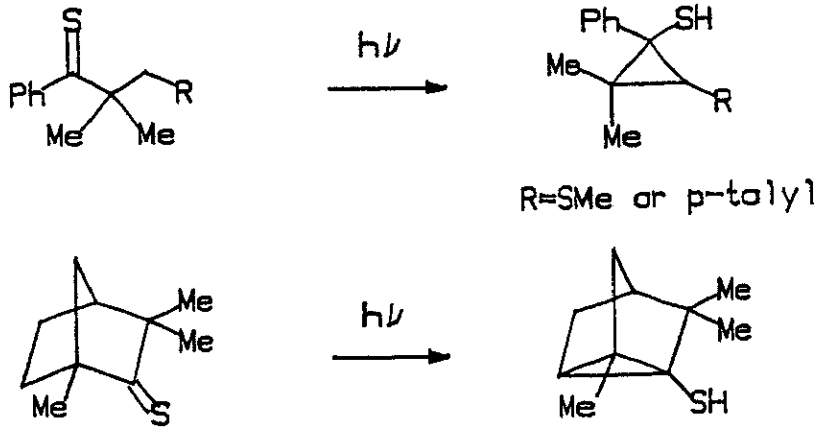


Scheme 62

compare the photochemical reactions of cyclic thioimides and ope chain thioimides.

II-4-1. Photochemical Reactions of Acyclic Monothioimides. A Novel Photorearrangement involving 1,2-Thiobenzoyl Shift via β-Hydrogen Abstraction of Thioimides

Although the photoreactions of thioketones and thioesters are well studied, those of thioimides have not been reported except for [2+2] cycloaddition of cyclic thioimides with olefins.[163)-167)] β-Hydrogen abstraction appears to be rare occurance in carbonyl photochemistry, giving precedence to the Norrish Type II, intermolecular hydrogen abstraction, or simply other photochemical reactions. Although a few instances of β-hydrogen abstraction of thioketones have been reported[170)-172)] (Scheme 63). They are limitted to thiones where only β-hydrogens are abstractable or β-hydrogens are strongly activated by substituents. The author investigated the photochemical β-hydrogen abstraction of acyclic monothioimides.



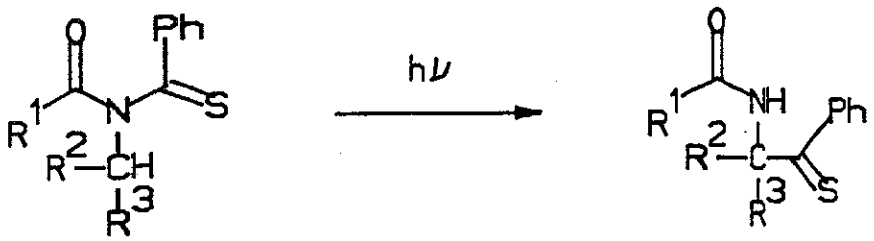
Scheme 63

The monothioimides (204-210) were obtained almost quantitatively by acylation of the corresponding N-alkylthiobenzamides.

The structure of these compounds was determined by the elemental analyses and spectral data. The visible spectrum of the monothioimide (204) in n-hexane showed a maximum at 456 nm (ε=160) assignable to $n\pi^*$ band of the thiocarbonyl group. Irradiation of N-isopropyl-N-benzoylthiobenzamide (204) in benzene with a high pressure mercury lamp under argon gave α-(benzoylamino)thioisobutyrophenone (211) in 62% yield. The structure of 211 was determined by the elemental analysis and spectral data. The IR spectrum (KBr) exhibited absorptions at 3260 (NH), 1630 (C=O), 1525 [C(=O)NH], and 1055 cm^{-1} (C=S). The mass spectrum showed the molecular peak at m/z 283 (M^+), and fragment peaks at m/e 187 (M-PhC=O), 163 [PhC(=S)C$(CH_3)_2$], 162 (M-PhC=S), 121 (PhC=S), and 105 (PhC=O). The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ 1.90 (s, 6H, 2*CH_3), 7.2-7.5 (m, 8H, Ph), 7.6-7.8 (m, 2H, Ph), and 7.9 (br, 1H, NH). The ^{13}C-NMR exhibited signals at δ 27.8 (q), 68.5 (s), 125.9 (d), 126.9 (d), 127.5 (d), 128.4 (d), 129.2 (d), 131.4 (d), 135.2 (s), 141.8 (s), 166.2 (s), and 255.6 (s). Furthermore, the visible spectrum of (211) showed a maximum at 524 nm (ε=90) assignable to the $n\pi^*$ band of thioketone moiety. Photolysis of other thioimides under the same conditions also gave the corresponding thioketones (211-216) in good yields (Table 18). Although photolysis of 209 also gave the thioketone (216) in 43% yield, this compound was unstable and decomposed gradually even at room temperature. The photoreaction of 210 was much slower than that of other monothioimides 204-209, and prolonged irradiation gave an intractable mixture.

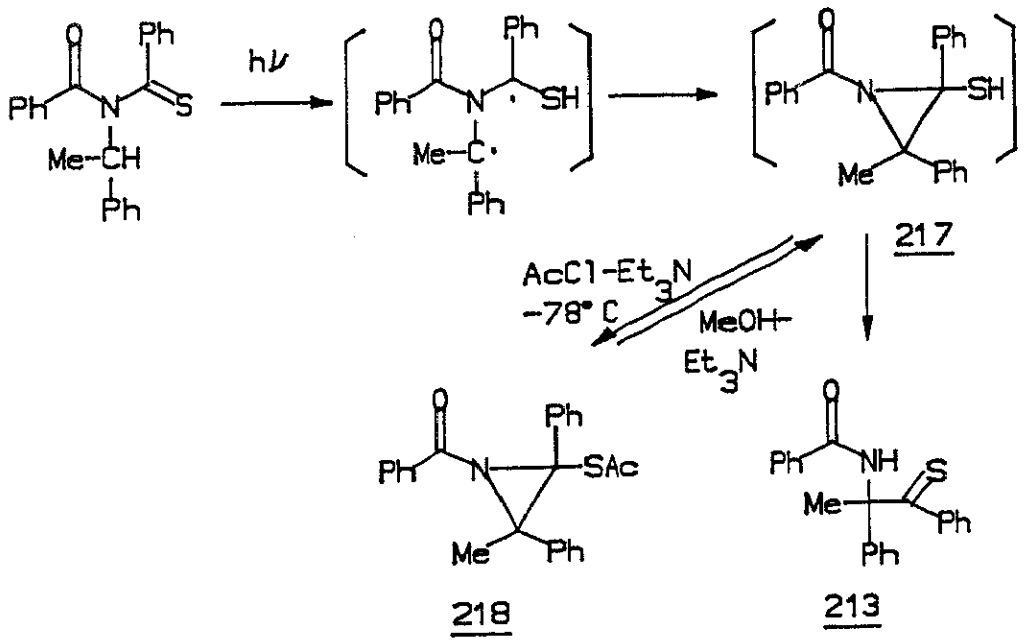
The formation of the thioketones (211-216) is reasonably explained in terms of ring opening of an aziridine (217), which

Table 18: Photolysis of Monothioimides



reactant No.	R^1	R^2	R^3	product No.	Yield (%)
204	Ph	Me	Me	211	62
205	Ph	Me	Et	212	80
206	Ph	Me	Ph	213	98
207	Me	Me	Me	214	64
208	Me	Me	Ph	215	95
209	Ph	H	Ph	216	43
210	Ph	H	Pr^i		0

is produced by cyclization of 1,3-diradical (Scheme 64). The intermediacy of 217 was confirmed by the following experiments. Irradiation of 206 in toluene at -78°C resulted in the loss of the red color. On warming to the room temperature, the colorless solution turned purple and 213 was obtained as a main product. This finding indicated the presence of an intermediate that did not possess a thiobenzoyl moiety. When the colorless solution obtained in the low temperature photolysis was treated with acetyl chloride in the presence of triethylamine at -78°C, 2,3-diphenyl-2-(acetylthio)-1-benzoyl-3-methylaziridine (218, 85%) was obtained, accompanied by a small amount of 213 (9%).



Scheme 64

The structure of 218 was assigned on the basis of elemental analysis and spectral data. The IR spectrum (KBr) exhibited carbonyl frequencies at 1705 and 1660 cm^{-1}. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ 1.14 (s, 3H, CH_3), 2.01 [s, 3H, $C(=O)CH_3$], 7.3-7.8 (m, 13H, Ph), and 8.1-8.2 (m, 2H, Ph), and ^{13}C-NMR exhibited resonances at 26.3 (q), 31.3 (q), 80.6 (s), 104.7 (s), 126.6 (d), 127.7 (d), 128.0 (d), 128.5 (d), 128.6 (d), 131.9 (s), 139.0 (s), 140.0 (s), 161.6 (s), and 191.8 (s) ppm. The mass spectrum showed molecular ion at m/z 387 (M^+) and fragment peaks at m/e 312 [M-SC(=O)Me], and 207 [M-SC(=O)Me-Ph(=O)]. Furthermore, the fact that the base-catalyzed methanolysis (MeOH-NEt_3) of 218 gives 213 almost quantitatively is also consistent with the mechanism (Scheme 64).

In conclusion Photolysis of N-acylthiobenzamides gave thioketones via a novel photorearrangement involving 1,2-thiobenzoyl shift via β-hydrogen abstraction by the thiocarbonyl

group. The present photorearrangement involving unprecedented 1,2-thiobenzoyl shift provides the first example of β-hydrogen abstraction of thioimides.

II-4-2. A New Synthesis of β-Lactams via Photochemical γ-Hydrogen Abstraction of Monothioimides

Synthesis of β-lactam compounds has been of continuing interest for many years because of the medical importance of penicillin and cephalosporin antibiotics. Much effort has been put into the preparation of simple β-lactams for testing as antibiotics, antidepresents, antisedatives[173] (Figure 15).

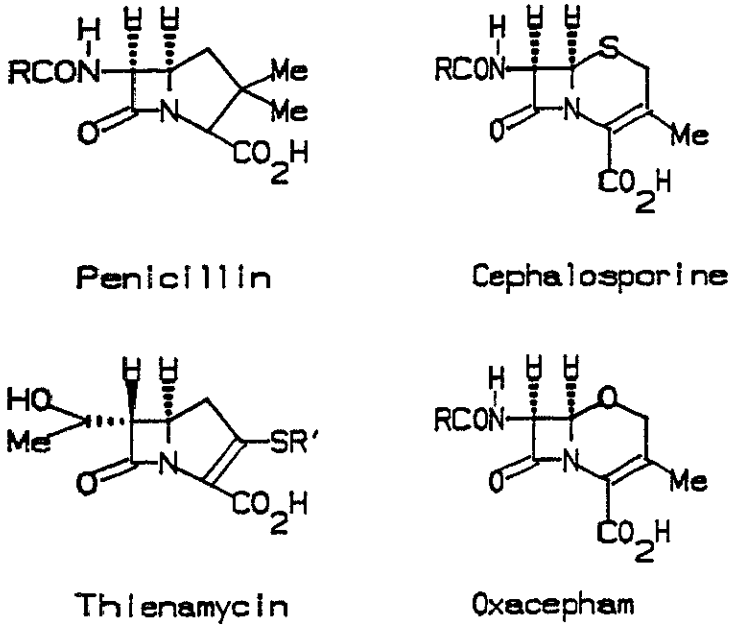


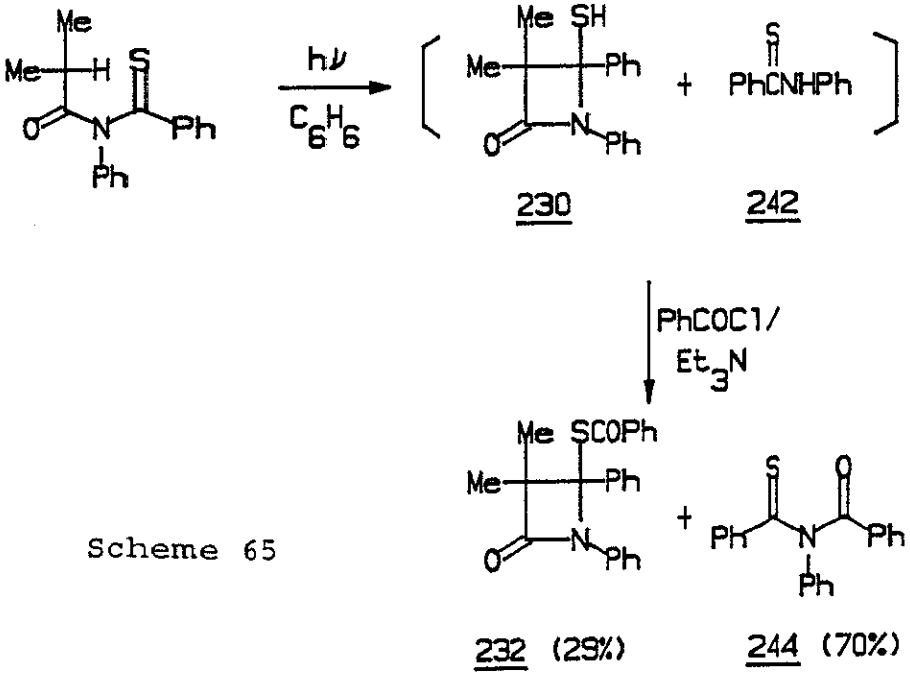
Figure 15

Syntheses involving photochemical reactions have been reported, most of them involving hydrogen abstraction,[174)-176)] ring contraction,[177)-182)] electro-cyclization,[183)-187)] or the rearrangement of diazo compounds.[188)-192)] Other photochemical reactions[193)-200)] have been used to synthesize a variety of β-lactam structures.

The author investigated the new synthesis of β-lactams involving

photochemical β-hydrogen abstraction of monothioimides.

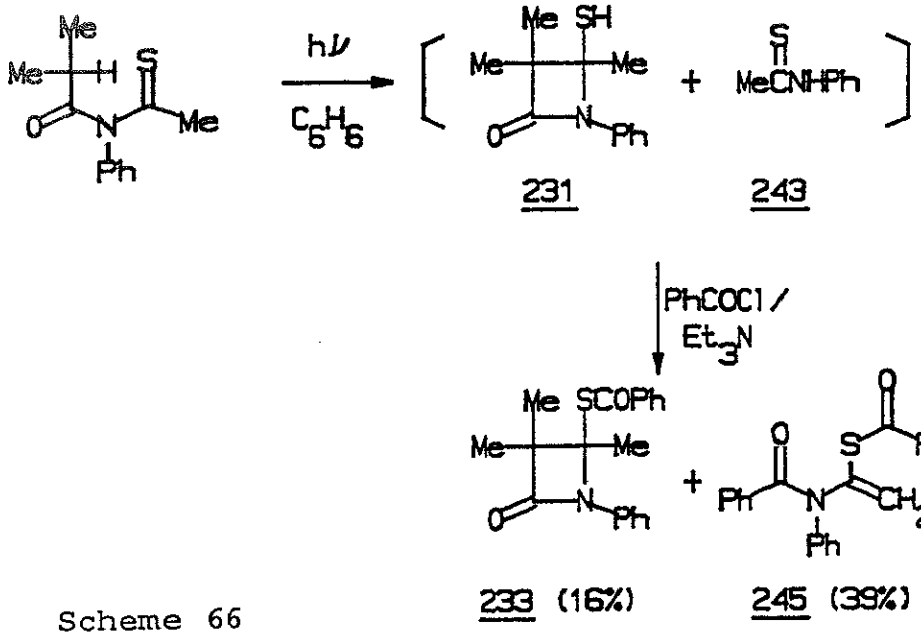
When N-isobutyroyl-N-phenylthiobenzamide (219) was irradiated with a 1000-W high pressure mercury lamp in benzene under argon, IR and NMR spectra of the reaction mixture indicated the formation of β-lactam (230) and thiobenzamide (242). The β-lactam was too unstable to isolate as such. Benzoylation of the reaction mixture with benzoyl chloride and triethylamine gave S-benzoyl β-lactam (232) in 29 % and N-thiobenzoylbenzanilide (244) in 70 %. The formation of 244 was reasonably explained in terms of benzoylation of 242 which was produced by Type II cleavage of 219 (Scheme 65).



Scheme 65

Photolysis of the monothioimide (220) followed by benzoylation gave the β-lactam (233) in 16 % and 245 in 39 %. The formation of 245 from 243 was confirmed by the fact that 245 was independently synthesized from 243 by benzoylation.

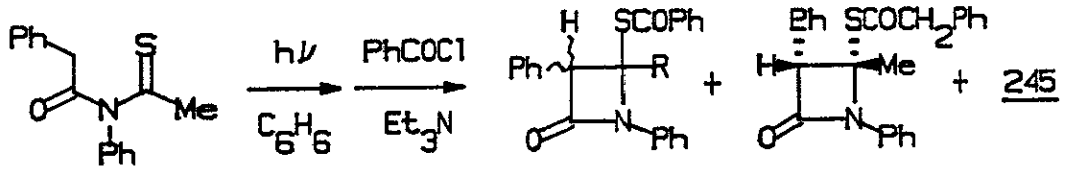
In the case of 221, in the same conditions, S-benzoyl β-lactams (234, about 1:1 mixture of stereoisomers), S-phenylacetyl



231 243

233 (16%) 245 (39%)

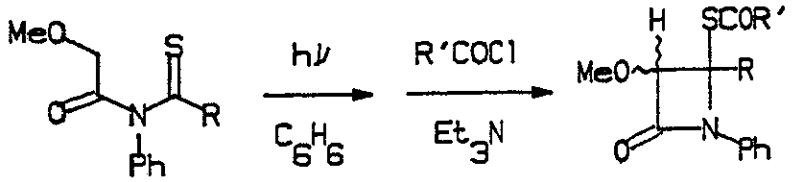
Scheme 66



234 (35%) 235 (13%) 245 (17%)

Scheme 67

β-lactam (235), and 245 were obtained in 35%, 13%, 17 %, respectively (Scheme 67). Photolysis of methoxy acetyl derivative (222) gave β-lactam (236) in high yield (76%) in the same manner. In this case, only cis isomer was obtained. Photolysis of 223 followed by acetylation with acetyl chloride and triethyamine gave S-acetyl β-lactam 239 as a mixture of two stereoisomers (cis, 63% : trans, 27%) in 90 % yield (Scheme 68).



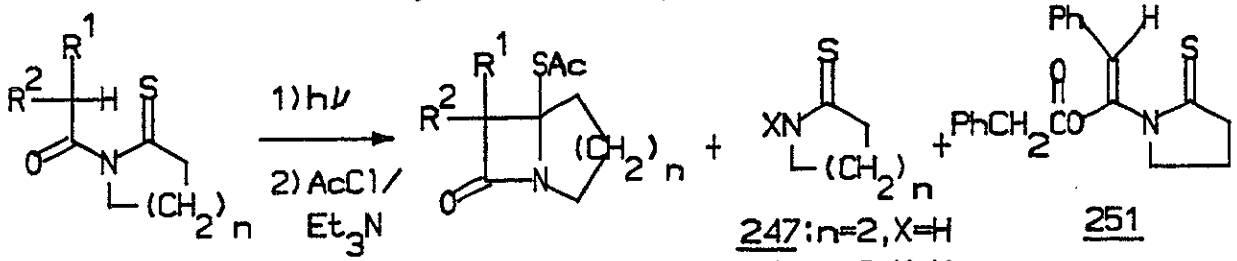
222: R=Me
223: R=Ph

236: R=Me, R'=Ph (76%)
237: R=Ph, R'=Me (90%)

Scheme 68

Next the author tried to synthesize bicyclic β-lactams via photochemical reaction of semicyclic monothioimides. Photolysis of five-membered semicyclic monothioimides 224 and 225 mainly undergo Type II cleavage process to produce pyrrolidine-2-thione (251) though that of 225 gave 251 (51%) accompanied by 246 (47%). When N-isobutyroly-piperidin-2-thione (226) was irradiated in benzene and the product was acetylated, an S-acetyl bicyclic β-lactam (238) was obtained in 21% yield along with a Type II cleavage product, N-acetylpiperidin-2-thione (249), in 39%. Photolysis of other semicyclic monothioimides (227-229) under the same conditions gave the corresponding β-lactams (Table 19). In the case of methoxy acetyl derivatives (227 and 229), only cis isomers (239 and 241) were obtained.

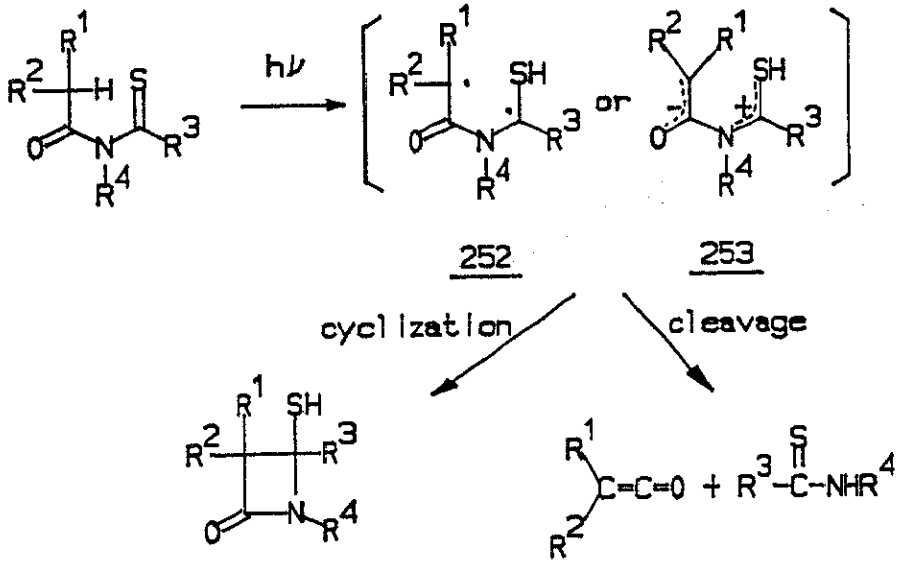
Table 19: Photolysis of Semicyclic Monothioimides



reactant				product						
No.	n	R^1	R^2	No.	Yield (%)		No.	X	n	Yield (%)
224	1	Me	Me		*a*		246	H	1	71
225	1	Ph	H		*a*		246	H	1	47 (51)[c]
226	2	Me	Me	238	21		249	Ac	2	39
227	2	MeO	H	239	49 (cis)		249	Ac	2	*b*
228	3	Me	Me	240	34		250	Ac	3	22
229	3	MeO	H	241	82 (cis)		250	Ac	3	9

a: Not detected. *b*: Trace. *c*: Yield of 251

The reaction of the monothioimides (219-229) is explainable in terms of the Type II process. The intermediacy of the zwitterion (252) is postulated because of the following reason (Scheme 69). In Chapter II-2, the author described the photochemical reaction of α-ketoamides (24) which gave β-lactams (26) and oxazolidinones (25) via zwitterionic intermediate (32) (Scheme 31). Zwitterion (253) quite resembles to 32. Zwitterion (253) may be more stable than 32 because of the sulfur atom attached at the cationic center. The formation of the ketenes (Type II cleavage products) was supported by the fact that S-phenyl-acetyl β-lactam (237) was obtained in the photolysis of 221 and 251 in the case of that of 225 (Scheme 69). As for the formation of 242, 243, and 246-248, direct homolysis of C-N bond of monothioimide (219-229) could not be excluded.



Scheme 69

Furthermore, the fact that stereo selective reaction proceeds in the case of N-methoxy acetyl derivatives (252 and 253) is explainable in terms of the hydrogen bond between the methoxy-oxygen and the mercapto group (Figure 16).

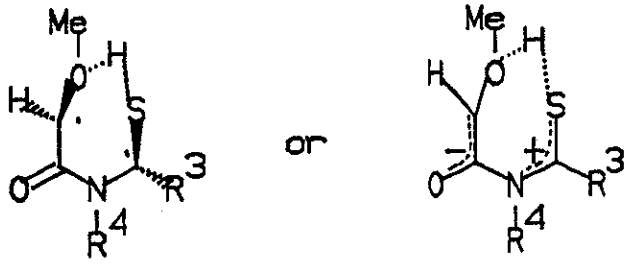


Figure 16

In the present reaction, Type II cyclization occurred as the main process. On the other hand, Mazzocchi et al. reported the photochemistry of acyclic imides,[28] in which the imides undergo type II eliminations across the imide moiety in addition to those on the C-alkyl chain and α-cleavage reaction. There is no satisfactory idea to explain the differences of photochemical behavior between acyclic imides and acyclic monothioimides at present.

In conclusion, acyclic and semicyclic monothioimides undergo photochemical γ-hydrogen abstraction to produce β-lactams (Type II cyclization products), ketenes, and thioamide (Type II cleavage products). The present reaction is not only the first example of γ-hydrogen abstraction of thioimide derivatives but also provides a useful method of synthesizing some β-lactams possessing sulfur atoms.

II-4-3. Photochemical Reactions of N-Acylthiourethanes

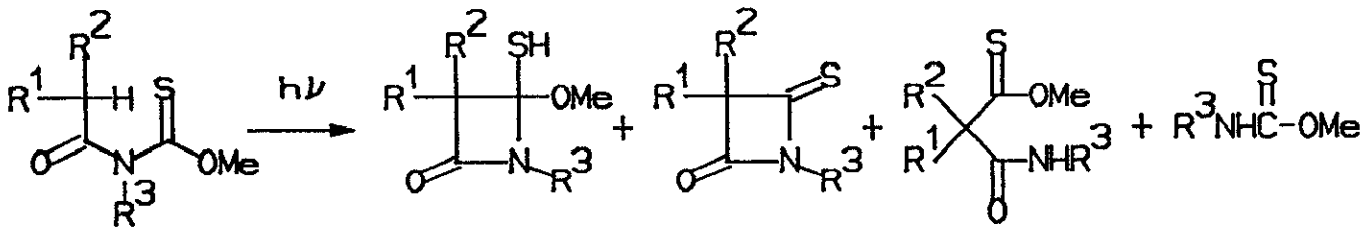
Next the author investigated the photochemical reaction of N-acylthiourethanes. There is no report on photochemistry of thiourethanes to my best knowledge.

N-Acylthiourethanes (254-259) were obtained by the reaction of corresponding thiourethanes with acid chlorides in good yields. N-Acylthiourethanes (254-259) were irradiated in benzene with a high pressure mercury lamp under argon. N-Isobutyroylthiourethane (254) was inert toward photolysis. In the case of (255), an intractable mixture was obtained. Photolysis of 256 gave a β-lactam (260), a thioxo-β-lactam (262), and a thiourethane (267) in the respective yields of 37, 26, and 29%. In the case of 257, a β-lactam (261) couldn't be isolated although the IR and NMR spectra of the reaction mixture indicated the formation of 261. Instead of 261, 264 was obtained as a main product accompanied with 263 and 268. Photolyses of 258 and 259 gave 265 and 266, respectively, as main products (Table 20). An attempt to trap the mercapto β-lactams by acetylation was unsuccessful.

The formation of all products is rationalized in terms of Type II reaction involving γ-hydrogen abstraction by thiocarbonyl group of thiourethane (Scheme 70).

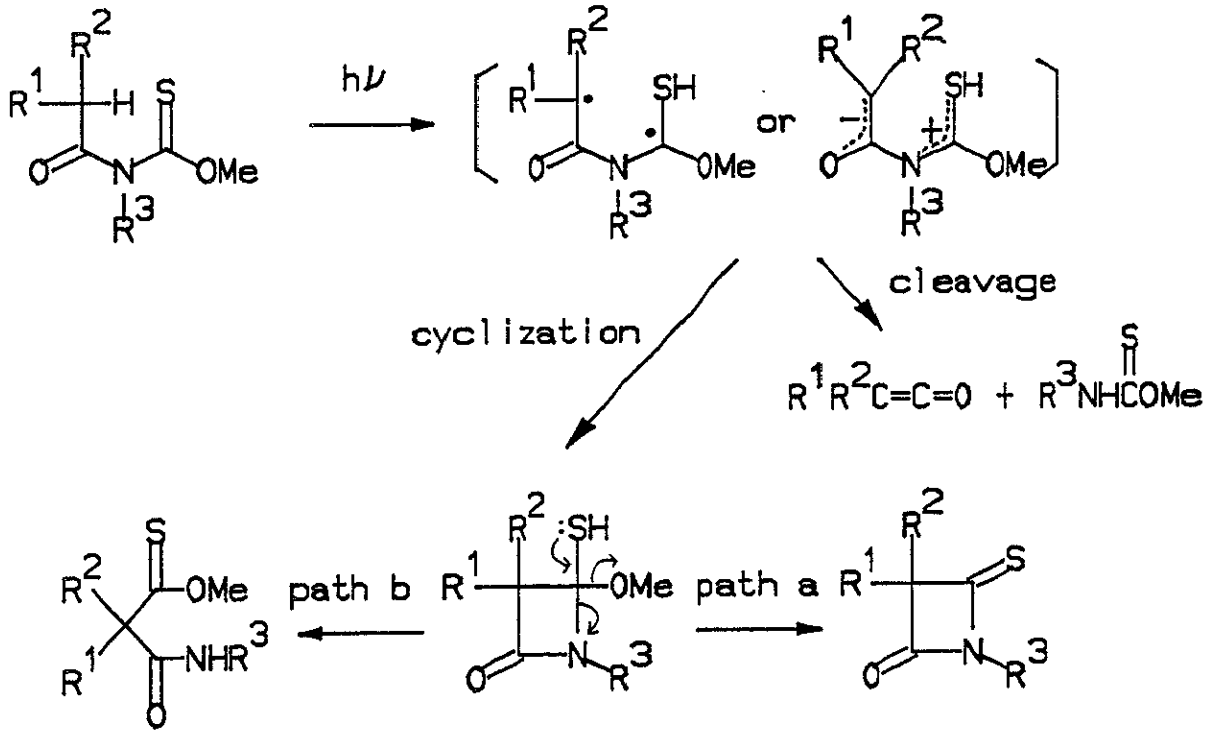
The photoreaction of 259 was sensitized by thioxanthone (E_T=65-69kcal/mol) but not by Michler's ketone (E_T=62 kcal/mol).[90] The quenching of the reaction by stilbene was quite inefficient.

Table 20:Photolysis of N-Acylthiourethanes



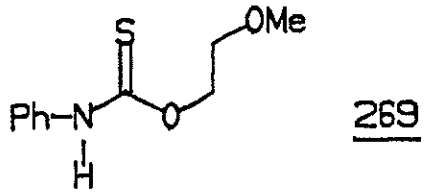
reactant				product							
No.	R^1	R^2	R^3	No.	Yield	No.	Yield	No.	Yield	No.	Yield
254	Me	Me	Ph		*a*		—		—	268	—
255	Ph	H	Ph		*b*		—		—	268	—
256	Ph	Ph	Me	260	37	262	26		0	267	29
257	Ph	Ph	Ph	261	0	263	13	264	46	268	29
258	MeO	H	Me		0		0	265	30	267	*c*
259	MeO	H	Ph		0		0	266	70	268	17

a:Recovered. *b*:Intractable mixture. *c*:Trace.



Scheme 70

When the thiourethane 259 was irradiated at its $n\pi^*$ band (346nm ε=120) selectively, the photoreaction also proceeded. These results indicate that the photoreaction proceeds from $n\pi^*$ state though the multiplicity of the excited state in the direct photolysis cannot be determined from the available data.



269

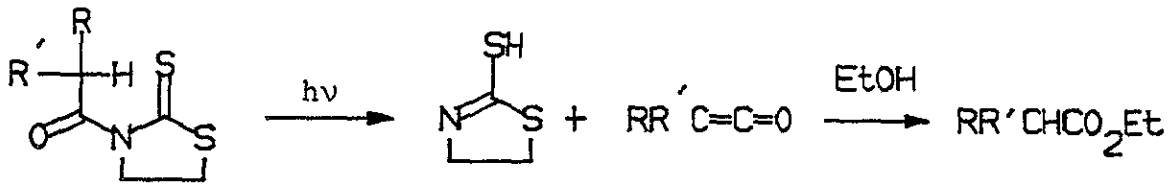
Figure 17

Thiourethane 269 was inert toward photolysis. Introduction of acyl groups on the nitrogen atoms of thiourethanes made these

compounds reactive but their reactivities were much lower than those of acyclic monothioimides (Chapter II-4-2). This reaction provides the first example in a series of photochemical reactions of thiourethane systems.

II-4-4. Photochemical Reactions of N-Acyldithiocarbamates

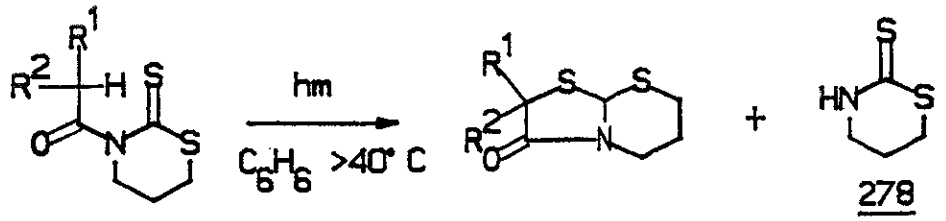
In relation to the photochemical reactions of acyclic and semicyclic monothioimides, the author investigated the photochemical reactions of N-acyldithiocarbamates. It has been reported that N-acyl-2-thionothiazolidines afforded only Type II cleavage products (Scheme 71).[202]



Scheme 71

When 3-acetyl-2-thiotetrahydro-1,3-thiazine (270) was irradiated in benzene with a 1000-W high pressure mercury lamp under argon above 40°C. Type II cleavage product, 2-thiotetrahydro-1,3-thiazine (278) was obtained in 48% yield. Photolysis of N-isobutyroyl derivative (271) gave a similar result. In the cases of 272-274, 2,9-dithia-6-azabicyclo[4,3,0]nonan-7-ones (275-277) were obtained as main products as shown in Table 21. When thiazine (272) was irradiated at low temperature (0-15°C), the IR spectrum of the photoreaction mixture indicated the presence of bicyclic β-lactam (279) (1760 cm^{-1}). However, the β-lactam (279) could not be isolated. Instead of 279, thioxo-β-lactam (280) was obtained in 55% by silica gel column chromatography of the mixture (Scheme 72).

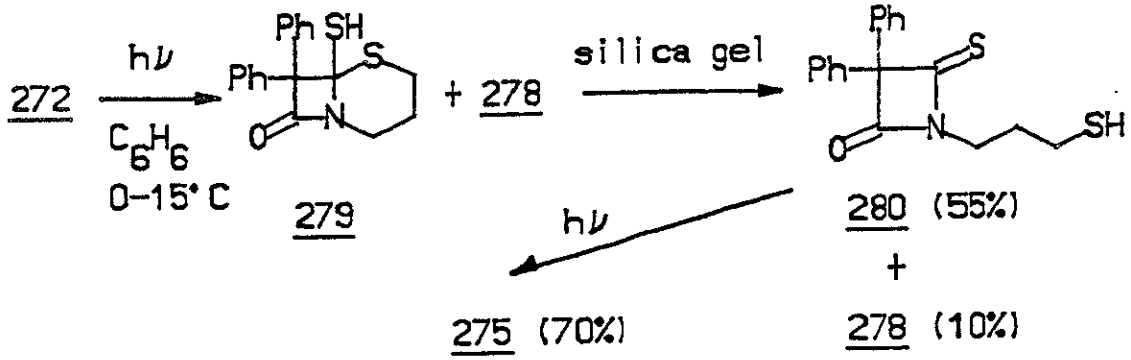
Table 21: Photolysis of Thiazines above 40°C



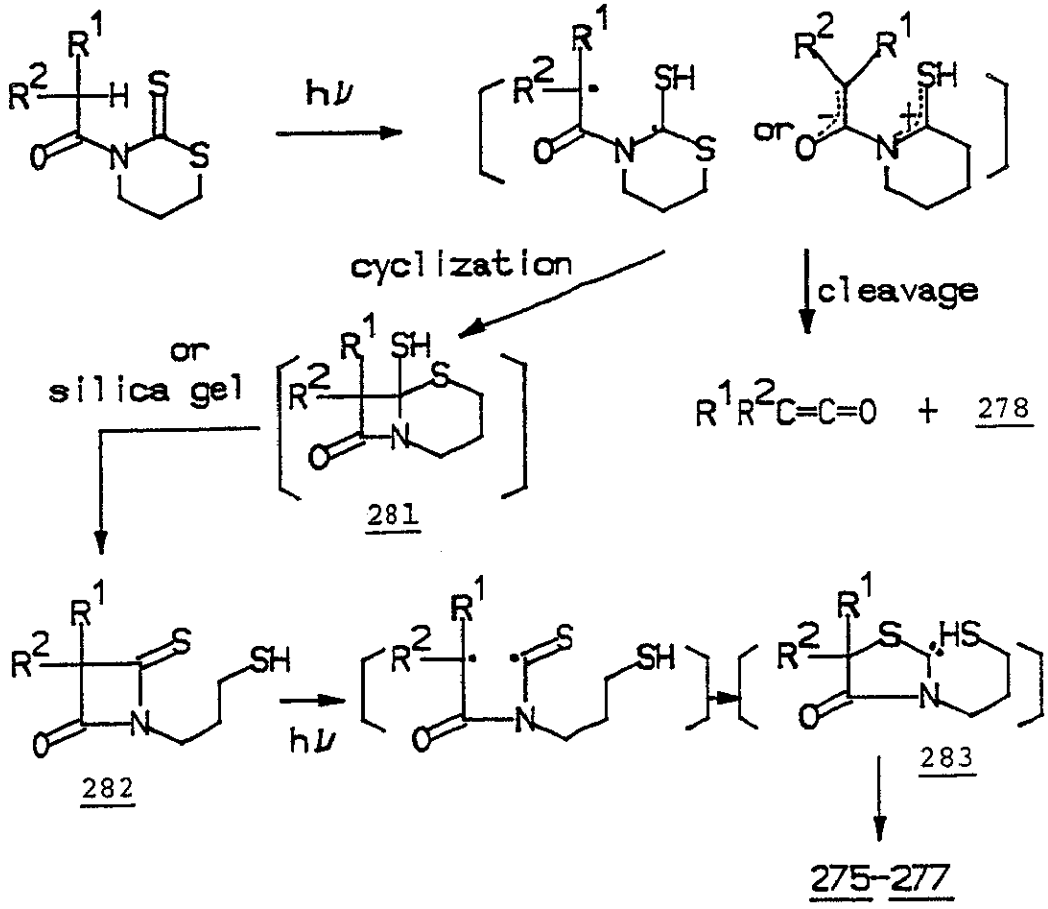
reactant No.	R^1	R^2	product No.	Yield (%)	278 Yield (%)
270	H	H		0	48
271	Me	Me		0	59
272	Ph	Ph	275	51	11
273	MeO	H	276	31	16
274	EtO	H	277	56	26

The mechanism for the formation of 275-277 is reasonably explained in terms of a thiacarbene 283 formed by α-cleavage reaction of 282 (Scheme 73). When 280 was irradiated in benzene, 275 was obtained in 70% yield as a sole product. It is known that azetidine-2,4-diones undergo ring expansion in irradiation in methanol to produce 5-methoxy-isoxazolid-3-ones via oxa-carbenes.[203),204)] In the thione photochemistry, α-cleavage reaction is not well documented although a few examples are reported with strained thioketones and dithioesters.[205)-209)] The photochemical reactions of the thioimides give hydrogen abstraction (Chapter II-4-1, 2) and [2+2] cycloaddition products.[163),182)] However, there has been no example of α-cleavage reaction with nitrogen-thiocarbonyl systems.

It is expected that protection of the mercapto group of 281 make it possible to isolate the β-lactam since 281 was stable at low temperature. When 272 was irradiated at low temperature (0-



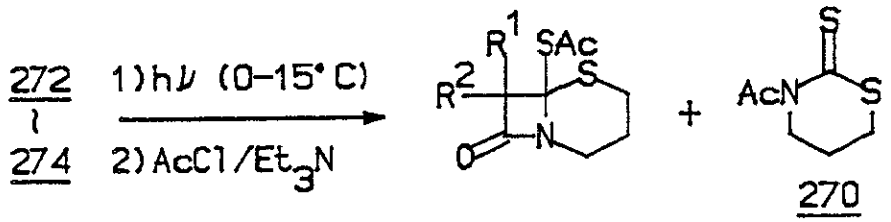
Scheme 72



Scheme 73

15 °C) and acetyl chloride and triethylamine were added, a S-acetyl β-lactam (284) was obtained as expected in 66% yield. In the similar manner, cepham analogues (285 and 286) were obtained (Table 22). The β-lactam (285) was obtained as a mixture of two stereoisomers (about 10:1), and 286 consistent of a single isomer. The stereochemistry of the β-lactams (285 and 286) can not be determined. The structures of the photoproducts were determined on the basis of elemental analyses and spectral data.

Table 22: Photochemical Reactions of Thiazines (272-274) at 0-15 °C



270

No.	R^1	R^2	Yield (%)	Yield (%)
284	Ph	Ph	66	10
285	MeO	H	57	15
286	EtO	H	65	23

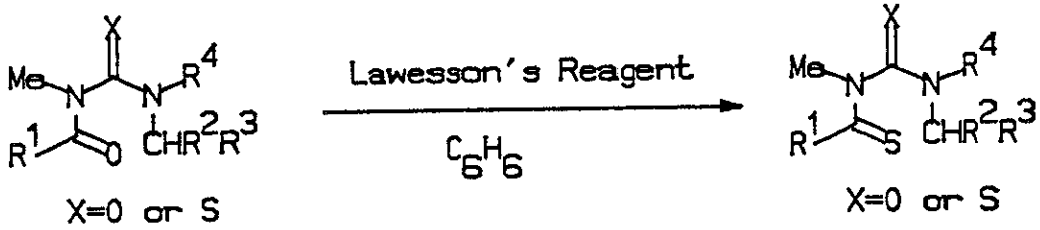
In conclusion, photolyses of 3-diphenylacetyl-, 3-methoxyacetyl, and 3-ethoxyacetyl-2-thiotetrahydro-1,3-thiazines followed by acetylation gave bicyclic β-lactams. High temperature photolysis of them gave 2,9-dithia-5-azabicyclo[4,3,0]-nonan-4-ones via α-cleavage of thioxo-β-lactams. In view of the results of the photoreactions of 270-274, radical-stabilizing substituents (Ph and OR) seem to enhance the cyclization. The

present reaction provides not only a useful synthesis of some β-lactams but also the first example of α-cleavage reaction in thioimide systems.

II-4-5. Photochemical Reactions of N-Thioaroylureas and N-Thioaroylthioureas

In relation to the photochemical reactions of thioimides involving hydrogen abstraction from β- and γ-positions, the author investigated the photochemical hydrogen abstraction from δ-positions by thiocarbonyl groups.

Thioaroylureas (287-292) were obtained in good yields by the reaction of the corresponding N-aroylureas with Lawesson's reagent, and N-thioaroylthioureas (293-298) were synthesized from N-aroylthioureas in the same manner (Scheme 74).

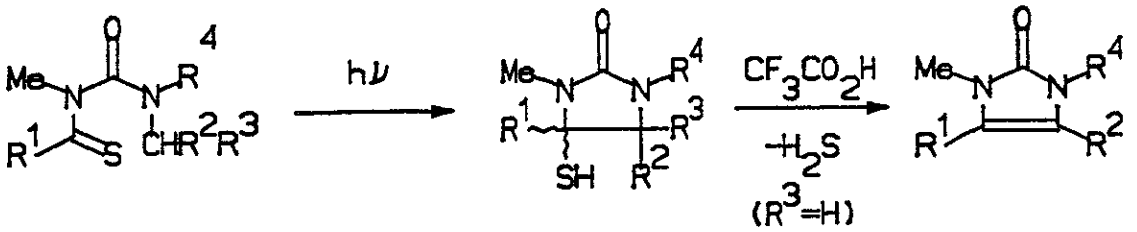


Scheme 74

N',N'-Dialkyl-N-methyl-N-thiobenzoylureas (287-289) were unreactive toward photolyses. On the other hand, when N',N'-dibenzyl-N-methyl-N-thiobenzoylurea (290) was irradiated with a 1000w high pressure mercury lamp under argon, 1-benzyl-4,5-diphenyl-4-mercapto-3-methylimidazolidin-2-one (299) was obtained in 68%. The NMR spectrum of the product indicated that it was a mixture of two stereoisomers. The separation of them was not achieved because they are unstable and converted to the imidazolone (192) gradually by spontaneous elimination of hydrogen sulfide at room temperature. Treatment of 299 with trifluoro-

acetic acid in benzene gave 195 in an excellent yield. The structure of 195 was confirmed by the direct comparison with authentic sample (Scheme 52).[131] Similarly, imidazolidinones (300 and 301) were obtained from N-thioaroylureas (291 and 292) and converted to imidazolones (294 and 195) in good yields (Table 23).

Table 23: Photochemical Reactions of N-Thioaoylureas (287-292)

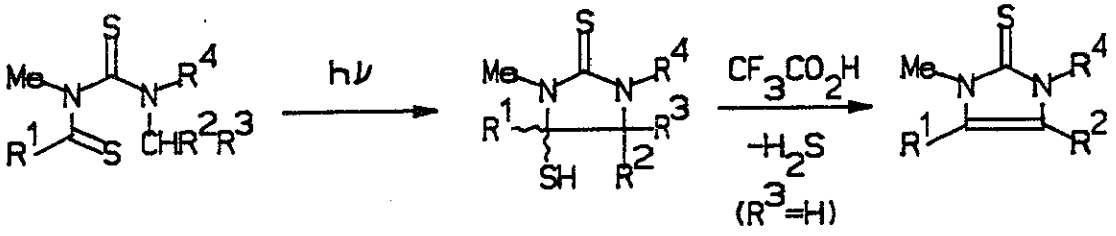


reactant					product			
No.	R^1	R^2	R^3	R^4	No.	Yield (%)	No.	Yield (%)[a]
287	Ph	H	H	Me		*b*		—
288	Ph	Me	H	Et		*b*		—
289	Ph	Me	Me	Pr^i		*b*		—
290	Ph	Ph	H	CH_2Ph	299	68	195	92
291	p-MeOPh	Ph	H	CH_2Ph	300	56	197	86
292	p-ClPh	Ph	H	CH_2Ph	301	54	198	84

a:Yields from 299-301. *b*:Recovered.

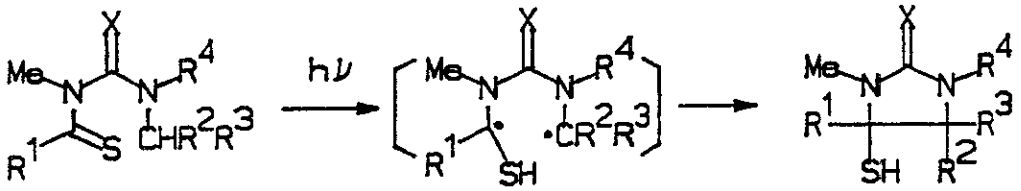
The photolysis of N-thioaroylthioureas (298-301) gave the corresponding imidazolidinethiones (305-308), while 296 and 297 were inert as in the case of 290 and 291. The products (306-308) were also converted to the imidazolethiones (309-311) by the acid-catalyzed elimination of hydrogen sulfide. (Table 24)

Table 24: Photolysis of N-Thioaroylthioureas (293-298)



reactant					product			
No.	R^1	R^2	R^3	R^4	No.	Yield (%)	No.	Yield (%)[a]
293	Ph	H	H	Me		*b*		—
294	Ph	Me	H	Et		*b*		—
295	Ph	Me	Me	Pr^i	302	61		—
296	Ph	Ph	H	CH_2Ph	303	56	306	84
297	p-MeOPh	Ph	H	CH_2Ph	304	45	307	99
298	p-ClPh	Ph	H	CH_2Ph	305	73	308	99

a:Yields from 302-305. *b*:Recovered.



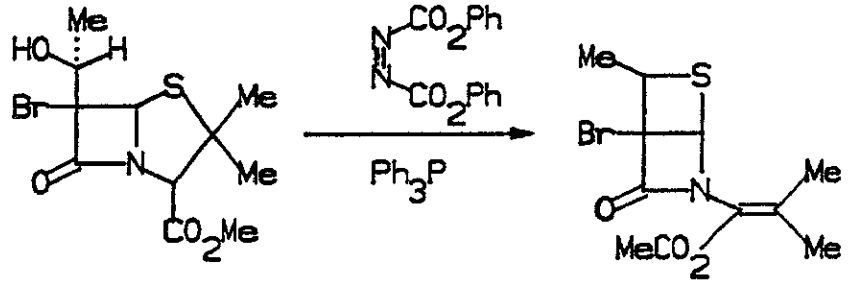
(X=O or S)

Scheme 75

The formation of 299-305 is reasonably explained in terms of hydrogen abstraction by the thioaroyl group via seven membered cyclic transition states and subsequent cyclization of the resulting 1,5-diradical (Scheme 75). This reaction provides the first example of δ-hydrogen abstraction of nitrogen-containing thiocarbonyl compounds. Furthermore, these reactions provide useful methods for synthesizing some imidazolones and imidazolethiones, since the syntheses of the starting materials (287-298) are easy.

II-4-6. Photochemical Reactions of N-Thioacyl-α,β-unsaturated Amides. A New Synthesis of β-Lactams

In relation to the studies of photochemical reactions of monothioimides, the author investigated a new synthesis of β-lactams involving photochemical reactions of N-thioacyl-α,β-unsaturated amides. This reaction provides structually interesting 3-oxo-6thia-2-azabicyclo[2,2,0]hexanes (thietane-fused β-lactams). Although transformation of a penicillin derivatives to a 3-oxo-6thia-2-azabicyclo[2,2,0]hexane was recently reported,[210] there have been no general synthesis of thietane-fused β-lactams (Scheme 76).

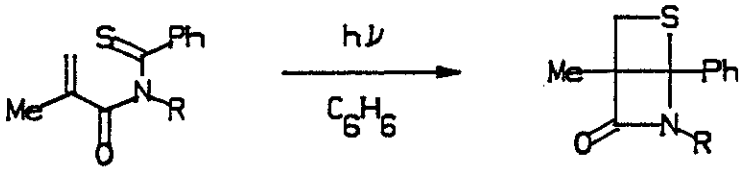


Scheme 76

N-(Thioacyl)-α,β-unsaturated amides were easily obtained by the reaction of the corresponding thioamides with α,β-unsaturated amides in the presence of triethylamine at room temperature. The UV spectrum of N-benzyl-N-(thiobenzoyl)methacrylamide (312) exhibited maxima at 298 nm (ε=9100), 322 nm (ε=9900), and 462 nm (ε=190). When 312 in benzene was irradiated with a high pressure mercury lamp under argon at room temperature and the crude product was chromatographed on silica gel, 2-benzyl-4-methyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (335) was obtained

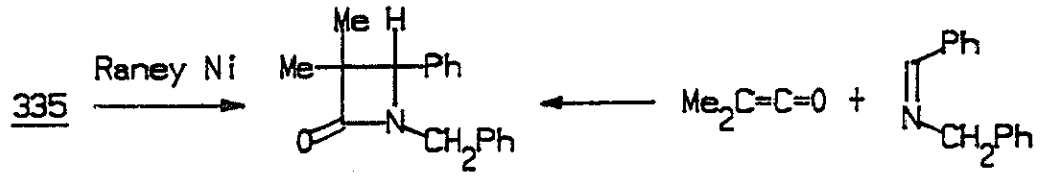
in 95% yield as a crystalline compound. Photolysis of other N-(thiobenzoyl)methacrylamides (309-311 and 313) under the same conditions gave the corresponding β-lactams in high yields (Table 25).

Table 25: Photochemical Reactions of 309-313



reactant		product	
No.	R	No.	Yield (%)
309	Me	332	55
310	Et	333	96
311	Pr^i	334	73
312	CH_2Ph	335	95
313	Ph	336	77

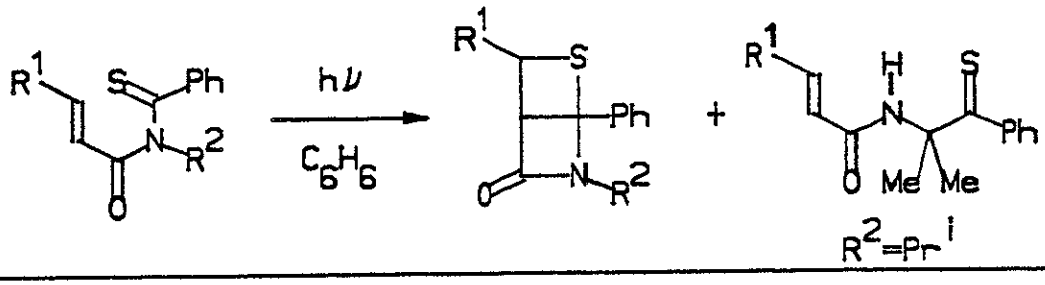
The structure of 335 was deduced from spectra. The IR spectrum ($CHCl_3$) exhibited a carbonyl frequency at 1750 cm^{-1} characteristic of β-lactams. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ 1.07 (s, 3H, CH_3), 3.10 and 3.41 (ABq, 2H, J=10.0 Hz, 5-CH_2), 4.46 and 4.51 (ABq, 2H, J=15.0 Hz, N-CH_2), and 7.1-7.4 (m, 10H, Ph), and ^{13}C-NMR exhibited resonances at δ 14.8 (q), 29.1 (t), 45.5 (t), 68.3 (s), 76.5 (s), 127.6 (d), 128.4 (d), 128.6 (d), 128.7 (d), 129.3 (d), 134.1 (s), 134.9 (s), and 171.4 (s). The mass spectrum (MS) showed peaks at m/e 295 (M+.), 262 (M-S), and 176 (M-$PhCH_2NCO$). In confirmation of the structure, 335 was desulfurized with Raney nickel to give 356 in 82%, which was identified by direct comparison with authentic sample (Scheme 77).[211]



Scheme 77

When N-isopropyl-N-(thiobenzoyl)acrylamide (314) was irradiated under the same conditions, thietane formation reaction and β-hydrogen abstraction occured competitively and the yield of β-lactam (337) decreased (9%). In stead of 337, thioketone (338) was obtained as a main product.

Table 26: Photochemical Reactions of 314-321

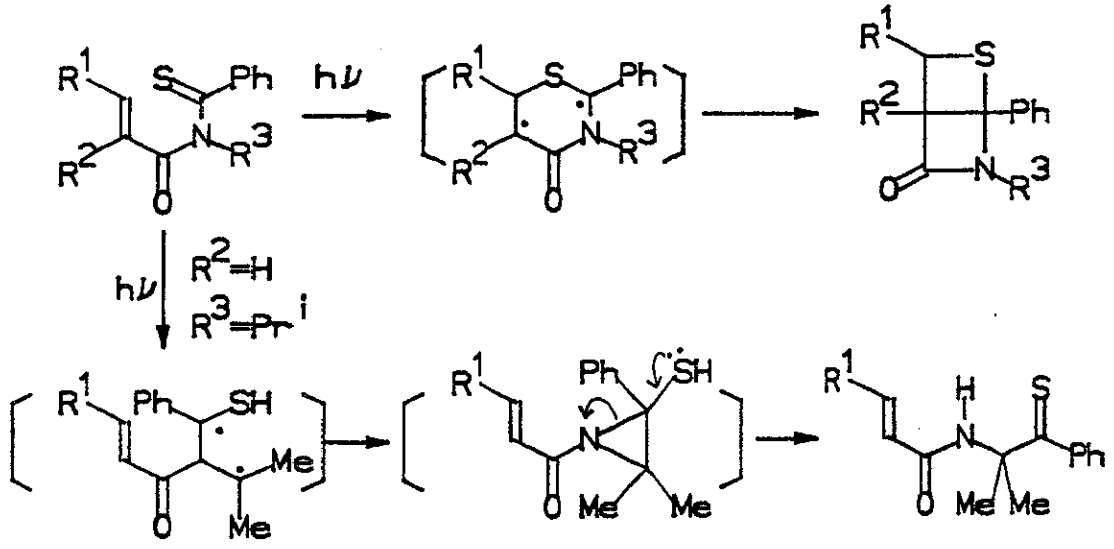


reactant No.	R^1	R^2	product No.	Yield (%)	No.	Yield (%)
314	H	Pr^i	337	9	338	38
315	H	CH_2Ph	339	13		—
316	H	Ph	340	47		—
317	Me	Pr^i	341	13	342 342'	52 (trans) 23 (cis)
318	Me	Ph	343	73		—
319	Ph	Pr^i		0	344	71 (trans)
320	Ph	CH_2Ph		*a*		—
321	Ph	Ph		*b*		—

a: Intractable mixture. *b*: Recovered

Photolysis of other N-acryl and N-crotonyl derivatives gave corresponding β-lactams as shown in Table 26, though thioketone (342) was obtained as main product when R^3 was isopropyl (317). In the case of N-cinnamamides, thietane formation did not proceed and the starting materials were recovered except for that of 319 which gave a thioketone (344) in 71%.

The formation of thioketones was explained in terms of β-hydrogen abstraction of thiocarbonyl groups as shown in Scheme 78 (β-hydrogen abstraction mechanism as explained in Chapter II-4-1).

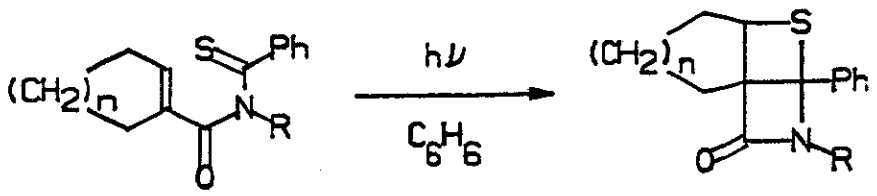


Scheme 78

In the case of cyclic olefins (322-326), tricyclic thietane-fused β-lactams (345-349) were obtained in excellent yields (Table 27).

Irradiation of N-methacryl-2-thionothiazolidine (327) gave β-lactam (350) and 351 in comparable yield (Table 28). Their structures of them were determined on the basis of elemental analyses and spectral data. The IR spectrum of 350 showed a

Table 27: Photolysis of 322-326

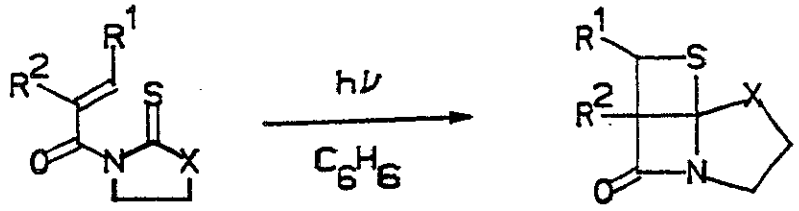


reactant			product	
No.	n	R	No.	Yield (%)
322	1	Pr^i	345	81
323	1	Ph	346	96
324	2	Pr^i	347	99
325	2	CH_2Ph	348	87
326	2	Ph	349	91

carbonyl frecuency at 1750 cm^{-1}. The ^{1}H-NMR spectrum ($CDCl_3$) of 350 showed signals at δ 1.36 (s, 3H, Me), 3.03 and 3.60 (ABq, J=11Hz, 2H, 8-CH_2), 3.1-4.2 (m, 4H, 3-CH_2 and 4-CH_2). The ^{13}C-NMR spectrum ($CDCl_3$) showed signals at δ 14.7 (q), 31.3 (t), 39.8 (t), 43.5 (t), 69.8 (t), 84.3 (s), and 172.7 (s). The IR spectrum of 351 exhibited a carbonyl frequency at 1750 cm^{-1} characteristic of five-membered monothioimides. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ 1.71 (s, 3H, Me), 2.95 and 3.69 (ABq, J=9Hz, 2H, 6-CH_2), 3.36 (t, J=8Hz, 2H, 3-CH_2), and 4.28 (t, J=8Hz, 2H, 2-CH_2). The ^{13}C-NMR spectrum ($CDCl_3$) of 351 showed siganls at δ 2.2 (q), 28.8 (t), 33.8 (t), 64.0 (t), 78.1 (s), 168.2 (s), and 192.0 (s).

Photolysis of other N-acyl-2-thionothiazolidines (328 and 329) and thionooxazolidines (330 and 331) gave β-lactams (352-355) as shown in Table 28.

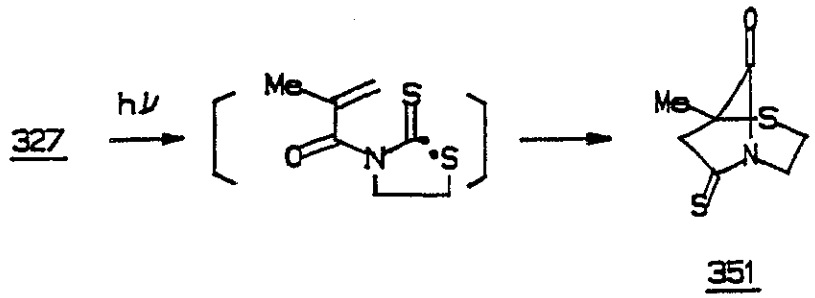
Table 28: Photolysis of 327-331



reactant				product	
No.	X	R^1	R^2	No.	Yield (%)
327	S	H	Me	350	30 (30)[a]
328	S	Me	Me	352	67
329	S	$-(CH_2)_4-$		353	15
330	O	H	Me	354	27
331	O	Me	Me	355	20

a:Yield of 351.

The mechanism for the formation of 351 is reasonably explained in terms of (C=S)-S bond cleavage (Scheme 79).



351

Scheme 79

The quantum yield of the photoreaction of 312 was 0.18 (for the formation of 335). The photoreaction also proceeded when 312 was irradiated in the $n\pi^*$ region of the thiocarbonyl group (>400 nm) selectively. The photocyclizations were sensitized by

Michler's ketone (E_T=62 kcal/mol).[90] Quenching of the reaction by 1,3-pentadiene or stilbene was quite inefficient. These results suggest that the cyclization proceeds from the $n\pi^*$ triplet state of the thiocarbonyl group, although a singlet-state reaction can not be excluded from the available data.

Photolysis of several types of N-acyl-α,β-unsaturated amides gave thietane-fused β-lactams in good yields. Although one example of thietane-fused β-lactam involving transformation of penicilin derivatives was reported, there have been no general methods for the synthesis of thietan-fused β-lactams. Since the starting materials are easily obtained by acylation of thioamides and the yields of these photoreactions are good, this reaction provides a useful synthesis of thietane-fused β-lactams.

III. EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point apparatus, and were uncorrected. IR spectra were measured on a Jasco IRA-1 Infrared spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on Hitachi R-24 and JEOL-100 spectrometer using tetramethylsilane as an internal standard. The chemical shifts are in δ-units (ppm) with coupling constants in Hz, and $CDCl_3$ was used as a solvent unless otherwise stated. UV spectra were measured on a Shimadzu UV-365 UV-VIS-NIR recording spectrophotometer. Absorption maxima are reported as wave lengths (nm) followed by the logarithm of the molar extinction coefficient (logε) in parentheses. GLC was run on a Hitachi 163 Gas Chromatograph using SE-30 column. A Taika low pressure mercury lamp, Eikohsha 300, Ushio 450, and Eikohsha 1000-W high pressure mercury lamp were used as irradiation sources. Silica gel (Merk, Kieselgel 60, 230-400 mesh) was used for a column chromatography. Elemental analyses were performed by Perkin-Elmer Model 240 elemental-analyzer.

Preparation of 1,2-Diphenylmaleilimides

1,2-Diphenylmaleilimides were prepared according to the method in the literature.[94)]

Preparation of 1,2-Diphenylmaleilimide Ozonides (1-5)

1,2-Diphenylmaleilimide (0.5g) was dissolved in acetone (30ml). Ozone in oxygen was bubbled through the solution at

-78 °C until the disappearance of the yellow color. The solution was then evaporated at room temperature and the title compound was recrystallized from ethanol or chloroform-hexane mixture.

1,2-Diphenylmaleilimide ozonide (1)

mp: 133-134 °C; IR(KBr): 1725 and 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.4-7.8 (m, 10H). Anal. Calcd for $C_{16}H_{11}NO_5$: C, 64.64; H, 3.72; N, 4.71. Found: C, 64.52; H, 3.62; N, 4.72%.

N-Methyl-1,2-diphenylmaleilimide ozonide (2)

mp: 137-138 °C; IR(KBr): 1705 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.23 (s, 3H) and 7.4-7.8 (m, 10H). Anal. Calcd for $C_{17}H_{13}NO_5$: C, 65.59; H, 4.20; N, 4.49. Found: C, 65.41; H, 4.08; N, 4.53%.

N-Isopropyl-1,2-diphenylmaleilimide ozonide (3)

mp: 97-98 °C; IR(KBr): 1705 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.48 (d, J=7.0Hz, 6H), 4.97 (sep, J=7.0Hz, 1H), and 7.3-7.9 (m, 10H). Anal. Calcd for $C_{19}H_{17}NO_5$: C,67.24; H, 5.04; N, 4.12. Found: C, 67.46; H, 5.02; N, 4.14%.

N-Phenethyl-1,2-diphenylmaleilimide ozonide (4)

mp: 100-101 °C; IR(KBr): 1705 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.92 (t, J=7.0Hz, 2H), 4.08 (t, J=7.0Hz, 2H), 7.30 (s, 5H), and 7.47 (s, 10H). Anal. Calcd for $C_{24}H_{19}NO_5$: C, 71.81; H, 4.77; N, 3.48. Found: C, 71.47; H, 4.72; N, 3.65%.

N-Phenyl-1,2-diphenylmaleilimide ozonide (5)

mp: 127-128 °C; IR(KBr): 1715 and 1765 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.1-7.9 (m, 15H). Anal. Calcd for $C_{22}H_{15}NO_5$: C, 70.77; H, 4.04; N, 3.80. Found: C, 70.58; H, 3.92; N, 3.80%.

Reaction of Diphenylmaleilimides with Dimethyl Sulfide

An ozonide was dissolved in benzene. Dimethyl sulfide was

added dropwise to the solution at room temperature, and the reaction mixture was left standing for 1 hr. The solvent was removed by evaporation and the crude product was purified by column chromatography on silica gel and then recrystallized from chloroform-hexane mixture.

Bisphenylglyoxalylimide (6)

mp: 105-106°C; IR(KBr): 1675, 1700, 1740, 1765, and 3340 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.4-7.8 (m, 6H), 8.2-8.4 (m, 4H), and 10.4 (br, 1H). Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.97. Found: C, 68.36; H, 3.81; N, 4.97%.

Bisphenylglyoxalyl-N-methylimide (7)

mp: 118.5-120°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.35 (s, 3H), 7.5-7.8 (m, 6H), and 7.9-8.2 (m, 4H). Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.43; N, 4.74. Found: C, 69.02; H, 4.27; N, 4.72%.

Bisphenylglyoxalyl-N-isopropylimide (8)

mp: 96.5-97.5°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.52 (d, J=7.0Hz, 6H), 4.56 (sep, J=7.0Hz, 1H), 7.4-7.7 (m, 6H), and 7.8-8.0 (m, 4H). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.29; N, 4.33. Found: C, 70.81; H, 5.22; N, 4.27%.

Bisphenylglyoxalyl-N-phenethylimide (9)

IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.00 (t, J=7.0Hz, 2H), 4.28 (t, J=7.0Hz, 2H), 7.0-7.8 (m, 11H), and 7.9-8.0 (m, 4H).

Bisphenylglyoxalyl-N-phenylimide (10)

mp: 131-132.5°C; IR(KBr): 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.2-7.7 (m, 11H) and 7.9-8.1 (m, 4H). Anal. Calcd for $C_{22}H_{15}NO_4$: C, 73.94;

H, 4.24; N, 3.91. Found: C, 73.74; H, 4.21; N, 3.91%.

Measurement of IR Spectra of Maleilimide Ozonide at 77K

The apparatus used in the present study consists of a pellet holder, a vacuum shroud, dewar, and CaF_2 windows. Irradiation and the measurement of IR spectra were carried out through the windows. A 300-W high pressure mercury lamp (Eikohsha) was used as an irradiation source.

Trapping of the Aziridine-2,3-dione (2)

The ozonide (2) in ethanol-ether-toluene glass (2:1:1) was photolyzed at 77K, and the resulting reaction mixture was allowed to melt (about -130 to -120 °C) and eventually warmed up to room temperature gradually. Examination of the mixture by GLC indicated the absence of N-methyloxamic acid ethyl ester which would be formed by addition of ethanol to 2.

Preparation of 4-Methyl-1,2,4-triazoline-3,5-dione (19)

The title compound (19) was prepared according to the method in the literature.[213]

Preparation of N,N-Disubstituted α-Ketoamides

The α-ketoamides (35-44) were prepared from α-ketoacid chlorides[214] and amines according to the literature.[63] The structure of α-ketoamides (34-37, 41-43) were determined on the basis of the spectral data in the literature.[63]

N,N-Di(p-cyanobenzyl)pyruvamide (38)

mp: 147-149 °C; IR(KBr): 2230, 1705, and 1620 cm^{-1}; NMR($CDCl_3$): δ

2.47 (s, 3H, Me), 4.53 (s, 4H, CH_2), 7.2-7.7 (m, 8H, aromatic protons). Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.60; H, 4.68; N, 13.18%.

N,N-Di(p-methoxybenzyl)pyruvamide (39)

mp: 50-51°C; IR($CHCl_3$): 1710 and 1630 cm^{-1}; NMR($CDCl_3$): δ 2.36 (s, 3H, COMe), 3.80 (s, 6H, OMe), 4.30 and 4.45 (two s, 4H, CH_2), 6.75-7.8 (m, 8H, aromatic protons). Anal. Calcd. for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.48; H, 6.53; N, 4.29%.

N-(1-Adamantyl)-N-methylpyruvamide (40)

mp: 87-89°C; IR($CHCl_3$): 1705 and 1635 cm^{-1}; NMR($CDCl_3$): δ 1.73 (br s, 6H, adamantyl), 2.17 (br s, 9H, adamantyl), 2.35 (s, 3H, COMe), 2.85 (s, 3H, NMe). Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 8.99; N, 5.95. Found: C, 71.24; H, 9.02; N, 5.95%.

N-Isopropylbenzoylformanilide (44)

mp: 133-136°C; IR($CHCl_3$): 1680 and 1635 cm^{-1}; NMR($CDCl_3$): δ 1.22 (d, 6H, J=7Hz, isopropyl methyl), 5.05 (sep, 1H, J=7Hz, NCH), 7.0-7.9 (m, 10H, aromatic protons). Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.25. Found: C, 76.21; H, 6.42; H, 5.19.

General Procedure for the Photochemical Reactions of α-Ketoamides

A solution of the amide (200mg) in a solvent (40ml) was irradiated in a Pyrex vessel under argon with a 300-W high-pressure mercury lamp (Eikohsha) in the presence or absence of the additives. After the starting material had disappeared, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (flash chromatography). In the case of the photolysis in methanol containing sodium methoxide or

sulfuric acid, the solution was neutralized with acetic acid or sodium bicarbonate before removal of the solvent. The structures of the products (45-47, 51-52, 55, and 58-59) were determined on the basis of spectral data in the literature.[63] N-Ethyllactamide (70) was identified by the direct comparison with an authentic sample.[215]

N-Ethyl-N-(1-methoxyethyl)lactamide (68)

bp: 80°C (3 torr) (bath temperature, Kugelrohr destillation); IR($CHCl_3$): 3340 and 1635 cm^{-1}; NMR($CDCl_3$): δ 1.0-1.7 (m, 9H, 3Me), 3.24 (s, 3H, OMe), 3.4 (m, 2H, CH_2), 3.8 (m, 1H, OH, D_2O exchangeable), 4.4 (m, 1H, CHOH), and 4.9 and 5.8 (both m, total 1H, NCH). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 54.83; H, 9.77; N, 7.99. Found: C, 54.51; H, 9.70; N, 8.09%.

2,5-Diphenyl-3-benzyloxazolidin-4-one (47)

mp: 95-97°C; IR($CHCl_3$): 1695 cm^{-1}; NMR($CDCl_3$): δ 3.60-4.98 (ABq, J=15Hz, 2H, CH_2), 5.38 (d, J=2Hz, 1H, 5-H), 5.83 (d, J=2Hz, 1H, 2-H), and 6.95-7.6 (m, 15H, aromatic protons). Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.21; H, 5.81; N, 4.25. Found: C, 80.50; H, 5.82; N, 4.26%.

3-(p-Cyanobenzyl)-2-(p-cyanophenyl)-5-methyloxazolidin-4-one (48)

mp: 196-198°C; IR($CHCl_3$): 2230 and 1700 cm^{-1}; NMR($CDCl_3$): δ 1.60 (d, J=7Hz, 3H, Me), 3.80 and 4.79 (ABq, J=16Hz, 2H, CH_2), 4.5 (m, 1H, 5-H), 5.75 (d, J=2Hz, 1H, 2-H), and 7.0-7.9 (m, 8H, aromatic protons). Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.90; H, 4.77; N, 13.20%.

1-(p-Cyanobenzyl)-4-(p-cyanophenyl)-3-hydroxy-3-methylazetidin-2-one (56)

mp: 141-147°C; IR($CHCl_3$): 3320, 2235, and 1740 cm^{-1}; NMR($CDCl_3$):

δ 1.61 (s, 3H, Me), 4.01 and 4.90 (ABq, J=16Hz, 2H, CH_2), 4.40 (s, 1H, 4-H), and 7.1-7.9 (m, 8H, aromatic protons). Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.90; H, 4.77; N, 13.20%.

3-(p-Methoxybenzyl)-2-(p-methoxyphenyl)-4-methyloxazolidin-2-one (49)

bp: 110°C(10^{-3} torr); IR($CHCl_3$): 1685 cm^{-1}; NMR($CDCl_3$): δ 1.54 (d, J=6Hz, 3H, Me), 3.46 and 4.85 (ABq, J=15Hz, 2H, CH_2), 3.75 and 3.80 (two s, each 3H, OMe), 4.43 (m, 1H, 5-H), 5.62 (d, J=2Hz, 1H, 2-H), and 6.7-7.3 (m, 8H, aromatic protons). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.29; H, 6.40; N, 4.20%.

1-(p-Methoxybenzyl)-4-(p-methoxyphenyl)-3-hydroxy-3-methylazetidin-2-one (57)

mp: 131-132°C; IR($CHCl_3$): 3360 and 1740 cm^{-1}; NMR($CDCl_3$): δ 1.49 (s, 3H, 3-Me), 3.75 and 4.80 (ABq, J=14Hz, 2H, CH_2), 3.77 and 3.80 (two s, each 3H, OMe), 4.22 (s, 1H, 4-H), and 6.7-7.4 (m, 8H, aromatic protons). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.29; H, 6.40; N, 4.20%.

3-(1-Adamantyl)-5-methyloxazolidin-4-one (50)

mp: 82-83°C; IR($CHCl_3$): 1690 cm^{-1}; NMR($CDCl_3$): δ 1.35 (d, J=6Hz, 3H, Me), 1.7 (br s, 6H, adamantyl), 2.1 (br s, 9H, adamantyl), 4.20 (q, J=6Hz, 1H, 5-H), and 5.05 (br s, 2H, CH_2). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 8.99; N, 5.95. Found: C, 71.35; H, 8.93; N, 5.92%.

N-(1-Adamantyl)-N-methoxymethyllactamide (69)

mp: 73-74°C; IR($CHCl_3$): 3410 and 1640 cm^{-1}; NMR($CDCl_3$): δ 1.30

(d, J=6Hz, 3H, Me), 1.71 (br s, 6H, adamantyl), 2.19 (br s, 9H, adamantyl), 3.24 (s, 3H, OMe), 3.85 (d, J=7Hz, 1H, OH, D_2O exchangeable), 4.4 (m, 1H, CHO), and 4.45 and 4.68 (ABq, J=12Hz, 2H, CH_2). Anal. Calcd for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.42; N, 5.23. Found: C, 67.33; H, 9.45; N, 5.25%.

2,2-Dimethyl-3,5-diphenyloxazolidin-4-one (54)

mp: 93-94°C; IR($CHCl_3$): 1700 cm^{-1}; NMR($CDCl_3$): δ 1.59 (s, 6H, Me), 5.48 (s, 1H, 5-H), and 7.1-7.9 (m, 10H, aromatic protons). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.23. Found: C, 76.20; H, 6.40; N, 5.22%.

4,4-Dimethyl-1,3-diphenyl-3-hydroxyazetidin-2-one (61)

mp: 112-113°C; IR($CHCl_3$): 3320 and 1720 cm^{-1}; NMR($CDCl_3$): δ 1.08 (s, 3H, Me), 1.71 (s, 3H, Me), and 7.0-7.8 (m, 10H, aromatic protons). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.23. Found: C, 76.20; H, 6.40; N, 5.22%.

Spectroscopic Detection of the Iminium Ions

NMR Spectra

A solution of the α-ketoamide (5mg) in 0.5ml of CH_3OD containing D_2SO_4 (5%) was irradiated in an NMR tube with a 300-W high pressure mercury lamp at -78°C for 10-20min. The NMR spectra were measured at -50°C immediately after the irradiation.

Visible Spectra

A solution of α-ketoamide (2-3mg) in 3ml of CH_3OH containing H_2SO_4 (5%) was irradiated in a cell for UV spectroscopy at -78°C for 10-20min. The visible spectra were recorded immediately after the irradiation.

Photolysis of Cyclohexyl Benzoylformate (85)

The ester (200mg) and an equimolar amount of the imine (63 or 64) were dissolved in dry benzene (10ml). The solution was placed in a Pyrex tube and 1.5g of moleclar sieves (4Å) was added. The tube was sealed, allowed to stand overnight, and then irradiated with a 1000-W high pressure mercury lamp at 80°C. After removal of the solvent, the product was isolated by flash chromatography on silica gel.

Preparation of Phenylglyoxalylimides

To a solution (30ml) of acetone containing a corresponding 1,2-disubstituted maleilimide (0.5g), ozone in oxygen was bubbled through the solution at -78°C until the blue color appeared. The solution was warmed up to the room temperature, and dimethyl-sulfide (0.3g) was added dropwise. The reaction mixture was left for 1hr and the solvent was removed by evaporation. The crude product was chromatographed on silica gel and then recrystallized from chloroform-hexane mixture.

Bisphenylglyoxalyl-N-benzylimide (91)

mp: 82-83°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.18 (s, 2H), 7.0-7.8 (m, 11H), and 7.8-8.0 (m, 4H). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.69; H, 4.53; N, 3.75%.

Bisphenylglyoxalyl-N-cyclohexylimide (92)

mp: 87-88°C; IR($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.8-2.8 (br, 10H), 4.0 (br, 1H), 7.3-7.7 (m, 6H), and 7.8-8.2 (m, 4H). Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85. Found: C,

72.57; H, 5.77; N, 3.95%.

Bisphenylglyoxalyl-N-(p-methylphenyl)imide (93)

mp: 119.5-120°C; IR($CHCl_3$): 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.31 (s, 3H), 7.15-7.25 (m, 4H), 7.5-7.8 (m, 6H), and 7.9-8.1 (m, 4H). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.24; H, 4.49; N, 3.72%.

Bisphenylglyoxalyl-N-(p-methoxyphenyl)imide (94)

mp: 152-153°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.76 (s, 3H), 6.7-7.8 (m, 13H), and 7.8-8.1 (m, 4H). Anal. Calcd for $C_{23}H_{17}NO_5$: C, 71.31; H, 4.42; N, 3.61. Found: C, 71.29; H, 4.36; N, 3.49%.

Bisphenylglyoxalyl-N-(p-chlorophenyl)imide (95)

mp: 150-151.5°C; IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.28 (s, 3H), 7.5-7.8 (m, 7H), and 7.9-8.1 (m, 4H). Anal. Calcd for $C_{22}H_{14}NO_4Cl$: C, 67.44; H, 3.60; N, 3.57. Found: C, 67.46; H, 3.56; N, 3.54%.

Bisphenylglyoxalyl-N-(o-methylphenyl)imide (96)

mp: 135.5-136°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.35 (s, 3H), 7.0-7.6 (m, 10H), and 7.8-8.1 (m, 4H). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.01; H, 4.51; N, 3.71%.

Bisphenylglyoxalyl-N-(2,6-dimethylphenyl)imide (97)

mp: 171-172.5°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.30 (s, 6H), 7.5-7.8 (m, 6H), and 7.9-8.1 (m, 4H). Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.96; N, 3.63. Found: C, 74.63; H, 4.86; N, 3.61%.

Bisphenylglyoxalyl-N-(2,6-dichlorophenyl)imide (98)

mp: 150-150.5°C; IR($CHCl_3$): 1680 and 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ

7.2-7.9 (m, 9H) and 8.0-8.3 (m, 4H). Anal. Calcd for $C_{22}H_{13}NO_4Cl_2$: C, 61.99; H, 3.07; N, 3.28. Found: C, 61.87; H, 3.01; N, 3.23%.

General Procedure for the Photoreaction of Bisphenylglyoxalylimides (6-10, 91-98)

A solution of bisphenylglyoxalylimide (200mg) in 40ml of benzene was deaerated with argon and irradiated in a Pyrex vessel with a 450-W high pressure mercury lamp for 1-4hr (until the starting material disappeared). After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene-ethyl acetate mixture afforded the photoproducts. Crystalline photoproducts were recrystallized from chloroform-hexane mixture.

3-Benzoyloxy-1-methyl-3-phenylazetidine-2,4-dione (99)

bp: 160°C (5 torr); IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.07 (s, 3H), 7.0-7.9 (m, 8H), and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.43; N, 4.74. Found: C, 68.82; H, 4.31; N, 4.76%.

3-Benzoyloxy-1-isopropyl-3-phenylazetidine-2,4-dione (100)

mp: 96-96.5°C; IR($CHCl_3$): 1730 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.48 (d, J=7Hz, 6H), 4.08 (sep, J=7Hz, 1H), and 7.2-7.9 (m, 8H), 7.9-8.2 (m, 2H). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.29; N, 4.33. Found: C, 70.58; H, 5.12; N, 4.12%.

3-Benzoyloxy-1-benzyl-3-phenylazetidine-2,4-dione (101)

mp: 102.5-103.5°C; IR($CHCl_3$): 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 4.67 (s, 2H), 7.2-7.7 (m, 13H), and 7.9-8.2 (m, 2H). Anal. Calcd for

$C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.61; H, 4.47; N, 3.83%.

3-Benzoyloxy-1-phenethyl-3-phenylazetidine-2,4-dione (102)

IR($CHCl_3$): 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.80 (t, J=7Hz, 2H), 3.90 (t, J=7Hz, 2H), 7.2-7.7 (m, 13H), and 7.9-8.2 (m, 2H).

3-Benzoyloxy-1-cyclohexyl-3-phenylazetidine-2,4-dione (103)

mp: 115.5-116.5°C; IR($CHCl_3$): 1720 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.9-2.4 (br, 10H), 3.3-4.3 (br, 1H), 7.1-7.9 (m, 8H), and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82; N, 3.85. Found: C, 72.95; H, 5.76; N, 3.76%.

3-Benzoyloxy-3-phenylazetidine-2,4-dione (104)

mp: 168.5-169°C; IR($CHCl_3$): 1740 and 3305 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-7.9 (m, 8H), 8.0-8.2 (m, 2H), and 8.67 (br, 1H). Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.32; H, 3.94; N, 4.97. Found: C, 68.19; H, 3.85; N, 4.96%.

Bis-5,5'-(oxazolidine-2,4-dione) (111)

IR($CHCl_3$): 1760, 1820, and 3390 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.2-7.9 (m, 10H) and 9.8 (br, 2H).

3-Benzoyloxy-1,3-diphenylazetidine-2,4-dione (105)

mp: 151-152°C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-7.9 (m, 13H) and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{22}H_{15}NO_4$: C, 73.94; H, 4.23; N, 3.91. Found: C, 74.00; H, 4.01; N, 3.92%.

Bis-5,5'-(3,5-diphenyloxazolidine-2,4-dione) (112)

mp: 290-291.5°C; IR($CHCl_3$): 1750 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.2-7.8 (m). Anal. Calcd for $C_{30}H_{20}N_2O_6$: C, 71.42; H, 4.00; N, 5.55. Found: C, 71.13; H, 3.89; N, 5.51%.

3,5-Diphenyloxazolidine-2,4-dione (118)

IR(KBr): 1735 and 1805 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.90 (s, 1H) and

7.48 (s, 5H).

3-Benzoyloxy-1-(p-methylphenyl)-3-phenylazetidine-2,4-dione (106)

mp: 143.5-144.5°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.37 (s, 3H), 7.2-8.0 (m, 12H), and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.44; H, 4.54; N, 3.81%.

Bis-5,5'-[3-(p-methylphenyl)-5-phenyloxazolidine-2,4-dione] (113)

mp: 281-282°C; IR($CHCl_3$): 1745 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.36 (s, 6H) and 6.9-7.9 (m, 18H). Anal. Calcd for $C_{32}H_{24}N_2O_6$: C, 72.17; H, 4.54; N, 5.26. Found: C, 72.36; H, 4.51; N, 5.18%.

3-(p-Methylphenyl)-5-phenyloxazolidine-2,4-dione (119)

mp: 100-101°C: IR($CHCl_3$): 1745 and 1800 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.36 (s, 3H), 5.86 (s, 1H), 7.29 (s, 4H), and 7.47 (s, 5H). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.71; H, 4.90; N, 5.22%.

Bis-5,5'-[3-(p-methoxyphenyl)-5-phenyloxazolidine-2,4-dione] (114)

mp: >300°C; IR(KBr): 1740 and 1815 cm^{-1}.

3-Benzoyloxy-1-(p-chlorophenyl)-3-phenylazetidine-2,4-dione (107)

mp: 128.5-129.5 C; IR($CHCl_3$): 1730 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-8.0 (m, 12H) and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{22}H_{14}NO_4Cl$: C, 67.44; H, 3.60; N, 3.57. Found: C, 67.58; H, 3.56; N, 3.52%.

Bis-5,5'-[3-(p-chlorophenyl)-5-phenyloxazolidine-2,4-dione] (115)

mp: 286-288°C; IR($CHCl_3$): 1750 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.0-7.9 (m). Anal. Calcd for $C_{30}H_{18}N_2O_6Cl_2$: C, 62.84; H, 3.16; N, 4.88. Found: C, 62.70; H, 3.08; N, 4.81%.

3-Benzoyloxy-1-(o-methylphenyl)-3-phenylazetidine-2,4-dione (108)

mp: 141.5-142.5°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.32

(s, 3H), 7.2-8.0 (m, 12H), and 8.0-8.3 (m, 2H). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.32; H, 4.54; N, 3.79%.

Bis-5,5'-[3-(o-methylphenyl)-5-phenyloxazolidine-2,4-dione] (116)
mp: >300°C; IR(KBr): 1745 and 1815 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.28 (s, 6H) and 7.1-7.8 (m, 18H).

3-(o-Methylphenyl)-5-phenyloxazolidine-2,4-dione (120)
mp: 137-138°C; IR($CHCl_3$): 1745 and 1815 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.13 and 2.30 (two s, total 3H), 5.97 and 6.00 (two s, total 1H), and 7.1-7.7 (m, 9H). Anal. calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.74; H, 4.93; N, 5.16%.

3-Benzoyloxy-1-(2,6-dimethylphenyl)-3-phenylazetidine-2,4-dione (109)
mp: 180-180.5°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.93 (s, 3H), 2.62 (s, 3H), 7.1-7.3 (m, 3H), 7.4-7.8 (m, 6H), and 7.8-8.2 (m, 4H). Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.96; N, 3.63. Found: C, 74.67; H, 4.86; N, 3.58%.

3-Benzoyloxy-1-(2,6-dichlorophenyl)-3-phenylazetidine-2,4-dione (110)
mp: 182.5-184°C; IR($CHCl_3$): 1740 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-8.0 (m, 11H) and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{22}H_{13}NO_4Cl_2$: C, 61.99; H, 3.07; N, 3.28. Found: C, 61.98; H, 3.02; N, 3.27%.

Irradiation of 100 in Methanol with a Low Pressure Mercury Lamp

A solution of 100 (180mg) in 20ml of methanol was deaerated with argon and irradiated with a low pressure mercury lamp. After removal of the solvent, the residue was chromatographed on

silica gel. Two products (121 and 122) were isolated.

5-Benzoyloxy-2-methoxy-5-phenyl-3-isopropyloxazolidin-4-one (121)

IR($CHCl_3$): 1720 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.31 (d, J=7Hz, 3H), 1.42 (d, J=7Hz, 3H), 3.52 (s, 3H), 4.17 (sep, J=7Hz, 1H), 6.23 (s, 1H), 7.3-7.6 (m, 6H), and 7.8-8.2 (m, 4H).

O-Benzoylmandelic acid methyl ester (122)

IR($CHCl_3$): 1720 cm^{-1}; ^1H-NMR($CDCl_3$): δ 3.73 (s, 3H), 6.15 (s, 1H), 7.3-7.7 (m, 8H), and 8.0-8.2 (m, 2H).

Unequivocal Synthesis of Bis-5,5'-(3,5-diphenyloxazolidin-2,4-dione) (112) from 118 and Nickel Peroxide

A mixture of 118 (100mg) and nickel peroxide (1g) in benzene (5ml) was stirred at room temperature for 2hr. The reaction mixture was filtered, and the filtrate was evaporated and the title compound was recrystallized from chloroform-hexane mixture.

Preparation of Bispyruvylimides (123-125) and N-Pyruvylphenylglyoxalylimides (126-129)

Corresponding 1,2-disubstituted maleilimide in acetone was ozonized as in the case of 1,2-diphenylmaleilimides. However, these imides were unstable to silica gel and produced morpholine derivatives by hydration. Therefore, the crude imides was used for irradiation.

Bispyruvyl-N-isopropylimide (123)

IR($CHCl_3$): 1665 and 1715 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.33 (d, J=7Hz, 6H), 2.34 (s, 6H), and 4.71 (sep, J=7Hz, 1H).

Bispyruvyl-N-benzylimide (124)

IR($CHCl_3$): 1665 and 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.33 (s, 6H), 5.23 (s, 2H), and 7.22 (s, 5H).

Bispyruvyl-N-phenylimide (125)

IR($CHCl_3$): 1675 and 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.34 (s, 6H) and 7.1-7.5 (m, 5H).

N-Isopropyl-N-pyruvylphenylglyoxalylimide (126)

IR($CHCl_3$): 1665 and 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.47 (d, J=7Hz, 6H), 2.68 (s, 3H), 4.80 (sep, J=7Hz, 1H), 7.4-7.8 (m, 3H), and 8.0-8.2 (m, 2H).

N-Benzyl-N-pyruvylphenylglyoxalylimide (127)

IR($CHCl_3$): 1665 and 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.28 (s, 3H), 5.03 (s, 2H), 7.1-7.7 (m, 8H), and 7.9-8.1 (m, 2H).

N-Phenyl-N-pyruvylphenylglyoxalylimide (128)

IR($CHCl_3$): 1680, 1695, and 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.43 (s, 3H), 7.1-7.7 (m, 3H), and 7.9-8.1 (m, 2H).

N-(2,6-Dimethylphenyl)-N-pyruvylphenylglyoxalylimide (129)

IR($CHCl_3$): 1675 and 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.22 (s, 6H), 2.40 (s, 3H), 7.0-7.7 (m, 6H), and 7.9-8.1 (m, 2H).

Irradiations of Bispyruvylimides and N-Pyruvylphenylglyoxalylimides

The imides (123-125, 126-129) were irradiated as soon as they were synthesized because they were unstable. The yields were determined by NMR spectroscopy. The reaction mixture was chromatographed on silica gel and the photoproducts were isolated. In the case of crystalline photoproducts, they were recrystallized from chloroform-hexane mixture.

3-Acetoxy-3-methyl-1-isopropylazetidine-2,4-dione (130)

IR($CHCl_3$): 1740 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.43 (d, J=7Hz, 6H), 1.69 (s, 3H), 2.11 (s, 3H), and 4.32 (sep, J=7Hz, 1H).

3-Acetoxy-1-benzyl-3-methylazetidine-2,4-dione (131)

IR($CHCl_3$): 1740 and 1880 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.53 (s, 3H), 2.05 (s, 3H), and 4.47 (s, 2H), and 7.28 (s, 5H).

3-Acetoxy-3-methyl-1-phenylazetidine-2,4-dione (132)

mp: 50-50.5°C; IR($CHCl_3$): 1745 and 1865 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.70 (s, 3H), 2.12 (s, 3H), 7.3-7.7 (m, 3H), and 7.8-8.0 (m, 2H). Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.00. Found: C, 61.86; H, 4.71; N, 6.01%.

3-Acetoxy-1-isopropyl-3-phenylazetidine-2,4-dione (134)

mp: 59-59.5°C; IR($CHCl_3$): 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.42 (d, J=7Hz, 6H), 2.18 (s, 3H), 4.02 (sep, J=7Hz, 1H), and 7.2-7.8 (m, 5H). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.78; N, 5.36. Found: C, 64.39; H, 5.77; N, 5.35%.

3-Acetoxy-1-benzyl-3-phenylazetidine-2,4-dione (135)

IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.12 (s, 3H), 4.56 (s, 2H), and 7.2-7.7 (m, 10H).

3-Acetoxy-1,3-diphenylazetidine-2,4-dione (136)

mp: 98.5-99.5°C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.19 (s, 3H) and 7.3-8.0 (m, 10H). Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.43; N, 4.74. Found: C, 69.21; H, 4.39; N, 4.76%.

3-Acetoxy-1-(2,6-dimethylphenyl)-3-diphenylazetidine-2,4-dione (137)

mp: 89-90°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.85 (s, 3H), 2.19 (s, 3H), 2.48 (s, 3H), and 6.9-7.9 (m, 8H). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.29; N, 4.33. Found: C, 70.73; H, 5.28;

N, 4.33%.

Quantum Yield Measurement

Valerophenone actinometry was used for quantum yield determination. The 313nm line was isolated with a filter solution containing 2.0mmol/l potassium chromate in 5% aqueous potassium carbonate. Samples in Pyrex tubes were degassed to ca. 10^{-3}torr in three freeze-pump-thaw cycles and sealed. For quantum yield of 7 for the formation of 99, photolysate was carried out 20-30% conversion. The degree of the reaction was determined by NMR spectroscopy. Quantum yield of 10 was determined by means of measuring of the degree of the forming of benzaldehyde in the presence of dodecan thiol (0.2mol/l) by gas chromatography.

Sensitization and Quenching of 7 and 10

Three Pyrex vessels were irradiated at 366nm line with merry-go-round apparatus. The first was a benzene solution containing 3-methoxyacetophenone and 7 or 10. The second was a benzene solution of Michler's ketone and 7 or 10, and the third was that of 7 or 10. After removal of benzene, the degree of the reaction of 7 was determined by NMR spectroscopy. The 366nm line was isolated with a filter solution containing 0.04mol/l naphthalene. Concentrations of the sensitizers were adjusted so that 5% or less of the incident light was absorbed by imide (7 or 10). Quenching of 7 and 10 was carried out as in the case of sensitization. A large excess of quencher was used.

Preparation of N-Formylphenylglyoxalylamide (138-142)

All these compounds were prepared from N-substituted formamide and phenylglyoxalyl chloride. A typical run is exemplified for the preparation of 141. To a solution of N-benzylformamide (680mg, 5mmol) in 25ml of dry ether was added phenylglyoxalyl chloride (850mg, 5mmol). The mixture was cooled at 0°C with magnetic stirring. Triethylamine (510mg, 5mmol) was added drop by drop, and then triethylamine hydrochloride was precipitated. Water was added, and the solution was extracted with ether. After the mixture was washed with water and dried with magnesium sulfate, the ether was removed by evaporation. N-Benzyl-N-formylphenylglyoxalylamide (141) was isolated by column chromatography on silica gel and purified by recrystallization from chloroform-hexane mixture.

N-Formyl-N-methylphenylglyoxalylamide (138)

IR($CHCl_3$): 1665 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.25 (s, 3H), 7.3-7.8 (m, 3H), and 9.00 (s, 1H).

N-Ethyl-N-formylphenylglyoxalylamide (139)

IR($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.25 (t, J=7Hz, 3H), 3.89 (q, J=7Hz, 2H), 7.3-7.8 (m, 3H), 7.9-8.2 (m, 2H), and 8.92 (s, 1H).

N-Formyl-N-isopropylphenylglyoxalylamide (140)

IR($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.50 (d, J=7Hz, 6H), 4.80 (sep, J=7Hz), 7.3-7.8 (m, 3H), 7.8-8.2 (m, 2H), and 8.86 (s, 1H).

N-Benzyl-N-formylphenylglyoxalylamide (141)

mp: 61.5-62°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.02 (s, 2H), 7.2-7.8 (m, 8H), 7.8-8.0 (m, 2H), and 8.98 (s, 1H). Anal.

Calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.97; H, 4.90; N, 5.23%.

N-Formyl-N-phenylphenylglyoxalylamide (142)

mp: 97-98°C; IR($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.1-7.8 (m, 8H), 7.9-8.1 (m, 2H), and 9.27 (s, 1H). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.13; H, 4.37; N, 5.53. Found: C, 70.84; H, 4.30; N, 5.47%.

General Procedure for the Photoreaction of N-Formylphenylglyoxalylamide

A solution (40ml) of the N-formylphenylglyoxalylamides (138-142: 200mg) were irradiated in a Pyrex vessel under argon with a 450-W high pressure mercury lamp for 2-3hr. After removal of the solvent, the residue was chromatographed on silica gel. The crystalline photoproducts were recrystallized from chloroform-hexane mixture.

3-Hydroxy-1-methyl-3-phenylazetidine-2,4-dione (143)

mp: 127-128.5°C; IR($CHCl_3$): 1710 and 3330 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.94 (s, 3H), 4.21 (br, 1H), and 7.3-7.7 (m, 5H). Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.32. Found: C, 62.98; H, 4.71; N, 7.30%.

1-Ethyl-3-hydroxyphenylazetidine-2,4-dione (144)

IR($CHCl_3$): 1735 and 3360 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.25 (t, J=7Hz, 3H), 3.40 (q, J=7Hz, 2H), 4.35 (br, 1H), and 7.0-7.8 (m, 5H).

3-Hydroxy-3-phenyl-1-isopropylazetidine-2,4-dione (145)

mp: 72-72.5°C; IR($CHCl_3$): 1735, 1860, and 3340 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.35 (d, J=6Hz, 6H), 3.94 (sep, J=7Hz, 1H), 4.7

(br, 1H), and 7.2-7.6 (m, 5H). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.97; N, 6.38. Found: C, 65.77; H, 5.94; N, 6.38%.

1-Benzyl-3-hydroxy-3-phenylazetidine-2,4-dione (146)

mp: 81.5-82.5°C; IR($CHCl_3$): 1740, 1800, and 3300 cm^{-1}; ^1H-NMR($CDCl_3$): δ 4.44 (s, 2H), 4.63 (br, 1H), and 7.1-7.6 (m, 10H). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.63; H, 4.85; N, 5.28%.

1-Formyl-3-hydroxy-3,4-diphenylazetidin-2-one (148)

mp: 143.5-145.5°C; IR($CHCl_3$): 1705, 1795, and 3300 cm^{-1}; ^1H-NMR($CDCl_3$): δ 5.30 (s, 1H), 6.8-7.6 (m, 10H), and 9.00 (s, 1H). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.71; H, 4.88; N, 5.24%.

3-Hydroxy-1,3-diphenylazetidine-2,4-dione (147)

mp: 117.5-118.5°C; IR($CHCl_3$): 1725 and 3300 cm^{-1}; ^1H-NMR($CDCl_3$): δ 7.1-7.8 (m, 8H), 7.8-8.2 (m, 2H), and 9.25 (s, 1H). Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.13; H, 4.37; N, 5.53. Found: C, 70.90; H, 4.34; N, 5.52%.

2-Hydroxy-2-methoxycarbonyl-2-phenylacetanilide (149)

IR($CHCl_3$): 1520, 1695, 1735 and 3380 cm^{-1}; ^1H-NMR($CDCl_3$): δ 3.29 (s, 3H), 7.1-7.8 (m, 10), and 8.80 (br, 1H).

Preparation of N-(Phenylthiocarbonyl)phenylglyoxalylamides (152-156)

All these compounds were prepared from N-substituted phenylthio- (or phenoxy) carbamates and phenylglyoxalyl chloride. To a solution of N-substituted phenylthiocarbamate in dry benzene was added phenylglyoxalyl chloride. Triethylamine was added drop by

drop with magnetic stirring at room temperature and stirred further 1-2hr (in the case of 54, refluxed for 2hr). The precipitated triethylamine hydrochloride was removed by filtration. The filtrate was condenced by evaporation. The title compound was isolated by column chromatography on silica gel and purified by recrystallization from chloroform-hexane mixture.

N-Phenyl-N-(phenylthiocabonyl)phenylglyoxalylamide (152)

mp: 156-157°C; IR($CHCl_3$): 1680 and 1705 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-7.7 (m, 13H) and 7.9-8.1 (m, 2H). Anal. Calcd for $C_{21}H_{15}NO_3S$: C, 69.78; H, 4.18; N, 3.87. Found: C, 69.47; H, 4.19; N, 3.79%.

N-(p-Methylphenyl)-N-(phenylthiocabonyl)phenylglyoxalylamide (153)

mp: 157-158°C; IR($CHCl_3$): 1685 and 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.47 (s, 3H), 7.0-7.7 (m, 12H) and 7.9-8.1 (m, 2H). Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.25; H, 4.59; N, 3.81%.

N-Isopropyl-N-(phenylthiocabonyl)phenylglyoxalylamide (154)

mp: 118-119°C; IR($CHCl_3$): 1670 and 1695 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.65 (d, J=7Hz, 6H), 4.40 (sep, J=7Hz, 1H), 7.4-7.7 (m, 8H), and 7.8-8.1 (m, 2H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.27. Found: C, 66.04; H, 5.24; N, 4.24%.

N-Benzyl-N-(phenylthiocarbonyl)phenylglyoxalylamide (155)

mp: 120-121°C; IR($CHCl_3$): 1680 and 1705 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.23 (s, 2H), 7.2-7.6 (m, 13H) and 7.7-8.2 (m, 2H). Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.19; H, 4.59; N, 3.66%.

N-Phenyl-N-phenoxyphenylglyoxalylamide (156)

mp: 167.5-168.5°C; IR($CHCl_3$): 1675, 1710, and 1740 cm^{-1}; ^1H-NMR($CDCl_3$): δ 7.3-7.7 (m, 13H) and 7.9-8.1 (m, 2H). Anal. Calcd for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.37; N, 4.05. Found: C, 73.08; H, 4.34; N, 4.06%.

General Procedure for the Photochemical Reactions of N-(Phenylthiocarbonyl)phenylglyoxalylamides

A solution of the amide (200 mg) in benzene was irradiated in a Pyrex vessel under argon with a 450-W high pressure mercury lamp. After the starting material disappeared, the solvent was removed by evaporation and the residue was chromatographed on silica gel. In the case of crystalline products, they were recrystallized from chloroform-hexane mixture.

Determination of the Yields of Isocyanates

The amides (152-156) were irradiated in Pyrex sealed tubes. In the case of those of 152 and 153, to the reaction mixtures acetophenone was added as standard compound. The yields of phenylisocyanate and p-tolylisocyanate were determined by GLC. The direct detection of benzylisocyanate and isopropylisocyanate was unsuccessful. Therefore, methanol was added to the photoreaction mixture and stood for over night. The yields of N-isopropyl and N-benzyl methylcarbamates were meassured by GLC. In the case of that of 156, phenylisocyanate was not detected by GLC.

3,5-Diphenyl-5-(phenylthio)oxazolidine-2,4-dione (157)

mp: 171-172°C; IR($CHCl_3$): 1750 and 1815 cm^{-1}; ^1H-NMR($CDCl_3$): δ

6.6-6.9 (m, 2H), 7.2-7.6 (m, 9H), and 7.7-8.1 (m, 4H). Anal. Calcd for $C_{21}H_{15}NO_3S$: C, 69.78; H, 4.18; N, 3.87. Found: C, 69.81; H, 4.14; N, 3.82%.

3-(p-Methylphenyl)-5-phenyl-5-(phenylthio)oxazolidine-2,4-dione (158)

mp: 119-119.5°C; IR($CHCl_3$): 1750 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.28 (s, 3H), 6.5-6.7 (m, 2H), 7.0-7.6 (m, 8H), and 7.7-8.1 (m, 4H). Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.38; H, 4.66; N, 3.64%.

3-Isopropyl-5-phenyl-5-(phenylthio)oxazolidine-2,4-dione (159)

IR($CHCl_3$): 1740 and 1810 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.87 (d, J=7Hz, 3H), 0.98 (d, J=7Hz, 3H), 3.95 (sep, J=7Hz, 1H), and 7.1-8.0 (m, 10H).

Bis-5,5'-(3,5-diisopropyloxazolidine-2,4-dione) (162)

IR($CHCl_3$): 1740 and 1815 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.0-1.5 (m, 12H), 4.22 (sep, J=7Hz, 2H), and 7.1-7.8 (m, 10H).

4,4-Dimethyl-3-hydroxy-3-phenyl-3-(phenylthiocarbonyl)azetidin-2-one (163)

mp: 160.5-162°C; IR($CHCl_3$): 1680, 1715, 1775, and 3300 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.10 (s, 3H), 1.70 (s, 3H), 3.70 (br, 1H), and 7.3-7.6 (m, 10H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.13; N, 4.27. Found: C, 66.15; H, 5.19; N, 4.21%.

3-Hydroxy-3,4-diphenyl-3-(phenylthiocarbonyl)azetidin-2-one (164)

mp: 189-191°C; IR($CHCl_3$): 1685, 1720, 1785, and 3300 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.00 (br, 1H), 5.40 (s, 1H), and 6.8-7.6 (m, 15H). Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.00; H, 4.49; N, 3.67%.

3,5-Diphenyl-5-phenoxyoxazolidine-2,4-dione (161)

mp; 78-79°C; IR($CHCl_3$): 1750 and 1820 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 7.3-8.0 (m, 15H). Anal. Calcd for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.37; N, 4.05. Found: C, 73.13; H, 4.66; N, 3.92%.

Preparation of N-Benzoylformyl-α,β-unsaturated Amides (166-175)

N-Benzoylformyl-α,β-unsaturated amides were obtained by condensation of corresponding α,β-unsaturated amides with phenylglyoxalyl chloride in the presence of triethylamine.

N-Benzoylformyl-N-methylmethacrylamide (166)

UV $\lambda_{max.}$ (Cyclohexane): 218 (ε=10400), 256 (10000), and 350nm (90); IR($CHCl_3$): 1625 and 1655 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.85 (d, J=1Hz, 3H), 3.33 (s, 1H), 5.23 (m, 1H), 5.40 (br s, 1H), 7.3-7.7 (m, 3H), and 7.9-8.1 (m, 2H). This material was liquid and underwent decarbonylation to produce N-benzoyl-N-methylmethacrylamide quantitatively by distillation.

N-Benzoylformyl-N-ethylmethacrylamide (167)

UV $\lambda_{max.}$ (Cyclohexane): 216 (ε=8400), 258 (7500), and 255nm (60); IR($CHCl_3$): 1620 and 1660 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.28 (t, J=7Hz, 3H), 1.83 (d, J=1Hz, 3H), 3.93 (q, J=7Hz, 2H), 5.13 (m, 1H), 5.33 (br s, 1H), 7.3-7.7 (m, 3H), and 7.9-8.1 (m, 2H). This material was unstable toward distillation as same as 166.

N-Benzoylformyl-N-isopropylmethacrylamide (168)

UV $\lambda_{max.}$ (Cyclohexane); 219 (ε=13200), 258 (14900), and 360nm (140); mp: 62-63°C; IR($CHCl_3$): 1625 and 1660 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.43 (d, J=7Hz, 6H), 1.70 (d, J=1Hz, 3H), 3.83 (sep, J=7Hz, 1H), 5.1 (m, 1H), 5.35 (m, 1H), 7.1-7.5 (m, 3H), and 7.7-8.0 (m, 2H). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.60; N, 5.40.

Found: C, 69.36; H, 6.63; N, 5.37%.

N-Benzoylformyl-N-benzylmethacrylamide (169)

UV $\lambda_{max.}$ (Cyclohexane); 214 (ε=15200), 257 (12200), and 360nm (30); mp: 115-116°C; IR($CHCl_3$): 1620 and 1660 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.75 (d, J=1Hz, 3H), 5.07 (br s, 3H), 5.26 (br s, 1H), 7.0-7.6 (m, 8H), and 7.8-8.1 (m, 2H). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 4.55. Found: C, 73.95; H, 5.59; N, 4.52%.

N-Benzoylformyl-N-(p-methylphenyl)methacrylamide (170)

UV $\lambda_{max.}$ (Cyclohexane); 213 (ε=17300) and 253nm (16500); mp: 109-110°C; IR($CHCl_3$): 1625 and 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.78 (d, J=1Hz, 3H), 2.40 (s, 3H), 5.43 (m, 1H), 5.62 (s, 1H), 7.1-7.7 (m, 7H), and 7.9-8.2 (m, 2H). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 4.55. Found: C, 73.93; H, 5.62; N, 4.52%.

N-Benzoylformyl-N-(2,6-dimethylphenyl)methacrylamide (171)

UV $\lambda_{max.}$ (Cyclohexane); 225 (ε=14000) and 253nm (16600); mp: 109-109.5°C; IR($CHCl_3$): 1625 and 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.72 (d, J=1Hz, 3H), 2.25 (s, 6H), 5.18 (m, 1H), 5.33 (br s, 1H), 7.0-7.6 (m, 6H), and 7.8-8.0 (m, 2H). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.95; N, 4.35. Found: C, 74.65; H, 5.99; N, 4.37%.

N-Benzoylformyl-N-isopropylcrotonamide (172)

UV $\lambda_{max.}$ (Cyclohexane); 229 (ε=14300) and 253nm (14400); IR($CHCl_3$): 1630 and 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.57 (d, J=7Hz, 6H), 1.88 (dd, J=1.5 and 7Hz, 3H), 4.54 (sep, J=7Hz, 1H), 6.29 (dq, J=15 and 1.5Hz, 1H), 6.67 (dq, J=15 and 7Hz, 1H), 7.3-7.7 (m, 3H), and 7.9-8.1 (m, 2H). This material was liquid and underwent decarbonylation to give N-benzoyl-N-isopropylcrotonamide by distillation.

N-Benzoylformyl-N-(p-methylphenyl)crotonamide (173)

UV $\lambda_{max.}$ (Cyclohexane); 240nm (ε=24900); mp: 118-119°C; IR($CHCl_3$) 1630 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.73 (dd, J=1.5 and 6Hz, 3H), 2.42 (s, 3H), 5.77 (dq, J=15 and 1.5Hz, 1H), 6.8-7.7 (m, 8H), and 7.9-8.2 (m, 2H). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 4.55. Found: C, 74.17; H, 5.56; N, 4.55%.

N-Benzoylformyl-N-isopropylcinnamamide (174)

UV λ_{max} (Cyclohexane); 221 (ε=11700), 222 (12100), 228 (12400), 258 (14200), and 291nm (18500); mp: 92.5-94 C; IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.60 (d, J=7Hz, 6H), 4.58 (sep, J=7Hz, 1H), 6.73 (d, J=16Hz, 1H), 7.2-7.6 (m, 4H), and 7.8-8.0 (m, 2H). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.95; N, 4.35. Found: C, 74.68; H, 6.00; N, 4.34%.

N-Benzoylformyl-N-(p-methylphenyl)cinnamamide (175)

UV $\lambda_{max.}$(Cyclohexane); 230 (ε=22700), 250 (19700), and 305nm (28100); mp: 113-114°C; IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.42 (s, 3H), 6.20 (d, J=16Hz, 1H), 7.0-7.7 (m, 13H), and 7.8-8.1 (m, 2H). Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 77.91; H, 5.24; N, 3.75%.

General Procedure for the Photochemical Reactions of 166-175

A solution of the amide (166-175) (200mg) in benzene (40ml) was irradiated in a Pyrex vessel under argon with a 450-W high pressure mercury lamp (USHIO). After the starting material had disappeared, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (flash chromatography).

3,5-Dimethyl-1-phenyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (176)

UV $\lambda_{max.}$ (Cyclohexane); 255 (ε=5600), 251 (490), 257 (500), and 264nm (400); mp: 89-90°C; IR($CHCl_3$): 1695 and 1750 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.66 (s, 3H), 3.10 and 3.29 (ABq, J=10Hz, 2H), 3.21 (s, 3H), and 7.2-7.5(m, 5H). ^{13}C-NMR($CDCl_3$): δ 19.9 (q), 25.3 (q), 48.4 (t), 82.5 (s), 84.3 (s), 125.1 (d), 128.3 (d), 128.8 (d), 135.7 (s), 172.4 (s), and 173.2 (s). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.66, N, 6.05. Found: C, 67.51; H, 5.68; N, 6.05%.

3-Ethyl-5-methyl-1-phenyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (177)

UV $\lambda_{max.}$ (Cyclohexane) 218 (ε=8300), 252 (360), 258 (390), and 264nm (320); mp: 74-75°C; IR($CHCl_3$): 1690 and 1750 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.17 (t, J=7Hz, 3H), 1.58 (s, 3H), 3.01 and 3.19 (ABq, J=9Hz, 2H), 3.79 (q, 2H), and 7.1-7.6 (m, 5H). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.52; H, 6.20; N, 5.69%.

3-Isopropyl-5-methyl-1-phenyl-3-aza-6-oxabicyclo[3,1,1]-heptane-2,4-dione (178)

UV $\lambda_{max.}$ (Cyclohexane); 218 (ε=10400), 252 (410), 257 (450), and 264nm (400); mp: 68.5-70.0°C; IR($CHCl_3$): 1685 and 1745 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.42 (d, J=7Hz, 3H), 1.57 (s, 3H), 2.94 and 3.11 (ABq, J=10Hz, 2H), 4.73 (sep, J=7Hz, 1H), and 7.0-7.4 (m, 5H). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.60; N, 5.40. Found: C, 69.47; H, 6.62; N, 5.38%.

3-Benzyl-5-methyl-1-phenyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (179)

UV $\lambda_{max.}$ (Cyclohexane); 215 (ε=15400), 252 (710), 258 (760), and 264nm (640); bp: 160°C (10^{-3} torr); IR($CHCl_3$): 1690 and 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.62 (s, 3H), 2.98 and 3.20 (ABq, J=10Hz, 2H), 4.87 (s, 2H), and 7.1-7.5 (m, 10H). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 4.55. Found: C, 74.15; H, 5.57; N, 4.55%.

5-Methyl-1-phenyl-3-(p-methylphenyl)-3-aza-6-oxabicyclo[3,1,1]-heptane-2,4-dione (180)

UV $\lambda_{max.}$ (Cyclohexane); 222 (ε=9700), 257 (1100), and 264nm (820); mp: 136.5-138.0°C; IR($CHCl_3$): 1700 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.67 (s, 3H), 2.33 (s, 3H), 3.25 (br, 2H), and 7.1-7.5 (m, 9H). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 5.55. Found: C,73.95, H; 5.56; N, 5.52%.

5-Methyl-1-phenyl-3-(2,6-dimethylphenyl)-3-aza-6-oxa-bicyclo[3,1,1]pentane-2,4-dione (181)

UV $\lambda_{max.}$ (Cyclohexane); 217 (ε=15600), 258 (810), 264 (850), and 272nm (610); mp: 168-170°C; IR($CHCl_3$): 1700 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.72 (s, 3H), 2.15 (s, 6H), 3.33 (br, 2H), and 7.0-7.4 (m, 8H). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.95; N, 4.35. Found: C, 74.44; H, 5.92; N, 4.32%.

7-Methy-1-phenyl-3-isopropyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (182)

UV $\lambda_{max.}$ (Cyclohexane); 218 (ε=18500), 252 (890), 258 (970), and 263nm (860); mp: 131-134°C; IR($CHCl_3$): 1690 and 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.50 (d, J=7Hz, 1H), 1.50 (d, J=7Hz, 6H), 3.83 (quint, J=7Hz, 1H), 4.82 (d, J=7Hz, 1H), 4.80 (m, 1H), and 7.2-7.5 (m, 5H). ^{13}C-NMR($CDCl_3$): δ 10.5 (q), 19.5 (q), 44.2 (d),

51.0 (d), 82.3 (d), 92.1 (s), 171.4 (s), and 172.1 (s). ^{1}H-NMR($CDCl_3$): δ 1.23 (d, J=7Hz, 6H), 1.45 (d, J=7Hz, 3H), 3.21 (qd, J=7 and 1Hz, 1H), 4.48 (d, J=1Hz, 1H), 4.80 (m, 1H), 7.2-7.5 (m, 5H). ^{13}C-NMR($CDCl_3$): δ 13.3 (q), 19.3 (q), 44.0 (d), 50.1 (d), 82.4 (d), 90.6 (s), 170.1 (s), and 171.8 (s). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.60; N, 5.40. Found: C, 69.49; H, 6.63; N, 5.36%.

1,7-Diphenyl-3-isopropyl-3-aza-6-oxabicyclo[3,1,1]heptane-2,4-dione (183)

UV $\lambda_{max.}$ (Cyclohexane); 218 (ε=19900), 253 (1400), 259 (1570), and 263nm (1460); mp: 92.5-94°C; IR($CHCl_3$): 1690 and 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.02 (d, J=7Hz, 6H), 4.55 (sep, J=7Hz, 1H), 5.16 (d, J=7Hz, 1H), 5.26 (d, J=7Hz, 1H), and 7.0-7.6 (m, 10H). ^{13}C-NMR($CDCl_3$): δ 18.7 (q), 43.7 (d), 57.0 (d), 81.6 (d), 91.8 (s), 170.8 (s), 170.4 (s). ^{1}H-NMR($CDCl_3$): δ 1.50 (d, J=7Hz, 3H), 1.52 (d, J=7Hz, 3H), 4.19 (br s, 1H), 4.86 (sep, J=7Hz, 1H), 5.01 (br s, 1H), and 7.0-7.6 (m, 10H). ^{13}C-NMR($CDCl_3$): δ 19.3 (q), 44.2 (d), 59.8 (d), 82.3 (d), 92.3 (s), 171.1 (s), and 171.5 (s). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.95; N, 4.35. Found: C, 74.52; H, 5.89; N, 4.31%.

Sensitization and Quenching of 169 for the Formation of 179

Irradiations were performed in a merry-go-round apparatus. The 366nm line was isolated with a filter solution containing 0.04M naphthalene. Concentration of the sensitizers was adjusted to that 95% or more of the incident light was absorbed by the sensitizers. In the case of 169, the sensitized reaction was efficient as same as the direct photolysis ($\Phi_{sens}/\Phi \simeq 1$).

Quenching of the photoreaction of 169 was carried out in the presence of stilbene (0.1M) or piperylene (1.0M). The efficiency of the photoreaction was not different from the direct photolysis.

Quantum Yield Determination of 169-171

Benzophenone-benzhydrol actinometry was used for the quantum yield determination. The 366nm line was isolated. Samples (0.05M benzene solution) in Pyrex tubes were degassed to ca. 10^{-3} torr in three freeze-thaw cycles and sealed. These samples were irradiated in a merry-go-round apparatus. Photolyses were carried out to 30-40% conversion. The degree of the reaction was determined by NMR spectroscopy. It was confirmed that the photoproducts (179-181) did not absorb the 366nm line.

Preparation of N-Aroylureas (184-191)

To a benzene solution of corresponding urea was added triethylamine and aroyl chloride. The mixture was refluxed for 2hr and then triethylamine hydrochloride was precipitated. The reaction mixture was extracted with benzene. After the mixture was washed with hydrogen chloride (1N) and aqueous sodium hydrogen carbonate, dried with magnesium sulfate. The solvent was removed by evaporation. The crude aroylurea was isolated by chromatography on silica gel with benzene-ethyl acetate solvent and then recrystallized from chloroform-hexane mixture.

1,3,3-Trimethyl-1-benzoylurea (184)

mp: 126-127°C; IR($CHCl_3$): 1640 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ

2.77 (s, 6H), 3.30 (s, 3H), and 7.2-7.9 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 33.2 (q), 37.0 (q), 127.4 (d), 128.1 (d), 131.2 (d), 135.2 (s), 158.2 (s), and 169.8 (s). Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.03; H, 6.81; N, 13.58%.

3,3-Diethyl-1-benzoyl-1-methylurea (185)

IR($CHCl_3$): 1640 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.90 (t, J=7Hz, 6H), 3.16 (q, J=7Hz, 4H), 3.21 (s, 3H), 7.2-7.8 (m, 5H).

3,3-Diisopropyl-1-benzoyl-3-methylurea (186)

mp: 74.5-76.5°C; IR($CHCl_3$): 1645 and 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.07 (d, J=6Hz, 12H), 3.21 (s, 3H), 3.50 (sep, J=6Hz, 2H), and 7.1-7.8 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 19.8 (q), 19.9 (q), 33.3 (q), 128.1 (d), 128.2 (d), 130.9 (d), 135.0 (s), 155.0 (s), and 169.1 (s). Anal. Calcd for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.67. Found: C, 68.71; H, 8.53; N, 10.63%.

3,3-Dibenzyl-1-benzoyl-3-methylurea (187)

mp: 86.5-87.5°C; IR($CHCl_3$): 1640 and 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.12 (s, 3H), 4.35 (s, 4H), and 6.8-7.7 (m, 15H); ^{13}C-NMR($CDCl_3$): δ 33.7 (q), 50.4 (t), 123.7 (d), 128.2 (d), 128.4 (d), 130.7 (d), 135.0 (s), 135.2 (s), 158.7 (s), and 170.0 (s); Anal. Calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.18; N, 7.81. Found: C, 76.86; H, 6.18; N, 7.79%.

3,3-Dibenzyl-1-(p-cyanobenzoyl)-1-methylurea (188)

mp: 128.5-130.0°C; IR($CHCl_3$): 1640, 1680, and 2240 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.07 (s, 3H), 4.30 (s, 4H), and 6.8-7.5 (m, 14H); ^{13}C-NMR($CDCl_3$): δ 33.7 (q), 50.7 (t), 117.8 (d), 126.5 (d), 127.9 (d), 128.0 (d), 128.8(d), 132.1 (d), 135.0 (s), 139.0 (s), 158.0 (s), and 168.5 (s).

3,3-Dibenzyl-1-(p-methoxypheny)-1-methylurea (189)

IR($CHCl_3$): 1635 and 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.09 (s, 3H), 3.75 (s, 3H), 4.33 (s, 4H), and 6.7-7.6 (m, 14H); ^{13}C-NMR($CDCl_3$): δ 34.1 (q), 50.7 (t), 55.3 (q), 126.4 (d), 127.3 (d), 127.7 (d), 127.8 (d), 128.6 (d), 129.8 (s), 135.6 (s), 162.0 (s), and 170.0 (s).

3,3-Dibenzyl-1-(p-chlorobenzoyl)-1-methylurea (190)

mp: 120.0-121.5 °C; IR($CHCl_3$): 1640 and 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.12 (s, 3H), 4.35 (s, 4H), and 6.9-7.6 (m, 14H); ^{13}C-NMR($CDCl_3$): δ 33.8 (q), 50.7 (t), 127.8 (d), 128.3 (d), 128.6 (d), 128.9 (d), 133.5 (s), 135.3 (s), 137.1 (s), 158.6 (s), and 169.0 (s); Anal. Calcd for $C_{23}H_{21}N_2O_2Cl$: C, 70.31; H, 5.38; N, 7.13. Found: C, 70.37; H, 5.37; N, 7.10%.

3,3-Dibenzyl-1-(2-naphthoyl)-1-methylurea (191)

IR($CHCl_3$): 1635 and 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.20 (s, 3H), 4.38 (s, 4H), and 6.7-8.2 (m, 17H).

3,3-Dimethyl-1-benzoyl-1-(2-phenethyl)urea (202)

IR($CHCl_3$): 1640 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.49 (br s, 6H), 3.03 (t, J=7Hz, 2H), 4.02 (t, J=7Hz, 2H), and 7.2-7.7 (m, 10H). ^{13}C-NMR($CDCl_3$): δ 34.6 (t), 36.9 (q), 47.4 (t), 126.1 (d), 126.3 (d), 127.4 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.7 (d), 129.8 (d), 130.2 (d), 131.3 (d), 132.9 (d), 135.3 (d), 138.2 (s), 157.6 (s), 169.6 (s).

3,3-Dimethyl-1-benzoyl-1-(2-methoxymethyl)urea (203)

IR($CHCl_3$): 1635 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.48 (br s, 6H), 3.30 (s, 3H), 3.41 (t, J=6Hz, 2H), 3.75 (t, J=6Hz, 2H), and 7.2-7.7 (m, 5H). ^{13}C-NMR($CDCl_3$): δ 36.0 (t), 37.0 (q), 57.8 (q),

65.2 (t), 127.3 (d), 128.0 (d), 131.0 (d), 135.3 (s), 158.9 (s), and 170.0 (s).

General Procedure for the Photoreaction of Aroylureas (184-191, 202-203)

A solution of aroylurea (200mg) in 40ml of acetonitrile was deaerated with argon and irradiated with a low pressure mercury lamp for 6-10hr. After removal of the solvent, the residue was chromatographed on silica gel with benzene-ethyl acetate solvent. The photoproducts were isolated and the crystalline products were recrystallized from chroloform-hexane mixture.

4-Hydroxy-1-isopropyl-4-phenyl-3,5,5-trimethylimidazolidin-2-one (192)

mp: 74.5-76°C; IR($CHCl_3$): 1680 and 3400 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.70 (s, 3H), 1.33 (s, 3H), 1.42 (d, J=7Hz, 6H), 2.35 (br, 1H), 2.68 (s, 3H), 3.35 (sep, J=7Hz, 1H), and 7.3-7.6 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 19.8 (q), 20.7 (q), 22.3 (q), 24.9 (q), 25.7 (q), 44.0 (d), 64.7 (s), 93.6 (s), 127.4 (d), 128.2 (d), 128.3 (d), 137.5 (s), and 158.9 (s). Anal. Calcd for $C_{15}H_{22}N_2O_2(H_2O)$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.34; H, 8.68; N, 9.79%.

1-Benzyl-4-hydroxy-3-methyl-4,5-diphenylimidazolidin-2-one (193)

IR($CHCl_3$): 1690 and 3580 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.70 (s, 3H), 3.70 and 5.10 (ABq, J=14Hz, 2H), 4.24 (s, 1H), 6.9-7.5 (m, 15H). ^{1}H-NMR ($CDCl_3$): δ 2.75 (s, 3H), 3.73 and 5.13 (ABq, J=14Hz, 2H), 4.52 (s, 1H), and 6.9-7.5 (m, 15H).

1-Benzyl-4,5-diphenyl-3-methylimidazol-2-one (195)

mp: 120.5-121.5°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.23 (s, 3H), 4.85 (s, 2H), and 7.0-7.4 (m, 15H); ^{13}C-NMR($CDCl_3$): δ

29.1 (q), 45.3 (t), 121.1 (s), 121.5 (s), 127.1 (d), 127.5 (d), 127.1 (d), 127.5 (d), 127.8 (d), 128.0 (d), 128.3 (d), 129.9 (s), 130.6 (s), 137.6 (s), and 153.8 (s). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.14; H, 5.92; N, 8.22. Found: C, 80.83; H, 5.95; N, 8.17%.

1-Benzyl-4-(p-cyanophenyl)-4-hydroxy-3-methyl-5-phenyl-imidazolidin-2-one (194)

IR($CHCl_3$): 1690, 2240, and 3580 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.80 (s, 3H), 3.73 and 5.13 (ABq, J=14Hz, 2H), 4.50 (s, 1H), and 6.8-7.8 (m, 15H). ^{1}H-NMR($CDCl_3$): δ 2.84 (s, 3H), 3.81 and 5.21 (ABq, J=14Hz, 2H), 4.64 (s, 1H), and 6.8-7.8 (m, 15H).

1-Benzyl-4-(p-methoxyphenyl)-3-methyl-5-phenylimidazol-2-one (197)

mp: 126-127°C; IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.13 (s, 3H), 3.62 (s, 3H), 4.73 (s, 2H), and 6.7-7.4 (m, 14H); ^{13}C-NMR($CDCl_3$): δ 28.8 (q), 45.2 (t), 55.0 (q), 120.4 (s), 121.1 (s), 127.0 (d), 127.3 (d), 127.8 (d), 128.2 (d), 128.5 (d), 128.8 (d), 129.2 (d), 130.4 (d), 131.2 (s), 137.6 (s), 137.8 (s), and 159.1 (s). Mass (C.I.): m/e 371 (M+1); Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.98; N, 7.56. Found: C, 77.82; H, 6.03; N, 7.44%.

1-Benzyl-3-methyl-7-methoxyphenanthro[9,10-d]imidazol-2-one (199)

mp: 209.5-211°C; IR($CHCl_3$): 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.95 (s, 3H), 4.10 (s, 3H), 5.60 (s, 2H), and 6.9-8.0 (m, 12H); Mass (C.I.): m/e 369 (M+1); Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 76.75; H, 5.54; N, 7.46. Found: C, 76.77; H, 5.45; N, 7.16%.

1-Benzyl-4-(p-chlorophenyl)-3-methyl-5-phenylimidazol-2-one (198)

mp: 123.5-125°C; IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.92 (s, 3H), 4.63 (s, 2H), and 6.9-7.8 (m, 14H); ^{13}C-NMR($CDCl_3$): δ 29.1

(q), 45.3 (t), 120.2 (s), 121.4 (s), 126.8 (d), 127.2 (d), 127.5 (d), 127.8 (d), 128.0 (d), 128.3 (d), 128.7 (d), 129.1 (d), 129.9 (d), 130.5 (d), 131.0 (s), 133.7 (s), 137.6 (s), and 135.8 (s); Mass (C.I.): m/e 375 (M+1).

1-Benzyl-7-chloro-3-methylphenanthro[9,10-d]imidazol-2-one (200) mp: 242.5-243.5°C; IR($CHCl_3$): 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 4.00 (s, 3H), 5.63 (s, 2H), and 7.0-8.0 (m, 12H); Mass (C.I.): m/e 373 (M+1); Anal. Calcd for $C_{23}H_{17}N_2O_2Cl(0.3H_2O)$: C, 73.04; H, 4.65; N, 7.37. Found; C, 73.02; H, 4.62; N, 7.25%.

Quenching of the Photoreaction of 187

Two Pyrex tubes were irradiated at 254nm line with merry-go-round apparatus. One was an acetonitrile solution of 187 containing excess of 1,3-pentadiene. The other was an acetonitrile solution of 187. After removal of acetonitrile, the degree of the reaction was determined by NMR spectroscopy.

Preparation of 187-d_2

To a solution of benzylamine in benzene was added dropwise benzoylchloride at room temperature and the mixture was stirred for 1hr. After removal of the solvent, N-benzylbenzamide was recrystallized from chloroform-hexane mixture. Lithium aluminum deuteride was added to a solution of N-benzylbenzamide in dry ether and the mixture was refluxed for 12hr. After filtration through celite column, washed with aqueous sodium hydroxide, and dried over anhydrous magnesium sulfate. After evaporation, dibenzyl amine-d_2 was dissolved in benzene and added dropwise a benzene solution of methyl isocyanate in an ice bath. After

removal of a solvent, N,N-dibenzyl-N'-methylurea-d_2 was obtained. The title compound was obtained from this urea and benzoyl chloride as in the case of 187.

Preparation of Monothioimides (204-210)

All these compounds were prepared by the reaction of N-substituted thiobenzamides with benzoyl chloride or acetyl chloride. A typical run is exemplified for the preparation of 204. To a solution of N-isopropyl thiobenzamide (600mg, 3.35mmol) and benzoyl chloride (560mg, 4mmol) in 20ml of dry benzene was added triethylamine (400mg, 4mmol) drop by drop at room temperature under argon. The reaction mixture was stirred further 2hrs. After benzene was removed by evaporation, the residue was chromatographed on silica gel. N-Benzoyl-N-isopropylthiobenzamide (204, 900mg, 95%) was isolated and recrystallized from chloroform-hexane mixture.

N-Benzoyl-N-isopropylthiobenzamide (204)

mp: 68.5-69.5°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.56 (d, J=6.8Hz, 6H), 5.80 (sep, J=6.8Hz, 1H), and 6.9-7.5 (m, 10H)); ^{13}C-NMR($CDCl_3$): δ 20.1 (q), 56.5 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.7 (d), 130.1 (d), 132.3 (d), 137.1 (s), 146.1 (s), 174.7 (s), and 207.3 (s). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.04; N, 4.91. Found: C, 71.92; H, 6.08; N, 4.91%.

N-Benzoyl-N-isobutylthiobenzamide (205)

bp: 60°C (10^{-3} torr); IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.05 (t, J=7.8Hz, 3H), 1.51 (d, J=6.8Hz, 3H), 1.7-2.3 (m, 2H), 5.4-5.8 (m, 1H), and 6.8-7.5 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 11.6 (q), 17.6

(q), 28.1 (t), 62.6 (d), 127.7 (d), 127.9 (d), 128.6 (d), 130.0 (d), 132.0 (d), 137.1 (s), 146.2 (s), 174.4 (s), and 208.9 (s). Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.43; N, 4.70. Found: C, 72.59; H, 6.45; N, 4.66%.

N-Benzoyl-N-(α-phenethyl)thiobenzamide (206)

mp: 102-104°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.97 (d, J=6.8Hz, 3H), 6.8-7.4 (m, 13H), and 7.5-7.8 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 17.8 (q), 62.5 (d), 126.6 (d), 126.8 (d), 127.6 (d), 127.8 (d), 130.1 (d), 132.0 (d), 137.1 (s), 139.8 (s), 146.3 (s), 174.1 (s), 208.2 (s). Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.48; H, 5.54; N, 4.05. Found: C, 76.51; H, 5.54; N, 4.06%.

N-Acetyl-N-isopropylthiobenzamide (207)

bp: 45°C (10^{-3} torr); IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.45 (d, J=6.8Hz, 6H), 1.79 (s, 3H), 5.31 (sep, J=6.8Hz, 1H), 7.2-7.7 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 20.0 (q), 28.4 (q), 56.2 (d), 127.9 (d), 128.6 (d), 131.7 (d), 145.8 (s), 174.3 (s), and 209.2 (s). Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.32. Found; C, 65.11; H, 6.84; N, 6.31%.

N-Acetyl-N-(α-phenethyl)thiobenzamide (208)

bp: 55°C (10^{-3} torr); IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.61 (s, 3H), 1.87 (d, J=7.3Hz, 3H), 6.64 (q, J=7.3Hz, 1H), and 7.1-7.7 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 17.1 (q), 28.7 (q), 62.1 (d), 127.2 (d), 127.3 (d), 127.9 (d), 128.2 (d), 128.7 (d), 131.7 (d), 139.9 (s), 145.8 (s), 174.4 (s), and 209.2 (s). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.04; N, 4.94. Found: C, 72.00; H, 6.05; N, 4.95%.

N-Acetyl-N-benzylthiobenzamide (209)

mp: 80.5-81.5°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.69 (s,

2H), 6.8-7.4 (m, 13H), 7.5-7.8 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 56.5 (t), 127.9 (d), 128.3 (d), 128.5 (d), 129.2 (d), 130.5 (d), 131.7 (d), 136.2 (s), 136.5 (s), 146.2 (s), 174.6 (s), and 209.4 (s). Anal. Calcd for $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.22. Found: C, 76.04; H, 5.17; N, 4.18%.

N-Benzoyl-N-isobutylthiobenzamide (210)

mp: 71.5-72.5°C; IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.06 (d, J=6.8Hz, 6H), 2.3-2.7 (m, 1H), 4.33 (d, J=7.3Hz, 2H), and 6.9-7.5 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 20.7 (q), 25.8 (d), 61.2 (t), 127.9 (d), 128.0 (d), 128.7 (d), 130.5 (d), 131.9 (d), 136.6 (s), 146.5 (s), 175.1 (s), and 210.2 (s). Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.43; N, 4.70. Found: C, 72.58; H, 6.38; N, 4.61%.

General Procedure for the Photoreaction of N-Acylthiobenzamides (204-210)

A benzene solution (40ml) of the monothioimide (1%) was irradiated in a Pyrex vessel under argon with a 1000-W high pressure mercury lamp for 0.5-2hr. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene-ethyl acetate afforded the photoproducts.

(α-Benzoylamino)thioisobutyrophenone (211)

mp: 123.5-125°C; IR($CHCl_3$): 1505, 1655 and 3310 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.90 (s, 6H), 7.2-7.5 (m, 8H), 7.6-7.8 (m, 2H), and 7.88 (br s, 1H); ^{13}C-NMR($CDCl_3$): δ 27.8 (q), 68.5 (s), 125.9 (d), 126.9 (d), 127.5 (d), 128.4 (d), 129.2 (d), 131.4 (d), 135.2 (s), 148.1 (s), 166.2 (s), and 255.6 (s). Mass (EI): m/e 283 (M+.) and 162 (M-PhCS). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.04;

N, 4.94. Found: C, 71.83; H, 6.04; N, 4.90%.

(α-Benzoylamino)-α-methyl-thiobutyrophenone (212)

mp: 99-100.5°C; IR($CHCl_3$): 1500, 1650, and 3300 cm^{-1}; ^1H-NMR($CDCl_3$): δ 0.85 (t, J=7.3Hz, 3H), 1.92 (s, 3H), 2.0-2.4 (m, 1H), 2.6-3.1 (m, 1H), 7.1-7.6 (m, 8H), 7.7-7.9 (m, 2H), and 8.30 (br s, 1H); ^{13}C-NMR($CDCl_3$): δ 8.51 (q), 25.4 (q), 29.9 (t), 72.3 (s), 125.7 (d), 126.8 (d), 127.6 (d), 128.4 (d), 129.2 (d), 131.2 (d), 135.3 (s), 147.8 (s), 165.5 (s), and 254.5 (s). Mass (EI): m/e 297 (M+.) and 176 (M-PhCS). Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.43; N, 4.70. Found: C, 72.58; H, 6.38; N, 4.61%.

(α-Benzoylamino)-α-phenylthiopropiophenone (213)

bp: 120°C (10^{-3} torr); IR($CHCl_3$): 1500, 1650 and 3360 cm^{-1}; ^1H-NMR($CDCl_3$): δ 2.19 (s, 3H), 6.7-7.6 (m, 13H), 7.7-7.9 (m, 2H), and 9.38 (br s, 1H); ^{13}C-NMR($CDCl_3$): δ 23.5 (q), 71.4 (s), 126.9 (d), 127.3 (d), 128.0 (d), 128.4 (d), 130.3 (d), 131.3 (d), 135.0 (s), 139.0 (s), 146.5 (s), 164.2 (s), and 249.5 (s). Mass (EI): m/e 345 (M+.) and 224 (M-PhCS). Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.48; H, 5.54; N, 4.05. Found: C, 76.88; H, 5.63; N, 4.04%.

(α-Acetylamino)thioisobutyrophenone (214)

mp: 150-151.5°C; IR($CHCl_3$): 1500, 1660 and 3300 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.78 (s, 6H), 1.85 (s, 3H), 7.03 (br s, 1H), and 7.1-7.5 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 23.7 (q), 28.6 (q), 68.0 (s), 125.8 (d), 127.3 (d), 129.1 (d), 148.4 (s), 168.9 (s), and 255.8 (s). Mass (EI): m/e 221 (M+.) and 100 (M-PhCS). Anal. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.32. Found: C, 64.86; H, 6.79; N, 6.25%.

(α-Acetylamino)-α-phenylthiopropiophenone (215)

bp: 100°C (10^{-3} torr); IR($CHCl_3$): 1480, 1660 and 3300 cm^{-1}; ^1H-

NMR($CDCl_3$): δ 1.88 (s, 3H), 2.07 (s, 3H), 6.7-7.5 (m, 10H), and 8.29 (br s, 1H); ^{13}C-NMR($CDCl_3$): δ 23.9 (q), 71.3 (s), 126.9 (d), 127.7 (d), 128.0 (d), 128.2 (d), 129.9 (d), 139.9 (s), 146.5 (s), 167.5 (s), and 248.8 (s). Mass (EI): m/e 283 (M+.) and 162 (M-PhCS). Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.04; N, 4.94. Found: C, 71.88; H, 6.07; N, 4.90%.

Trapping of the Intermediate (217) by Acetyl Chloride

A toluene solution (40ml) of 206 (200mg, 0.52mmol) was irradiated with a high pressure mercury lamp under argon at -78°C until the solution became colorless. Then, acetyl chloride (80mg, 1.0mmol) and triethylamine (100mg, 1.0mmol) were added to the reaction mixture. After standing over night at -78°C, the reaction mixture was warmed up to the room temperature gradually. The toluene was removed by evapcration and the residue was chromatographed on silica gel to give 2,3-diphenyl-2-acetothioxy-1-benzoyl-3-methylaziridine (218, 190mg, 85%) and (213, 18mg, 9%).

2,3-Diphenyl-2-acetothioxy-1-benzoyl-3-methylaziridine (218)

mp: 100-101 °C; IR($CHCl_3$): 1660 and 1705 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.14 (s, 3H), 2.01 (s, 3H), 7.3-7.8 (m, 13H), and 8.1-8.2 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 26.3 (q), 31.3 (q), 80.6 (s), 104.7 (s), 126.6 (d), 127.7 (d), 128.0 (d), 128.5 (d), 128.6 (d), 131.9 (d), 139.0 (s), 140.9 (s), 161.6 (s), and 191.8 (s). Mass (EI): m/e 387 (M+.) and 312 [M-SC(=O)Me], and 207 [M-SC(=O)Me-Ph(C=O)]. Anal. Calcd for $C_{23}H_{21}NO_2S.CHCl_3$: C, 59.25; H, 4.38; N, 2.76. Found: C, 59.47; H, 4.42; N, 2.77%.

Preparation of Monothioimides

All monothioimides were synthesized from corresponding thioamides and acid chlorides as in the case of 204-210.

N-Isobutyroylthiobenzanilide (219)

mp: 100-101 °C; IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.15 (d, J=7Hz, 6H), 2.81 (sep, J=7Hz, 1H), 7.1-7.5 (m, 8H), and 7.5-7.7 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 19.6 (q), 36.0 (d), 127.3 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.7 (d), 131.2 (d), 145.1 (s), 143.6 (s), 180.7 (s), 212.2 (s). Anal. Calcd for $C_{17}H_{17}NOS$; C, 72.05; H, 6.04; N, 4.94. Found: C, 72.08; H, 6.06; N, 4.92%.

N-Isobutyroylthioacetanilide (220)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.13 (s, 3H), 2.75 (sep, J=7Hz, 1H), 2.97 (s, 3H), and 7.1-7.6 (m, 5H).

N-Phenylacetylthioacetanilide (221)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.03 (s, 3H), 3.63 (s, 2H), and 6.9-7.5 (m, 15H).

N-Methoxyacetylthioacetanilide (222)

IR($CHCl_3$): 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.21 (s, 3H), 3.65 (s, 3H), 4.60 (s, 2H), and 7.0-7.8 (m, 5H).

N-Methoxyacetylthiobenzanilide (223)

IR($CHCl_3$): 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.30 (s, 3H), 4.07 (s, 2H), and 7.2-7.9 (m, 10H).

N-Isobutyroylpyrrolidine-2-thione (224)

IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.18 (d, J=7Hz, 6H), 2.03 (quint, J=7Hz, 2H), 3.20 (t, J=7Hz, 2H), 4.13 (t, J=7Hz, 2H), and 4.53 (sep, J=7Hz, 1H).

N-Phenylacetylpyrrolidine-2-thione (225)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.98(quint, J=7Hz, 2H), 3.17 (t, J=7Hz, 2H), 4.12 (t, J=7Hz, 2H), 4.62 (s, 2H), and 7.22 (s, 5H).

N-Isobutyroylpiperidine-2-thione (226)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.21 (d, J=7Hz, 6H), 1.6-2.1 (br, 4H), and 2.7-3.9 (br, 5H).

N-Methoxyacetylpiperidine-2-thione (227)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.6-2.1 (br, 4H), 2.7-3.9 (br, 4H), 3.50 (s, 3H), and 4.50 (s, 2H).

N-Isobutyroylthio-ε-caprolactam (228)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.44 (d, J=7Hz, 6H), 1.5-2.0 (br, 6H), and 2.1-4.8 (br, 5H).

N-Methoxyacetylthio-ε-caprolactam (229)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.5-2.0 (br, 6H), 2.1-4.8 (br, 4H), 3.50 (s, 3H), and 4.50 (s, 2H).

General Procedure for the Photochemical Reaction of Monothioimides (219-229)

A benzene solution of monothioimide was irradiated with a 1000-W high pressure mercury lamp under argon at 10-15 °C until the starting material disappeared. Then, three equivalent molar acid chloride and triethylamine were added to the reaction mixture was stood for over night. Precipitated triethylamine hydrochloride was filtered through a celite column and the resulting mixture was chromatographed on silica gel. The crystalline products were recrystallized from chloroform-hexane mixture.

3,3-Dimethyl-1,4-diphenyl-4-benzoylthioazetidin-2-one (232)

mp: 152.5-153°C; IR($CHCl_3$): 1665 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.95 (s, 3H), 1.61 (s, 3H), 6.9-7.6 (m, 13H), and 7.7-7.9 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 19.4 (q), 22.2 (q), 62.4 (s), 82.7 (s), 117.9 (d), 123.9 (d), 126.2 (d), 127.3 (d), 128.6 (d), 133.6 (d), 136.9 (s), 137.5 (s), 170.6 (s), and 190.0 (s). Anal. Calcd for $C_{24}H_{21}NO_2S$: C, 74.39; H, 5.46; N, 3.61. Found: C, 74.35; H, 5.44; N, 3.60%.

N-Benzoylthiobenzanilide (244)

IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 6.9-8.2 (m).

3,3,4-Trimethyl-4-benzoylthio-1-phenylazetidin-2-one (233)

IR($CHCl_3$): 1660 and 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.52 (s, 3H), 1.56 (s, 3H), 2.18 (s, 3H), 7.0-7.8 (m, 8H), and 7.8-8.0 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 18.6 (q), 20.2 (q), 22.8 (q), 60.5 (s), 76.7 (s), 118.1 (d), 124.2 (d), 127.0 (d), 128.5 (d), 128.9 (d), 133.6 (d), 136.4 (s), 169.9 (s), and 190.4 (s).

1-(N-Benzoylanilino)-1-(benzoylthio)ethylene (245)

IR($CHCl_3$): 1670 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.7 (m, 2H), 7.1-7.7 (m, 11H), and 7.8-8.1 (m, 4H).

1,3-Diphenyl-4-benzoylthio-4-methylazetidin-2-one (234)

(cis: 17%); IR($CHCl_3$): 1660 and 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.22 (s, 3H), 4.75 (s, 1H), and 6.9-7.8 (m, 15H); ^{13}C-NMR($CDCl_3$): δ 25.8 (q), 69.2 (d), 74.6 (s), 118.2 (d), 124.6 (d), 126.6 (d), 127.3 (d), 127.7 (d), 128.2 (d), 129.0 (d), 130.4 (d), 132.1 (s), 133.1 (d), 136.2 (s), 136.5 (s), 164.2 (s), and 188.6 (s).

(trans: 18%); IR($CHCl_3$): 1660 and 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.73 (s, 3H), 5.06 (s, 1H), and 7.0-8.0 (m, 15H); ^{13}C-NMR($CDCl_3$): δ 22.5 (q), 69.0 (d), 72.6 (s), 118.1 (d), 124.7 (d), 127.2 (d),

128.2 (d), 128.7 (d), 129.7 (d), 129.8 (d), 132.3 (s), 133.9 (d), 136.4 (s), 136.6 (s), 164.4 (s), and 190.1 (s).

1,3-Diphenyl-4-phenylacetylthio-4-methylazetidin-2-one (235) (cis); IR($CHCl_3$): 1670 and 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.24 (s, 3H), 3.30 (s, 2H), 4.63 (s, 1H), 6.7-6.9 (m, 2H), and 7.0-7.9 (m, 13H); ^{13}C-NMR($CDCl_3$): δ 25.7 (q), 50.3 (t), 69.0 (d), 74.4 (s), 118.2 (d), 124.6 (d), 127.2 (d), 127.5 (d), 127.8 (d), 128.4 (d), 129.1 (d), 129.3 (d), 130.5 (d), 132.2 (s), 132.3 (s), 136.2 (s), 164.1 (s), and 194.0 (s).

1-Benzoylthio-3-methoxy-4-methyl-1-phenylazetidin-2-one (236) (cis); IR($CHCl_3$): 1670 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.15 (s, 3H), 3.58 (s, 3H), 4.54 (s, 1H), 7.0-7.7 (m, 8H), and 7.8-8.0 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 24.1 (q), 60.5 (q), 75.6 (s), 91.5 (d), 118.3 (d), 124.7 (d), 127.0 (d), 128.4 (d), 129.0 (d), 133.4 (d), 135.6 (s), 136.6 (s), 162.9 (s), and 189.0 (s).

1,4-Diphenyl-4-acetylthio-3-methoxyazetidin-2-one (237) (trans); mp: 100-101°C; IR($CHCl_3$): 1700 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.30 (s, 3H), 3.58 (s, 3H), 4.42 (s, 1H), and 7.0-7.6 (m, 10H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.27. Found: C, 66.02; H, 5.29; N, 4.25%.

(cis); mp: 100-101 C; IR($CHCl_3$): 1690 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.32 (s, 3H), 3.32 (s, 3H), 5.28 (s, 1H), and 7.0-7.8 (m, 10H). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.27. Found: C, 65.95; H, 5.25; N, 4.20%.

7,7-Dimethyl-6-acetylthio-8-oxo-1-azabicyclo[4,2,0]octane (238) IR($CHCl_3$): 1680 and 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.9-3.0 (m, 6H), 1.40 (s, 3H), 1.45 (s, 3H), 2.35 (s, 3H), and 3.5-4.0 (m, 2H).

N-Acetylpiperidine-2-thione (249)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.0-2.0 (m, 4H), 2.65 (s, 3H), 2.9-3.3 (m, 2H), and 3.7-4.0 (m, 2H).

6-Acetylthio-7-methoxy-8-oxo-1-azabicyclo[4,2,0]octane (239)

mp: 78-79°C; IR($CHCl_3$): 1690 and 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.2-1.9 (br, 4H), 2.3-2.9 (br, 2H), 2.35 (s, 3H), 3.53 (s, 3H), 3.6-3.9 (m, 2H), and 4.44 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 20.3 (t), 24.0 (t), 31.2 (q), 34.2 (t), 37.5 (t), 60.6 (q), 74.4 (s), 93.6 (d), 163.5 (s), and 194.3 (s). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.10. Found: C, 52.39; H, 6.65; N, 6.11%.

8,8-Dimethyl-7-acetylthio-9-oxo-1-azabicyclo[5,2,0]nonane (240)

mp: 100-101°C; IR($CHCl_3$): 1680 and 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.0-2.6 (br, 6H), 1.37 (s, 6H), 2.33 (s, 3H), 2.8-3.2 (br, 2H), and 2.3-2.8 (br, 2H); ^{13}C-NMR($CDCl_3$): δ 18.2 (q), 20.8 (q), 26.5 (t), 29.1(t), 31.0 (q), 36.7 (t), 42.3 (t), 60.4 (s), 80.5 (s), 172.1 (s), and 194.7 (s). Anal. Calcd for $C_{12}H_{19}NO_2S$: C, 59.71; H, 7.93; N, 5.80. Found: C, 59.99; H, 8.13; N, 5.95%.

7-Acetylthio-8-methoxy-9-oxo-1-azabicyclo[5,2,0]nonane (241)

mp: 100-101°C; IR($CHCl_3$): 1680 and 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.2-1.9 (br, 6H), 2.0-2.6 (br, 2H), 2.35 (s, 3H), 2.8-3.8 (br, 4H), 3.53 (s, 3H), and 4.34 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 25.0 (t), 28.0 (t), 29.2 (t), 31.4 (q), 38.6 (t), 42.2 (t), 60.1 (q), 79.5 (s), 89.9 (d), 165.2 (s), and 194.5 (s). Anal. Calcd for $C_{11}H_{17}NO_3S$: C, 54.29; H, 7.04; N, 5.75. Found; C, 54.11; H, 7.02; N, 5.76%.

Preparation of N-Acylthiourethanes (254-259)

Title compounds were obtained by the reactions of correspon-

ding thiourethanes and acyl chlorides as in the case of the synthesis of monothioimides (204-210).

N-Isobutyroyl-N-phenylthiocarbamic acid O-methyl ester (254)

UV $\lambda_{max.}$ (Cyclohexane): 275nm (ε=27600); IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.20 (d, J=7Hz, 2H), 2.57 (sep, J=7Hz, 1H), 4.07 (s, 3H), and 7.0-7.5 (m, 5H).

N-Phenyl-N-phenylacetylthiocarbamic acid O-methyl ester (255)

UV $\lambda_{max.}$ (Cyclohexane): 274 (ε=9800) and 366nm (160); IR($CHCl_3$): 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.60 (s, 2H), 3.92 (s, 3H), and 6.8-7.4 (m, 10H).

N-Diphenylacetyl-N-methylthiocarbamic acid O-methyl ester (256)

mp: 65.5-66.5°C; UV $\lambda_{max.}$ (Cyclohexane): 270 (ε=18300) and 331nm (100); IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.48 (s, 3H), 3.89 (d), 5.75 (s, 1H), and 7.0-7.4 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 38.5 (q), 58.8 (q), 59.9 (d), 127.1 (d), 128.5 (d), 128.6 (d), 139.1 (s), 175.1 (s), and 192.4 (s). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.67. Found: C, 68.13; H, 5.69; N, 4.61%.

N-Diphenylacetyl-N-phenylthiocarbamic acid O-methyl ester (257)

mp: 53.4-54.5°C; UV $\lambda_{max.}$ (Cyclohexane): 273 (ε=11500) and 365nm (94); IR($CHCl_3$): 1705 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 4.05 (s, 3H), 5.46 (s, 1H), and 6.9-7.4 (m, 15H); ^{13}C-NMR($CDCl_3$): δ 58.9 (q), 59.2 (d), 127.3 (d), 128.6 (d), 128.9 (d), 129.3 (d), 138.4 (s), 173.8 (s), and 193.0 (s). Anal. Calcd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.29; N, 3.87. Found: C, 73.15; H, 5.31; N, 3.86%.

N-Methoxyacetyl-N-methylthiocarbamic acid O-methyl ester (258)

UV $\lambda_{max.}$ (Cyclohexane): 264 (ε=11400) and 346nm (120); IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.42 (s, 3H), 3.52 (s, 3H), 4.14 (s,

3H), and 4.43 (s, 2H); ^{13}C-NMR($CDCl_3$): δ 37.1 (q), 59.2 (q), 59.3 (q), 74.9 (t), 172.4 (s), and 192.2 (s).

N-Methoxyacetyl-N-phenylthiocarbamic acid O-methyl ester (259)

mp: 74.0-75.0°C; UV $\lambda_{max.}$ (Cyclohexane): 268 (ε=11400) and 350nm (130); IR($CHCl_3$): 1710 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.44 (s, 3H), 4.11 (s, 3H), 4.40 (s, 2H), and 7.1-7.5 (m, 5H); ^{13}C-NMR($CDCl_3$): δ 59.4 (q), 74.1 (t), 128.5 (d), 129.4 (d), 140.6 (s), 172.1 (s), and 192.4 (s). Anal. Calcd for $C_{11}H_{11}NO_3S$: C, 55.21; H, 5.47; N, 5.85. Found: C, 55.19; H, 5.39; N, 5.77%.

General Procedure for the Photolysis of N-Acylthiourethanes (254-259)

A benzene solution (70ml) containing N-acylthiourethane (300mg) was deaerated with argon and irradiated with a 1000-W high pressure mercury lamp until the starting material disappeared (4-8hr). After removal of the solvent, the residue was chromatographed on silica gel and the photoproducts were isolated.

3,3-Diphenyl-4-mercapto-4-methoxy-1-methylazetidin-2-one (260)

mp: 138-140°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.21 (s, 3H), 3.28 (s, 3H), 3.70 (s, 1H), and 7.3-7.6 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 26.8 (q), 49.1 (q), 95.7 (s), 126.7 (d), 128.0 (d), 128.5 (d), 135.6 (s), and 171.3 (s). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 4.91; N, 4.67. Found: C, 68.00; H, 5.65; N, 4.64%.

3,3-Diphenyl-1-methyl-4-thioxoazetidin-2-one (262)

mp: 109-110°C; IR($CHCl_3$): 1810 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.15 (s, 3H) and 7.2-7.6 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 26.8 (q), 96.1 (s), 126.9 (d), 128.2 (d), 128.6 (d), 135.9 (s), 171.9 (s), and 209.0

(s). Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.23. Found: C, 71.80; H, 4.89; N, 5.21%.

1,3,3-Triphenyl-4-thioxoazetidin-2-one (263)

IR($CHCl_3$): 1800cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 6.6-8.1 (m, 15H).

2,2-Diphenyl-2-methoxythiocarbonyl acetanilide (264)

IR($CHCl_3$): 1680 and 3340 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 4.13 (s, 3H), 7.0-7.5 (m, 15H), and 8.06 (br, 1H); ^{13}C-NMR($CDCl_3$): δ 60.1 (q), 119.8 (d), 124.5 (d), 127.7 (d), 127.9 (d), 128.9 (d), 130.1 (d), 137.6 (s), 164.4 (s), and 214.0 (s). Mass (C.I.): m/e 362 (M+1).

2-Methoxy-2-methoxythiocarbonyl-N-methyl acetamide (265)

IR($CHCl_3$): 1680 and 3420 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.83 (d, J=8.3Hz, 3H), 3.45 (s, 3H), 4.17 (s, 1H), 4.53 (s, 3H), and 6.82 (br, 1H). ^{13}C-NMR($CDCl_3$): δ 25.6 (q), 57.5 (q), 59.2 (q), 88.1 (d), 166.1 (s), and 214.5 (s). Mass (C.I.): m/e 178 (M+1).

2-Methoxy-2-methoxythiocarbonyl acetanilide (266)

IR($CHCl_3$): 1680 and 3380 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.50 (s, 3H), 4.14 (s, 3H), 4.64 (s, 1H), 7.0-7.6 (m, 5H), and 8.46 (br, 1H). ^{13}C-NMR($CDCl_3$): δ 57.9 (q), 59.6 (q), 88.3 (d), 119.7 (d), 124.6 (d), 128.9 (d), 137.0 (s), 163.7 (s), and 214.0 (s). Mass (C.I.): m/e 240 (M+1).

Quenching and Sensitization of N-Acylthiourethane (259)

Three Pyrex tubes were irradiated at 366nm line with a high pressure mercury lamp in a merry-go-round apparatus. The first was a benzene solution of only 259. The second was that of stilbene (0.1M) and 259. The third was that of Michler's ketone and 259. Other two Pyrex tubes were irradiated at 313nm

line. One was a benzene solution of 259. The other was that of thioxanthone and 259. After removal of the solvent, the degree of the reaction was determined by NMR spectroscopy. The 313nm line was isolated with a filter solution containing 2mmol/l potassium chromate in 5% aqueous sodium carbonate. The 366nm line was isolated with a filter solution containing 0,04mol/l naphthalene. Concentration of sensitizers were adjusted so that 5% or less of the incident light was absorbed by 259 (in quenching) or sensitizers (in sensitization).

Preparation of 3-Acyl-2-thiotetrahydro-1,3-thiazine (270-274)

These compounds were prepared by the acylation of 2-thiotetrahydro-1,3-thiazine with corresponding acid chloride in the presence of triethylamine as same as the synthesis of monothioimides.

3-Acetyl-2-thiotetrahydro-1,3-thiazine (270)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.28 (quint, J=6Hz, 2H), 2.70 (s, 3H), 3.10 (t, J=6Hz, 2H), and 4.0 (t, J=6Hz, 2H).

3-Isobutyroyl-2-thiotetrahydro-1,3-thiazine (271)

IR($CHCl_3$): 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.22 (d, J=7Hz, 6H), 2.23 (quit, J=6Hz, 2H), 3.05 (t, J=6Hz, 2H), and 3.6-4.0 (m, 3H).

3-Diphenylacetyl-2-thiotetrahydro-1,3-thiazine (272)

IR($CHCl_3$): 1715 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.20 (quint, J=6Hz, 2H), 3.15 (t, J=6Hz, 2H), 3.95 (t, J=6Hz, 2H), 5.30 (s, 1H) and 6.9-7.5 (m, 10H). Anal. Calcd for $C_{18}H_{17}NOS_2$: C, 66.02; H, 5.23; N, 4.27. Found; C, 66.04; H, 5.27; N, 4.22%.

3-Methoxyacetyl-2-thiotetrahydro-1,3-thiazine (273)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.25 (quint, J=6Hz, 2H),

3.10 (t, J=6Hz, 2H), 3.40 (s, 3H), 3.90 (t, J=6Hz, 2H), and 4.60 (s, 2H).

3-Ethoxyacetyl-2-thiotetrahydro-1,3-thiazine (274)

IR($CHCl_3$): 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.23 (t, J=7Hz, 2H), 2.25 (quint, J=6Hz, 2H), 3.03 (t, J=6Hz, 2H), 3.62 (q, J=7Hz, 2H), 3.98 (t, J=6Hz, 2H), and 4.77 (s, 2H).

General Procedure for the Photochemical Reaction of N-Acyl-thiazines (270-274) above 40°C

A solution of the thiazine (300mg) in benzene (60ml) was irradiated in a Pyrex vessel under argon with a 1000-W high pressure mercury lamp. After the starting material disappeared, benzene was removed by evaporation and the residue was chromatographed on silica gel.

8,8-Diphenyl-2,9-dithia-6-azabicyclo[4,3,0]nonan-7-one (275)

mp: 99-100°C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.9-2.2 (m, 5H), 3.9-4.1 (m, 1H), 5.40 (s, 1H), and 7.1-7.6 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 30.6 (t), 40.3 (t), 41.9 (t), 71.1 (s), 74.8 (d), 126.7 (d), 127.3 (d), 127.4 (d), 128.1 (d), 128.7 (d), 136.3 (s), 140.3 (s), and 168.6 (s). Anal. Calcd for $C_{18}H_{17}NOS(0.2H_2O)$: C, 65.53; H, 5.24; N, 4.23. Found; C, 65.56; H, 5.24; N, 4.18%.

8-Methoxy-2,9-dithia-6-azabicyclo[4,3,0]nonan-7-one (276)

(major); IR($CHCl_3$): 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.6-2.2 (m, 4H), 2.6-3.5 (m, 5H), 3.47 (s, 3H), 4.3-4.6 (m, 1H), 5.54 (s, 1H), and 5.71 (s, 1H); ^{13}C-NMR($CDCl_3$) δ 24.8 (t), 30.1 (t), 43.7 (t), 55.5 (q), 60.9 (d), 84.1 (d), and 165.7 (s).

(minor); IR($CHCl_3$): 1760 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.6-2.2 (m, 4H),

2.6-3.5 (m, 5H), 3.41 (s, 3H), 4.3-4.6 (m, 1H), 5.62 (s, 1H), and 5.78 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 24.7 (t), 29.5 (t), 43.1 (t), 55.4 (q), 60.0 (d), 83.7 (d), and 166.2 (s).

3,3-Diphenyl-1-(3-mercaptopropane)-3-thioxoazetidin-2-one (280)

IR($CHCl_3$): 1800 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.98 (quint, J=7Hz, 2H), 2.40 (q, J=7Hz, 2H), 3.73 (t, J=7Hz, 2H), and 7.1-7.3 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 21.7 (t), 31.0 (t), 39.4 (t), 81.2 (s), 126.9 (d), 128.3 (d), 128.8 (d), 171.5 (d), 135.9 (s), and 208.9 (s).

General Procedure for the Photochemical Reaction at Low Temperature Followed by Acetylation

A benzene solution of thiazine was irradiated in the presence of molecular sieves with a 1000-W high pressure mercury lamp under argon at 10-15 °C until the starting material disappeared. Then, three equivalent molar acetyl chloride and triethylamine were added at 0 °C and stood for over night at room temperature. Precipitated triethylamine hydrcchloride was filtered through a celite column and the filtrate was concentrated by evaporation. The reaction mixture was chromatographed on silica gel.

7,7-Diphenyl-6-acetylthio-5-thia-1-azabicyclo[4,2,0]octan-8-one (284)

mp: 99-100°C; IR($CHCl_3$): 1755 and 1695 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.5-2.0 (m, 2H), 1.96 (s, 3H), 2.5-3.4 (m, 5H), 3.9-4.2 (m, 1H), and 7.0-7.6 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 23.6 (t), 28.5 (t), 30.4 (q), 37.3 (t), 81.1 (s), 81.7 (s), 127.6 (d), 127.8 (d), 128.3 (d), 128.7 (d), 136.5 (s), 137.5 (s), 165.0 (s), and 192.8 (s). Anal. Calcd for $C_{20}H_{19}NO_2S_2$: C, 65.01; H, 5.18; N, 3.80. Found:

C, 64.86; H, 5.19; N, 3.74%.

7-Acetoxy-6-acetylthio-5-thia-1-azabicyclo[4,2,0]octan-8-one (285)

(major); IR($CHCl_3$): 1695 and 1765 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.6-2.2 (m, 2H), 2.34 (s, 3H), 2.6-4.1 (m, 4H), 3.54 (s, 3H), and 4.66 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 23.2 (t), 27.2 (t), 30.9 (q), 37.2 (t), 60.8 (q), 76.0 (s), 95.3 (d), 161.5 (s), and 193.5 (s). (minor): IR($CHCl_3$): 1695 and 1765 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.6-2.2 (m, 2H), 2.34 (s, 3H), 2.6-4.1 (m, 4H), 3.65 (s, 3H), and 4.97 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 23.7 (t), 25.5 (t), 30.8 (q), 36.4 (t), 60.4 (q), 74.0 (s), 94.4 (d), 162.6 (s), and 194.3 (s).

6-Acetylthio-7-ethoxy-5-thia-1-azabicyclo[4,2,0]octan-8-one (286)

mp: 83-84°C; IR($CHCl_3$): 1690 and 1765 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.22 (t, J=7Hz, 3H), 1.6-2.1 (m, 2H), 2.34 (s, 3H), 2.7-3.4 (m, 3H), 3.72 (q, J=7Hz, 2H), 3.8-4.1 (m, 1H), and 4.76 (s, 1H); ^{13}C-NMR($CDCl_3$): δ 15.1 (q), 23.4 (t), 27.3 (t), 30.9 (t), 37.3 (q), 69.1 (t), 77.3 (s), 94.1 (d), 162.0 (s), and 193.5 (s). Anal. Calcd for $C_{10}H_{15}NO_3S_2$: C, 45.95; H, 5.78; N, 5.35. Found: C, 45.99; H, 5.86; N, 5.38%.

Preparation of N-Thioacylureas (287-292) and Thioacylthioureas (293-298)

To a benzene solution of N-acylurea (or N-acylthiourea) was added a half molar amount of Lawesson's reagent. Then the reaction mixture was refluxed 1-2hr until the N-acylurea disappeared. After removal of the solvent, the residue was chromatographed on silica gel. N-Thioacylurea (or N-thioacyl-

thiourea) was obtained almost quantitatively.

N,N',N'-Trimethyl-N-thiobenzoylurea (287)

mp: 74-75°C; IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.68 (s, 6H), 3.56 (s, 3H), and 7.2-7.8 (m, 5H). Anal. Calcd for $C_{11}H_{14}N_2OS$: C, 59.43; H, 6.34; N, 12.60. Found: C, 59.44; H, 6.38; N, 12.54%.

N',N'-Diethyl-N-methyl-N-thiobenzoylurea (288)

bp: 60°C (10^{-3} torr); IR($CHCl_3$): 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-1.8 (br, 6H), 2.5-3.9 (br, 4H), 3.60 (s, 3H), and 7.3-7.7 (m, 5H). Anal. Calcd for $C_{13}H_{18}N_2OS$: C, 62.36; H, 7.24; N, 11.18. Found; C, 62.37; H, 7.15; N, 10.93%.

N',N'-Diisopropyl-N-methyl-N-thiobenzoylurea (289)

mp: 70-71°C; IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-1.5 (m, 12H), 3.37 (br, 2H), 3.57 (s, 3H), and 7.1-7.8 (m, 5H). Anal. Calcd for $C_{15}H_{22}N_2OS$: C, 64.71; H, 7.96; N, 10.06. Found: C, 64.34; H, 8.03; N, 9.87%.

N',N'-Dibenzyl-N-methyl-N-thiobenzoylurea (290)

mp: 82-83°C; UV $\lambda_{max.}$(EtOH): 243 (ε=9200), 290 (9600), and 413nm (250); IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.4 (s, 3H), 4.2 (br, 4H), and 6.8-7.8 (m, 15H). Anal. Calcd for $C_{23}H_{22}N_2OS$: C, 73.76; H, 5.92; N, 7.48. Found: C, 73.58; H, 5.92; N, 7.39%.

N',N'-Dibenzyl-N-methyl-N-(p-methoxythiobenzoyl)urea (291)

mp: 95-96°C; UV $\lambda_{max.}$(EtOH): 285 (ε=15800) and 410nm (420); IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.42 (s, 3H), 3.83 (s, 3H), 4.17 (br, 4H), and 6.6-7.8 (m, 14H). Anal. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.25; H, 5.98; N, 6.92. Found: C, 71.26; H, 5.98; N, 6.83%.

N',N'-Dibenzyl-N-methyl-N-(p-chlorothiobenzoyl)urea (292)

mp: 100-101°C; UV $\lambda_{max.}$(EtOH): 253 (ε=11800), 280 (10500), and 414nm (300); IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.40 (s, 3H), 4.2 (br, 4H), and 7.0-7.9 (m, 14H). Anal. Calcd for $C_{23}H_{21}N_2OSCl$: C, 67.55; H, 5.17; N, 6.85. Found: C, 67.52; H, 5.18; N, 6.82%.

N,N',N'-Trimethyl-N-thiobenzoylthiourea (293)

mp: 64.5-66°C; IR(film): 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.5-4.0 (br, 9H) and 7.0-8.0 (m, 5H). Anal. Calcd for $C_{11}H_{14}N_2S_2$: C, 55.42; H, 5.92; N, 11.75. Found: C, 55.27; H, 5.97; N, 11.71%.

N',N'-Diethyl-N-methyl-N-thiobenzoylthiourea (294)

mp: 88-89°C; IR(film): 1070, 1275, and 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.3-1.5 (br, 6H), 3.0-4.5 (br, 7H), and 7.3-7.8 (m, 5H). Anal. Calcd for $C_{13}H_{18}N_2S_2$: C, 58.60; H, 6.81; N, 10.51. Found: C, 58.58; H, 6.83; N, 10.47%.

N',N'-Diisopropyl-N-methyl-N-thiobenzoylthiourea (295)

mp: 68-69°C; IR(film): 1330, 1440, and 1495 cm^{-1}; (major): ^{1}H-NMR($CDCl_3$): δ 0.88 (d, J=6.3Hz, 3H), 1.17 (d, J=6.9Hz, 3H), 1.20 (d, J=6.9Hz, 3H), 1.57 (d, J=6.9Hz, 3H), 3.71 (s, 3H), 3.9-4.5 (m, 2H), 7.2-7.4 (m, 3H), and 7.7-7.8 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 17.2 (q), 19.1 (q), 19.4 (q), 21.6 (q), 44.2 (q), 50.4 (d), 55.7 (d), 127.2 (d), 128.0 (d), 129.5 (d), 141.9 (s), 183.7 (s), 199.0 (s). (minor); ^{1}H-NMR($CDCl_3$): δ 1.29 (d, J=6.9Hz, 3H), 1.44 (d, J=6.8Hz, 3H), 1.71 (d, J=6.9Hz, 3H), 1.78 (d, J=6.9Hz, 3H), 3.28 (s, 3H), 3.9-4.5 (m, 2H), 7.2-7.4 (m, 3H), and 7.7-7.8 (m, 2H); ^{13}C-NMR($CDCl_3$): δ 17.8 (q), 18.7 (q), 20.4 (q), 20.9 (q), 42.6 (q), 50.7 (d), 55.7 (d), 125.8 (d), 128.3 (d), 129.0 (d), 142.1 (s), 184.2 (s), 199.0 (s). Anal. Calcd for $C_{15}H_{22}N_2S_2$: C, 61.18;

H, 7.53; N, 9.51. Found: C, 61.07; H, 7.56; N, 9.37%.

N',N'-Dibenzyl-N-methyl-N-thiobenzoylthiourea (296)

mp: 76-77°C; IR(film): 1420 and 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.0-5.0 (br, 7H) and 6.8-7.9 (m, 15H). Anal. Calcd for $C_{23}H_{22}N_2S_2$: C, 70.73; H, 5.67; N, 7.17. Found: C, 70.68; H, 5.78; N, 7.09%.

N',N'-Dibenzyl-N-methyl-N-(p-methoxythiobenzoyl)thiourea (297)

mp: 92-93°C; IR(film): 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.57 (s, 3H), 3.82 (s, 3H), 4.0-5.2 (br, 4H), and 6.7-7.9 (m, 14H). Anal. Calcd for $C_{24}H_{24}N_2S_2$: C, 68.53; H, 5.75; N, 6.66. Found: C, 68.52; H, 5.87; N, 6.61%.

N',N'-Dibenzyl-N-methyl-N-(p-chlorothiobenzoyl)thiourea (298)

mp: 79-80°C; IR(film): 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.6 (br, 3H), 3.8-6.0 (br, 4H), and 6.8-7.8 (br, 14H). Anal. Calcd for $C_{23}H_{21}N_2S_2Cl$: C, 64.99; H, 4.98; N, 6.59. Found: C, 64.34; H, 5.02; N, 6.58%.

General Procedure for the Photochemical Reactions of N-Thioacylureas and Thioacylthioureas

An urea (300mg) was dissolved in dry benzene (70ml) and deaerated with argon. The benzene solution was irradiated with a 1000-W high pressure mercury lamp at 10-15°C until the starting material disappeared. Benzene was removed by evaporation and the residue was chromatographed on silica gel. However, produced imidazolidinones were unstable. Therefore, isolated imidazolidinones were immediately desulflized by trifluoroacetic acid. An imidazolidinone was dissolved in dry benzene, and a few drops of trifluoroacetic acid was added. The mixture was refluxed for 1hr and concentrated by evaporation. The residue was chromatographed

on silica gel and an imidazolone was isolated.

4,5-Diphenyl-1-benzyl-4-mercapto-3-methylimidazolidin-2-one (299)

The title compound was obtained as a mixture of two stereo isomers in a ratio about 2:1. IR($CHCl_3$): 1685 cm^{-1}; (major isomer); ^{1}H-NMR($CDCl_3$): δ 1.94 (s, 1H), 2.85 (s, 3H), 3.80 and 5.10 (ABq, J=15Hz, 2H), 4.21 (s, 1H), and 6.8-7.6 (m, 15H); ^{13}C-NMR($CDCl_3$): δ 34.5 (q), 46.3 (t), 71.4 (d), 79.7 (s), 126.8 (d), 127.5 (d), 127.6 (d), 128.2 (d), 128.4 (d), 128.6 (d), 128.8 (d), 129.2 (d), 132.2 (s), 133.1 (s), 135.7 (s), 140.1 (s), and 160.4 (s).

1-Benzyl-4-mercapto-4-(p-methoxyphenyl)-3-methyl-5-phenylimidazolidin-2-one (300)

The title compound was obtained as a mixture of two stereo isomers in a ratio about 2:1. IR($CHCl_3$): 1680 cm^{-1}; (major isomer); ^{1}H-NMR($CDCl_3$): δ 1.93 (s, 1H), 2.83 (s, 3H), 3.77 (s, 3H), 3.71 and 5.08 (ABq, J=15Hz, 2H), 4.18 (s, 1H), and 6.7-7.5 (m, 14H).

1-Benzyl-4-(p-chlorophenyl)-4-mercapto-3-methyl-5-phenylimidazolidin-2-one (301)

The title compound was obtained as a mixture of two stereo isomers in a ratio about 2:1. IR($CHCl_3$): 1680 cm^{-1}; (major isomer); ^{1}H-NMR($CDCl_3$): δ 1.95 (s, 1H), 2.83 (s, 3H), 3.80 and 5.07 (ABq, J=15Hz, 2H), 4.17 (s, 1H), and 6.8-7.6 (m, 14H).

3,5,5-Trimethyl-1-isopropyl-4-mercapto-3-methyl-4-phenylimidazolidine-2-thione (302)

mp: 125.5-127°C; IR(KBr): 1440 and 1465 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.76 (s, 3H), 1.59 (s, 3H), 1.63 (d, J=7Hz, 6H), 3.10 (s, 3H),

4.25 (sep, J=7Hz, 1H), 7.43 (s, 5H). Anal. Calcd for $C_{15}H_{22}N_2S_2$: C, 61.18; H, 7.53; N, 9.51. Found: C, 61.02; H, 7.68; N, 9.34%. This compound was unstable toward silica gel and converted to hydroxy derivative, 3,5,5-trimethyl-4-hydroxy-1-isopropyl-3-methyl-4-phenylimidazolidine-2-thione, mp: 149-150 C; IR(KBr): 3320 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.76 (s, 3H), 1.42 (s, 3H), 1.62 (d, J=7Hz, 6H), 3.00 (s, 3H), 3.01 (br s, 1H, D_2O exchangeable), 4.08 (sep, J=7Hz, 1H), 7.39 (s, 5H); ^{13}C-NMR($CDCl_3$): δ 19.8 (q), 20.6 (q), 21.1 (q), 24.9 (q), 30.3 (q), 47.6 (d), 69.1 (s), 96.5 (s), 127.3 (d), 128.3 (d), 128.8 (d), 136.8 (s), 180.9 (s). Anal. Calcd for $C_{15}H_{22}N_2OS$: C, 64.71; H, 7.96; N, 10.06. Found: C, 64.56; H, 8.00; N, 10.00%.

4,5-Diphenyl-1-benzyl-4-mercapto-3-methylimidazolidine-2-thione (303)

IR($CHCl_3$): 1500 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.97 (s, 1H), 3.23 (s, 3H), 3.93 and 5.89 (ABq, J=15Hz, 2H), 4.45 (s, 1H), and 6.9-7.5 (m, 15H).

3,4-Diphenyl-1-benzyl-3-methylimidazole-2-thione (306)

mp: 164-165°C; IR(KBr): 1400 and 1440 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.63 (s, 3H), 5.38 (s, 2H), and 6.8-7.6 (m, 15H). Anal. Calcd for $C_{23}H_{20}N_2S$: C, 77.49; H, 5.65; N, 7.85. Found: C, 77.35; H, 5.69; N, 7.88%.

1-Benzyl-4-mercapto-4-(p-methoxyphenyl)-3-methyl-5-phenylimidazolidine-2-thione (304)

IR(film): 1435 and 1505 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.98 (s, 1H), 3.18 (s, 3H), 3.77 (s, 3H), 3.95 and 5.88 (ABq, J=15Hz, 2H), 4.42 (s, 1H), and 6.7-7.5 (m, 14H).

1-Benzyl-4-(p-methoxyphenyl)-3-methyl-5-phenylimidazole-2-thione

(307)

IR($CHCl_3$): 1400 and 1440 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.57 (s, 3H), 3.72 (s, 3H), 5.32 (s, 2H), and 6.7-7.3 (m, 14H).

1-Benzyl-4-(p-chlorophenyl)-4-mercapto-3-methyl-5-phenylimidazolidine-2-thione (305)

IR(film): 1440 and 1490 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 2.02 (s, 1H), 3.18 (s, 3H), 3.90 and 5.85 (ABq, J=15Hz, 2H), 4.32 (s, 1H), and 6.8-7.6 (m, 14H).

1-Benzyl-4-(p-chlorophenyl)-3-methyl-5-phenylimidazole-2-thione (308)

mp: 177.5-178.5°C; IR(KBr): 1440 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.63 (s, 3H), 5.38 (s, 2H), and 6.8-7.6 (m, 14H). Anal. Calcd for $C_{23}H_{21}N_2SCl$: C, 70.66; H, 4.89; N, 7.16. Found: C, 70.58; H, 4.97; N, 7.21%.

General Procedure for the Synthesis of N-Thioacyl-α,β-unsaturated Amides (309-331)

These compounds were obtained by the reaction of thioamides and corresponding α,β-unsaturated amides as in the case of the synthesis of monothioimides (204-210).

N-Methyl-N-thiobenzoylmethacrylamide (309)

IR($CHCl_3$): 1625 and 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.48 (d, J=1Hz, 3H), 3.65 (s, 3H), 5.10 (br s, 1H), 5.28 (br s, 1H), and 6.9-7.4 (m, 5H).

N-Ethyl-N-thiobenzoylmethacrylamide (310)

IR($CHCl_3$): 1625 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.32 (t, J=7Hz, 3H), 1.45 (d, J=1Hz, 3H), 4.30 (q, J=7Hz, 2H), 5.03 (br s, 1H),

5.27 (br s, 1H), and 7.0-7.4 (m, 5H).

N-Isopropyl-N-thiobenzoylmethacrylamide (311)

IR($CHCl_3$): 1625 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.41 (d, J=1Hz, 3H), 1.47 (d, J=7Hz, 6H), 5.39 (br s, 1H), 5.65 (sep, J=7Hz, 1H), 5.53 (br s, 1H), and 7.2-7.5 (m, 5H).

N-Benzyl-N-thiobenzoylmethacrylamide (312)

IR($CHCl_3$): 1625 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.38 (d, J=1Hz, 3H), 5.23 (br s, 1H), 5.50 (s, 2H), 5.48 (br s, 1H), and 7.1-7.5 (m, 10H).

N-Phenyl-N-thiobenzoylmethacrylamide (313)

IR($CHCl_3$): 1610 and 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.79 (d, J=1Hz, 3H), 5.38 (br s, 1H), 5.85 (br s, 1H), and 6.9-7.6 (m, 10H).

N-Isopropyl-N-thiobenzoylacrylamide (314)

IR($CHCl_3$): 1610 and 1685 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.51 (d, J=7Hz, 6H), 5.1-5.7 (m, 2H), 5.8-6.1 (m, 2H), and 7.0-7.6 (m, 5H).

N-Benzyl-N-thiobenzoylacrylamide (315)

IR($CHCl_3$): 1615 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.0-5.2 (m, 1H), 5.4 (s, 2H), 5.7-6.1 (m, 2H), and 6.9-7.5 (m, 10H).

N-Phenyl-N-thiobenzoylacrylamide (316)

IR($CHCl_3$): 1615 and 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.3-5.5 (m, 2H), 6.0-6.3 (m, 2H), and 6.8-7.7 (m, 10H).

N-Isopropyl-N-thiobenzoylcrotonamide (317)

IR($CHCl_3$): 1630 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.43 (d, J=7Hz, 6H), 1.50 (dd, J=6 and 2Hz, 3H), 5.47 (m, 2H), 6.45 (dq, J=15 and 6Hz, 1H), and 7.1-7.6 (m, 5H).

N-Phenyl-N-thiobenzoylcrotonamide (318)

IR($CHCl_3$): 1635 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.50 (dd, J=6 and 2Hz, 3H), 5.40 (m, 1H), 6.00 (dq, J=15 and 6Hz, 1H), and 7.1-7.6

(m, 10H).

N-Isopropyl-N-thiobenzoylcinnamamide (319)

IR($CHCl_3$): 1610 and 1690 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.48 (d, J=7Hz, 6H), 5.55 (sep. J=7Hz, 1H), 6.50 (d, J=15Hz, 1H), and 7.0-7.6 (m, 11H).

N-Benzyl-N-thiobenzoylcinnamamide (320)

IR($CHCl_3$): 1615 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 5.52 (m, 1H), 6.07 (d, J=15Hz, 1H), and 6.9-7.5 (m, 11H).

N-Phenyl-N-thiobenzoylcinnamamide (321)

mp: 106-108°C; IR($CHCl_3$): 1605 and 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 6.57 (d, J=16Hz, 1H) and 7.0-8.0 (m, 16H). Anal. Calcd for $C_{22}H_{17}NOS$: C, 76.93; H, 4.98; N, 4.07. Found: C, 76.83; H, 4.96; N, 4.02%.

N-Isopropyl-N-thiobenzoyl-1-cyclopentenylamide (322)

IR($CHCl_3$): 1610 and 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.2-1.7 (m, 2H), 1.43 (d, J=6Hz, 6H), 1.8-2.4 (m, 4H), 5.58 (sep, J=6Hz, 1H), 6.17 (br, 1H), and 7.1-7.3 (m, 5H).

N-Phenyl-N-thiobenzoyl-1-cyclopentenylamide (323)

IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.2-2.4 (m, 6H), 6.15 (br, 1H), and 7.0-7.5 (m, 10H).

N-Isopropyl-N-thiobenzoyl-1-cyclohexenylamide (324)

IR($CHCl_3$): 1680 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.47 (d, J=7Hz, 6H), 0.7-2.1 (m, 8H), 5.65 (sep, J=7Hz, 1H), 6.3 (br s, 1H), and 7.2-7.4 (m, 5H).

N-Benzyl-N-thiobenzoyl-1-cyclohexenylamide (325)

IR($CHCl_3$): 1675 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.0-1.3 (m, 4H), 1.6-2.0 (m, 4H), 5.38 (s, 2H), 5.93 (br s, 1H), and 7.0-7.4 (m, 10H).

N-Phenyl-N-thiobenzoyl-1-cyclohexenylamide (326)

IR($CHCl_3$): 1675 cm^{-1}; ^1H-NMR($CDCl_3$): δ 0.8-2.0 (m, 8H), 6.2 (br s, 1H), and 7.0-7.5 (m, 10H).

3-Methacryl-2-thioxo-1,3-thiazine (327)

IR($CHCl_3$): 1680 cm^{-1}; ^1H-NMR($CDCl_3$): δ 2.00 (br s, 3H), 3.37 (t, J=7Hz, 2H), 4.30 (t, J=7Hz, 2H), 5.38 (m, 1H), and 5.52 (m, 1H).

3-Tiglyl-2-thioxo-1,3-thiazine (328)

IR($CHCl_3$): 1680 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.25 (q, J=1.5Hz, 3H), 1.50 (br d, J=7Hz, 3H), 3.40 (t, J=7Hz, 2H), 4.30 (t, J=7Hz, 2H), and 6.15 (qq, J=1.5 and 7Hz, 1H).

3-(1-Cyclohexenecarbonyl)-2-thioxo-1,3-thiazine (329)

IR($CHCl_3$): 1675 cm^{-1}; ^1H-NMR($CDCl_3$): δ 0.7-2.0 (br, 8H), 3.40 (t, J=7Hz, 2H), 4.30 (t, J=7Hz, 2H), and 6.20 (br s, 1H).

3-Methacryl-2-thioxo-1,3-oxazine (330)

IR($CHCl_3$): 1680 cm^{-1}; ^1H-NMR($CDCl_3$): δ 2.07 (br s, 3H), 4.20 (t, J=7Hz, 2H), 4.67 (t, J=7Hz, 2H), and 5.4-5.6 (m, 2H).

3-Tiglyl-2-thioxo-1,3-oxazine (331)

IR($CHCl_3$): 1680 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.25 (q, J=1.5Hz, 3H), 1.50 (br s, J=7Hz, 3H), 6.15 (qq, J=1.5 and 7Hz, 1H), 4.20 (t, J=7Hz, 2H), and 4.60 (t, J=7Hz, 2H).

General Procedure for the Photochemical Reaction of N-α,β-Unsaturated Thioamides (309-331)

Usually these monothioimides were unstable toward moisture. Synthesized monothioimides were immediately photolyzed in dry benzene in the presence of molecular sieves with a 1000-W high pressure mercury lamp under argon at 10-15°C. After the starting material disappeared, benzene was removed by evaporation. The

residual mixture was chromatographed on silica gel and the photoproducts were isolated.

2,4-Dimethyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (332)

mp: 103-104.5°C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.02 (s, 3H), 2.83 (s, 3H), 3.07 and 3.27 (ABq, J=10Hz, 2H), and 7.1-7.5 (m, 5H). Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.47; H, 5.94; N, 6.34. Found: C, 65.72; H, 5.97; N, 6.38%.

2-Ethyl-4-methyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (333)

IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.02 (s, 3H), 1.24 (t, J=7Hz, 3H), 3.03 and 3.30 (ABq, J=10Hz, 2H), 3.33 (q, J=7Hz, 2H), and 7.1-7.6 (m, 5H).

2-Isopropyl-4-methyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]-hexane (334)

mp: 82-83°C; IR($CHCl_3$): 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.00 (s, 3H), 1.33 (d, J=7Hz, 3H), 1.35 (d, J=7Hz, 3H), 2.94 and 3.34 (ABq, J=10Hz, 2H), 3.60 (sep, J=7Hz, 1H), and 7.0-7.4 (m, 5H). Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.92; N, 5.66. Found: C, 67.83; H, 6.98; N, 5.59%.

2-Benzyl-4-methyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (335)

mp: 81-82°C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.02 (s, 3H), 3.00 and 3.30 (ABq, J=10Hz, 2H), 4.37 (s, 2H), and 7.0-7.4 (m, 10H). Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 72.95; H, 5.79; N, 4.72%.

1,2-Diphenyl-4-methyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (336)

mp: 103-104 °C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.08 (s, 3H), 3.16 and 3.47 (ABq, J=10Hz, 2H), and 6.8-7.5 (m, 10H). Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.56; H, 5.37; N, 4.97. Found: C, 72.61; H, 5.51; N, 4.92%.

2-Isopropyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (337)

IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.29 (d, J=7Hz, 3H), 1.30 (d, J=7Hz, 3H), 3.24 (dd, J=3 and 10Hz, 1H), 3.48 (dd, J=9 and 10Hz, 1H), 3.72 (sep, 7Hz, 1H), 4.11 (dd, J=3 and 9Hz, 1H), and 7.0-7.6 (m, 5H), ^{13}C-NMR($CDCl_3$): δ 21.1 (q), 20.8 (q), 21.3 (t), 46.7 (d), 61.6 (d), 70.5 (s), 128.3 (d), 126.4 (s), 137.4 (s), and 167.5 (s).

(α-Acrylamino)thioisobutyrophenone (338)

mp: 103-104 °C; IR($CHCl_3$): 1670 and 3320 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.82 (s, 6H), 5.43 (t, J=6Hz, 1H), 6.07 (d, J=6Hz, 2H), 7.1-7.6 (m, 5H), and 7.85 (br s , 1H). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.98; H, 6.58; N, 5.85. Found: C, 66.91; H, 6.48; N, 6.00%.

2-Benzyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (339)

IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.18 (dd, J=3 and 10Hz, 1H), 3.46 (dd, J=9 and 10Hz, 1H), 4.16 (s, 2H), and 7.0-7.4 (m, 10H); ^{13}C-NMR($CDCl_3$): δ 21.7 (t), 45.3 (t), 62.3 (d), 71.7 (s), 126.5 (d), 126.5 (d), 127.3 (d), 128.2 (d), 128.3 (d), 128.5 (d), 128.8 (d), 134.2 (s), 136.0 (s), and 167.8 (s).

1,2-Diphenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (340)

mp: 119-120 °C; IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 3.28 (dd, J=3 and 10Hz, 1H), 3.62 (dd, J=9 and 10Hz, 1H), 4.17 (dd, J=3 and 9Hz, 1H), and 7.1-7.6 (m, 10H). Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.23. Found: C, 71.89; H, 4.99; N, 5.24%.

2-Isopropyl-5-methyl-1-phenyl-3-oxo-6-thia-2-azabicyclo[2,2,0]-

hexane (341)

IR($CHCl_3$): 1740 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.28 (d, J=7Hz, 6H), 1.58 (d, J=6Hz, 3H), 3.3-4.2 (m, 3H), and 7.0-7.7 (m, 5H).

(α-Crotonylamino)thioisobutyrophenone (342)

(trans); mp: 125-126 °C; IR($CHCl_3$): 1635, 1665, 3320, and 3430 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.50 (dd, J=6 and 1Hz, 3H), 1.80 (s, 6H), 5.45 (m, 1H), 6.20 (dq, J=15 and 1Hz, 1H), 7.1-7.7 (m, 5H), and 7.90 (br s, 1H). Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.92; N, 5.66. Found: C, 67.96; H, 6.90; N, 5.65%.

(α-Crotonylamino)thioisobutyrophenone (342')

(cis); mp: 102-103 °C; IR($CHCl_3$): 1640, 1675, 3320, and 3430 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.72 (s, 6H), 1.90 (br d, J=6Hz, 3H), 5.50 (br d, J=12Hz, 1H), 5.81 (dq, J=12 and 6Hz, 1H), and 7.1-7.4 (m, 5H). Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.92; N, 5.66. Found: C, 67.83; H, 6.89; N, 5.64%.

1,2-Diphenyl-5-methyl-3-oxo-6-thia-2-azabicyclo[2,2,0]hexane (343)

IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.67 (d, J=6Hz, 3H), 3.2-4.8 (m, 2H), and 6.8-7.2 (m, 10H).

(α-Cinnamylamino)thioisobutyrophenone (344)

mp: 102-103 °C; IR($CHCl_3$): 1625, 1665, 3310, and 3430 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.87 (d, J=15Hz, 1H), 7.0-7.5 (m, 11H), and 7.8 (br, 1H). Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.18; N, 4.52. Found: C, 73.90; H, 6.25; N, 4.53%.

8-Isopropyl-7-phenyl-9-oxo-8-azatricylo[3,2,1]nonane (345)

mp: 115-116 °C; IR($CHCl_3$): 1730 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.31 (d, J=6Hz, 3H), 1.33 (d, J=6Hz, 3H), 3.70(sep, J=6Hz, 1H), 4.05 (br,

1H), and 7.1-7.5 (m, 5H). Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.00; N, 5.12. Found: C, 70.33; H, 7.06; N, 5.02%.

7,8-Diphenyl-9-oxo-8-azatricyclo[3,1,2]nonane (346)

mp: 184-185 °C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.3-2.3 (m, 6H), 4.1-4.3 (m, 1H), and 7.0-7.7 (m, 10H).

9-Isopropyl-8-phenyl-10-oxo-9-azatricyclo[4,1,2]decane (347)

mp: 94.5-95 °C; IR($CHCl_3$): 1735 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-2.5 (m, 8H), 1.28 (d, J=7Hz, 3H), 1.37 (d, J=7Hz, 3H), 3.63 (sep, J=7Hz, 1H), 3.78 (t, J=6Hz, 1H), and 7.1-7.7 (m, 5H). Anal. Calcd for $C_{17}H_{21}NOS$: C, 71.04; H, 7.36; N, 4.87. Found: C, 71.21; H, 7.44; N, 4.87%.

9-Benzyl-8-phenyl-10-oxo-9-azatricyclo[4,1,2]decane (348)

mp: 89-90 °C; IR($CHCl_3$): 1745 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-2.5 (m, 8H), 3.80 (t, J=7Hz, 1H), 4.40 (s, 2H), and 7.0-7.5 (m, 10H). Anal. Calcd for $C_{21}H_{21}NOS$: C, 75.18; H, 6.31; N, 4.17. Found: C, 74.84; H, 6.30; N, 4.14%.

8,9-Diphenyl-10-oxo-9-azatricyclo[4,1,2]decane (349)

mp: 164-165.5 °C; IR($CHCl_3$): 1750 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-2.5 (m, 8H), 3.85 (t, J=7Hz, 1H), 6.9-7.6 (m, 10H). Anal. Calcd for $C_{20}H_{19}NOS$: C, 74.37; H, 5.95; N, 4.35. Found: C, 74.68; H, 6.03; N, 4.33%.

7-Methyl-6-oxo-2,9-dithia-5-azatricyclo[3,1,2]nonane (350)

mp: 97.5-99 °C; IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.36 (s, 3H), 3.03 and 3.60 (ABq, J=11Hz, 2H), 3.0-3.4 (m, 3H), and 3.9-4.2 (m, 1H); ^{13}C-NMR($CDCl_3$): δ 14.7 (q), 31.3 (t), 39.8 (t), 43.5 (t), 69.8 (s), 84.3 (s), and 172.7 (s). Anal. Calcd for $C_7H_9NOS_2$: C, 44.89; H, 4.84; N, 7.47. Found: C, 44.70; H, 4.85; N, 7.47%.

5-Methyl-8-oxo-7-thioxo-4-thia-1-azabicyclo[3,2,1]octane (351)

bp: 60°C (10^{-3} torr); IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.71 (s, 3H), 2.95 and 3.69 (ABq, J=8.8Hz, 2H), 3.36 (t, J=7.8Hz, 2H), and 4.28 (t, J=7.8Hz, 2H); ^{13}C-NMR($CDCl_3$): δ 22.2 (q), 28.8 (t), 33.8 (t), 64.0 (t), 78.1 (s), 168.2 (s), and 192.0 (s). Anal. Calcd for $C_7H_9NOS_2$: C, 44.89; H, 4.84; N, 7.47. Found: C, 45.15; H, 4.85; N, 7.34%.

7,8-Dimethyl-6-oxo-2,9-dithia-5-azatricyclo[3,1,2]nonane (352)

mp: 100-101°C; IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.27 (s, 3H), 1.46 (d, J=6.8Hz, 3H), 3.0-3.4 (m, 3H), 3.9-4.2 (m, 1H), and 4.15 (q, J=6.8Hz, 1H); ^{13}C-NMR($CDCl_3$): δ 9.5 (q), 18.6 (q), 39.6 (t), 40.0 (d), 43.4 (t), 64.4 (s), 72.4 (s), and 173.7 (s). Anal. Calcd for $C_8H_{11}NOS_2$: C, 47.73; H, 5.50; N, 6.95. Found: C, 47.77; H, 5.58; N, 6.99%.

13-Oxo-12-aza-7,9-dithiatetracyclo[4,1,1,3]tridecane (353)

IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 0.5-2.5 (br, 8H), 2.9-3.2 (m, 3H), and 3.7-4.2 (m, 2H).

7-Methyl-6-oxo-5-aza-2-oxa-9-thiatricyclo[3,1,2]nonane (354)

IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.33 (s, 3H), 2.77 and 3.30 (ABq, J=10Hz, 2H), 2.9-3.1 (m, 1H), and 3.53-4.53 (m, 3H).

7,8-Dimethyl-6-oxo-5-aza-2-oxa-9-thiatricyclo[3,1,2]nonane (355)

IR($CHCl_3$): 1755 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 1.25 (s, 3H), 1.45 (d, J=7Hz, 3H), 2.8-3.2 (m, 1H), and 3.5-4.5 (m, 4H).

IV. SUMMARY

The photochemical reactions of several types of nitrogen-containing carbonyl and thiocarbonyl compounds were investigated. These photoreactions provided not only new types of reactions but also useful methods for synthesizing nitrogen-containing heterocycles, such as, aziridine-2,3-diones, azetidin-2-ones (β-lactams), azetidine-2,4-diones, oxazolidine-2,4-diones, etc.

(1) 1,2-Diphenylmaleilimide ozonides were prepared by ozonolysis of the corresponding maleilimides. When they were photolyzed at room temperature, isocyanates carbon monoxide, and benzoic anhydride were obtained quantitatively. The low temperature photolyses of them in KBr pellets were followed by IR spectroscopy. Unstable intermediates produced in the photolyses were assignable to be hitherto unknown three-membered cyclic imides, aziridine-2,3-diones. Photolysis of 1,2,4-triazoline-3,5-dione gave similar results. However, the yield of aziridine-2,3-dione was lower than that in the case of maleilimide ozonides.

(2) Photochemical reactions of α-ketoamides were proved to proceed via zwitterionic intermediates. The remarkable substituent and solvent effects can be rationalized on the basis of the mechanism involving zwitterionic intermediates. The iminium ions which were produced by protonation of the zwitterions were detected by NMR and UV spectra. The photo-

cyclization of α-ketoamides which yields the β-lactams and the photoelimination which affords the hydroxyketene and imines can be regarded as Norrish Type II reactions, because the former involves γ-hydrogen abstraction by the excited carbonyl group followed by cyclization to give the four-membered cyclic compounds (β-lactams), and the latter involves the hydrogen abstraction and subsequent cleavage of the β-bond. Therefore, these photoreactions provide the first example of Type II reactions involving zwitterionic intermediates.

(3) Photolysis of N-alkyl-α-ketoimides gave azetidine-2,4-diones in good yields. On the other hand, irradiation of N-aryl and unsubstituted imides yielded dimers of oxazolidine-2,4-dione as main products in addition to azetidine-2,4-diones. The distribution of the products were dependent on the steric bulkiness of the aryl groups. α-Cleavage mechanism was posturated and the intermediates, oxazolidine-2,4-dione radical and benzoyl radical, were trapped by mercaptane. The conformations of imides play important roles in the photochemistry of imides. It is well-known that azetidine-2,4-diones are pharmacologically highly active. This photoreaction provides useful synthesis of azetidine-2,4-diones bearing an oxygen function atom at the 3-position since the previously reported syntheses were tedious, sluggish, and the yields of the azetidine-2,4-diones were generally poor.

(4) Photolysis of N-formylphenylglyoxalylamides in tert-butanol gave 3-hydroxyazetidine-2,4-diones via formyl-hydrogen abstraction. This photoreaction provides an excellent methods for synthesizing azetidine-2,4-diones, since the syntheses of the starting materials were easy.

(5) Photolysis of N-phenylglyoxalyl-N-(phenylthiocarbonyl)amides gave 4-phenylthiooxazolidine-2,4-diones. In the cases of N-benzyl and N-isopropyl derivatives, β-lactams were obtained as main products. The formation of oxazolidine-2,4-diones was reasonably explained in terms of the cleavage of C(=O)-S bond followed by cyclization of the resulting acyl radical and recombination of the cyclic radical with thiyl radical. Oxazolidine-2,4-diones are pharmacologically highly active. Those possessing sulfur function at the 5-position are hitherto unknown. Since the starting materials can be easily obtained by acylation of S-phenylthiocarbamates, this photoreaction provides a useful method for the synthesis of some oxazolidine-2,4-diones.

(6) [2+2]Photocycloaddition of α-dicarbonyl compounds with electron-rich olefins are well studied. Furthermore, it is known that α-diketones do not undergo intermolecular Paterno-Büchi reaction with electron-deficient olefins. Photolysis of N-phenylglyoxalyl-α,β-unsaturated amides gave bicyclic oxetanes. The efficiency of them was controlled by the substituents of the nitrogen atom. The differences of

quantum yields and the chemical yields were dependent on the conformations of imides. This photochemical reaction provides the first example of Paterno-Büchi reaction of α-dicarbonyl compounds with electron-deficient olefins.

(7) Amides are photochemically unreactive in comparison with ketones and esters. The amides usually do not undergo hydrogen abstraction, whereas the imides which have two carbonyl groups and one nitrogen atom exhibit photochemical reactivities similar to those of ketones. This has been explained in terms of the difference between the π-electron donating effects of nitrogens of amides and those of imides. Therefore, the photoreaction of N-aroylureas which possess two nitrogen atoms and two carbonyl groups was investigated. Photolysis of them gave imidazolidin-2-ones, imidazolones, and phenanthlene derivatives. The results lead to the conclusion that these ureas undergo photochemical hydrogen abstraction as imides but their reactivities are much lower than those of imides.

(8) Photolysis of acyclic monothioimides gave thioketones. The mechanism for the formation of thioketones was explainable in terms of β-hydrogen abstraction of thiocarbonyl groups. Resulting 1,3-diradical cyclize to mercaptoaziridines followed by ring opening reaction. The intermediate, mercaptoaziridine, was trapped by acetylation at low temperature. β-Hydrogen abstraction appears to be rare occurance in carbonyl photochemistry, giving precedence to

the Norrish Type II, intermolecular hydrogen abstraction, or simply other photochemical reactions. Although a few instances of β-hydrogen abstraction of thioketones have been reported, they are limitted to thiones where only β-hydrogens abstractable or β-hydrogens are strongly activated. This photorearrangement involving unprecedented 1,2-thiobenzoyl shift provides the first example of β-hydrogen abstraction of nitrogen-containing thiocarbonyl systems.

(9) Photolyses of acyclic and semicyclic monothioimides followed by acylation gave β-lactams via Norrish Type II reactions of thiocarbonyl groups. N-Methoxyacetyl derivatives undergo photocyclization effectively and stereoselectively. The stereoselective reaction was explainable in terms of the hydrogen bond between mercapto group and methoxy oxygen. This photoreaction provides not only the first example of γ-hydrogen abstraction in nitrogen-containing thiocarbonyl systems but also provides a useful method of synthesizing some β-lactams possessing sulfur atoms.

(10) Thiourethanes were inert toward photolysis. N-Acylthiourethanes underwent photochemical γ-hydrogen abstraction to produce 4-mercapto-4-methoxy-β-lactams, thioxo-β-lactams, thiourethanes, and ring opening products of β-lactams.

(11) Photolysis of 3-acyl-2-thiotetrahydro-1,3-thiazines above 40 C gave 2,9-dithia-6-azabicyclo[4,3,0]nonan-7-ones.

Photolysis of them at low temperature gave mercapto β-lactams but they are too unstable to isolate. Instead of them, thioxo-β-lactam was obtained by column chromatography on silica gel. Low temperature photolysis of the thiazines followed by acetylation gave cepham analogues accompanied by a small amount of Type II cleavage products.

(12) Thioaroylureas were obtained by the reaction of the corresponding N-aroylureas with Lawesson's reagent, and N-thioaroylthioureas were synthesized from N-aroylthioureas quantitatively. Photolysis of them gave corresponding imidazolidin-2-ones or imidazolidine-2-thiones. Furthermore, they are desulfurized by the acid catalized reaction (trifluoroacetic acid) to produce imidazol-2-ones or imidazol-2-thiones in good yields. This photoreaction provides the first example of δ-hydrogen abstraction of nitrogen-containing thiocarbonyl compounds. Furthermore, the reactions provide a useful syntheses of imidazolones and thioimidazolones.

(13) Photolysis of several types of N-acyl-α,β-unsaturated amides gave thietane-fused β-lactams in good yields. Since the starting materials are easily obtained by acylation of thioamides, these reactions provide a useful methods for synthesizing thietane-fused β-lactams.

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