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ELECTRON TRANSFER FROM AROMATIC COMPOUNDS
THROUGH PHOTOCHEMICAL AND ANODIC PROCESSES

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DECEMBER 1981

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GENERAL INTRODUCTION

Recently, much attention has been paid to photochemical electron transfer processes from the view point of mechanistic photochemistry, energy storage, photoimaging, preparative chemistry, and so on.

The present investigation concerns with photochemically induced electron transfer from organic molecules.

Chapter 1 describes that photoexcitation of charge transfer complexes of 4-methoxy- and 4-methyl-styrene with oxygen in a polar solvent like acetonitrile results in electron transfer from the styrenes to oxygen to generate radical cations of the styrenes followed by their addition to the styrenes finally affording dimers of the styrenes.

In Chapters 2 and 4, attempts have been undertaken to examine the electron transfer from excited organic compounds, particularly aromatic olefins and phenols, to copper(II) and iron(III) salts finally giving definite reaction products which have hitherto not extensively investigated. Such photochemical electron transfer from the excited aromatic olefins and phenols giving their cation radicals is compared with the electron transfer in electrochemical oxidation as described in Chapters 3 and 4, where the reaction intermediates, their reactivity, and selectivity for reaction products in both processes are discussed.

CHAPTER 1

ELECTRON TRANSFER RESULTING FROM EXCITATION OF CHARGE
TRANSFER COMPLEXES BETWEEN SOME STYRENE DERIVATIVES AND
OXYGEN. THE ROLE OF OXYGEN AS AN ELECTRON ACCEPTOR IN
PHOTODIMERIZATION OF SOME STYRENE DERIVATIVES

SUMMARY

Formation of a charge transfer (CT) complex between 4-methoxystyrene (1) and molecular oxygen is observed in the range of 320-370 nm in acetonitrile and benzene. Irradiation of the CT complex results in the excited state in which higher proportion of electron transfer takes place from the olefin moiety to the oxygen moiety than the ground state CT complex; the excited CT complex will, in a polar solvent like acetonitrile, undergo dissociation into the cation radical of 1 and superoxide anion to give finally trans-1,2-bis(4-methoxyphenyl)cyclobutane (3) through the dimer cation radical of 1, while in a nonpolar solvent such as benzene, the excited CT complex cannot dissociate into the solvated cation radical of 1 and superoxide anion to deactivate into the ground state.

On the other hand, 1 was irradiated under nitrogen atmosphere to afford cis-1,2-bis(4-methoxyphenyl)cyclobutane (2) via the excimer of 1.

Similar irradiation of 4-methylstyrene (5) under oxygen atmosphere afforded 6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalen-1-one (9), which seems to be a quenching product of tetralin-type dimer cation radicals by oxygen species (O_2 or $O_2^{\cdot -}$).

INTRODUCTION

In photochemical reactions, oxygen has often been investigated only as an oxidant. It is well known that singlet oxygen generated by dye-sensitization oxidizes olefins to afford hydroperoxides, endoperoxides, dioxetanes, carbonyl compounds, and epoxides.¹⁾ In contrast to active studies of singlet oxygen, another role of oxygen as an electron acceptor has hardly attracted attention.²⁾

Formation of charge transfer complexes between organic compounds and oxygen has been observed.³⁾ However, its role in photochemical reactions had not been recognized until a few years ago. Recently, copolymerization of styrene and α -methylstyrene with oxygen was reported to be initiated by irradiation of the CT bands between the olefins and oxygen.⁴⁾ Also, excitation of charge transfer bands between hexamethylbenzene and oxygen in methanol-benzene was shown to produce 2,3,4,5,6-pentamethylbenzyl cations followed by reaction with methanol to give 1-methoxy-2,3,4,5,6-pentamethylbenzene.^{2b)} Furthermore, in dye-sensitized photooxygenation of trans-stilbene, oxygen was reported to serve as an electron acceptor.⁵⁾

This chapter aims to report that photoexcitation of charge transfer complexes between 4-methoxy- and 4-methylstyrene and oxygen in acetonitrile results in electron

transfer from the styrenes to oxygen to generate radical cations of the styrenes followed by their addition to the styrenes finally affording dimers of the styrenes. This role of oxygen as an electron acceptor in the photo-dimerization is in keeping with that of the well-known electron acceptors like nitriles, anhydrides, pyrylium salts, and iron(III) salts.⁶⁾ Therefore, the result of this work provides clear evidence for the role of oxygen as an electron acceptor and must give deep insight into elucidation of the mechanism of photooxygenation.

RESULTS

Formation of Charge Transfer (CT) Complexes between 4-Methoxy- and 4-Methyl-styrene and Oxygen.

The longest wavelength end of the absorption band of 4-methoxystyrene (1, 0.59 mol/dm^3) lies at 325 nm in acetonitrile or benzene. On saturation of the solution with oxygen a new absorption band appeared in the range of 320-370 nm in both solvents (Figure 1). This band disappeared reversibly on introduction of argon to exclude oxygen. Therefore, the new absorption band is reasonably assigned to the charge transfer (CT) resulting between 1 and oxygen.⁶⁾

Similarly, 4-methylstyrene (5) also exhibited an absorption due to the CT complex with oxygen at the region of 310-370 nm in acetonitrile (Figure 1).

Formation of a CT complex between 4-Methoxystyrene and 1,4-Dicyanobenzene.

Under nitrogen atmosphere, olefin 1 absorbs the light shorter than 325 nm and also 1,4-dicyanobenzene (DCNB) the light shorter than 300 nm in acetonitrile.

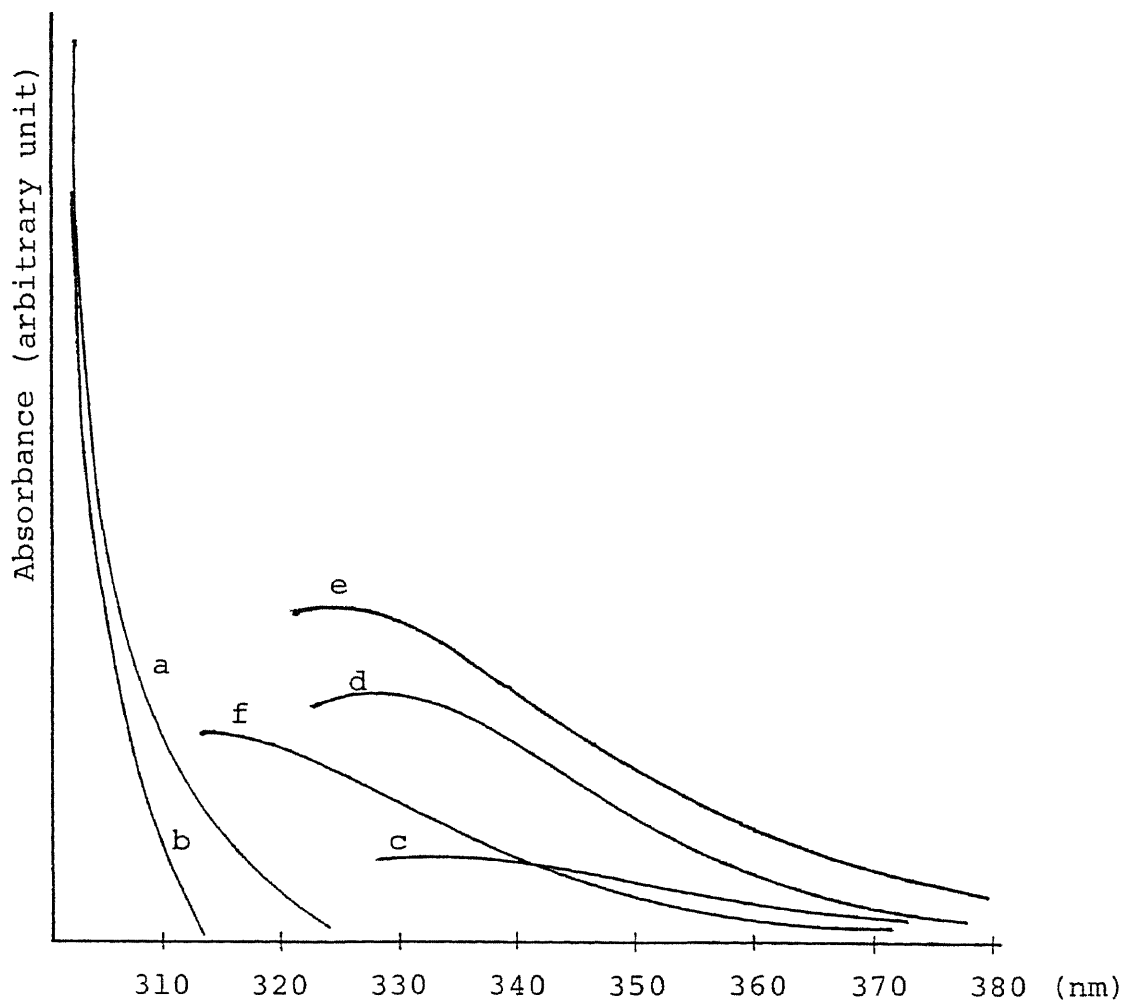


Fig. 1. UV spectra of CT complexes:

- a: 4-methoxystyrene; b: 4-methylstyrene;
- c: between 4-methoxystyrene and oxygen in MeCN;
- d: between 4-methoxystyrene and oxygen in PhH;
- e: between 4-methoxystyrene and DCNB in MeCN;
- f: between 4-methylstyrene and oxygen in MeCN.

However, a solution of 1 (0.59 mol/dm^3) in the presence of DCNB (0.08 mol/dm^3) in acetonitrile under nitrogen atmosphere exhibited a new absorption band at the region of 320-390 nm to be assigned to the CT complex between 1 and DCNB (Figure 1).

Irradiation of 4-Methoxystyrene.

Typical Run.

A solution of 1 (0.59 mol/dm^3) in acetonitrile was irradiated under oxygen in a uranium glass tube (effective at 366 nm) with a high pressure mercury lamp to give cis- and trans-1,2-diarylcyclobutane (the head-to-head cyclo-adducts, 2 and 3, respectively; conversion 43 %; yield 31 %; 2/3 = 5/95) together with the product by oxidative cleavage, 4-methoxybenzaldehyde (4, 32 %). The yields of the products were determined by GLPC analyses and the structure of 2 and 3 was confirmed on the basis of their spectral data after separation by chromatography on silica gel.

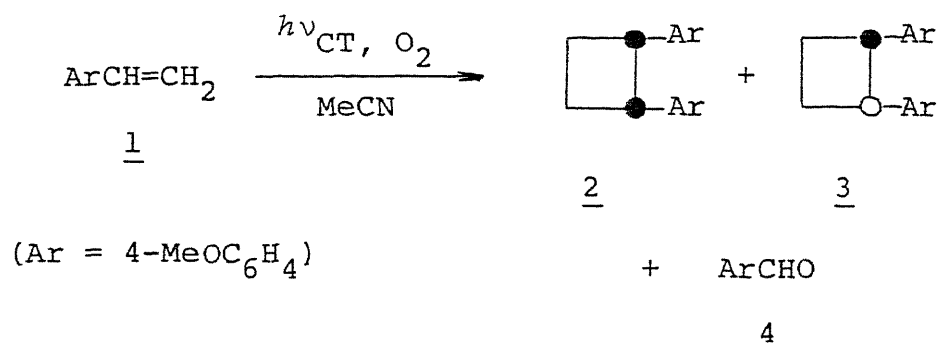


Table 1. Photodimerization of 4-Methoxystyrene (0.59 mol/dm³)

Run	Conditions	Filter	Conv. (%)	Isomer Ratio			4 (Yield, %)
				2 + 3 (Yield, %)	2 : 3	3	
1)	MeCN, O ₂	Quartz ^a	34	56	63 : 37	9	
2)	MeCN, O ₂	Pyrex ^b	63	47	16 : 84	14	
3)	MeCN, O ₂	Uranium ^c	43	31	5 : 95	32	
4)	MeCN, N ₂	Quartz ^a	23	65	90 : 10	trace	
5)	MeCN, N ₂	Pyrex ^b	26	63	87 : 13	trace	
6)	MeCN, N ₂	Uranium ^c	3	trace	— : —	trace	
7)	PhH, O ₂	Pyrex ^b	37	18	80 : 20	11	
8)	PhH, O ₂	Uranium ^c	—	trace	— : —	trace	
9)	MeCN, N ₂	Pyrex ^b	28	75	22 : 78	trace	
	4-MeOC ₆ H ₄ CHO ^d						
10)	MeCN, N ₂	Uranium ^c	12	50	13 : 87	trace	
	Ph ₂ CO ^e						
11)	MeCN, N ₂	Pyrex ^b	95	42	2 : 98	0	
	DCNB ^f						
12)	MeCN, N ₂	Uranium ^c	77	68	2 : 98	0	
	DCNB ^g						

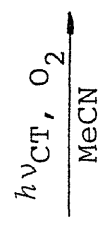
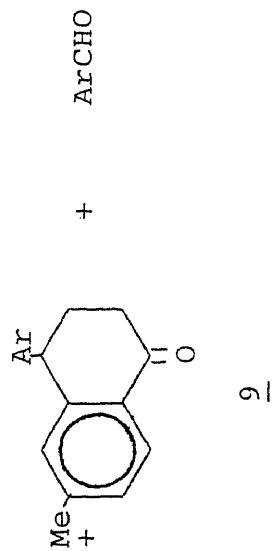
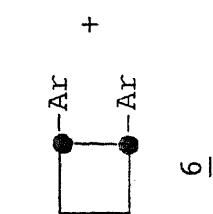
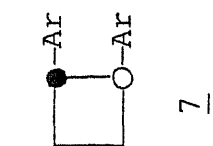
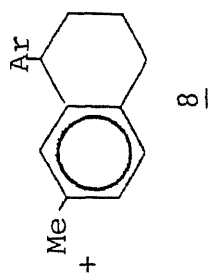
^aEffective at 254 nm. ^bEffective at 313 nm. ^cEffective at 366 nm.
^d0.12 mol/dm³. ^e0.17 mol/dm³. ^f0.13 mol/dm³. ^g0.08 mol/dm³.

The aldehyde 4 was identified by comparison of the retention time with that of the authentic sample on GLPC.

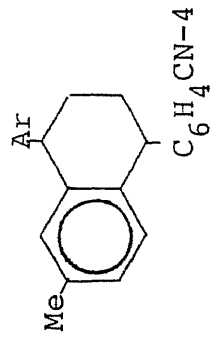
The results of the irradiations of 1 under various conditions are summarized in Table 1.

Irradiation of 4-Methylstyrene.

Irradiation of 5 (0.61 mol/dm^3) in acetonitrile under oxygen atmosphere in a Pyrex tube with the high pressure mercury lamp led to the formation of three cyclodimers (20 %), cis- and trans-1,2-bis(4-methylphenyl) cyclobutane (the head-to-head adducts 6 and 7, respectively) and the tetralin derivative, 7-methyl-1-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (8) (isomer ratio; 6 : 7 : 8 = 1 : 2 : 1), and a dimeric ketone of the olefin (20 %), 6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalen-1-one (9) together with 4-methylbenzaldehyde (8 %). On the other hand, irradiation of 5 (0.61 mol/dm^3) in acetonitrile under nitrogen atmosphere gave the cyclodimers 6, 7 and 8 in a ratio of 65 : 20 : 15, but no dimeric ketone 9. The yields of the products were determined by GLPC analyses. The structure of dimeric ketone 9 was identified by its spectral data and the preparation of its phenylhydrazone derivative after separation by column chromatography on silica gel, while that of 6, 7, and 8



(Ar = 4-MeC₆H₄)



by their spectral data or by comparison of the retention time with authentic samples.^{6d)}

Photosensitized Dimerization of 4-methylstyrene with DCNB.

Irradiation of 4-methylstyrene (5, 0.69 mol/dm³) in the presence of DCNB (0.13 mol/dm³) instead of oxygen under nitrogen atmosphere afforded 1-(4-cyanophenyl)-6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (10) as a main product (30 %), together with the olefin dimers (5 %, 6 : 7 : 8 = 12 : 16 : 72). Tetralin 10 was separated by column chromatography on silica gel and its structure was determined on the basis of its spectral data and the elemental analysis.

DISCUSSION

(I) Photochemical Reaction of 4-Methoxystyrene.

Wavelength Effect on the Photodimerization of 4-Methoxystyrene under Oxygen.

4-Methoxystyrene (1) absorbs the light shorter than 325 nm (Figure 1). The direct irradiation of 1 under nitrogen atmosphere in acetonitrile with 254-nm or 313-nm light gave cis- and trans-cyclodimers 2 and 3 in a ratio of ca. 90/10. In this case the dimerization is assumed to proceed through an excimer as has previously been proposed for styrene⁷⁾ (Runs 4 and 5 in Table 1).

Wavelength Effect

Run	Condition	Wavelength	Isomer Ratio	
			<u>2</u>	<u>3</u>
1)	MeCN, O ₂	254 nm	63	: 37
2)	MeCN, O ₂	313 nm	16	: 84
3)	MeCN, O ₂	366 nm	5	: 95
4)	MeCN, N ₂	254 nm	90	: 10
5)	MeCN, N ₂	313 nm	87	: 13
6)	MeCH, N ₂	366 nm	no reaction	

On the contrary, irradiation of 1 under oxygen atmosphere in acetonitrile with 366-nm light gave 2 and 3 in a ratio of 5/95 (yield 31 %), together with 4-methoxybenzaldehyde (4) (Run 3 in Table 1). Because the CT absorption band between 1 and oxygen was observed in the range of 320-390 nm, 366-nm light can excite only the CT complex. On the contrary, no reaction products were essentially detected on irradiation under nitrogen in acetonitrile with 366-nm light which cannot be absorbed by any species (Run 6 in Table 1).

However, under oxygen, the irradiation with shorter wavelength lights tended to decrease the ratio of the resulting trans-isomer. Irradiation in a Pyrex tube with the high pressure mercury lamp (effective at 313 nm) resulted in the cis/trans ratio of 16/84 (47 % yield, Run 2) and irradiation in a quartz tube with a low pressure mercury lamp (effective at 254 nm) resulted in the ratio of 63/37 (56 % yield, Run 1). These results can be understood in terms that with the decrease of the excitation wavelength higher proportion of uncomplexed olefins are excited which result in the production of the cis-dimer.

Solvent Effect.

Although the CT band between 1 and oxygen was observed in benzene in a similar region to that in acetonitrile (Figure 1), irradiation of 1 under oxygen in this solvent with 366-nm light gave no dimers (Run 8 in Table 1). This remarkable solvent effect suggests

Solvent Effect

Run	Condition	Wavelength	Isomer Ratio
			<u>2</u> : <u>3</u>
2)	MeCN, O ₂	313 nm	16 : 84
3)	MeCN, O ₂	366 nm	5 : 95
7)	PhH, O ₂	313 nm	80 : 20
8)	PhH, O ₂	366 nm	no reaction

that excitation of the charge transfer complex between 1 and oxygen results in the excited state in which higher proportion of electron transfer takes place from the olefin moiety to the oxygen moiety than the ground state CT complex; the excited CT complex will, in a polar solvent like acetonitrile (dielectric constant: 37.5), undergo dissociation into the cation radical of 1 and superoxide anion. However, in a nonpolar solvent such as benzene (dielectric constant: 2.3), the excited CT complexes cannot dissociate into the solvated cation radical of 1 and superoxide anion.

The free-energy change (ΔG) associated with the electron transfer process is given by Eq. 1⁸⁾ where $E(D/D^+)$ and $E(A^-/A)$ are the oxidation potential of the donor (D) and the reduction potential of the acceptor (A), respectively, and $e_0^2/\epsilon\alpha$ is the energy (ca. 0.06 eV in MeCN) gained by bringing the two radical ions to the encounter distance (α) in a solvent of dielectric constant ϵ .

$$\Delta G \text{ (kcal/mol)} = 23.06[E(D/D^+) - E(A^-/A) - e_0^2/\epsilon\alpha] - \Delta E_{0-0} \text{ (kcal/mol)}$$

(Eq. 1)

The calculation of the free-energy change in the photochemical electron transfer process from olefin 1 to oxygen gives the negative value of ΔG , which indicates that the photochemical electron transfer can reasonably take place in the primary process of the photochemical reaction (Table 2). Similar calculation shows that the photochemical electron transfer between olefin 1 and DCNB can also occur (Table 2).

The result of irradiation at 313 nm showed that the reaction in benzene under oxygen atmosphere was initiated from light-absorption by 1 but not by the CT complex, which enforces the photodimerization via the excimer of 1 to give dimers 2 and 3 in a ratio of 80/20 (yield 18 %) together with 4 (11 %) (Run 7 in Table 1).

Table 2. The Free-Energy Change (ΔG) Associated with the Photochemical Electron Transfer Process from 4-Methoxystyrene to Oxygen or DCNB.

	E_{ox}/V	E_{red}/V	Calculated $\Delta G, \text{kcal/mol}$
4-MeOC ₆ H ₄ CH=CH ₂	1.15	—	
O ₂	—	1.28	-39 ^{a)} or -23 ^{b)}
1,4-(CN) ₂ C ₆ H ₄	—	2.00	-23 ^{a)} or -7 ^{b)}

a) ΔG was calculated using 94 kcal/mol (the energy of the singlet excited state of 1) as ΔE_{0-0} .

b) ΔG was calculated using 78 kcal/mol (the energy of 366-nm light employed to excite the CT complex) as ΔE_{0-0} .

Photosensitized Dimerization.

a) Photosensitized Electron-Transfer Dimerization of 4-Methoxystyrene.

Irradiation of a solution of 1 (0.59 mol/dm^3) in the presence of 1,4-dicyanobenzene (DCNB, 0.12 mol/dm^3) in acetonitrile in a uranium glass tube (366 nm) and in a Pyrex tube with the high pressure mercury lamp (313 nm) gave the cis- and trans-dimer (yield: 68 % in Run 12, 42 % in Run 11) in a ratio of 2/98 as previously reported by Yamamoto et al.^{6b)}

Photosensitized Dimerization

Run	Condition	Wavelength	Isomer Ratio	
			<u>2</u>	<u>3</u>
3)	MeCN, O ₂	366 nm	5	: 95
9)	MeCN, N ₂	313 nm	22	: 78
10)	MeCN, N ₂ 4-MeOC ₆ H ₄ CHO Ph ₂ CO	366 nm	13	: 87
11)	MeCN, N ₂ DCNB	313 nm	2	: 98
12)	MeCN, N ₂ DCNB	366 nm	2	: 98

The resulting isomer ratio in this reaction is very similar to that obtained from the dimerization in the presence of oxygen (Runs 3, 11, and 12). Yamamoto mentioned that no photodimerization of 1 occurred in the absence of DCNB and proposed a mechanism through which the excited 1 interacts with DCNB to give the cation radical of 1 finally resulting in dimerization of 1.^{6b)} However, in view of the present observation of the formation of the CT complex between 1 and DCNB in the ground state, the reaction must proceed through excitation of the CT complex followed by dissociation into olefin radical cations and DCNB anion radicals. The olefin radical cations add to the ground state olefins to give olefin dimer cation radicals which accept an electron from superoxide anion, finally to give the olefin dimer.

b) Triplet Sensitized Dimerization of 4-Methoxystyrene.

On triplet sensitization with benzophenone under nitrogen (366 nm) in acetonitrile, 1 gave the dimers (50 % yield) in a different isomer ratio (2/3 = 13/87) from that in the dimerization under oxygen mentioned above (Runs 3 and 10). 4-Methoxybenzaldehyde (4) hardly sensitized the dimerization on irradiation in a uranium glass tube (366 nm); however, 4 in a Pyrex tube (313 nm) under nitrogen in acetonitrile sensitized the dimerization

to produce 2 and 3 in a ratio of 22/78 (75 % yield) (Run 9).

These results rule out a possibility that on the irradiation of 1 under oxygen with 366-nm light the resulting 4 would sensitize the reaction and also the reaction would proceed through triplet sensitization.

Machanism.

The results of irradiations of 1 under various conditions are simply summarized in Table 3.

As Table 3 shows, the higher ratio of cis-dimer 2 to trans-dimer 3 is observed in the direct irradiations of 1 with 313-nm light under nitrogen in acetonitrile, with 254-nm light under nitrogen or oxygen in acetonitrile, and with 313-nm light under oxygen in benzene, while the higher ratio of trans-dimer 3 to cis-dimer 2 is obtained in the irradiations of the CT complexes between 1 and oxygen and between 1 and DCNB with 366-nm light in acetonitrile, and in the benzophenone-sensitized reaction with 366-nm light. In a benzene solution where the CT complex between 1 and oxygen was observed in a similar wavelength region to that in acetonitrile, the irradiation of the CT complex with 366-nm light caused no reaction.

Therefore, these results are most plausibly explained by consideration of two intermediates, the excimer for direct irradiation and the cation radical of 1 for

Table 3. Summary of Photodimerization of 4-Methoxystyrene under Various Conditions

Solvent	Condition	Excitation Wavelength	Isomer Ratio	Intermediate
CH ₃ CN	CT (<u>1</u> ^{δ+} ...O ₂ ^{δ-})	313 nm or 366 nm	c ≪≪ t	Radical Cation
	Direct	313 nm, N ₂	c ≫≫ t	Excimer
	Direct	254 nm, N ₂ ^{O₂}	c ≫≫ t	Excimer
C ₆ H ₆	CT (<u>1</u> ^{δ+} ...O ₂ ^{δ-})	366 nm	no reaction	—
	Direct	313 nm	c ≫≫ t	Excimer
CH ₃ CN	CT (<u>1</u> ^{δ+} ...DCNB ^{δ-})	366 nm	c ≪≪ t	Radical Cation
	Ph ₂ CO, Sens.	366 nm	c ≪≪ t	Excited Triplet

1 = 4-methoxystyrene, DCNB = 1,4-dicyanobenzene

excitation of CT complex. As Scheme 1 explains, on direct excitation the excited olefin will interact with a ground state olefin molecule to give an excimer with the geometry in which the aromatic rings are overlapped with each other. Finally, the excimer will collapse into cis-dimer 2. On irradiation of the CT complex in acetonitrile, the excited CT complex will undergo dissociation into the cation radicals of 1 and superoxide anions. These radical ions will either behave like the radical ions produced from excitation of the CT complex between the olefin and DCNB or will undergo back electron transfer to generate the triplet state of the olefin by conserving the triplet nature of the radical pair formed initially.

To examine the latter possibility, an attempt was done to compare the energy between the radical ion pairs and the olefin triplet state.

The free energy of the pair of the radical cation of 1 and a superoxide anion in acetonitrile can be estimated by Eq. 2 to be + 54 kcal/mol over their ground state molecules.

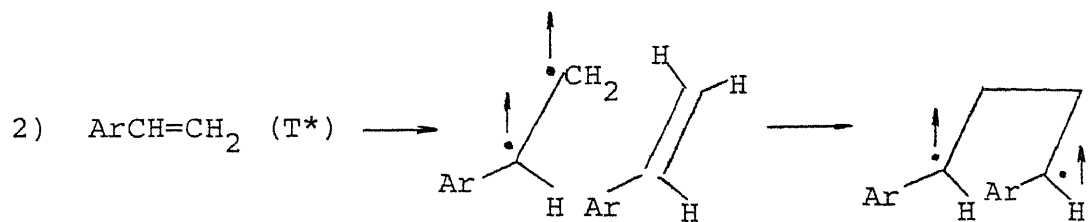
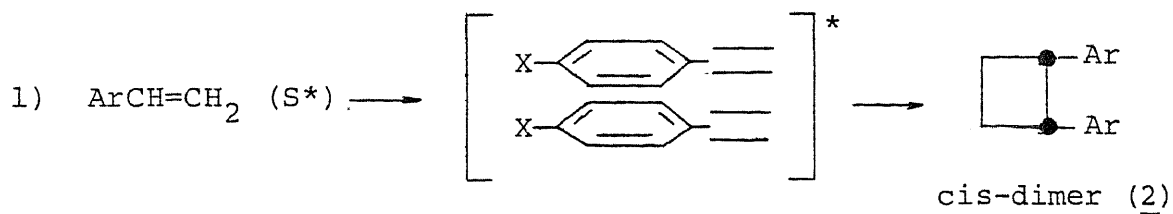
$$\Delta G \text{ (kcal/mol)} = 23.06 [E(D/D^+) - E(A^-/A) - e_o^2/\epsilon a]$$

(Eq. 2)

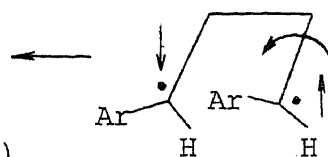
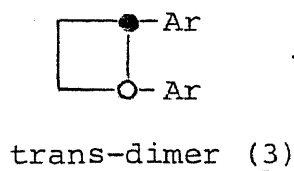
The energy of the singlet excited state of 1 is estimated to be 94 kcal/mol from its fluorescence spectrum and that of the triplet excited state is assumed to be nearly 60 kcal/mol because the triplet energy of styrene was reported to be 62 kcal/mol.⁹⁾ Such estimation for the excited state enables to depict the energy diagram in Figure 2. This diagram excludes the possibility for production of the triplet olefin from the pair of the olefin radical cation and the superoxide anion, since this process is endothermic by ca. 6 kcal/mol.

Therefore, it is reasonable to conclude that on excitation of the CT complex the resulting olefin radical cations add to ground state olefin to give olefin dimer cation radicals to which an electron is reverted from superoxide anions finally to give the olefin dimer. In the interaction of the radical cation and the olefin molecule to give the dimer cation radical, the aromatic rings substituted in the ethylenic linkages will avoid steric crowding, therefore to take a trans-configuration. The mechanism for photodimerization of 4-methoxystyrene is summarized as shown in Scheme 2.

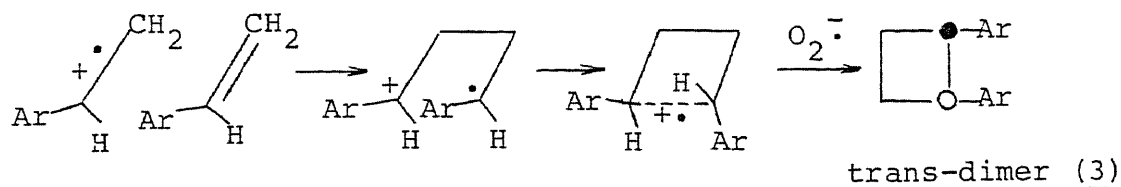
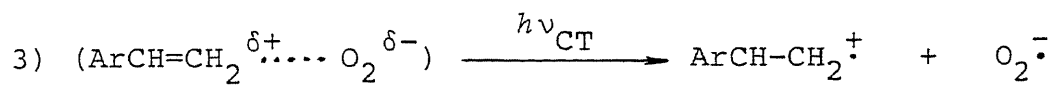
Scheme 1



triplet
biradical



singlet
biradical



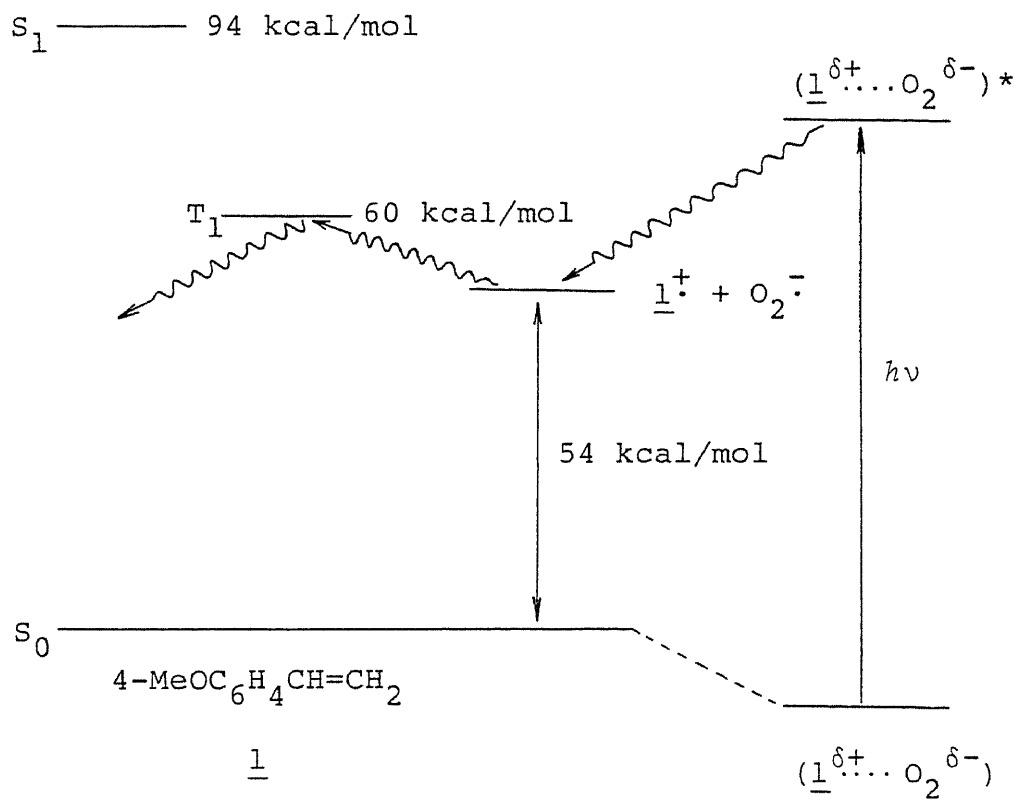
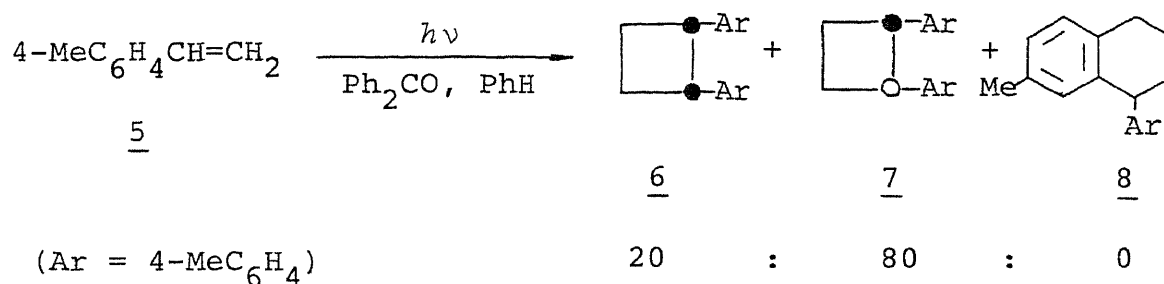


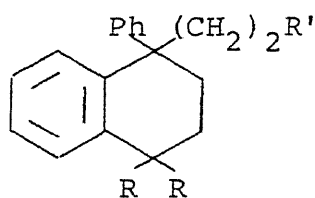
Fig. 2. Energy diagram of a triplet mechanism through the excited CT complex between 1 and oxygen

(II) Photochemical Reaction of 4-Methylstyrene.

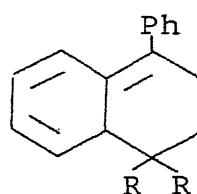
Irradiation of 4-methylstyrene (5) under oxygen in acetonitrile gives the three cyclodimers, 6, 7, and 8, and the dimeric ketone of the olefin, 9 (Scheme 3). Irradiation of 5 in the presence of DCNB as an electron acceptor affords 1-(4-cyanophenyl)-6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (10), together with the olefin dimers (6 : 7 : 8 = 12 : 16 : 72). Comparing the present results with that reported previously by Yamamoto et al., ketone 9 and diaryltetralin 10 seem to be quenching products of tetralin-type dimer cation radicals by oxygen species (O_2 or $O_2^{\cdot-}$) and DCNB (neutral molecule or anion radical), respectively, as depicted in Scheme 3, because tetralin-type dimer 8 is reported to be produced only through the olefin cation radicals:^{6d)} the triplet sensitized dimerization of 5 by benzophenone in benzene gave only cyclodimers 6 and 7 in a ratio of 20/80 but no tetralin-type dimer 8.^{6d)} Therefore, the production of dimeric ketone 9 indicates that excitation of the CT complex between 5 and oxygen in acetonitrile causes the dissociation into the cation radical of 5 and superoxide anion from the excited CT complex.



Recently, Arnold et al. reported that photochemical dimerization of Ph₂C=CH₂ (I) or cross-cycloaddition of I with Me₂C=CH₂ in the presence of CH₂=CHR (R=CN, CO₂Me) and 4-NCC₆H₄CO₂Me, 4-NCC₆H₄CN, or 1,4-dicyanonaphthalene as a photosensitizer gave the appropriate tetrahydronaphthalene II (R=Ph, Me; R'=CN, CO₂Me) through trapping of the triene intermediate III by an ene reaction.¹⁰⁾ However, it should be noted that such quenching products of dimer cation radicals like 9 and 10 have been scarcely reported.



(II)



(III)

EXPERIMENTAL

All the melting points and boiling points are uncorrected. ^1H -NMR and ^{13}C -NMR spectra were recorded on a JEOL JMN-MH-100 spectrometer and a JEOL FX-100 spectrometer, respectively, in deuteriochloroform with TMS as an internal standard. Infrared (IR) spectra were obtained from a Hitachi 260-50 spectrophotometer and UV spectra were measured by means of a Hitachi 200-20 spectrophotometer. Mass spectra were determined with a Hitachi RMU-6MC mass spectrometer. Column chromatography was carried out under pressure on silica gel (Merk Kieselgel 60, Art. 9385) using benzene and dichloromethane as eluents. Irradiations for photochemical reactions were carried out with a 400-W high pressure mercury lamp (Riko UVL-400HA) or with a 160-W low pressure mercury lamp (Riko UVL-160LA).

Materials.

4-Methoxystyrene and 4-methylstyrene were prepared by decarboxylation of the corresponding cinnamic acids as described in the literature.¹¹⁾ Acetonitrile and benzene, purchased from Wako Pure Chemical Industries, were guaranteed reagents and were distilled before use.

Charge Transfer (CT) Absorption Spectra of Styrene Derivatives.

CT Spectra with Molecular Oxygen.

Samples of 1 (0.59 mol/dm^3 in acetonitrile or benzene) were placed in a sample cell and a reference cell, and a stream of oxygen was passed for several minutes through the sample in the sample cell. Spectra were measured at room temperature. Immediately after a spectrum was recorded argon was passed through the sample and a spectrum was again measured. The band observed under oxygen atmosphere completely disappeared at room temperature by argon bubbling.

Similarly, CT spectra of 5 (0.61 mol/dm^3 in acetonitrile) with molecular oxygen were measured.

CT Spectra with 1,4-Dicyanobenzene (DCNB).

A solution of the CT complex was prepared immediately before measurement by mixing an acetonitrile solution of 1 (0.59 mol/dm^3) with DCNB (50 mg, 0.39 mmol). The spectrum was measured at room temperature by a conventional method using a Hitachi 200-20 spectrophotometer. In a reference cell was placed an acetonitrile solution of a

donor at the same concentration as in a sample cell.

(I) Photochemical Reaction of 4-Methoxystyrene.

a) Irradiations with a High Pressure Mercury Lamp.

A solution (3 cm^3) of 4-methoxystyrene (238 mg, 1.78 mmol) in acetonitrile or benzene was irradiated under oxygen or nitrogen atmosphere in a Pyrex tube or a uranium glass tube with a 400-W high pressure mercury lamp for 16 h at room temperature. The yields of all products were determined by GLPC analysis on a Hitachi 163 gas chromatograph equipped with a flame ionization detector using 2 m columns of 5 % Polyethylene glycol 20M and 5 % Silicone GE SE-30 (Table 1).

b) Irradiations with a Low Pressure Mercury Lamp.

A solution (3 cm^3) of 4-methoxystyrene (238 mg, 1.78 mmol) in acetonitrile was irradiated in a quartz tube with a 160-W low pressure mercury lamp under oxygen or nitrogen atmosphere for 16 h at room temperature. The yields of products were determined by GLPC analysis (Table 1).

c) Sensitized Photodimerization.

A solution (3 cm³) of 4-methoxystyrene (238 mg, 1.78 mmol) in acetonitrile was irradiated in the presence of 4-methoxybenzaldehyde (56 mg, 0.41 mmol) or 1,4-dicyanobenzene (50 mg, 0.39 mmol) in a Pyrex or a uranium glass tube with the high pressure mercury lamp under nitrogen atmosphere at room temperature. The yields of products were determined by GLPC analysis (Table 1).

Isolation of Reaction Products.

a) cis-1,2-Bis(4-methoxyphenyl)cyclobutane (2)

4-Methoxystyrene (2 g, 15 mmol) was irradiated in acetonitrile (25 cm³) with a 160-W low pressure mercury lamp under nitrogen stream at room temperature. After 48 h, 4-methoxystyrene was completely consumed as determined by GLPC analysis. Column chromatography on silica gel of the reaction mixture gave a dimer. The structure of the dimer was identified as cis-1,2-bis(4-methoxyphenyl)-cyclobutane from the following spectra data. GLPC analysis showed the formation of the trans dimer (3) as well as 2 (2/3 = 91/9).

2: Oil; MS: m/e 268 (M⁺), 240, 225, 134 (M⁺/2, 100 %), 119:

$^1\text{H-NMR}(\text{CDCl}_3)$: δ 2.36 (q, 4H, CH_2), 3.64 (s, 6H, OMe),
3.86 (m, 2H, CH), 6.52-6.84 (q, 8H, aromatic H);
 $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 157.4 (s), 133.7 (s), 128.8 (d), 113.0
(d), 55.0 (q), 44.5 (d), 24.5 (t).

b) trans-1,2-Bis(4-methoxyphenyl)cyclobutane (3)^{6b)}

Irradiation of 4-methoxystyrene (500 mg, 3.7 mmol) in acetonitrile (5 cm³) under oxygen atmosphere through a Pyrex filter with a 400-W high pressure mercury lamp for 24 h gave trans-dimer 3 (320 mg, 64 %) after separation by chromatography on silica gel with benzene as an eluent.

3: Oil; MS: m/e 268 (M^+), 266, 240, 225, 160, 134 ($\text{M}^+/2$, 100 %), 119; IR(neat): 2940, 1600, 1500, 1450, 1280, 1250, 1170, 1030, 820 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$: δ 2.12 (m, 4H, 2 CH_2), 3.40 (m, 2H, 2CH), 3.72 (s, 6H, 2OMe), 6.72-7.12 (q, 8H, aromatic H); $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 158.0 (s), 136.8 (s), 127.6 (d), 113.7 (d), 55.2 (q), 47.8 (d), 26.0 (t).

(II) Photochemical Reaction of 4-Methylstyrene.

General Procedure.

A solution (3 cm³) of 4-methylstyrene (216 mg, 1.83 mmol) in acetonitrile was irradiated under oxygen or nitrogen atmosphere in a Pyrex or a uranium glass tube with a 400-W high pressure mercury lamp at room temperature for 20 h using a merry-go-round apparatus. The yields of the products were determined by GLPC analysis.

Isolation of Reaction Products.

a) 6-Methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalen-1-one (9)

4-Methylstyrene (1.8 g, 15 mmol) was irradiated in acetonitrile (60 cm³) under oxygen atmosphere through a Pyrex filter with a 400-W high pressure mercury lamp at room temperature. After 72 h, 4-methylstyrene was completely consumed as determined by GLPC analysis and 9 was separated from other dimers (6, 7, and 8) by chromatography on silica gel using benzene as an eluent.

9: Oil; MS: m/e 250 (M⁺, 100 %), 235, 222, 208; IR(neat): 1670 cm⁻¹, $\nu_{C=O}$; ¹H-NMR(CDCl₃): δ 2.34 (s, 3H, CH₃), 2.30

(s, 3H, CH₃), 2.3-2.65 (m, 4H, CH₂CH₂), 4.0-4.25 (m, 1H, CH), 6.7-8.0 (m, 7H, aromatic H); ¹³C-NMR(CDCl₃): δ 197.7, 146.4, 144.3, 140.7, 136.2, 130.6, 129.8, 129.2, 128.4, 127.9, 127.2, 44.8, 36.5, 31.9, 21.7, 21.0. The phenylhydrazone of 9, mp 131-133 °C (dec); Anal. Found: C, 84.73; H, 7.10; N, 8.26 %. Calcd for C₂₄H₂₄N₂: C, 84.66; H, 7.10; N, 8.22 %.

b) 1-(4-Cyanophenyl)-6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (10).

4-Methylstyrene (1.8 g, 15 mmol) was irradiated in the presence of 1,4-dicyanobenzene (1 g, 8 mmol) in acetonitrile (250 cm³) with the high pressure mercury lamp under nitrogen stream at room temperature. After 44 h, the solvent was evaporated in vacuo and silica gel chromatography of the residue gave dimers (7 and 8, trace) and 10 (yield 570 mg, 21 %) as a 1 : 1 mixture of cis- and trans-isomers, the assignment of which was carried out with ¹³C-NMR spectrum.

10: Colorless amorphous; mp 111-112 °C from hexane-methanol; MS: m/e 337 (M⁺), 245 (100 %), 234, 219, 208; IR(KBr): 2210 cm⁻¹, ν_{C≡N}; ¹H-NMR(CDCl₃): δ 1.6-2.1 (m, 4H, CH₂CH₂), 2.16 and 2.18 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 3.95-4.35 (m, 2H, 2CH), 6.6-7.55 (m, 11H, aromatic H); ¹³C-NMR (CDCl₃): δ 153.3,

153.2, 144.0, 143.9, 140.0, 139.6, 136.3, 136.1, 135.7,
135.3, 135.2, 132.1, 131.0, 130.7, 129.9, 129.6, 129.0,
128.6, 127.5, 127.3, 119.0, 109.9, 45.7, 45.6, 45.3, 44.8,
30.9, 30.1, 29.7, 21.0. Anal. Found: C, 89.03; H, 6.87;
N, 4.16 %. Calcd for $C_{25}H_{23}N$: C, 88.97; H, 6.87; N, 4.15 %.

1-(4-Methylphenyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (8)^{6d})

8: Oil; MS: m/e 236 (M^+), 221, 208, 193, 144 ($M^+ - 4-MeC_6H_4$,
100 %), 129, 118; ^{13}C -NMR($CDCl_3$): δ 144.5 (s), 139.1 (s),
135.1 (s), 134.8 (s), 134.3 (s), 130.4 (d), 128.7 (d),
128.6 (d), 126.6 (d), 45.0 (d), 33.3 (t), 29.3 (t), 21.0
(t and q).

c) cis-1,2-Bis(4-methylphenyl)cyclobutane (6)^{6d})

4-Methylstyrene (1.8 g, 15 mmol) was irradiated in
acetonitrile (250 cm^3) with a 160-W low pressure mercury
lamp under argon stream at room temperature for 48 h.
The solvent was evaporated in vacuo and the residue was
separated by chromatography on silica gel to give 6 (1 g,
56 %) and trace amounts of 7 and 8.

6: Oil; MS: m/e 236 (M^+), 208, 193, 178, 132, 118 ($M^+/2$,
100 %), 90: IR(neat): 2930, 1500, 1440, 1310, 1130, 810,

730 cm^{-1} ; $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 138.6 (s), 134.7 (s), 128.3 (d), 127.8 (d), 44.9 (d), 24.6 (t), 21.0 (q).

d) trans-1,2-Bis(4-methylphenyl)cyclobutane (7)^{6d})

A solution (3 cm^3) of 4-methylstyrene (216 mg, 1.83 mmol) in acetonitrile was irradiated in the presence of benzophenone (100 mg, 0.55 mmol) in a uranium glass tube with a 400-W high pressure mercury lamp under argon atmosphere at room temperature to give 6 and 7 in a ratio of 30/70 but no tetralin dimer 8. The structural assignment of trans-cyclobutane dimer 7 was made by GC/mass.

7: MS: m/e 236 (M^+), 234, 221, 219, 206, 193, 191, 179, 178, 144, 118 ($\text{M}^+/2$, 100 %), 105, 90.

(III) Irradiation of 1,2-Bis(4-methoxyphenyl)cyclobutanes
(2 and 3) under Oxygen Atmosphere.

Solutions (3 cm^3) of 2 (105 mg, 0.4 mmol; purity 75 %) or 3 (120 mg, 0.45 mmol; purity 86 %) in acetonitrile were irradiated in Pyrex tubes or uranium glass tubes with a 400-W high pressure mercury lamp using a merry-go-round apparatus under oxygen atmosphere at room temperature for 16 h. After the irradiation, the conversion of the starting materials and the isomer ratio of the cis- and trans-cyclobutane dimers were analyzed by GLPC. The results are shown in Table 7.

Table 7. Irradiation of 1,2-Bis(4-methoxyphenyl)cyclobutanes
in Acetonitrile under Oxygen Atmosphere

Run	Cyclo- butane	Conc. (mol/dm ³)	Tube	Irr. Time (h)	Conv. (%)	Isomer Ratio <u>2</u> : <u>3</u> (%)
a)	<u>2</u>	0.13	Pyrex or uranium	0	0	92 : 8
b)	<u>2</u>	0.13	Pyrex	16	51	71 : 29
c)	<u>2</u>	0.13	uranium	16	24	84 : 16
d)	<u>3</u>	0.15	Pyrex or uranium	0	0	1 : 99
e)	<u>3</u>	0.15	Pyrex	16	24	0.3 : 99.7
f)	<u>3</u>	0.15	uranium	16	10	0.8 : 99.2

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CHAPTER 2

PHOTOCHEMICAL ELECTRON TRANSFER FROM AROMATIC OLEFINS
TO METALLIC IONS. DEPENDENCE OF THE REACTION COURSE
ON THE STRUCTURE OF THE OLEFINS

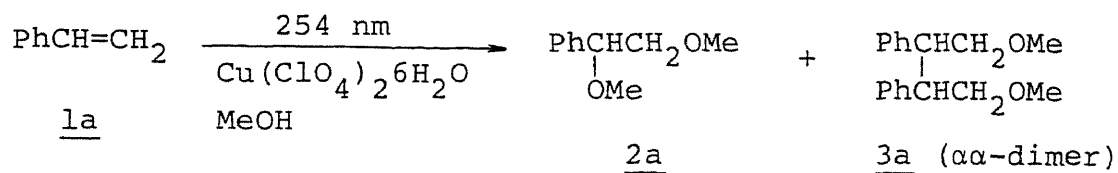
SUMMARY

To examine the photochemical electron transfer from aromatic olefins to copper(II) or iron(III) ions, irradiation of a series of substituted styrenes (1) was carried out in the presence of copper(II) or iron(III) salts in methanol, which gave dimethoxylated monomers (2) and one or more of three types [$\alpha\alpha$ - (3), $\alpha\beta$ - (4), and $\beta\beta$ - (5)] of dimethoxylated dimers. The formation of these products are reasonably attributed to the participation of the cation radicals of the olefins generated by electron transfer from the excited olefins to the metallic ions. Substituents on the substrates are found to govern the reaction products.

INTRODUCTION

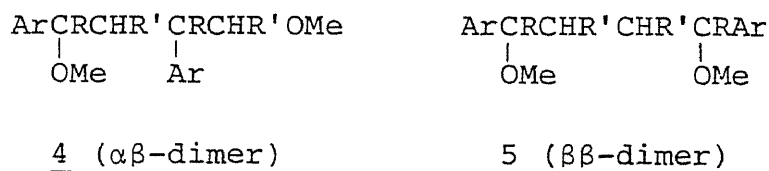
Recently, much attention has been paid to the photochemical electron transfer processes from the view point of mechanistic photochemistry, energy storage, photoimaging, preparative chemistry, and so on.¹⁾ In this chapter, attempts have been undertaken to examine the electron transfer from excited organic compounds, particularly aromatic olefins, to copper(II) and iron(III) salts finally giving definite reaction products which have hitherto not been extensively investigated. Photochemical electron transfer from styrenes giving their cation radicals has been investigated through excitation of organic electron acceptors like 1,4-dicyanobenzene or methyl 4-cyanobenzoate followed by electron transfer to their excited state from ground-state styrenes.²⁻⁴⁾

Tsutsumi and Murai reported previously that the photochemical reaction of styrene (1a) in the presence of copper(II) perchlorate in methanol gave a dimethoxylated monomer 2a and a dimethoxylated dimer ($\alpha\alpha$ -dimer 3a) as isolable products.⁵⁾



However, the mechanism has been unobvious until now.

I carried out this photochemical reaction for a series of styrene derivatives 1 to find other isomeric dimethoxylated dimers 4 ($\alpha\beta$ -dimer) and 5 ($\beta\beta$ -dimer), that the reaction products are obtained through photochemical electron transfer from the excited olefins 1 to the metallic ions, that the reaction course of the cation radicals of 1 was controlled by the substituents on the α -, β -, and p-carbons of the olefins 1, and that the reaction products are similar to those of the electrolysis of the styrene derivatives 1 with a platinum anode in the same solvent as described in Chapter 3.



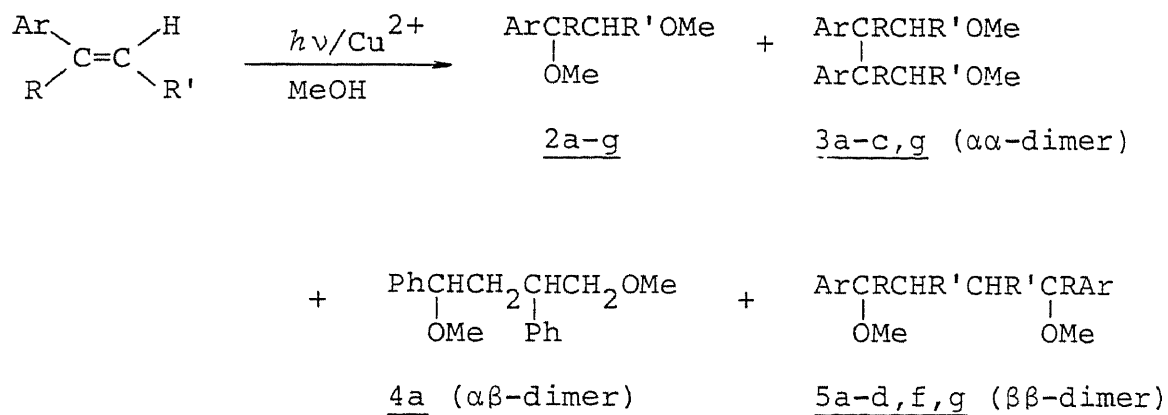
RESULTS

Photochemical Reaction of Substituted Styrenes in the Presence of Metallic Ions in Methanol

Typical Run. Styrene (1a, 28 mmol) was irradiated in the presence of copper(II) perchlorate (56 mmol) in methanol (300 cm³) under nitrogen stream at room temperature with a 160-W low pressure mercury lamp for 40 h. After the irradiation, 70 % of 1a was consumed and a dimethoxylated monomer 2a (yield 41 %) was obtained in addition to three types [$\alpha\alpha$ - (3a, yield 4 %), $\alpha\beta$ - (4a, 0.7 %), $\beta\beta$ - (5a, 1.5 %)] of dimethoxylated dimers (see Scheme 1). During the irradiation, a small amount of metallic copper was precipitated. The structure of the products was identified by GC/mass spectra in comparison with authentic samples obtained from the anodic oxidation of 1a in methanol with a platinum or a graphite anode as described in Chapter 3. Yields of the reaction products were determined by GLPC analysis.

In control experiments, when 1a was left standing in methanol with $\text{Cu}(\text{ClO}_4)_2$ for 25 days under nitrogen atmosphere at room temperature, 1a was completely recovered, and also irradiation of 1a in the presence of $\text{Cu}(\text{ClO}_4)_2$ in methanol with visible light through a Pyrex filter under nitrogen atmosphere at room temperature gave only a trace amount of 2a.

Scheme 1.



a: Ar=Ph, R=R'=H; b: Ar=4-ClC₆H₄, R=R'=H; c: Ar=Ph, R=Me, R'=H; d: Ar=R=Ph, R'=H; e: Ar=Ph, R=H, R'=Me; f: Ar=4-MeC₆H₄, R=R'=H; g: Ar=4-MeOC₆H₄, R=R'=H.

Similar irradiations of styrene derivatives 1 in the presence of $\text{Cu}(\text{ClO}_4)_2$ in methanol were carried out. The results are summarized in Table 1. The use of iron(III) perchlorate instead of copper(II) perchlorate in the photochemical reaction of 1a-d in methanol gave 2a (12 %), 2b (13 %), 2c (24 %), and 2d (24 %), respectively, but other products were not isolated in all the cases.

Oxidation Potentials.

The oxidation potentials of olefins 1 were determined in acetonitrile by cyclic voltammetry with an electrochemical cell composed of a platinum wire as an anode, a platinum gauze as a cathode, and a $\text{Ag}/0.1 \text{ mol/dm}^3 \text{ AgNO}_3$ reference electrode. The results are shown in Table 1.

Table 1. Photochemical Reaction of Styrene Derivatives in the Presence of Copper
(II) Ion

<u>1</u>	ArCR=CHR'	E_{ox}/V^a	Conv. (%)	ArCRCHR'OMe OMe (2, %) ^b	Dimethoxylated Dimers (%) ^c		
					$\alpha\alpha$ (3)	$\alpha\beta$ (4)	$\beta\beta$ (5)
1a	PhCH=CH ₂	1.95	70	41	0.7	1.5	
1b	4-ClC ₆ H ₄ CH=CH ₂	1.76	58	13	—	6	
1c ^d	PhCMe=CH ₂	1.60	54	45	—	2	
1d ^e	Ph ₂ C=CH ₂	1.48	53	39	—	2	
1e	PhCH=CHMe	1.38	67	12	—	—	
1f	4-MeC ₆ H ₄ CH=CH ₂	1.38	63	42	—	5	
1g ^f	4-MeOC ₆ H ₄ CH=CH ₂	1.15	79	trace	—	34	

^aOxidation potential vs. Ag/0.1 mol/dm³ AgNO₃ in MeCN. ^bYield for 2: [(moles of 2)/(moles of 1 consumed)] x 100. ^cYield for 3, 4, or 5: [(moles of 3, 4, or 5)/(moles of 1 consumed)] x 200. ^dAnother product: PhCMe₂OMe (20 %). ^eOther products: Ph₂CO (10 %) and Ph₂C(OMe)Me (28 %). ^fOther products: 4-MeOC₆H₄CH(OMe)Me (12 %) and trans-1,2-bis(4-methoxyphenyl)cyclobutane (10 %).

DISCUSSION

Substituent Effect on the Selectivity for Products.

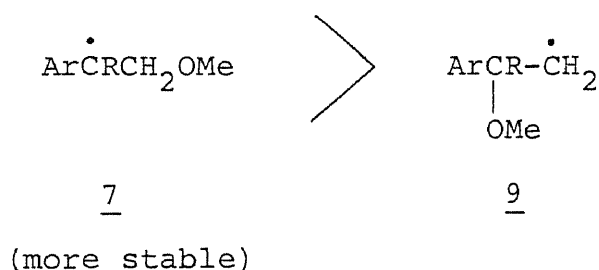
As Table 1 shows, 1a, 1b, and 1c with the higher oxidation potentials among 1's afforded 2, $\alpha\alpha$ -dimer 3, and $\beta\beta$ -dimer 5, accompanying $\alpha\beta$ -dimer 4 from 1a. On the other hand, 1d, 1f, and 1g with the lower oxidation potentials gave no $\alpha\alpha$ -dimer 3 but exclusively $\beta\beta$ -dimer 5 together with 2. On the basis of the above selectivity for the production of the dimethoxylated dimers, 1a, 1b, and 1c are now classified as group I olefins, while 1d, 1f, and 1g as group II olefins. Although 1e with the same oxidation potential as 1f seems to be involved in group II olefins based on the criterion of the oxidation potential, irradiation of 1e with $\text{Cu}(\text{ClO}_4)_2$ in methanol gave exclusively $\alpha\alpha$ -dimer 3e but no $\beta\beta$ -dimer 5e together with 2e. These results point out that the selectivity which dimethoxylated dimers are produced in the photochemical reaction is governed by the effect of the substituent on the α -, β -, or p-carbon of 1: group II olefins with electron donating groups such as methyl or methoxy group tend to produce $\beta\beta$ -dimer 5 selectively, while group I olefins with no electron donating groups tend to give $\alpha\alpha$ -dimer 3 rather than $\beta\beta$ -dimer 5.

Machanism.

The production of $\alpha\alpha$ -dimer 3 can be explained only by dimerization of radical 7 (see Scheme 2), since its intervention gives plausible explanation for dimethoxylated monomer 2 and $\alpha\beta$ -dimer 4: radical 7 would collapse into $\alpha\beta$ -dimer 4 through addition to the olefins, or be further oxidized by copper(II) ion into carbocations 8 finally giving rise to 2. Generation of radical 7 would come from addition of methanol to β -carbon of cation radical 6 which would be produced through photochemical one electron transfer from excited olefin 1 to copper(II) ion. However, in the photochemical reactions of group II olefins, production of neither $\alpha\alpha$ -dimer 3 nor $\alpha\beta$ -dimer 4 suggests that radical 7 does not participate as a reaction intermediate. Radical cations 6 arising from group II olefins seem to have more delocalized distribution of the positive charge on the aromatic ring and concurrent higher density of the unpaired electron on the terminal carbon than those from group I olefins as schematically expressed by a resonance canonical form (6a) and as actually observed with ESR technique for the radical cations of N,N-dimethylamino-alkenes generated by electrolysis.⁶⁾ Therefore, 6 from group II olefins, owing to their higher spin density on their terminal carbon atoms, will more facilely add to olefins than those from group I olefins finally leading to $\beta\beta$ -dimer 5, and consequently, due to the less positive

charge population on their terminal carbon atoms, will react with methanol on their α -carbon atoms to give radical 9, which will be further oxidized by copper(II) ion to give carbocations 10 finally affording 2.

The possibility that methoxy radicals generated from oxidation of methanol by excited copper(II) ion add to olefins 1 can be ruled out by the fact that $\beta\beta$ -dimers 5 were obtained (except for 1e) in addition to $\alpha\alpha$ -dimers 3, although methoxy radicals seem to attack more facilely on the β -carbon of 1 to give more stable radicals 7 than 9.^{5,7)}



Therefore, the present result shows that radical 9 must be produced through the reaction between the olefin radical cations with methanol.

The free-energy change (ΔG) involved in an electron transfer process is given by Eq. 1,⁸⁾ where $E(D/D^+)$ and $E(A^-/A)$ are the oxidation potential of the donor (D) and the reduction potential of the acceptor (A), respectively, and $e_o^2/\epsilon\alpha$ is the energy gained by bringing the two radicals to the encounter distance (α) in a solvent of dielectric constant ϵ (methanol, $\epsilon_{25^\circ} = 32.7$) and estimated to be 0.065

$$\Delta G \text{ (kcal/mol)} = 23.06 [E(D/D^+) - E(A^-/A) - e_0^2/\epsilon\alpha] - \Delta E_{0-0} \text{ (kcal/mol)} \quad (\text{Eq. 1})$$

eV (1.5 kcal/mol) in methanol. The singlet energies of 4-methoxystyrene and styrene were obtained from the fluorescence spectrum or literature,⁹⁾ respectively. In Table 2 are listed the calculated values of ΔG for the olefins. The electron-transfer process from the excited olefins to copper(II) ion is shown to be exothermic.

The proposed mechanism in Scheme 2 requires the second electron transfer from radical 7 or radical 9 to metallic ions. The free-energy change of this process cannot be calculated because the oxidation potentials of radical 7 and 9 cannot be measured. However, their oxidation potentials would lie at more cathodic levels than the reduction potentials of the metallic ions. Therefore, the second electron transfer process would be also exothermic (Figure 1).

Table 2. Singlet Energies of the Olefins and Calculated ΔG Values, Using Eq. 1, for the Electron-transfer Process Involving the Singlets of the Olefins and Copper(II) Ion

	E_{ox}/V^a	E_{red}/V^b	Es (kcal/mol)	ΔG (kcal/mol)
PhCH=CH ₂	1.95	—	98 ^c	-33
4-MeOC ₆ H ₄ CH=CH ₂	1.15	—	94 ^d	-48
Cu(ClO ₄) ₂	—	-0.88		

^aOxidation potential. ^bReduction potential.

^cTaken from S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, p. 20 (1973).

^dObtained from the fluorescence spectrum.

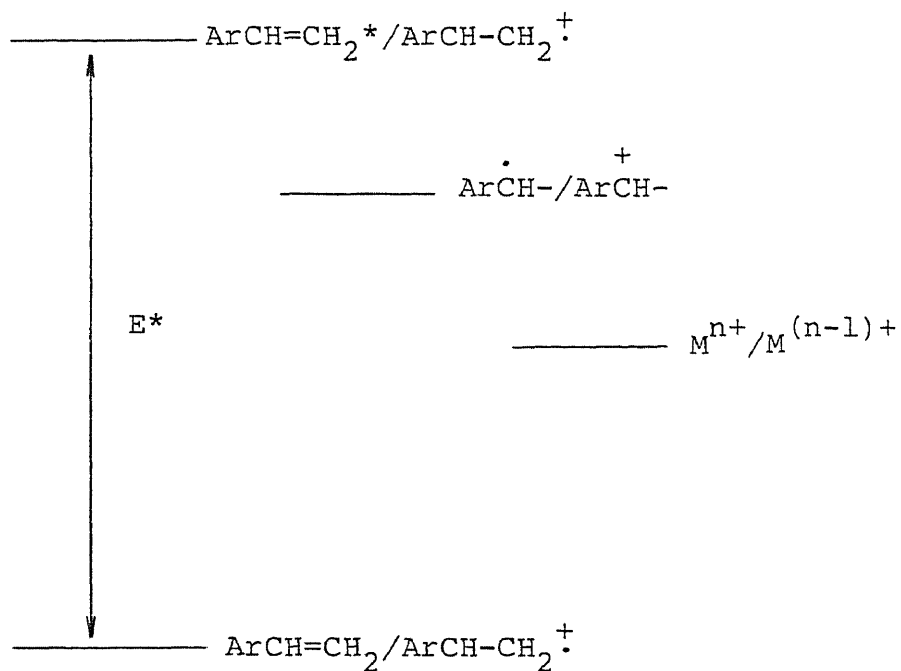
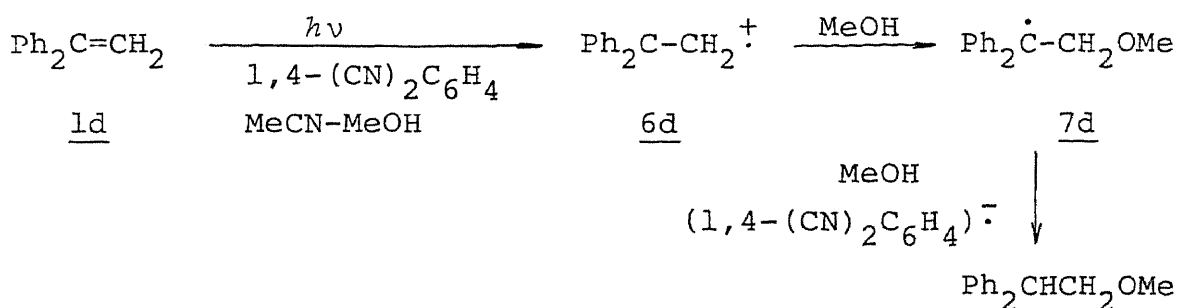


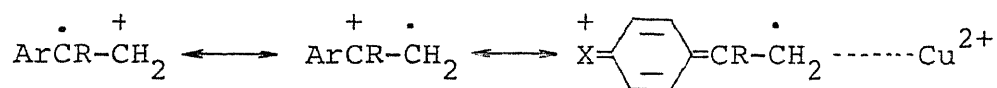
Fig. 1. Energy level diagram showing electron transfer processes

Comparison between "Organic" and "Inorganic" Electron Acceptors.

Arnold and Maroulis reported that cation radical 6d generated through photochemical electron transfer between 1d and "organic" electron acceptors like 1,4-dicyanobenzene and 1-cyanonaphthalene in methanol gave an anti-Markownikoff adduct of methanol to olefin 1d which suggests the formation of radical 7d as an intermediate.^{2d)}



This orientation for methanolysis of cation radical 6d seems to be different from that in the presence of metallic ions ("inorganic" electron acceptor). Thus, the increase of the electron density on β -carbons of radical cations 6 caused by introducing electron donating groups on the α - or p -carbon of 1 would be enhanced by the interaction with copper(II) ion on the β -carbon of 6.



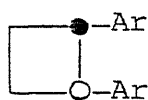
In the case of 1e with the same oxidation potential as 1f, which gave $\beta\beta$ -dimer 5f selectively in the photochemical reaction with the metallic ions, the result that $\alpha\alpha$ -dimer 3e was selectively obtained but no $\beta\beta$ -dimer 5e was obtained suggests that cation radical 6e scarcely interacts with copper(II) ion because of the presence of a methyl group on the β -carbon.

It should be noted that the behavior of the cation radicals of styrene derivatives generated photochemically with "organic" and "inorganic" electron acceptors are not always identical with each other, although the same cation radicals seem to be produced in both processes.

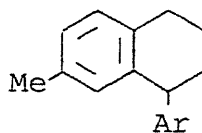
Selectivity for Dimerization in Acetonitrile.

As described in Chapter 1, trapping of the cation radicals of 1 unreacted olefins followed by back electron transfer from the anion radicals of electron acceptors affords the dimers of trans-cyclobutane- (t-CB) or tetralin-type (T) (Scheme 3),²⁾ depending on the structure of olefin 1 as summarized in Table 3.

Table 3 shows that olefins la-e with higher oxidation potentials than 4-methoxystyrene (lg) give T-type dimers, while lg and lh with lower oxidation potentials among 1's prefer t-CB-type to T-type dimers. Such selectivity for the dimerization through electron transfer suggests that the cation radicals of the olefins have different reactivity, which comes from the substituent effect on the p- or α -carbon in the olefins as discussed about the selectivity for the production of dimethoxylated dimers 3, 4, and 5.



t-CB-type Dimer



T-type Dimer

Table 3. Type of Dimers of Styrene Derivatives Produced through Photosensitized Electron Transfer Reaction

	Olefin	E_{ox}/V^a	Type of Dimer
<u>la</u>	PhCH=CH ₂	1.95	T ^b
<u>lb</u>	4-ClC ₆ H ₄ CH=CH ₂	1.76	(?) ^c
<u>lc</u>	PhCMe=CH ₂	1.60	T ^b
<u>ld</u>	Ph ₂ C=CH ₂	1.48	T ^d
<u>lf</u>	4-MeC ₆ H ₄ CH=CH ₂	1.38	T ^{b, e}
<u>lg</u>	4-MeOC ₆ H ₄ CH=CH ₂	1.15	t-CB ^{b, e}
<u>lh</u>	4-Me ₂ NC ₆ H ₄ CH=CH ₂	< 1.15	t-CB ^b

^aOxidation potential vs. Ag/0.1 mol/dm³ AgNO₃ in acetonitrile.

^bYamamoto et al., ref. 2a-c.

^cnot reported yet.

^dArnold et al., ref. 2d.

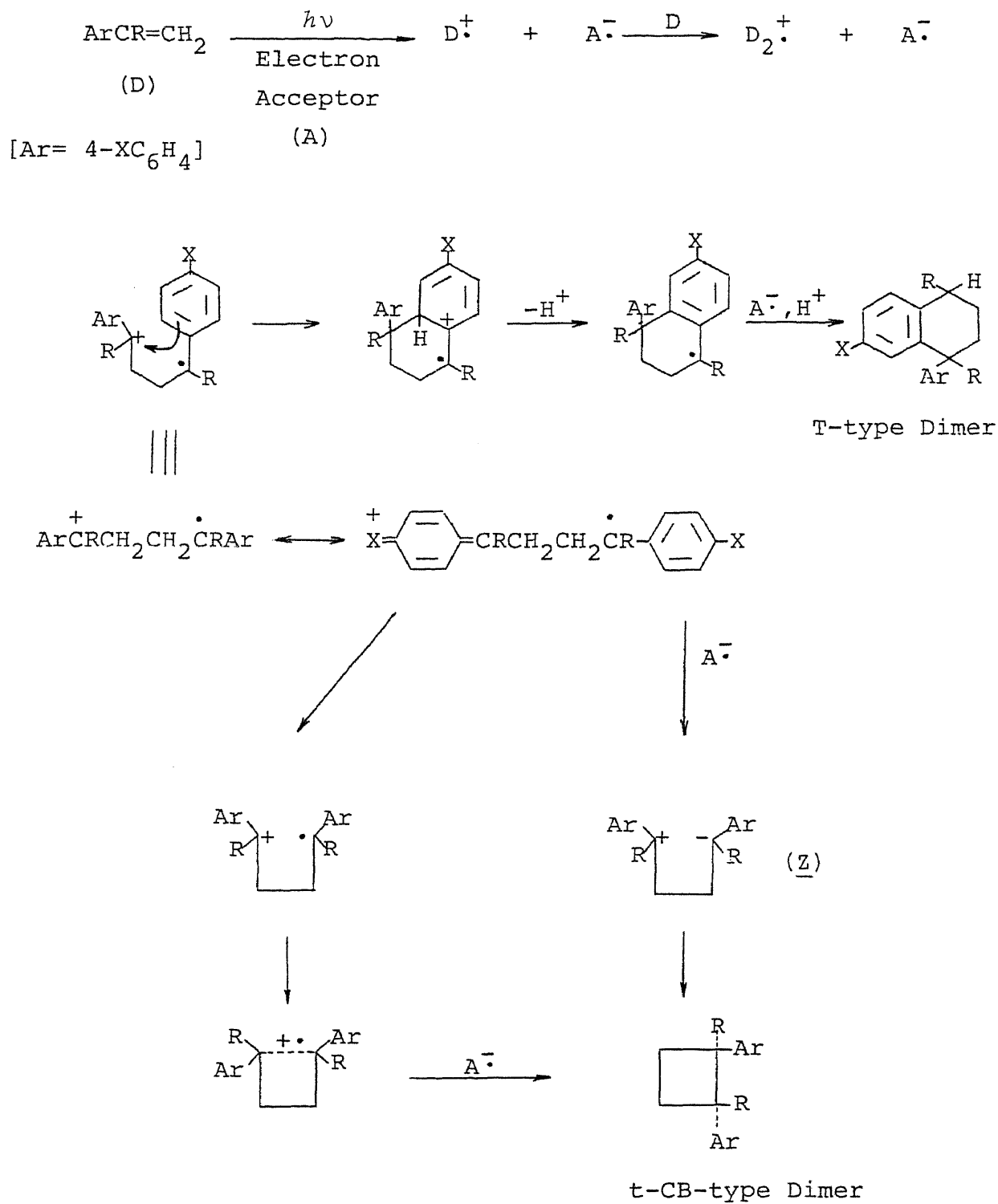
^edescribed in Chapter 1.

T-type dimers are formed by ring-closure at an α -carbon atom of one olefin part and an o-carbon atom of another olefin part in a dimer cation radical, followed by back electron transfer from an anion radical. However, the electron donating substituents such as methoxy and N,N-dimethylamino groups on the p-carbon atom of the aromatic ring would stabilize the positive charge on the α -carbon by resonance effect (see Scheme 3) to prevent the ring-closure to a T-type dimer.

Furthermore, the lifetime of the dimer cation radicals might be another important factor to govern the structure of the dimers: it is reported that the monomer cation radical of lh to give a t-CB-type dimer, has a lifetime of 10^{-6} sec in acetonitrile matrix,¹⁰⁾ while that of ld to give a T-type dimer a much longer lifetime (0.5 msec in acetonitrile, 5×10^2 times of that of lh).^{2d)} If the lifetime of the dimer cation radicals has a linear relationship to that of the monomer cation radicals, the dimer cation radical of lh would have a shorter lifetime than that of ld, which would be caused by the rapid back electron transfer from anion radicals to the dimer cation radicals to make an intramolecular attack by the aromatic ring to the positive charge on the α -carbon difficult, because the zwitter ion (Z) might favor collapsing into t-CB-type rather than into T-type dimers.

Such selectivity for the dimerization also would come from the substituent effect on cation radical 6. Therefore, the direct measurement of the distribution of electron density in 6 by ESR technique or the lifetime of 6 by flash-photolysis technique would give important information about the nature of 6 to allow the elucidation of the selectivity for reaction products mentioned above.

Scheme 3



EXPERIMENTAL

Materials.

Styrene, 4-chlorostyrene, α -methylstyrene, 1,1-diphenylethylene, and trans- β -methylstyrene were commercial samples from Wako Pure Chemical Industries. 4-Methylstyrene and 4-methoxystyrene were prepared by decarboxylation of the corresponding cinnamic acids as described in the literature.¹¹⁾ Copper(II) perchlorate and iron(III) perchlorate were purchased from Kanto Chemical.

Preparation of Authentic Samples.

Authentic samples of dimethoxylated monomers 2 (except for 2c) and dimethoxylated dimers (except for 3b, 3c, and 3e) were prepared by anodic oxidation of olefins 1 in methanol as described in Chapter 3.

Preparation of 1,2-Dimethoxy-1-phenylpropane (2e):

Metallic sodium (1 g, 43 mmol) was dissolved in 100 cm³ of methanol, and then freshly distilled β -methylstyrene (4.5 g, 38 mmol) was added to the mixture. The mixture was subjected to constant-current (1 A) electrolysis at a platinum plate anode (approximate area 60 cm²) with a platinum wire

as a cathode and SCE as a reference electrode under argon atmosphere at room temperature for 2 h. Because a current was not able to be maintained at 1 A after 2 h, constant-current electrolysis was continued at 0.1 A for 3 h. The electrolysis mixture was diluted with water (300 cm³) and extracted with dichloromethane (80 cm³ x 2). The organic layer was washed with water, dried (Na₂SO₄), and analyzed by GLPC. The products obtained by evaporation of the dichloromethane solution were separated with flash-column chromatography. The structures of the products were determined on the basis of their spectral data and elemental analysis.

PhCH(OMe)CH(Me)OMe (2e): erythro-form: bp 59 °C/4mm; MS: m/e 180 (M⁺), 149, 121 (100 %), 117, 105, 91; IR(neat): 1100 cm⁻¹, ν_{C-O} ; ¹H-NMR(CDCl₃): δ 1.12 (d, J=8 Hz, 3H, Me), 3.16 (s, 6H, 2MeO), 3.18 (m, 1H, CH), 4.14 (d, J=4 Hz, 1H, CH), 7.30 (s, 5H, Ph); ¹³C-NMR(CDCl₃): δ 139.2 (s), 128.0 (d), 127.4 (d), 86.0 (d), 80.6 (d), 57.1 (q), 57.0 (q), 14.3 (q); Anal. Found: C, 73.30; H, 8.92 %. Calcd for C₁₁H₁₆O₂: C, 73.29; H, 8.94 %.

threo-form: bp 62 °C/4mm; MS: m/e 180 (M⁺), 149, 121 (100 %), 117, 105, 91; IR(neat): 1100 cm⁻¹, ν_{C-O} ; ¹H-NMR(CDCl₃): δ 0.92 (d, J=7 Hz, 3H, Me), 3.24 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.50 (m, 1H, CH), 4.08 (d, J=7 Hz, 1H, CH), 7.28 (s, 5H, Ph); ¹³C-NMR(CDCl₃): δ 139.1 (s), 128.2 (d), 127.8 (d),

127.6 (d), 87.4 (d), 80.0 (d), 57.3 (q), 57.0 (q), 15.6 (q); Anal. Found: C, 73.19; H, 8.86 %. Calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.94 %.

Measurements of Oxidation and Reduction Potential.

Cyclic voltammetric data were obtained using a three-electrode cell with a Hokuto HA-201 potentiostat and a Hokuto HB-104 function generator. The working electrode was a platinum wire (1 mm diameter) sealed into glass and a counter electrode was a platinum gauze. A Ag/AgNO₃ (0.1 mol/dm³) electrode was used as a reference electrode and 0.1 mol/dm³ tetraethylammonium perchlorate as supporting electrolyte. The current-potential curves were recorded directly from the output of the potentiostat on a Rika Denki RW-11 X-Y recorder. The results are summarized in Table 1.

Irradiation of Styrenes with Copper(II) Salt in Methanol.

A solution of styrenes 1 (5 g, 28-48 mmol) in methanol (300 cm³) containing copper(II) perchlorate (21-36 g, 56-96 mmol) was irradiated under a nitrogen stream at room temperature with a 160-W low pressure mercury lamp (Riko UVL-160LA) for 40 h. The reaction mixture was diluted with water (500 cm³) and extracted with dichloromethane (100

cm³ x 2). The organic layer was washed with water and dried (Na₂SO₄). After evaporation of the solvent, the residue was subjected to flash-column chromatography on silica gel to give 2, 3, 4, and 5. The structures of the products (2, 3, 4, and 5) were confirmed from their spectral data and elemental analysis, or by comparison of their spectral data with those of authentic samples, which were prepared as described in Chapter 3. The organic layer was analyzed by GLPC to determine the yields of the products (Table 1).

1,2-Dimethoxy-2-phenylpropane (2c): PhCMe(OMe)CH₂OMe:

oil; bp 64 °C/3mmHg; MS: m/e 165, 149, 134 (100 %);
IR(neat): 2980, 2930, 2880, 1500, 1200, 1140, 1120, 1070,
760, 700; ¹H-NMR(CDCl₃): δ 1.52 (s, 3H, Me), 3.1 (s, 3H,
OMe), 3.3 (s, 3H, OMe), 3.4-3.5 (ss, 2H, OCH₂), 7.15-7.5
(m, 5H, aromatic H); ¹³C-NMR(CDCl₃): δ 142.5 (s), 128.1
(d), 127.2 (d), 126.5 (d), 80.8 (t), 78.9 (s), 59.5 (q),
50.6 (q), 20.1 (q); Anal. Found: C, 72.97; H, 9.02 %.
Calcd for C₁₁H₁₆O₂: C, 73.30; H, 8.95 %.

1,4-Dimethoxy-2,3-dimethyl-2,3-diphenylbutane (3c):

$\text{Ph} \underset{|}{\text{C}} \text{MeCH}_2 \text{OMe}$: Oil; a 1 : 1 mixture of meso- and d,l-form;
 $\text{Ph} \underset{|}{\text{C}} \text{MeCH}_2 \text{OMe}$ MS: m/e 221, 149 ($\text{M}^+ / 2$, 100 %), 134;
 $^1\text{H-NMR}(\text{CDCl}_3)$: δ 1.3 and 1.4 (s, 6H, 2Me), 3.15 and 3.18
(s, 6H, 2MeO), 3.34 and 3.6 (ss, 4H, 2OCH₂), 6.8-7.4 (m,
10H, 2Ph).

2,5-Dimethoxy-3,4-diphenylhexane (3e):

$\text{Ph} \underset{|}{\text{C}} \text{HCH}(\text{Me}) \text{OMe}$ (3e): mp 175-176 °C; MS: m/e 267, 209
 $\text{Ph} \underset{|}{\text{C}} \text{HCH}(\text{Me}) \text{OMe}$ (100 %), 150; IR(KBr): 1130-1070
 cm^{-1} , $\nu_{\text{C-O}}$; $^1\text{H-NMR}(\text{CDCl}_3)$: δ 0.74 (d, 6H, 2Me), 3.20 (m,
2H, 2CH), 3.20 (s, 6H, 2MeO), 3.22 (broad s, 2H, 2CH),
7.24-7.60 (m, 10H, 2Ph); $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 140.9 (s),
130.4 (d), 127.7 (d), 126.1 (d), 76.1 (d), 56.3 (q), 54.3
(d), 17.0 (q); Anal. Found: C, 80.69; H, 8.82 %. Calcd
for $\text{C}_{20}\text{H}_{26}\text{O}_2$: C, 80.54; H, 8.72 %.

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CHAPTER 3

ELECTROCHEMICAL OXIDATION OF AROMATIC OLEFINS.
DEPENDENCE OF THE REACTION COURSE ON THE STRUCTURE
OF THE OLEFINS AND ON THE NATURE OF THE ANODES

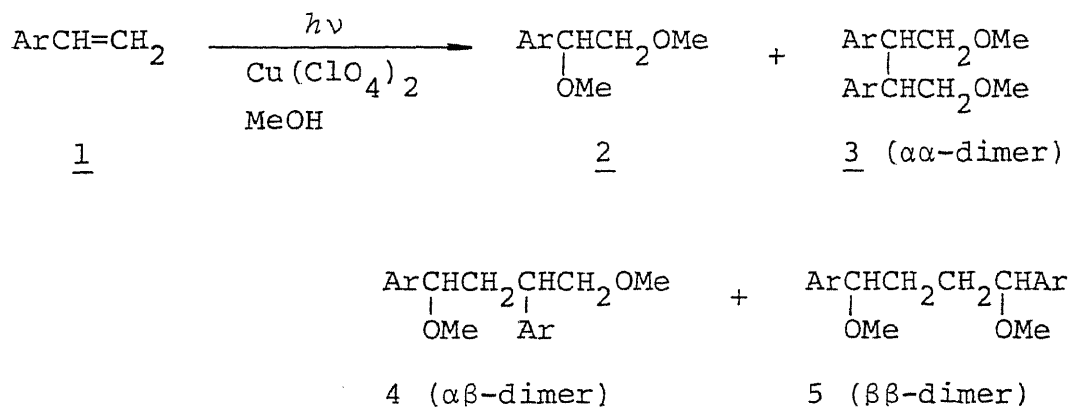
SUMMARY

Anodic oxidation of a series of substituted styrenes was investigated in methanol with a platinum and a graphite electrode. The results are compared with those of the photochemical electron transfer reaction discussed in Chapter 2. Use of the platinum anode gave mainly dimethoxylated monomers accompanied with one or more of three types of dimethoxylated dimers ($\alpha\alpha$ -, $\alpha\beta$ -, and $\beta\beta$ -dimers) depending on the substituents in the same manner as did the photochemical reaction of olefins 1 in the presence of metallic ions. Use of the graphite anode, however, afforded the $\beta\beta$ -dimers as the main product together with dimethoxylated monomers because of the stronger adsorption effect of the graphite electrode than the platinum anode.

The results of anodic oxidation of the olefins give clear evidence for the intervention of olefin radical cations (6) as reaction intermediates, which are the same as generated through the electron transfer from the excited olefins to metallic ions as discussed in Chapter 2.

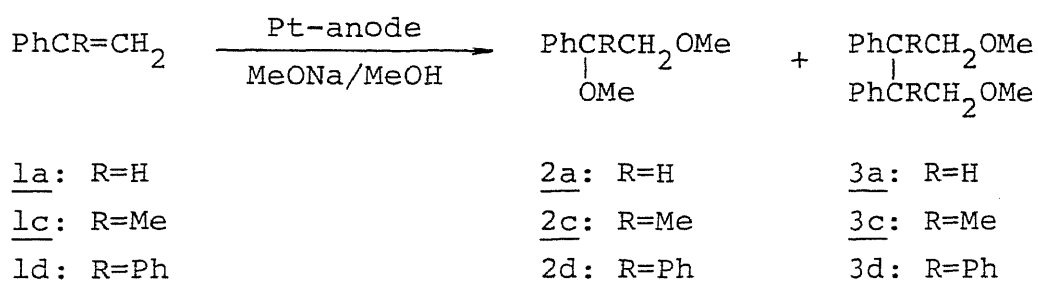
INTRODUCTION

In Chapter 2, it was discussed that irradiation of styrenes 1 in the presence of metallic salts such as copper(II) perchlorate in methanol gave the dimethoxylated monomers 2 and one or more of three types [$\alpha\alpha$ - (3), $\alpha\beta$ - (4), and $\beta\beta$ - (5)] of dimethoxylated dimers through the cation radicals of the olefins (6) generated by electron transfer from the excited olefins to metallic ions.

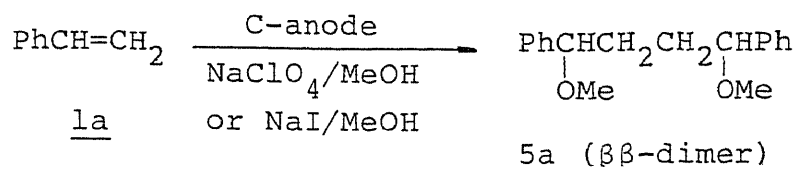


To confirm the intervention of the cation radicals of the olefins (6) in the photoexcitation of the olefins in the presence of metallic ions in methanol, an attempt has been undertaken to carry out anodic oxidation of the olefins in methanol and to compare the reaction products with those from the photochemical reactions as described in this chapter.

Recently, active investigations have been reported in electroorganic chemistry.¹⁾ Anodic oxidations of aromatic olefins like styrene have been carried out in several laboratories employing different experimental conditions.^{2,3)} However, the results are not necessarily consistent, and what factors actually govern the reaction course has not been clear.^{2,3)} Inoue and Tsutsumi carried out a pioneering work to describe that, on electrolysis at a platinum anode in methanol in the presence of sodium methoxide, styrene (1a) afforded a dimethoxylated monomer (2a) and a dimethoxylated dimer (α -dimer 3a, see below), and that α -methylstyrene (1c) and 1,1-diphenylethylene (1d) likewise gave the corresponding dimethoxylated monomers, and production of dimethoxylated dimers (3c and 3d) was suggested without actual determination of their structures.



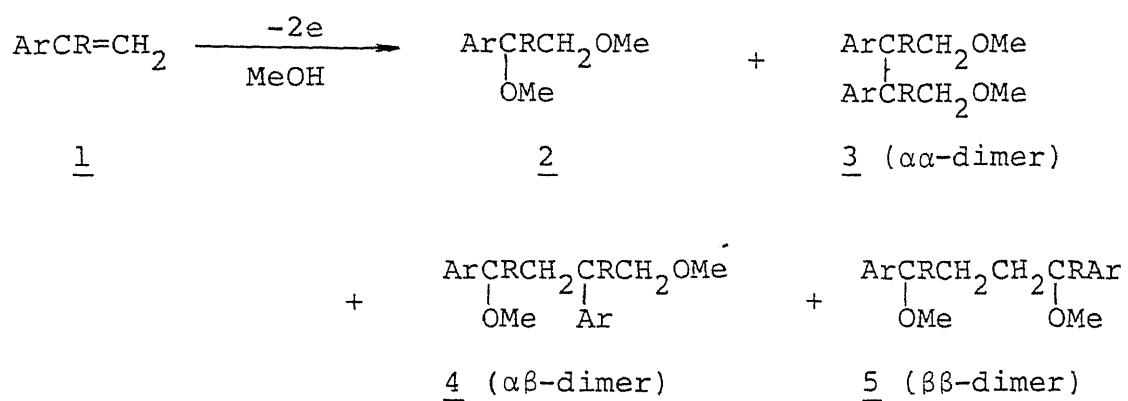
On the other hand, Schäfer and coworkers reported that oxidation of 1a on a graphite anode in methanol in the presence of sodium perchlorate or sodium iodide gave rise to another dimethoxylated dimer ($\beta\beta$ -dimer, 5a) a structural



isomer of 3a.³⁾

An attempt has been undertaken to conduct anodic oxidation of a series of styrenes (1) in methanol on a platinum and a graphite anode by the same worker, myself. It is found that styrenes (1), in general, afford dimethoxylated monomers (2) and one or more of three types of dimethoxylated dimers [$\alpha\alpha$ - (3), $\alpha\beta$ - (4), and $\beta\beta$ -dimers (5)] as indicated in Scheme 1 in the same manner as did the photochemical reaction of 1 in the presence of metallic ions in the same solvent. Substituents on the olefins and the nature of the electrodes is revealed to show remarkable effects upon the course of the reaction; particularly, it is worth to mention that the characterization of the resulting dimethoxylated dimers in low yields enables us to get deeper insight into the reaction course than that based mainly on the major products.²⁾

Scheme 1



RESULTS

The present investigation employed three kinds of procedures, A, B, and C, for anodic oxidation of styrene derivatives 1. In the procedure A, 1 (10-50 mmol) was electrolyzed in methanol (120 cm³) containing sodium methoxide (52 mmol) under a constant current (1 A) using a platinum plate with many holes as an anode (approximate area, 60 cm²), a platinum wire as a cathode, and SCE as a reference electrode under argon atmosphere at room temperature. Procedure B is similar to the procedure A except that tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte instead of sodium methoxide under constant-current electrolysis (0.1 or 1 A). This procedure was employed to examine the effect of supporting electrolyte: in procedure A, methoxide ions might be facilely oxidized than olefins 1 to generate methoxy radicals.²⁾ Procedure C was employed to examine the effect of electrodes on adsorption: 1 (10-25 mmol) was electrolyzed under a constant current (1 A) in methanol (120 cm³) in the presence of sodium perchlorate (82 mmol) or sodium iodide (10 mmol) at a graphite cylindrical anode (effective area, 80 cm²; thickness, 0.3 cm) with a graphite rod (diameter, 1 cm; length 8 cm) as a cathode and a Ag/AgCl reference electrode. The results of electrolyses of the styrenes

with procedures A, B, and C are summarized in Table 1.

Apparatus.

Figure 1 shows a schematic diagram of the electrolysis cell employed in the present investigation. The cell (volume, 150 cm³) consists of three parts: a platinum plate (60 cm²) or a graphite cylindrical anode (80 cm²), a platinum wire or a graphite rod (diameter, 1 cm; length, 8 cm) as a cathode, and SCE or a Ag/AgCl electrode as a reference electrode. Argon can be passed into the solution in the cell. If necessary, one can stir the solution by a magnetic stirrer.

Table 1. Electrochemical Oxidation of Styrene Derivatives (1) in Methanol^a

<u>1</u> ArCR=CH ₂	E _{ox} /V ^b	Procedure ^c	ArCRCH ₂ CH ₂ OMe OMe (2, %) ^d	Dimethoxylated Dimers (%) ^e		
				αα (3)	αβ (4)	ββ (5)
<u>1a</u> PhCH=CH ₂	1.95	A	19	0.5	1	1
		B	36	1	2	2
		C ^f	trace	—	—	15
<u>1b</u> 4-ClC ₆ H ₄ CH=CH ₂	1.76	A	31	0.3	—	3
		B	31	0.7	—	2
		C ^g	—	—	—	26
<u>1d</u> Ph ₂ C=CH ₂	1.48	A	40	—	—	1
		B	69	—	—	5
		C ^h	17	—	—	2
<u>1f</u> 4-MeC ₆ H ₄ CH=CH ₂	1.38	A	36	—	—	4
		B	30	—	—	3
		C	5	—	—	4
		C ⁱ	6	—	—	20
<u>1g</u> 4-MeOC ₆ H ₄ CH=CH ₂	1.15	A	17	—	—	(3.5) ^j
		B	—	—	—	13
		C	10	—	—	25

Table 1. (footnotes)

^aElectrolysis was carried out until the starting olefins were completely consumed except for the following runs where conversion (%) of the olefins was indicated in parentheses: 1a by procedure A (32 %), 1b by procedure A (79 %), and 1d by Procedure B (67 %). ^bOxidation potential vs. Ag/0.1 mol/dm³ AgNO₃ in MeCN.

^cProcedure A: working electrode (WE), platinum (Pt); counter electrode (CE), Pt; reference electrode (RE), SCE; Supporting electrolyte (SE), MeONa. Procedure B: WE, Pt; CE, Pt; RE, SCE; SE, TEAP. Procedure C: WE, graphite; CE, graphite; RE, Ag/AgCl; SE, NaClO₄. ^dYield for 2: [(moles of 2)/(moles of 1 consumed)] x 100. ^eYield for 3, 4, or 5: [(moles of 3, 4, or 5)/(moles of 1 consumed)] x 200. ^fOther products: PhCHO and PhCO₂Me. ^gOther products: 4-ClC₆H₄CHO and 4-ClC₆H₄CH(OMe)₂ (11 %). ^hAnother product: Ph₂CO (30 %). ⁱNaI was used as a supporting electrolyte. ^j(4-MeOC₆H₄COCH₂-)₂ (1.5 %) and [4-MeOC₆H₄C(OMe)₂CH₂-]₂ (2 %) were isolated, which are considered to be derived from 5g.

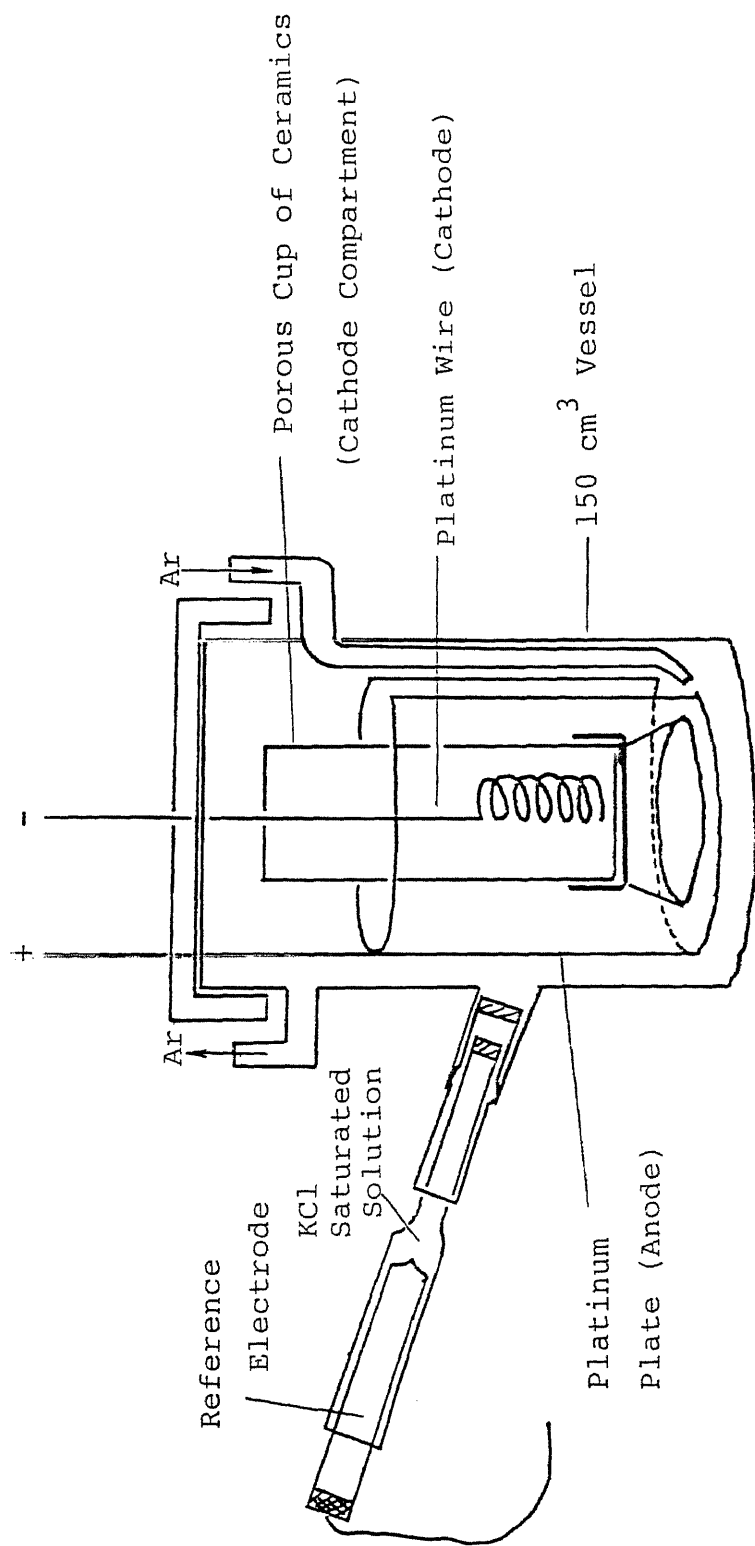
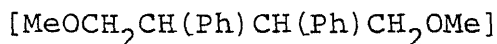


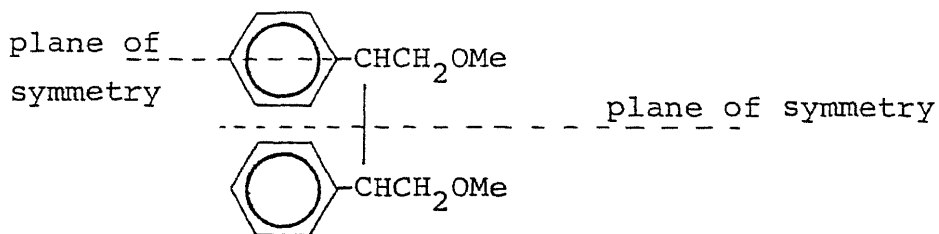
Fig. 1. Schematic diagram of electrolysis cell

Identification of Dimethoxylated Dimers.

1,4-Dimethoxy-2,3-diphenylbutane (3a, $\alpha\alpha$ -dimer):



This compound has been reported by Inoue and Tsutsumi.²⁾ The ^1H -NMR spectrum of 3a is shown in Figure 2. A broad signal arising from methine and methylene protons is seen around 3.3 ppm. The peak (3.08 ppm, s, 3H) due to the methoxy groups is also observed. The ^{13}C -NMR spectrum is shown in Figure 3, which exhibits the result of heteronuclear decoupling of all protons in compound 3a, and Figure 4 shows the off-resonance proton-decoupled spectrum to allow assignment of the number of protons directly attached to each carbon atom. Figure 3 indicates that there are seven unique types of carbon atoms but eighteen carbons in the formula of 3a ($\text{C}_{18}\text{H}_{22}\text{O}_2$); therefore, 3a has two symmetry planes as shown below.

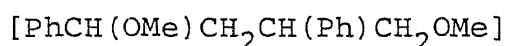


Simple inspection shows that the peak at 74.9 ppm is a triplet (i.e. a CH_2O group) because the chemical shift is moderately deshielded, which implicates that the carbon is attached to a single electronegative (deshielding)

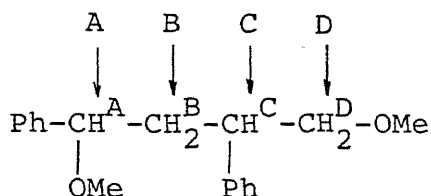
element. The peak at 58.7 ppm is a quartet (i.e. CH₃O group) and that at 48.5 ppm a doublet (i.e. CH group).

Other α-dimers were identified based on the patterns of ¹H- and ¹³C-NMR spectra as mentioned above.

1,4-Dimethoxy-1,3-diphenylbutane (4a, αβ-dimer):

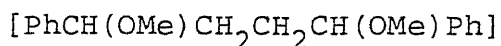


This compound was isolated from the electrolysis products of styrene with procedure B. Figures 5 and 6 show the ¹H-NMR and decoupled ¹H-NMR spectra of 4a, respectively. Figure 5 shows that there are seven hydrogen units: δ 6.96-7.36 (m, 10H, 2Ph), 3.90 (t, 1H, CH), 3.38 (d, 2H, CH₂), 3.18 (s, 3H, OMe), 3.04 (s, 3H, OMe), 2.72 (m, 1H, CH), 2.12 (t, 2H, CH₂). The decoupled ¹H-NMR shows that irradiation at H^A changes H^B to a doublet from a triplet of triplets, irradiation at H^B changes H^A to a singlet from a triplet, irradiation of H^C changes H^D to a singlet from a doublet, and irradiation at H^D changes H^C to a triplet from a quintet. The structure of 4a is consistent with the decoupling observed above.



Figures 7 and 8 show the fully decoupled and off-resonance decoupled spectra of ^{13}C -NMR concerning 4a, respectively. It is observed that there are two doublet signals at 81.8 (-CH-O-R group) and 42.1 ppm (-CH-R group), two triplet signals at 77.48 (-CH₂OR group) and 40.6 (-CH₂-group), and two quartet signals at 58.7 and 56.2 ppm (two MeO group). This pattern of the ^{13}C -NMR spectrum is consistent with the assigned structure to 4a ($\alpha\beta$ -dimer).

1,4-Dimethoxy-1,4-diphenylbutane (5a, $\beta\beta$ -dimer):

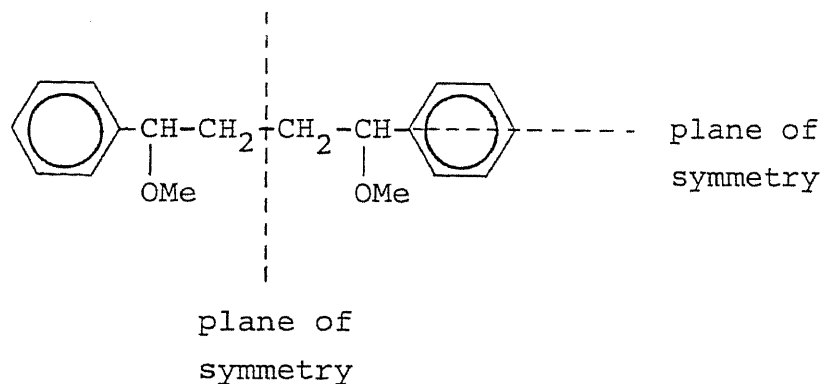


This compound has been reported by Schäfer et al.³⁾ By electrolysis of styrene (1a) with procedure C, 5a was prepared. Figure 9 shows the ^1H -NMR spectrum and Figures 10 and 11 show the ^{13}C -NMR spectra (fully decoupled and off-resonance decoupled, respectively).

As Figure 9 indicates, the methylene protons (1.8 ppm) of 5a ($\beta\beta$ -dimer) are observed in higher field than that of $\alpha\alpha$ -dimer 3a (3.3 ppm), while the methine protons shift to lower field than that of $\alpha\alpha$ -dimer 3a (from 3.3 ppm to 4.1 ppm). The peak due to the methoxy groups is seen at 3.2 ppm with a singlet. The pattern of ^1H -NMR also points out high symmetry in 5a ($\beta\beta$ -dimer).

The ^{13}C -NMR spectrum (Figure 10) shows that 5a is a mixture of meso- and dl-form, because pairs of peaks due to methine and methylene carbons are observed at 84.1 and 83.8 ppm, and at 34.7 and 34.2 ppm, respectively.

Compared to $\alpha\alpha$ -dimer 3a, the methine carbons shift to lower field (from 48.5 to 84 ppm), while methylene carbons to higher field (from 74.9 to 34 ppm). Also, the ^{13}C -NMR spectrum exhibits the presence of two symmetry planes as below.



The patterns of these spectra are consistent with the assigned structure to 5a ($\beta\beta$ -dimer). Other $\beta\beta$ -dimers were identified based on the patterns of ^1H - and ^{13}C -NMR spectra as mentioned above.

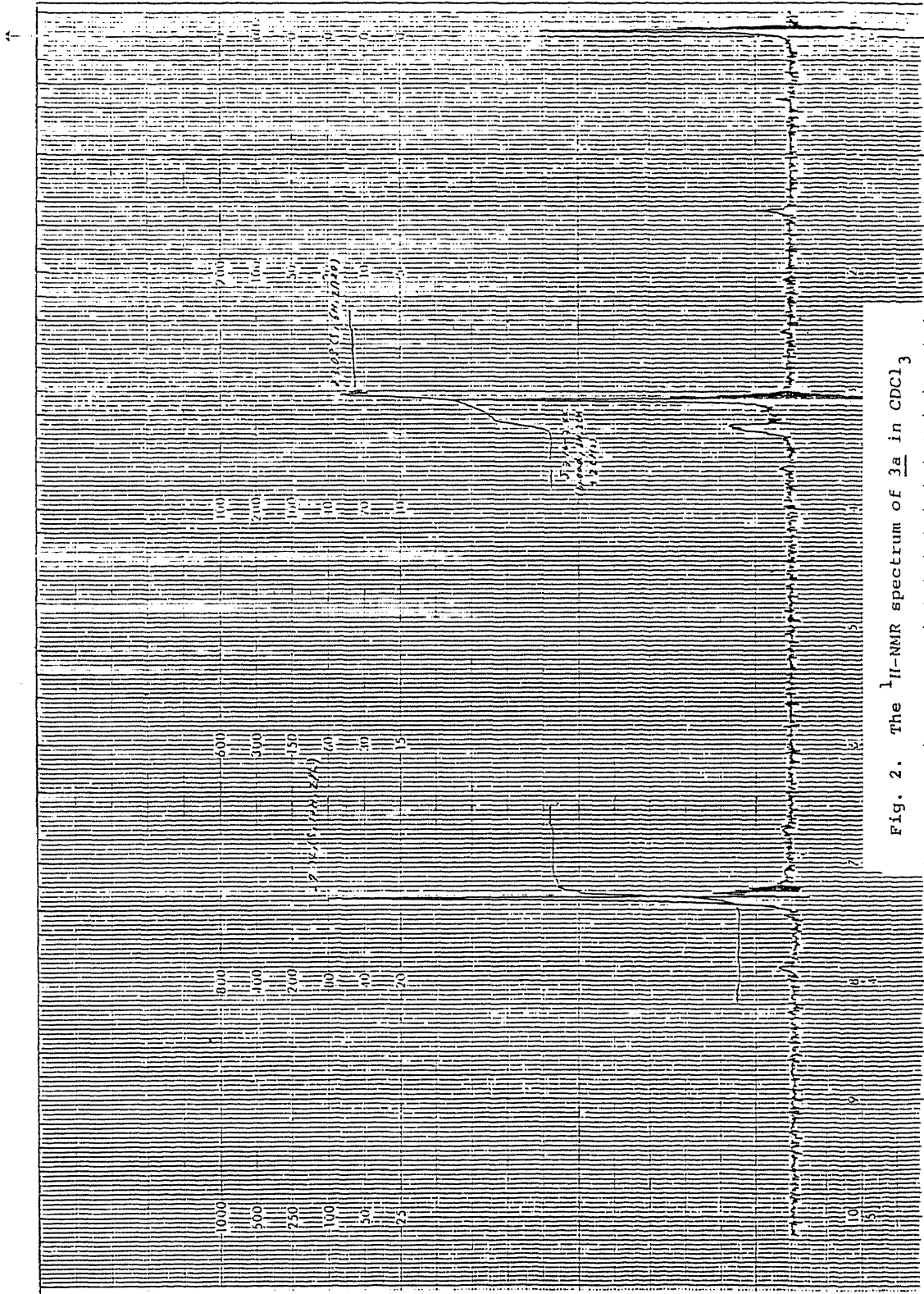


Fig. 2. The ^1H -NMR spectrum of $3a$ in CDCl_3

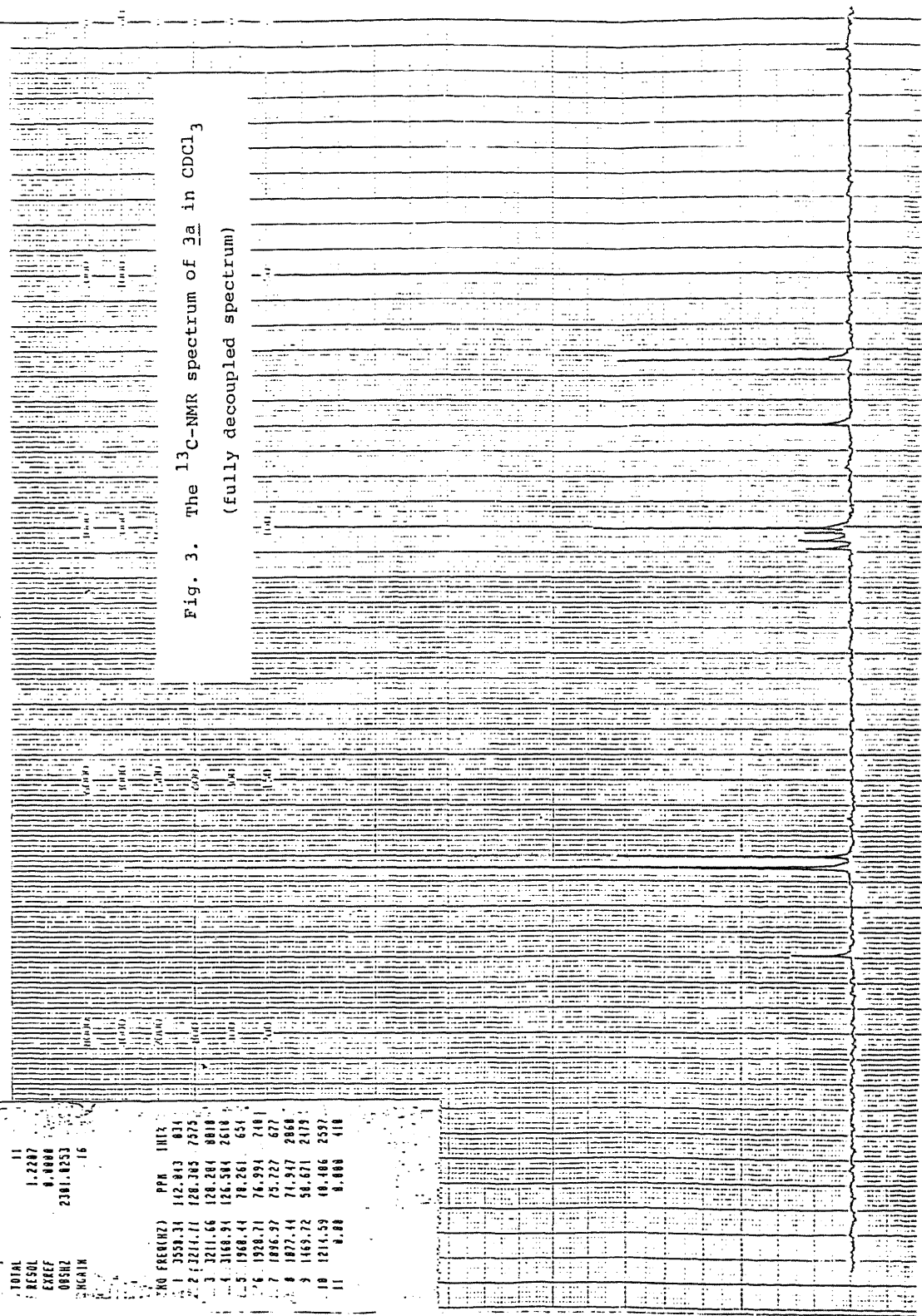


Fig. 3. The ^{13}C -NMR spectrum of 3a in CDCl_3
(fully decoupled spectrum)

NO	FREQ(CZ)	PPM	INT
1	3550.31	142.843	834
2	3214.71	128.383	7575
3	3211.66	128.284	8818
4	3188.91	126.584	2618
5	1968.44	78.261	654
6	1928.71	76.994	7481
7	1896.97	75.727	677
8	1877.44	74.947	2868
9	1469.72	58.671	2475
10	1214.59	48.186	2597
11	8.88	8.688	418

TOTAL 11
RESOL 1.2287
EXREF 8.4888
ORSHZ 2381.8253
NCALIB 16

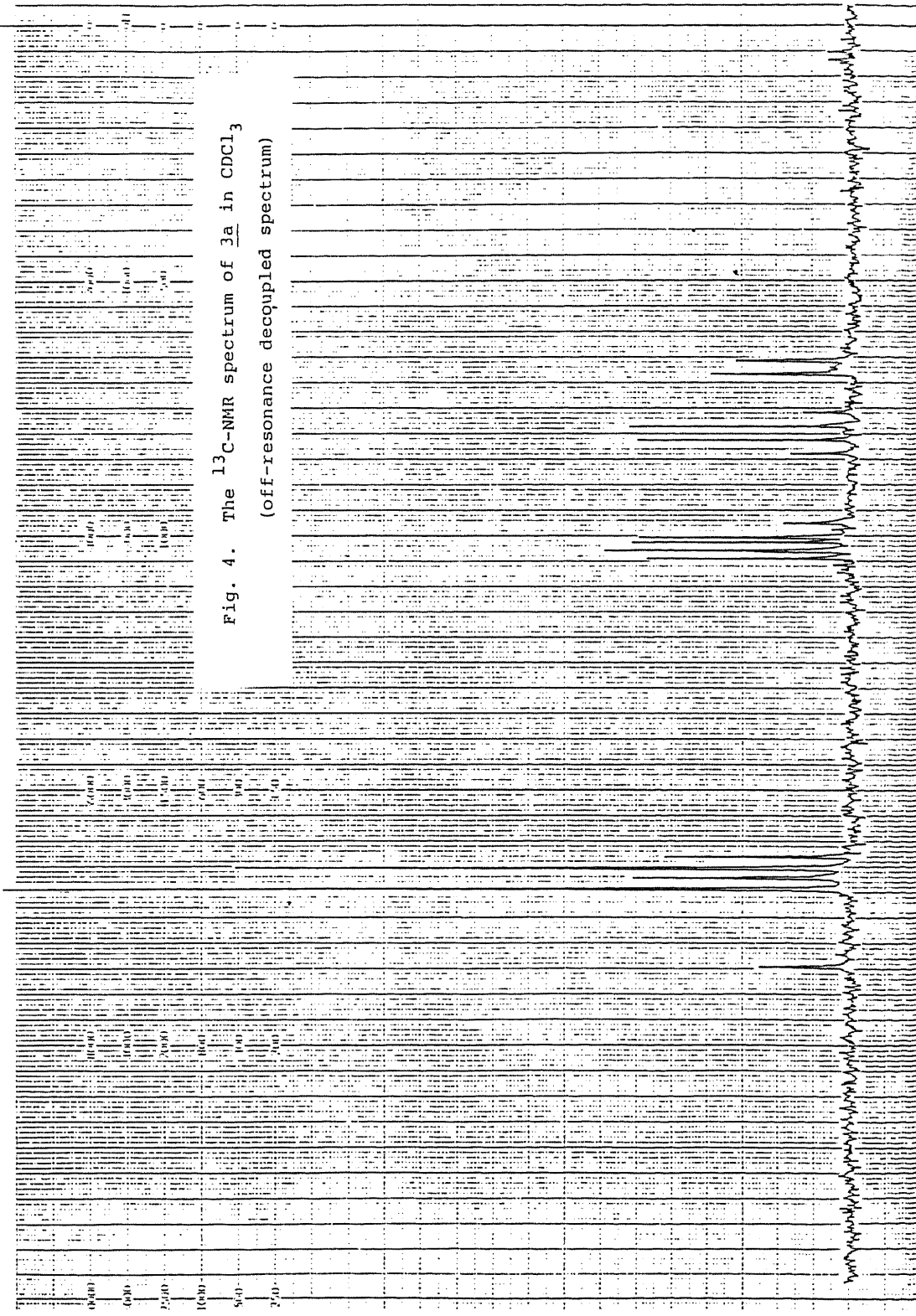


Fig. 4. The ^{13}C -NMR spectrum of **3a** in CDCl_3
 (off-resonance decoupled spectrum)

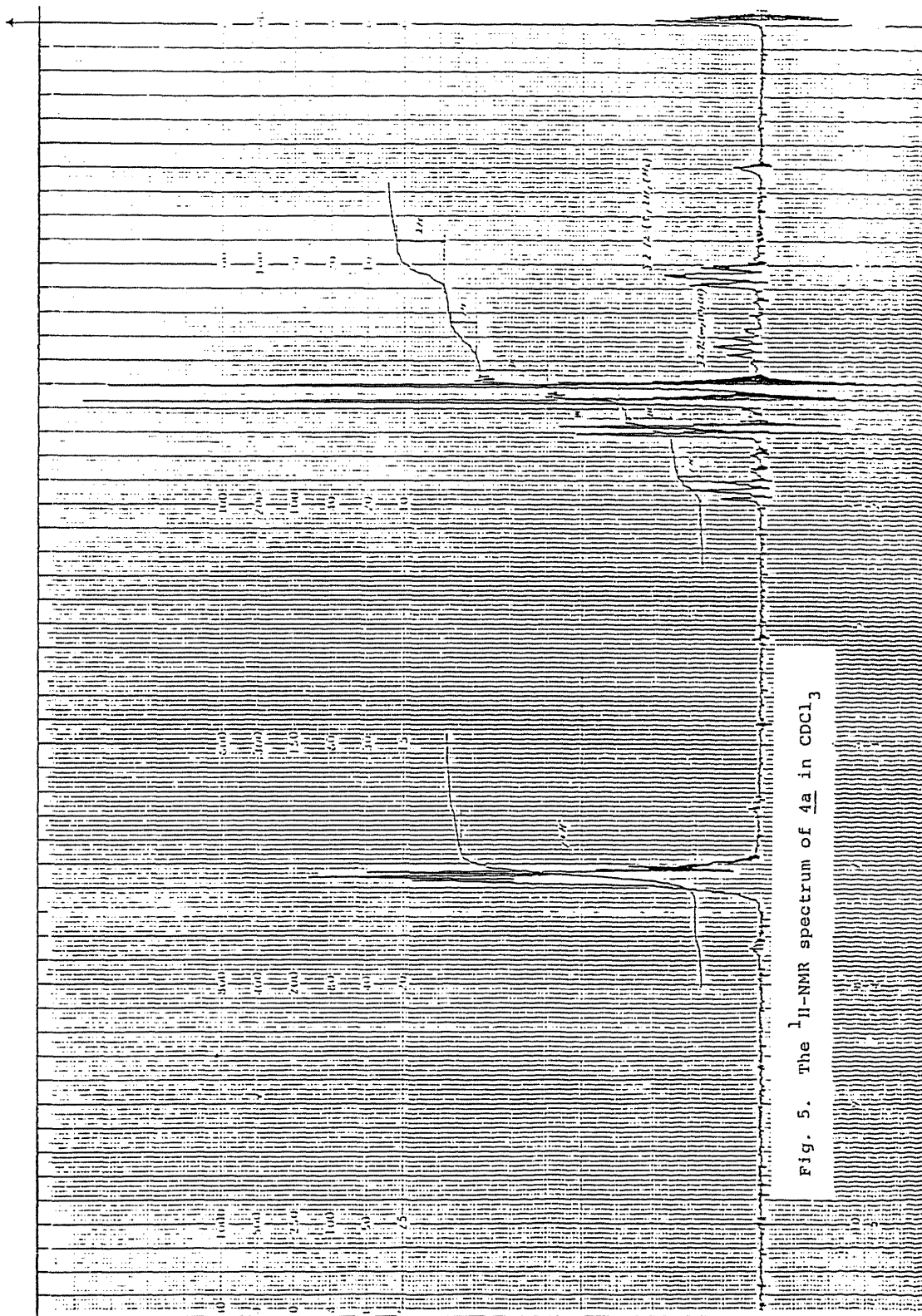


Fig. 5. The $^1\text{H-NMR}$ spectrum of **4a** in CDCl_3

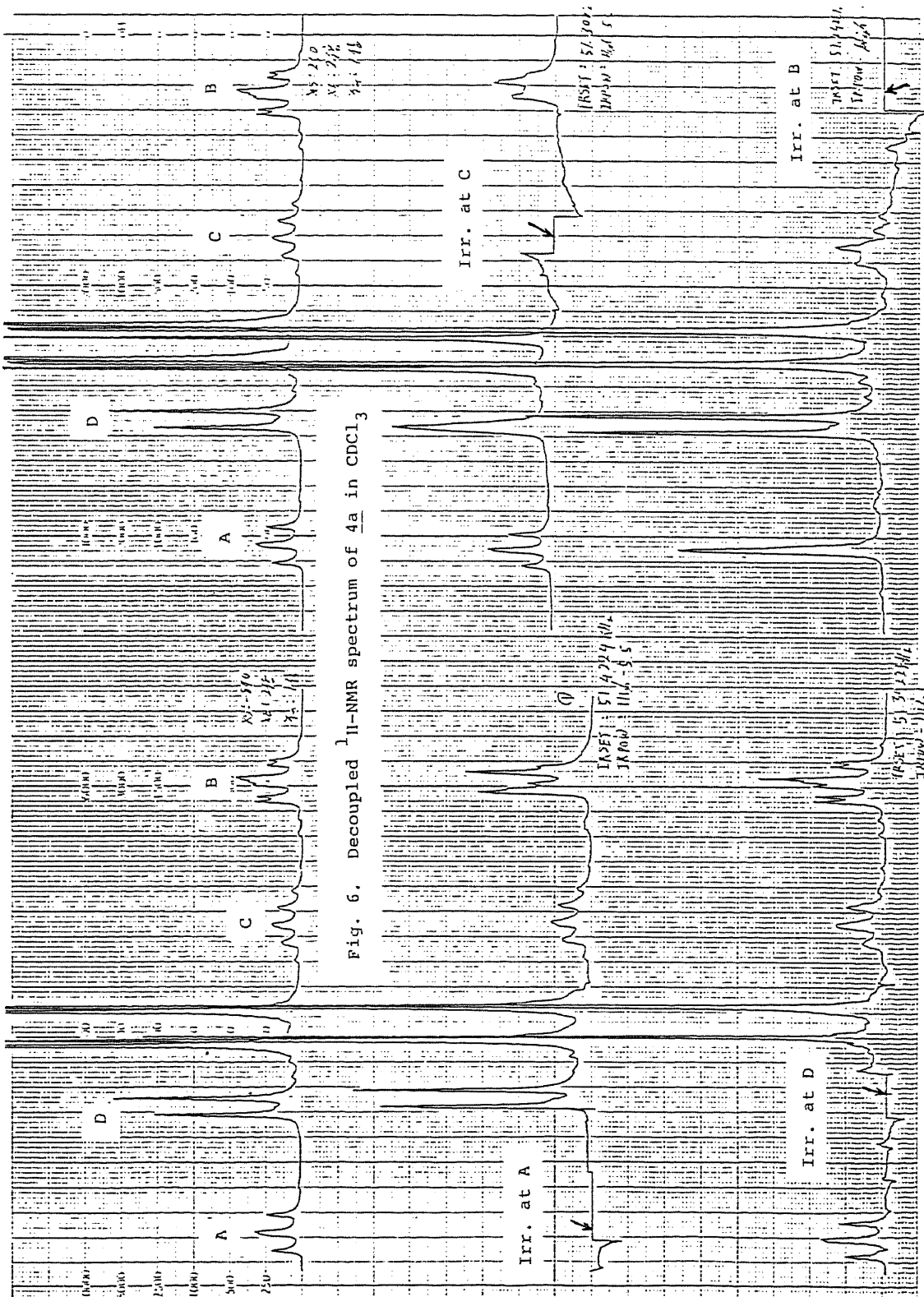


Fig. 6. Decoupled $^1\text{H-NMR}$ spectrum of 4a in CDCl_3

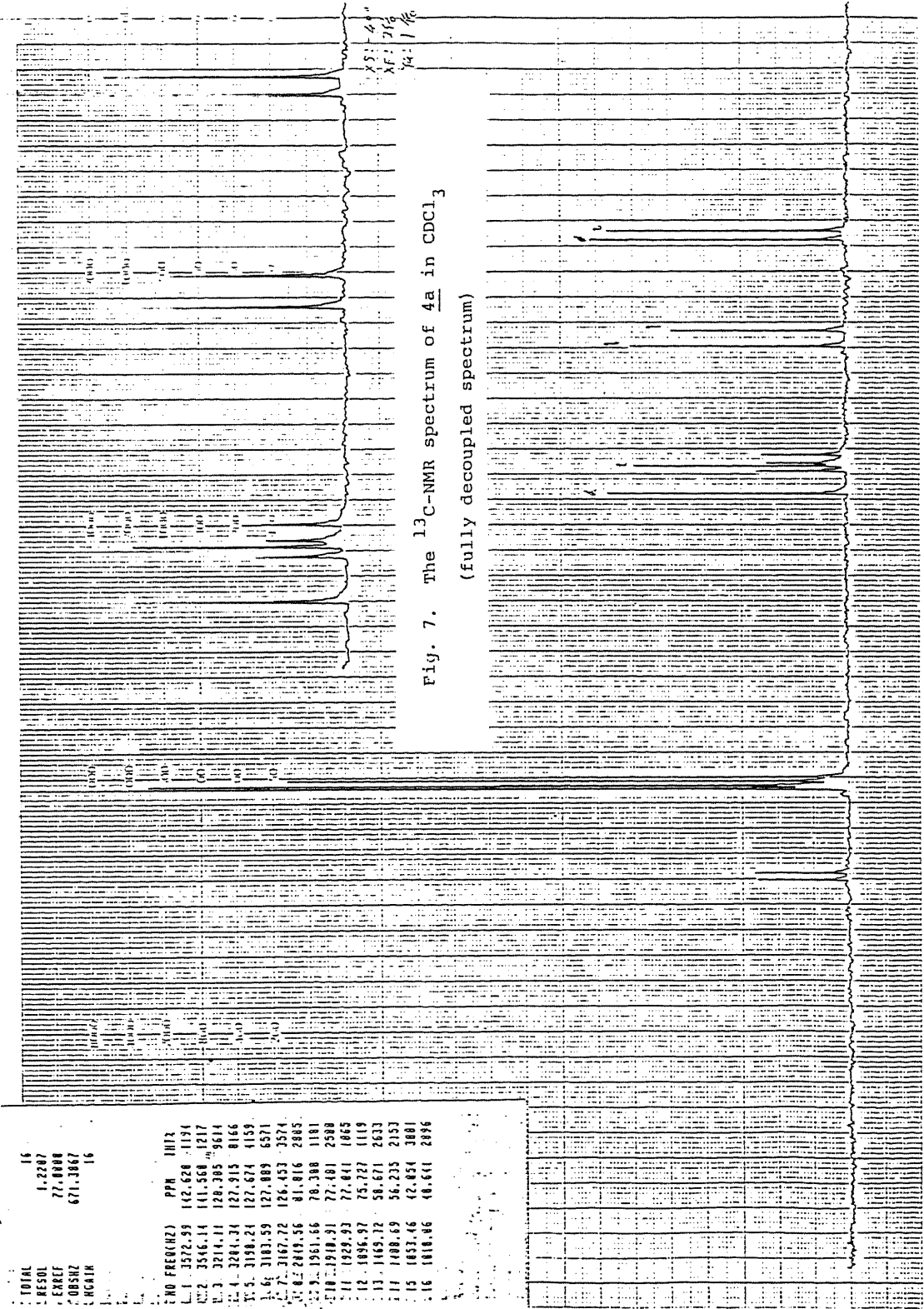


Fig. 7. The ^{13}C -NMR spectrum of 4a in CDCl_3
(fully decoupled spectrum)

CH0 FREQ(HZ)	PPM	INT12
1	1572.59	142.628
2	1546.14	141.568
3	1214.11	128.305
4	1244.34	127.915
5	1198.24	127.674
6	1183.59	127.889
7	1167.72	126.453
8	1019.56	81.816
9	1961.66	78.388
10	1918.91	77.481
11	1929.93	77.641
12	1896.97	75.727
13	1465.72	58.671
14	1488.69	56.235
15	1653.46	42.854
16	1818.86	48.641

TOTAL 16
 RESOL 1.2287
 EXCF 77.8008
 SUBSZ 671.3867
 SCALN 16

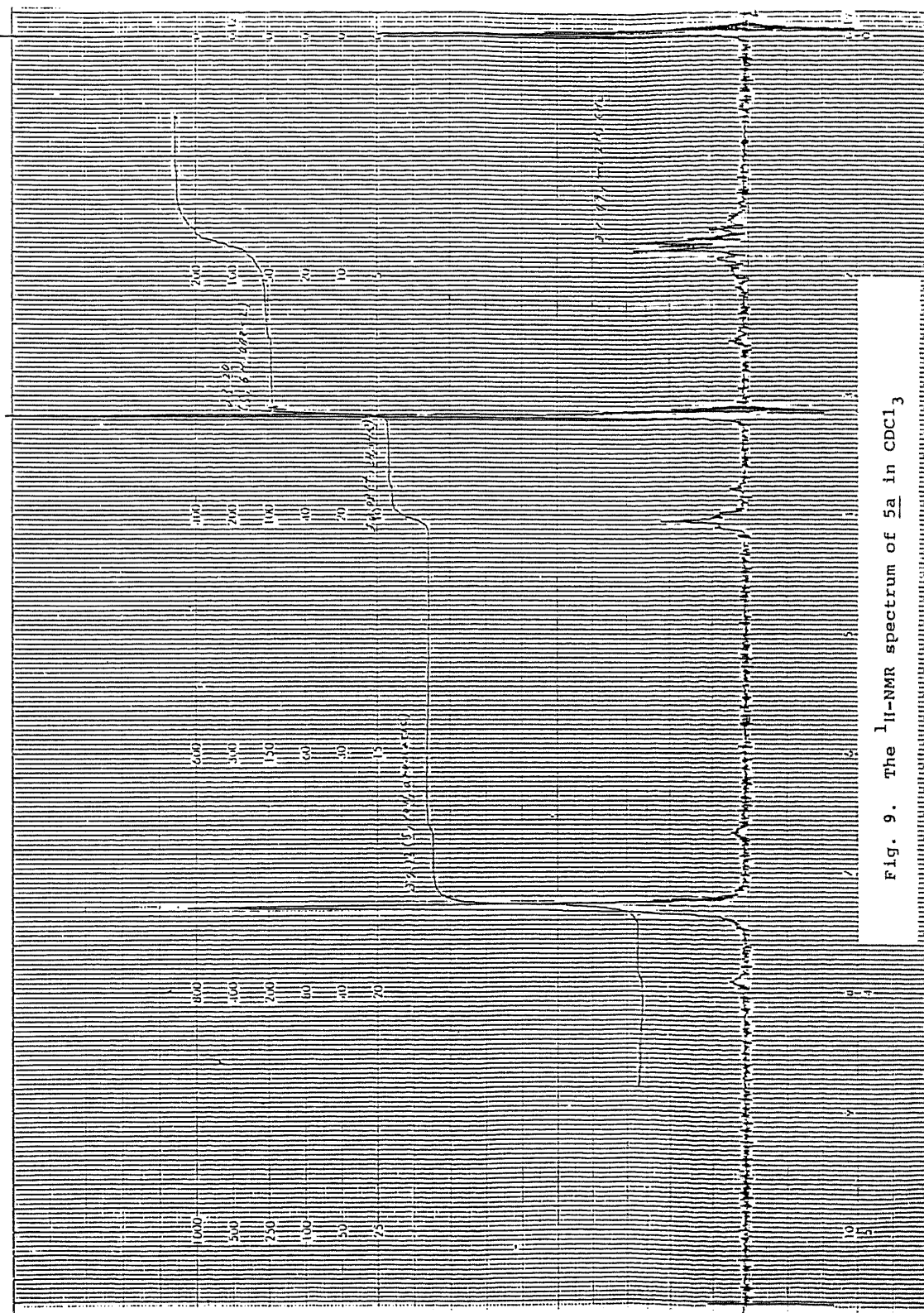


Fig. 9. The $^1\text{H-NMR}$ spectrum of **5a** in CDCl_3

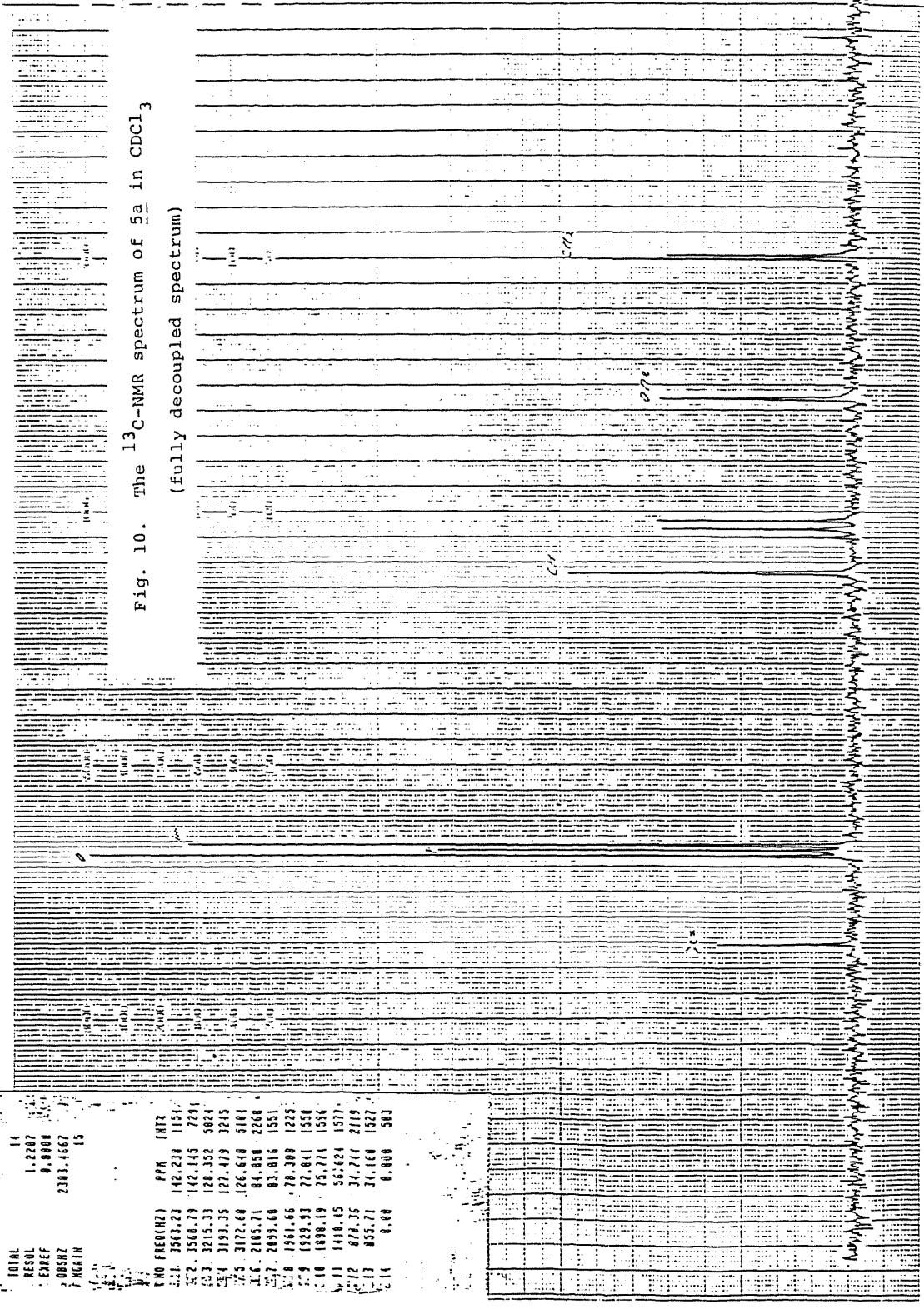


Fig. 10. The ¹³C-NMR spectrum of 5a in CDCl₃
(fully decoupled spectrum)

PPM	INT
142.238	1151
142.145	7291
128.352	3824
127.479	3245
126.648	5181
84.858	2268
83.816	1351
78.388	1225
77.841	1558
75.771	1536
58.621	1577
31.711	2119
31.160	1527
0.000	503

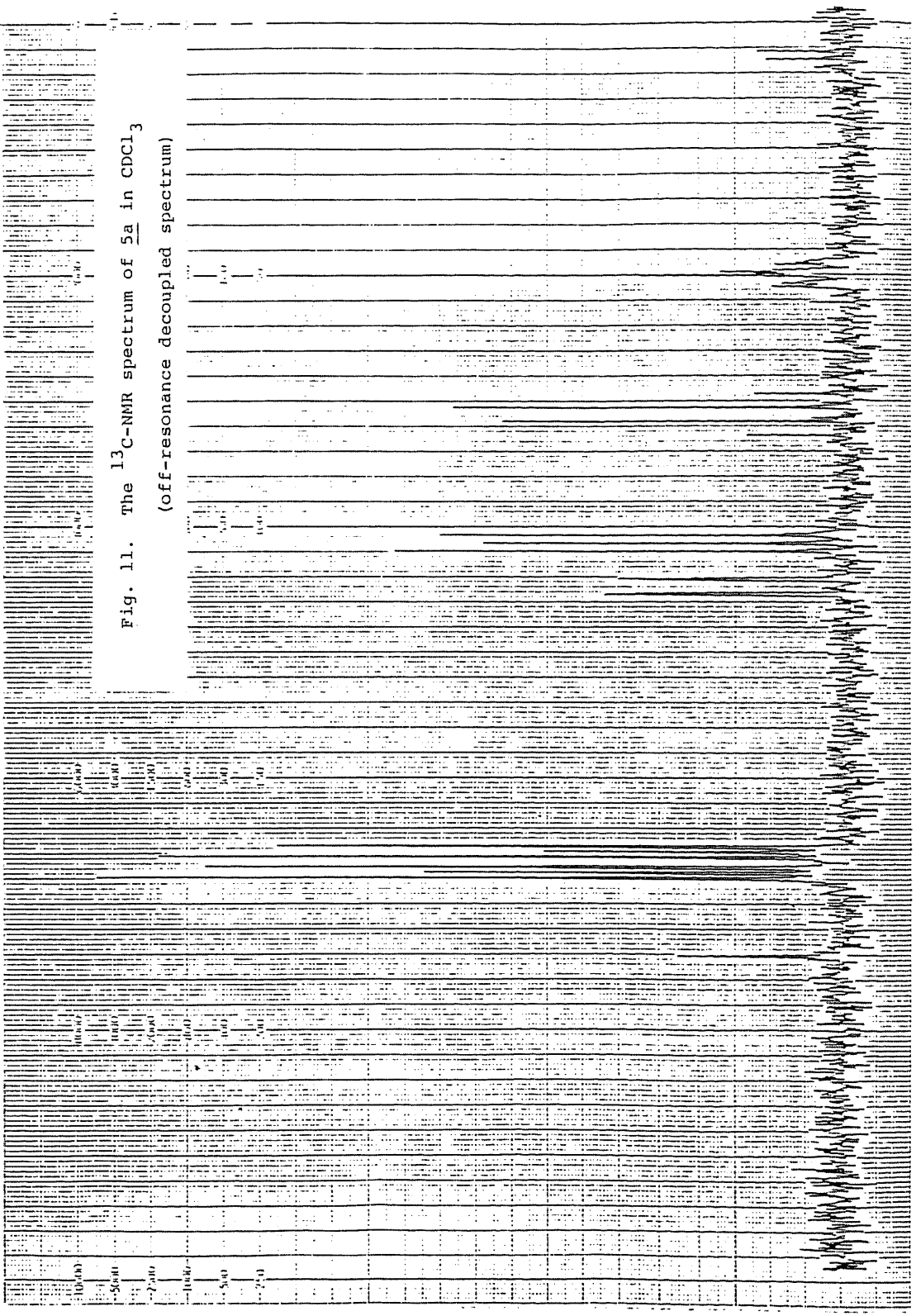


Fig. 11. The ^{13}C -NMR spectrum of 5a in CDCl_3
 (off-resonance decoupled spectrum)






DISCUSSION

As Table 1 indicates, use of the platinum electrode (Procedures A and B) leads to nearly the same results for each olefin except lg, irrespective of the supporting electrolyte employed. Thus, la and lb afford 2a and 2b, respectively, together with both of the corresponding $\alpha\alpha$ -dimers 3 and $\beta\beta$ -dimers 5; furthermore, $\alpha\beta$ -dimer 4a was obtained from la. On the other hand, ld, lf, and lg gave 2d, 2f, and 2g, respectively, along with the corresponding $\beta\beta$ -dimers exclusively; however, no $\alpha\alpha$ -dimers 3 were obtained. Olefins la and lb exhibit higher oxidation potentials among l's and are now classified as group I olefins based on the selectivity for production of dimethoxylated dimers, while the other olefins (ld, lf, and lg) with lower oxidation potentials are classified as group II olefins. Use of the graphite anode produced solely $\beta\beta$ -dimers 5 as the main products regardless of the structure of the olefins employed (except ld); however, 2's were obtained only from ld, lf, and lg, and 2's resulted from la and lb seem to be further oxidized into the corresponding benzaldehydes, acetals, and methyl benzoates under the reaction conditions. A control experiment showed that the anodic oxidation of 2a in the condition for procedure C afforded benzaldehyde and methyl benzoate. The mode of

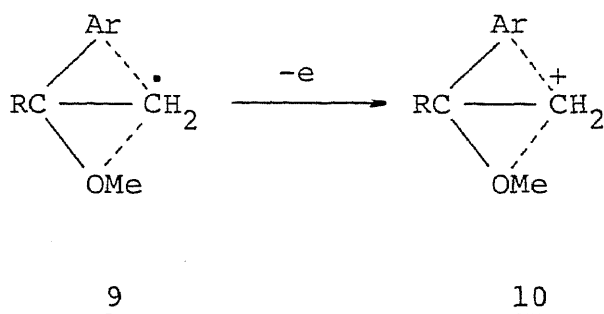
dimer production is simply summarized in Table 2 in addition to that in the photochemical electron transfer reaction between olefins 1 and metallic ions in methanol.

A mechanistic scheme essential to understand the reaction could be depicted as shown below (Scheme 2). With the use of the platinum anode the olefins are oxidized into their radical cations 6 irrespective of the supporting electrolytes employed. The production of 2, 3, and 4 can be understood by intervention of radicals 7 followed by their further anodic oxidation, dimerization, and addition to the olefins. For the formation of radicals 7, a possibility for anodic oxidation of methanol or methoxide ions into methoxy radicals followed by their addition on the terminal carbon atoms of the olefins²⁾ is ruled out because the production of 5 from all of the olefins examined needs the participation of radical cations 6. Thus, the radical cations 6 from group I olefins will react with alcohols or alkoxide ions to give radicals 7 which may collapse into 2, 3, or 4 as depicted in Scheme 2. On the contrary, in the oxidation of group II olefins, production of neither α -dimers 3 nor $\alpha\beta$ -dimers 4 suggests that radicals 7 will not participate as reaction intermediates. In the radical cations 6 arising from group II olefins, the positive charge seems to be more delocalized on the aromatic ring, and concurrently the unpaired electron density on the terminal carbon may be higher than in the case of group I olefins as schematically expressed by a resonance

Table 2. Mode of Dimer Production in Photochemical Electron Transfer Reaction and Anodic Oxidation of Olefins (1)

Classified Group	Olefin Compound	$h\nu, Cu^{2+}$	Anodic Oxidation		
			Pt/MeONa (A)	Pt/TEAP (B)	Graphite/NaClO ₄ (C)
I		$\alpha\alpha, \alpha\beta, \beta\beta$	$\alpha\alpha, \alpha\beta, \beta\beta$	$\alpha\alpha, \alpha\beta, \beta\beta$	$\beta\beta$
		$\alpha\alpha, \beta\beta$	$\alpha\alpha, \beta\beta$	$\alpha\alpha, \beta\beta$	$\beta\beta$
II		$\beta\beta$	$\beta\beta$	$\beta\beta$	$\beta\beta$
		$\beta\beta$	$\beta\beta$	$\beta\beta$	$\beta\beta$
		$\beta\beta$	$\beta\beta$	$\beta\beta$	$\beta\beta$

canonical form (6a), which was actually observed for the radical cations of N,N-dimethylaminoalkenes as described in Chapter 2.⁴⁾ Therefore, it is reasonable to suppose that 6 arising from group II olefins will more facilely add to the olefins than those from group I olefins finally leading to $\beta\beta$ -dimers 5, and consequently will react with methanol or methoxide ions on their α -carbon atoms to give radicals 9, which are further oxidized on the anode to carbocations 10 finally affording 2. Radicals 9 are thermodynamically less stable than the alternative radicals 7, but might be, to more or less extent, stabilized through the possible anchimeric effect of the aryl group on the carbon atom adjacent to the radical center. Also, on further oxidation of radical 9 on the anode, the adjacent methoxy group as well as the aryl group might participate in assisting the oxidation of the radicals to the carbocations 10 which subsequently collapse into 2.



However, the fact that 1g gives 2g only in procedure A but not in procedure B suggests that its radical cations 6g can react with methoxide ions but not effectively with methanol probably due to their reduced positive charge density on the ethylenic carbons through delocalization with the methoxy group.

The graphite electrode generally seems to adsorb substrates more strongly than the platinum electrode. Therefore, the results with a graphite anode can be accounted for by strong adsorption of the olefins and their radical cations 6 on the electrode at their β -carbon atoms. The presence of the adsorbed species in high concentration around the electrode will effect their facile combination subsequently giving 5.

Finally, it should be noted that the precise determination of the minor products which have hitherto not been isolated contributes to elucidation of the mechanism of electrochemical reactions, and the remarkable effects of the substituents to control the reaction course would result from sensitive electronic effects of the substituents exerted in the radical cation species. Moreover, as Table 2 shows the mode of dimer production in the anodic oxidation of olefins 1 with a platinum anode is quite the same as that of the photochemical reaction of the olefins in the presence of copper(II) ions in the same solvent, which affords clear evidence for the intervention of radical cations 6 as reaction intermediates in the photochemical reactions.

EXPERIMENTAL

All the melting points and boiling points are uncorrected. ^1H -NMR and ^{13}C -NMR spectra were recorded on a JEOL JMN-MH-100 spectrometer and a JEOL FX-100 spectrometer, respectively, in deuteriochloroform with TMS as an internal standard. Infrared (IR) spectra were obtained from a Hitachi 260-50 spectrophotometer. Mass spectra were determined with a Hitachi RMU-6MC mass spectrometer. Column chromatography was carried out under pressure on silica gel (Merck Kieselgel 60, Art 9385) using benzene and dichloromethane as eluents.

Materials.

Styrene, 4-chlorostyrene, 1,1-diphenylethylene, sodium perchlorate, and tetraethylammonium perchlorate (TEAP) were commercial samples from Wako Pure Chemical Industries or Nakarai Chemicals. 4-Methylstyrene and 4-methoxystyrene were prepared by decarboxylation of the corresponding cinnamic acids as described in literature.⁵⁾

Anodic Oxidation of Styrenes.

Electrolyses of styrenes (1) are carried out with three kinds of procedures, A, B, and C. The results are

shown in Table 1 and the structure of the products are summarized in Tables 3 and 4.

Procedure A.

Metallic sodium (1.2 g, 52 mmol) was dissolved in 120 cm³ of methanol, and then a freshly distilled styrene (10-50 mmol) was added to the mixture. The mixture was subjected to constant-current (1 A) electrolysis at a platinum plate (approximate area, 60 cm²) anode with a platinum wire as a cathode and SCE as a reference electrode under argon atmosphere at room temperature. When a current was not able to be maintained at 1 A during the electrolysis, constant-current electrolysis at 0.1 A was carried out. The electrolysis mixture was diluted with water (300 cm³) and extracted with dichloromethane (80 cm³ x 2). The organic layer was washed with water, dried (Na₂SO₄) and analyzed by GLPC. After evaporation of the solvent, the reaction mixture was subjected^V flash-column chromatography. The structures of the products^{to} were determined on the basis of their spectral data and elemental analysis, or identified by comparison of the retention time with those of authentic samples on GLPC. The conditions of the electrolysis were summarized in Table 5.

Procedure B.

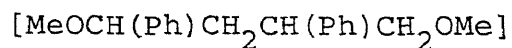
A styrene (10-40 mmol) was dissolved in a mixture solution of methanol and acetonitrile (3 : 2, 100 cm³) containing TEAP (3-10 g, 13-44 mmol) and subjected to constant-current (0.1 or 1 A) electrolysis at the platinum anode with the platinum wire as a cathode and the SCE as a reference electrode under argon stream at room temperature. The reaction mixture was worked up as mentioned in Procedure A. The conditions of the electrolyses are summarized in Table 6.

Procedure C.

A mixture of a styrene (10-25 mmol), $\sqrt{\text{ sodium perchlorate and sodium iodide (10 mmol) in methanol (130 cm}^3\text{)}}$ was electrolyzed under a constant current of 1 A (with NaClO₄) or 0.1 A (with NaI) at a carbon cylindrical anode (effective area, 80 cm²; thickness, 0.3 cm) with a carbon rod (diameter, 1 cm; length 8 cm) as a cathode and a Ag/AgCl as a reference electrode under argon stream at room temperature. The electrolyzed solution was worked up as mentioned in Procedure A. The conditions of the electrolyses are summarized in Table 7.

Isolation of Reaction Products.

1,4-Dimethoxy-1,3-diphenylbutane (4a):



After electrolytic oxidation of styrene (1a, 30 g, 0.29 mol) according to the procedure B (see Table 6), the reaction mixture was worked up as mentioned in the procedure A. The resulting residue was distilled under diminished pressure to give the following fractions.

Fraction	Bp (°C/mmHg)	Weight (g)
1	49/20-23	2.25
2	60-78/6	0.95
3	78-80/6	15.9
4	residue	8

Gas chromatographic analysis on a Hitachi 163 chromatograph with a flame ionization detector, using columns packed with 5 % silicone GE SE-30 on Chromosorb W (60-80 mesh) and 5 % PEG-20 M on Chromosorb W AW (60-80 mesh) showed fraction 1 was a mixture of unreacted styrene and ethylbenzene, and fraction 2 was a mixture of styrene, 2-methoxyethylbenzene, and 1,2-dimethoxy-1-phenylethane. Fraction 3 was 1,2-dimethoxy-1-phenylethane. The total amounts of these products estimated by GLPC analysis were as follow: unreacted styrene, 1.3 g; ethylbenzene, 1 g; 2-methoxy-

ethylbenzene, trace; 1,2-dimethoxy-1-phenylethane, 16.8 g. Fraction 4 was chromatographed on silica gel. Elution with benzene gave the mixture of 1,4-dimethoxy-2,3-diphenyl- (3a), 1,4-dimethoxy-1,3-diphenyl- (4a), and 1,4-dimethoxy-1,4-diphenyl-butane (5a). Compound 4a was separated by a Shimadzu LC-2 liquid chromatograph, using a Zorbax-ODS column (diameter, 4.6 mm; length, 25 cm) and a mixture solution of acetonitrile and water (1 : 1) as a carrier solvent under pressure (90-95 kg/cm²). The spectral data are shown in Table 3.

The methods of preparation and identification of other reaction products are summarized in Table 8.

Table 3. Dimethoxylated Monomers (2)

Compound (Formula)	Bp, °C(mmHg) or mp, °C	IR (cm ⁻¹) ^v C-O	¹ H-NMR, δ (ppm)	¹³ C-NMR, δ (ppm)	MS, m/e	Elemental Analysis (%) Found Calcd
PhCHCH ₂ OMe OMe	60-70 (4) (lit. 72-73 (1.5)) ²⁾	1100	3.28 (s, 3H, OMe) 3.39 (s, 3H, OMe)	138.8(s), 128.4 (d), 127.9(d),	122, 121 (100%), 91, 77	
<u>2a</u> (C ₁₀ H ₁₄ O ₂)			3.50 (m, 2H, CH ₂) 4.38 (dd, 1H, CH) 7.40 (s, 5H, Ph)	126.9(d), 82.9 (d), 77.2(t), 59.1(q), 56.9(q)		
4-ClC ₆ H ₄ CHCH ₂ OMe OMe	84 (4)	1100	3.28 (s, 3H, OMe) 3.36 (s, 3H, OMe) 3.44 (m, 2H, CH ₂) 4.32 (dd, 1H, CH) 7.26 (s, 4H, Ar)	137.4(s), 133.7 (s), 128.6(d), 128.3 (d), 82.3 (d), 76.9(t), 59.7(q), 57.0(q)	157, 155 (100%), 149, 91	C: 59.57 59.85 H: 6.51 6.53 Cl: 17.48 17.66
<u>2b</u> (C ₁₀ H ₁₃ ClO ₂)						
Ph ₂ CCH ₂ OMe OMe	63-66 (lit. 65.5-66.5) ²⁾	1180- 1040	3.20 (s, 3H, OMe) 3.30 (s, 3H, OMe) 4.10 (s, 2H, CH ₂) 7.10-7.50 (broad, 10H, 2Ph)	143.0(s), 127.8 (d), 127.3(d), 127.0(d), 82.2 (s), 76.3(t), 59.5(q), 51.5(q)	211, 197 (100%), 165	C: 79.46 79.34 H: 7.50 7.44
<u>2d</u> (C ₁₆ H ₁₈ O ₂)						

Table 3. (Continued)

Compound (Formula)	Bp, °C(mmHg) or mp, °C	IR (cm ⁻¹) ^v C-O	¹ H-NMR, δ(ppm)	¹³ C-NMR, δ(ppm)	MS, m/e	Elemental Analysis (%) Found Calcd
4-MeC ₆ H ₄ CHCH ₂ OMe OMe	58 (4)	1100	2.32 (s, 3H, Me) 3.26 (s, 3H, OMe) 3.38 (s, 3H, OMe) 3.46 (m, 2H, CH ₂) 4.34 (dd, 1H, CH) 7.20 (s, 4H, Ar)	139.1(s), 128.2(d) 127.8(d), 127.6(d) 87.4(d), 80.0(t) 57.3(q), 57.0(d) 15.6(q)	180(M ⁺), 135(100%), 119, 105, 91	C: 73.04 73.29 H: 8.89 8.94
<u>2f</u> (C ₁₁ H ₁₆ O ₂)						
4-MeOC ₆ H ₄ CHCH ₂ OMe OMe	120-130 (4)	1300- 1030	3.28 (s, 3H, OMe) 3.40 (s, 3H, OMe) 3.50 (m, 2H, CH ₂) 3.82 (s, 3H, OMe) 4.36 (dd, 1H, CH) 6.92 (d, 2H, Ar) 7.20 (d, 2H, Ar)	159.3(s), 130.8(s) 128.1(d), 113.8(d) 82.4(d), 77.2(t) 59.1(q), 56.7(q) 55.2(q)	196(M ⁺), 165, 164, 151(100%), 135, 136, 121, 91	C: 67.08 67.32 H: 8.00 8.21
<u>2g</u> (C ₁₁ H ₁₆ O ₃)						

Table 4. Dimethoxylated Dimers (3, 4, and 5)

Compound (Formula)	Mp, °C	IR, cm ⁻¹ ν _{C-O}	¹ H-NMR, δ(ppm)	¹³ C-NMR, δ(ppm)	MS, m/e	Elemental Analysis (%)	Found	Calcd
$\begin{array}{c} \text{PhCHCH}_2\text{OMe} \\ \\ \text{PhCHCH}_2\text{OMe} \end{array}$	130-131	1100	3.08 (s, 6H, 2MeO),	142.0(s), 128.3(d)	238, 206,			
			3.16-3.44 (broad, 6H, 2CH + 2CH ₂),	128.2(d), 126.5(d)	193, 135			
$\underline{3a^2} \text{ (C}_{18}\text{H}_{22}\text{O}_2\text{)}$			7.34 (s, 10H, 2Ph)	74.9(t), 58.7(q)	(100 %),			
				48.5(d)	134, 121,			
$\begin{array}{c} 4\text{-ClC}_6\text{H}_4\text{CHCH}_2\text{OMe} \\ \\ 4\text{-ClC}_6\text{H}_4\text{CHCH}_2\text{OMe} \end{array}$	127-128	1100	3.08 (s, 6H, 2MeO),	140.4(s), 132.4(s)	342, 340	C: 63.81	63.72	
			3.16-3.34 (broad, 6H, 2CH + 2CH ₂),	129.8(d), 128.5(d)	(M ⁺), 310,	H: 5.93	5.94	
$\underline{3b} \text{ (C}_{18}\text{H}_{20}\text{Cl}_2\text{O}_2\text{)}$			7.20 (s, 8H, Ar)	74.5(t), 58.9(q)	308, 172	Cl: 20.80	20.90	
				47.7(d)	170(100 %),			
$\begin{array}{c} \text{PhCHCH}_2\text{CHCH}_2\text{OMe} \\ \quad \\ \text{OMe} \quad \text{Ph} \end{array}$	Bp, 140 °C/4 mm	1100	2.12 (t, 2H, CH ₂),	142.6(s), 141.6(s)	270(M ⁺),	C: 79.77	79.96	
			2.72 (m, 1H, CH),	128.3(d), 127.9(d)	255, 223,	H: 8.22	8.20	
$\underline{4a} \text{ (C}_{18}\text{H}_{22}\text{O}_2\text{)}$			3.04 (s, 3H, OMe),	127.7(d), 127.1(d)	194, 193,			
			3.18 (s, 3H, OMe),	126.5(d), 81.8(d)	134, 121			
			3.38 (d, 2H, CH ₂),	77.5(t), 58.7(q)	(100 %),			
			3.90 (t, 1H, CH),	56.2(q), 42.1(d)	104, 91			
			6.96-7.36 (10H, 2Ph)	40.6(t)				

Table 4. (Continued)

Compound (Formula)	Mp, °C	IR, cm ⁻¹ ν _{C-O}	¹ H-NMR, δ(ppm)	¹³ C-NMR, δ(ppm)	MS, m/e	Elemental Analysis (%)		
						Found	Calcd	
PhCHCH ₂ CH ₂ CHPh OMe	71-73	1100	1.79 (m, 4H, 2CH ₂) 3.20 (s, 6H, 2MeO) 4.08 (t, 2H, 2CH) 7.32 (s, 10H, 2Ph)	142.2(s), 142.1(s) 128.4(d), 127.5(d) 126.6(d), 84.1(d) 83.8(d), 56.6(q) 34.7(t), 34.2(t)	238, 134, 121 (100%), 91	C: 79.80 H: 8.22	79.96 8.20	
<u>5a</u> ³ (C ₁₈ H ₂₂ O ₂)								
(4-ClC ₆ H ₄ CHCH ₂ -) ₂ OMe	60-64	1090	1.40-1.90(m, 4H, 2CH ₂), 3.12 (s, 6H, 2MeO) 3.98 (t, 2H, 2CH) 7.0-7.28 (q, 8H, Ar)	140.5(s), 133.0(s) 128.5(d), 127.9(d) 83.2(d), 82.9(d) 56.6(q), 34.4(t) 33.9(t)	170, 168, 157, 155 (100%)	C: 64.03 H: 5.87 Cl: 20.84	63.72 5.94 20.90	
<u>5b</u> (C ₁₈ H ₂₀ Cl ₂ O ₂)								
Ph ₂ CHCH ₂ CH ₂ CHPh OMe	226-228	1065	2.10 (s, 4H, 2CH ₂) 2.80 (s, 6H, 2MeO) 7.10-7.4 (broad, 20H, 4Ph)	145.5(s), 127.8(d) 126.7(d), 126.5(d) 82.2(s), 49.9(q) 28.0(t)	358, 313, 281, 211, 197(100%), 196, 180, 167, 105	C: 85.29 H: 7.00	85.31 7.11	
<u>5d</u> (C ₃₀ H ₃₀ O ₂)								

Table 4. (Continued)

Compound (Formula)	Mp, °C	IR, cm^{-1} $\nu_{\text{C=O}}$	$^1\text{H-NMR}$, δ (ppm)	$^{13}\text{C-NMR}$, δ (ppm)	MS, m/e	Elemental Analysis (%)
						Found Calcd
(4-MeC ₆ H ₄ CHCH ₂ -) ₂ OMe	96-99	1070, 1100	1.32-2.12 (m, 4H, 2CH ₂), 2.30 (s, 6H, 2Me) 3.14 (s, 6H, 2MeO) 3.98 (t, 2H, 2CH) 7.06 (s, 8H, Ar)	139.1(s), 137.0(s) 128.9(d), 126.6(d) 83.9(d), 83.6(d) 56.4(q), 34.8(t) 34.2(t), 21.1(q)	266, 149, 148, 136, 135(100%)	C: 80.34 80.49 H: 8.73 8.78
<u>5f</u> (C ₂₀ H ₂₆ O ₂)						
(4-MeOC ₆ H ₄ CHCH ₂ -) ₂ OMe	102-104	1300, 1240, 1160, 1045, 1015	1.5-1.8 (m, 4H, 2CH ₂), 3.20 (s, 6H, 2MeO) 3.80 (s, 6H, 2MeO) 3.9-4.1 (broad, 2H, 2CH), 6.7-7.3 (q, 8H, Ar)	159.0(s), 134.3(s) 127.8(d), 113.7(d), 83.6(d), 83.4(d) 56.4(q), 55.2(q) 34.6(t), 34.1(t)	299, 165 (100%)	C: 72.70 72.87 H: 7.93 7.82
<u>5g</u> (C ₂₀ H ₂₆ O ₄)						
(4-MeOC ₆ H ₄ C(=O)CHCH ₂ -) ₂	150-152	1660 ($\nu_{\text{C=O}}$)	3.42 (s, 4H, 2CH ₂) 3.90 (s, 6H, 2MeO) 7.00 (d, 4H, Ar) 8.08 (d, 4H, Ar)		298(M ⁺), 296(100%), 280, 163, 135	C: 72.05 72.46 H: 6.05 6.08
<u>6</u> (C ₁₈ H ₁₈ O ₄)						

Table 4. (Continued)

Compound (Formula)	Mp, °C	IR, cm ⁻¹ ν _{C-O}	¹ H-NMR, δ(ppm)	¹³ C-NMR, δ(ppm)	MS, m/e	Elemental Analysis (%)
						Found Calcd
$\begin{array}{c} \text{OMe} \\ \\ (4\text{-MeOC}_6\text{H}_4\text{CCH}_2\text{-})_2 \\ \\ \text{OMe} \end{array}$	175-178	1290- 1040	1.60 (s, 4H, 2CH ₂) 2.96 (s, 12H, 4MeO) 3.84 (d, 6H, 2MeO) 6.83-7.38 (q, 8H, Ar)	158.9(s), 132,7(s) 128.0(d), 113.2(d) 103.3(s). 55.2(q) 48.3(q), 31.2(t)	326(100%), 311, 283, 175, 135	C: 67.56 67.67 H: 7.71 7.74
<u>7</u> (C ₂₂ H ₃₀ O ₆)						
<u>4</u> -ClC ₆ H ₄ CH(OMe) ₂	Bp, 76 °C/6 mm	1050, 1090	3.24 (s, 6H, 2MeO) 5.28 (s, 1H, CH) 7.23 (s, 4H, Ar)	136.7(s), 134.2(s) 128.4(d), 128.2(d) 102.2(d), 52.5(q)	188, 187, 186, 185, 157, 155 (100%), 91	C: 57.87 57.91 H: 5.59 5.94 Cl: 19.41 18.99
<u>8</u> (C ₉ H ₁₁ ClO ₂)						

Table 5. Anodic Oxidation of Styrenes (1):

Pt-Pt/MeONa-MeOH, RE = SCE

Olefin	g, (mmol)	MeOH (cm ³)	Na g, (mmol)	Amp. x h	(Volt)	Conv. (%)
<u>1a</u>	5.0 (48)	120	1.2 (52)	1 x 1.3	(1.35-7.5)	32
				0.1 x 3	(7.4-7.5)	
<u>1b</u>	4.0 (29)	120	1.2 (52)	1 x 2	(1.3-2.2)	79
				0.1 x 18	(1.0-1.55)	
<u>1d</u>	1.85 (10)	130	1.3 (56)	1 x 3	(1.3-1.9)	100
<u>1f</u>	3.4 (29)	130	1.1 (48)	1 x 2	(1.34-10)	100
				0.1 x 19	(1.3-1.6)	
<u>1g</u>	2.0 (15)	130	1.3 (56)	1 x 2.5	(1.2-3.0)	100

Table 6. Anodic Oxidation of Styrenes (1): Pt-Pt/TEAP/MeOH-MeCN, RE = SCE

Olefin	g, (mmol)	MeOH : MeCN (total, cm ³)	TEAP g, (mmol)	Amp. x h	(Volt)	Conv. (%)
<u>1a</u>	1.8 (17)	10 : 3 (130)	3 (13)	0.1 x 10	(1.7-2.2)	100
<u>1a</u>	30 (290)	3 : 2 (100)	10 (44)	1.0 x 8.7 0.1 x 15	(1.75-2.1) (1.75-2.1)	97
<u>1b</u>	5.8 (42)	3 : 2 (100)	8 (35)	1.0 x 4	(1.62-1.9)	100
<u>1d</u>	2 (11)	10 : 3 (130)	3 (13)	0.1 x 5	(1.4-1.5)	67
<u>1f</u>	4 (34)	3 : 2 (100)	8 (35)	0.1 x 23.5	(1.35-1.87)	100
<u>1g</u>	2.3 (18)	2 : 1 (150)	2.6 (11)	0.1 x 3	(1.1-1.4)	100

Table 7. Anodic Oxidation of Styrenes (1): Graphite-Graphite/NaClO₄/MeOH,
RE = Ag/AgCl

Olefin	g, (mmol)	MeOH (cm ³)	NaClO ₄ g, (mmol)	Amp. x h	(Volt)	Conv. (%)
<u>1a</u>	1.8 (17)	130	5 (41)	1 x 8	(1.0-1.3)	100
<u>1b</u>	3.5 (25)	120	10 (82)	1 x 2.7	(1.1-1.4)	100
<u>1d</u>	2 (11)	130	10 (82)	1 x 2	(1.1-1.3)	100
<u>1f</u>	2 (17)	130	10 (82)	1 x 1.7	(1.0-1.4)	100
<u>1f</u>	2 (17)	120	1.5 (10) ^a	0.2 x 20	(0.23-0.48)	100
<u>1g</u>	2 (15)	130	10 (82)	1 x 0.8	(0.86-0.95)	100

^aSodium iodide was used as a supporting electrolyte.

Table 8. The Methods of Preparation and Identification of Reaction Products in Anodic Oxidation of 1

Compound	Preparation	Identification
<u>2a</u>	($h\nu$, Cu^{2+} or Fe^{3+}) Procedure A, B	Isolation
<u>2b</u>	($h\nu$, Cu^{2+} or Fe^{3+}) Procedure A, B	Isolation
<u>2d</u>	($h\nu$, Cu^{2+} or Fe^{3+}) Procedure A, B	Isolation
<u>2f</u>	($h\nu$, Cu^{2+}) Procedure A, B, C	Isolation
<u>2g</u>	Procedure A, C	Isolation
<u>3a</u>	Procedure A, B	Isolation
<u>3b</u>	$h\nu$, Cu^{2+}	GLPC Analysis
<u>5a</u>	Procedure C	Isolation
<u>5b</u>	Procedure C	Isolation
<u>5d</u>	($h\nu$, Cu^{2+}) Procedure A, B, C	Isolation
<u>5f</u>	Procedure C	Isolation
<u>5g</u>	($h\nu$, Cu^{2+}) Procedure B, C	Isolation
<u>6</u>	Procedure A	Isolation
<u>7</u>	Procedure A	Isolation
<u>8</u>	Procedure C	Isolation

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CHAPTER 4

COMPARISON BETWEEN PHOTOCHEMICAL ELECTRON TRANSFERRING
AND ELECTROCHEMICAL OXIDATIONS OF 2,6-DIALKYL-4-METHYL-
PHENOLS

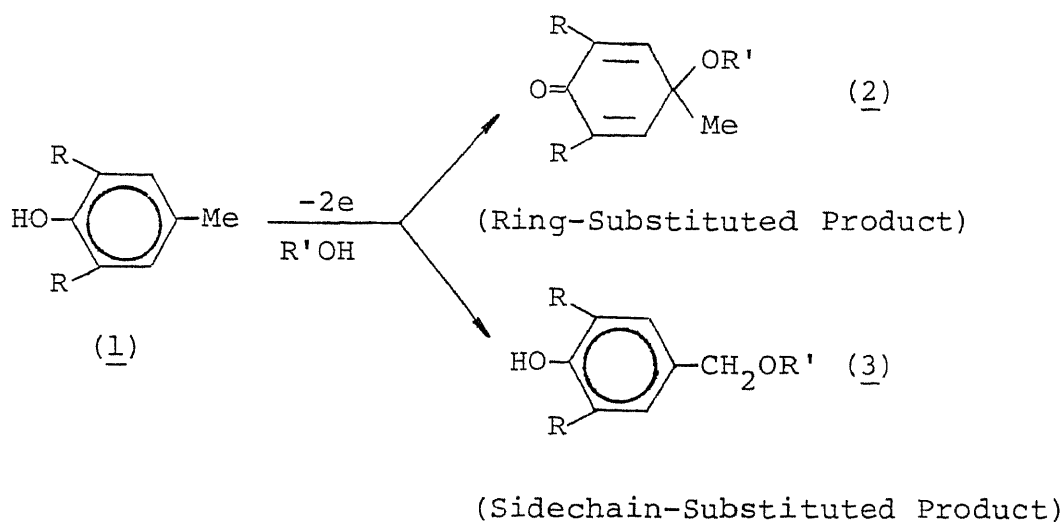
SUMMARY

Irradiation of 2,6-dialkyl-4-methylphenols in alcohols in the presence of Fe(III) or Cu(II) salts affords the corresponding 4-alkoxymethylphenols, being in contrast with anodic oxidation in alcohols which gives 4-alkoxy-4-methyl-cyclohexadienones.

INTRODUCTION

Oxidation of 2,6-dialkyl-4-methylphenols (1) in alcohol with various methods has been reported to give the corresponding 4-alkoxy-4-methyl-2,5-cyclohexadienones (2) (Ring-Substituted Products) or 4-alkoxymethylphenols (3) (Sidechain-Substituted Products) depending on the conditions:¹⁻⁵⁾ the oxidation of 1 with lead dioxide,¹⁾ active manganese dioxide,¹⁾ 2,6-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),²⁾ and iodic acid (HIO_3)³⁾ gave 4-alkoxymethylphenols (3), while that with hydrogen (hexacyanoferrate(III)) [$\text{H}_3\text{Fe}(\text{CN})_6$]⁴⁾, periodic acid (H_5IO_6)³⁾, and by anodic oxidation on a platinum anode⁵⁾ gave 4-alkoxy-4-methyl-2,5-cyclohexadienones (2).

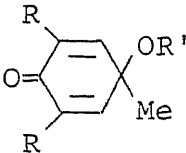
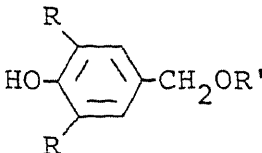
In these reactions, a variety of intermediates such as the benzyl cations (B), the quinonemethide (Q), the phenoxonium ions (P), and the dimer of 1 followed by the cleavage to 1 and



Q, were proposed.¹⁻⁵⁾

The photochemical electron transfer⁶⁾ gives ion radicals which are in most cases considered to afford the same reaction products as arising from the electrochemical electron transfer process of the same substrates.⁷⁾ In this chapter, it is reported that photochemical electron transfer from 2,6-dialkyl-4-methylphenols, 1a and 1b, to Fe³⁺ or Cu²⁺ in alcohols as a new method regarding to the oxidation of phenols leads to alkoxylation of their 4-methyl group affording 4-alkoxymethylphenols. This is in contrast with the reported one electron oxidation of 1a⁵⁾ and 1b through anodic reaction. This study seems to be the first report to show different behavior between the photochemical and the anodic electron transfer reactions.

Table 1. Selectivity for Production of Ring- (2) and Sidechain-Substituted Products (3) under Various Conditions

Method		
	(2)	(3)
	Condition	Condition
(A) Anodic Oxidation	Pt-anode/NaClO ₄ ⁵⁾	<i>(under active investigation)</i>
(B) Thermal Reaction	a) ⁴⁾ H ₃ Fe(CN) ₆ b) ³⁾ H ₅ IO ₆	a') ¹⁾ MnO ₂ or PbO ₂ b') ²⁾ DDQ c') ³⁾ HIO ₃
(C) Photochemical Reaction	(?)	Cu(ClO ₄) ₂ or Fe(ClO ₄) ₃ <i>(present investigation)</i>

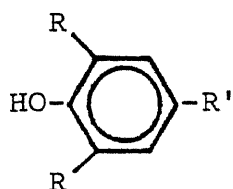
RESULTS AND DISCUSSION

Photolysis of Phenols in the Presence of Metallic Ions in Alcohols.

When 2,6-di-t-butyl-4-methylphenol (1a, 0.03 mol/dm³) was irradiated in methanol in the presence of iron(III) perchlorate (0.06 mol/dm³) with a low pressure mercury lamp under nitrogen stream at room temperature, the starting red-brown solution became completely colorless and 2,6-di-t-butyl-4-methoxymethylphenol (3a) was obtained in 73 % yield based on 1a consumed.⁸⁾ Similar irradiation of 1a in ethanol and 2-propanol produced the corresponding 4-ethoxymethyl- (3a') and 4-isopropoxymethyl-phenol (3a''), respectively. 3,5-Di-t-butyl-4-hydroxybenzaldehyde (4a) was also obtained as a by-product in methanol and ethanol (Table 2). Use of copper(II) perchlorate instead of iron(III) perchlorate gave similar results in methanol, ethanol, and 2-propanol as summarized in Table 2. In these reactions, metallic copper was precipitated during the irradiation.

Irradiation of 2,4,6-trimethylphenol (1b, 0.05 mol/dm³) under nitrogen stream at room temperature in methanol with the low pressure mercury lamp afforded 4-methoxymethyl-2,6-dimethylphenol (3b, 30 % yield) in the presence of iron(III)

perchlorate, but with copper(II) ions 1b was not consumed at all. However, 4-methylphenol (1c) and 2,4,6-tri-*t*-butylphenol (1d) failed in undergoing the alkoxylation in methanol: 1c gave polymeric matter and 1d was nearly quantitatively recovered.

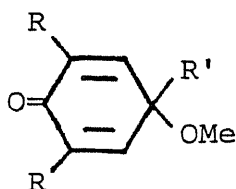


1a: R=^tBu, R'=Me

1b: R=Me, R'=Me

1c: R=H, R'=Me

1d: R=^tBu, R'=^tBu

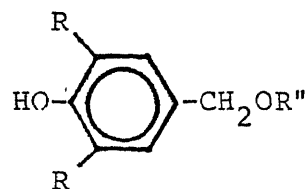


2a: R=^tBu, R'=Me

2b: R=Me, R'=Me

2c: R=H, R'=Me

2d: R=^tBu, R'=^tBu

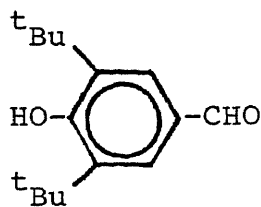


3a: R=^tBu, R''=Me

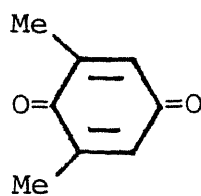
3a': R=^tBu, R''=Et

3a'': R=^tBu, R''=ⁱPr

3b: R=Me, R''=Me



4a



5

Table 2. Photochemical Alkoxylation of Phenols in the Presence of Transition Metal Ions

Phenol	Solvent	Metallic Ion ^a	Irradiation Time/h	Conversion/%	Product (yield/%) ^b
<u>1a</u>	MeOH	Fe ³⁺	10	75 ^c	<u>3a</u> (73) ^c <u>4a</u> (3) ^c
	MeOH	Fe ³⁺	10	91	<u>3a</u> (34) <u>4a</u> (5)
	MeOH	Cu ²⁺	50	47	<u>3a</u> (36)
	EtOH	Fe ³⁺	24	64	<u>3a'</u> (59) <u>4a</u> (3)
	EtOH	Cu ²⁺	60	14	<u>3a'</u> (34)
	i-PrOH	Fe ³⁺	17	33	<u>3a''</u> (32)
<u>1b</u>	i-PrOH	Cu ²⁺	91	89	<u>3a''</u> (32) <u>4a</u> (8)
	MeOH	Fe ³⁺	18	80	<u>3b</u> (30)
	MeOH	Cu ²⁺	66	0	—
	MeOH	Cu ²⁺	66	0	—

^aMetal perchlorates, Cu(ClO₄)₂·6H₂O and Fe(ClO₄)₃·6H₂O, were used.

^bIsolated yields unless otherwise noted.

^cYield determined by GLPC analysis.

In control experiments, when 1a was left standing in methanol with $\text{Cu}(\text{ClO}_4)_2$ for 3 days at room temperature, 1a was completely recovered. Also, irradiation of 1a in the presence of $\text{Cu}(\text{ClO}_4)_2$ in methanol with a high pressure mercury lamp instead of the low pressure mercury lamp gave only a trace amount of 3a. 4-Methoxycyclohexadienone 2a was irradiated with the low pressure mercury lamp in methanol in the presence and absence of the copper(II) salt to give only a trace amount of 3a and many unidentified products. These results eliminate the possibility that 3a would be produced through photorearrangement of 2a which would be formed as a primary product.

Anodic Oxidation of the Phenols.

Anodic oxidation of 1a,^{5a,b)} 1c,^{5c)} and 1d^{5b)} in methanol was reported to give 2a, 2c, and 2d, respectively.

Anodic oxidation of 1b (0.125 mol/dm^3) on a platinum electrode in a mixture of methanol and acetonitrile (3 : 1) containing sodium perchlorate (0.5 mol/dm^3) under constant-current (1 A) gave 4-methoxy-2,4,6-trimethyl-2,5-cyclohexadienone 2b (56 % yield) and 2,6-dimethylbenzoquinone 5 (4 %). Reexamination of electrolysis of 1a under similar conditions gave 2a (46 %) and 3a (trace) as reported

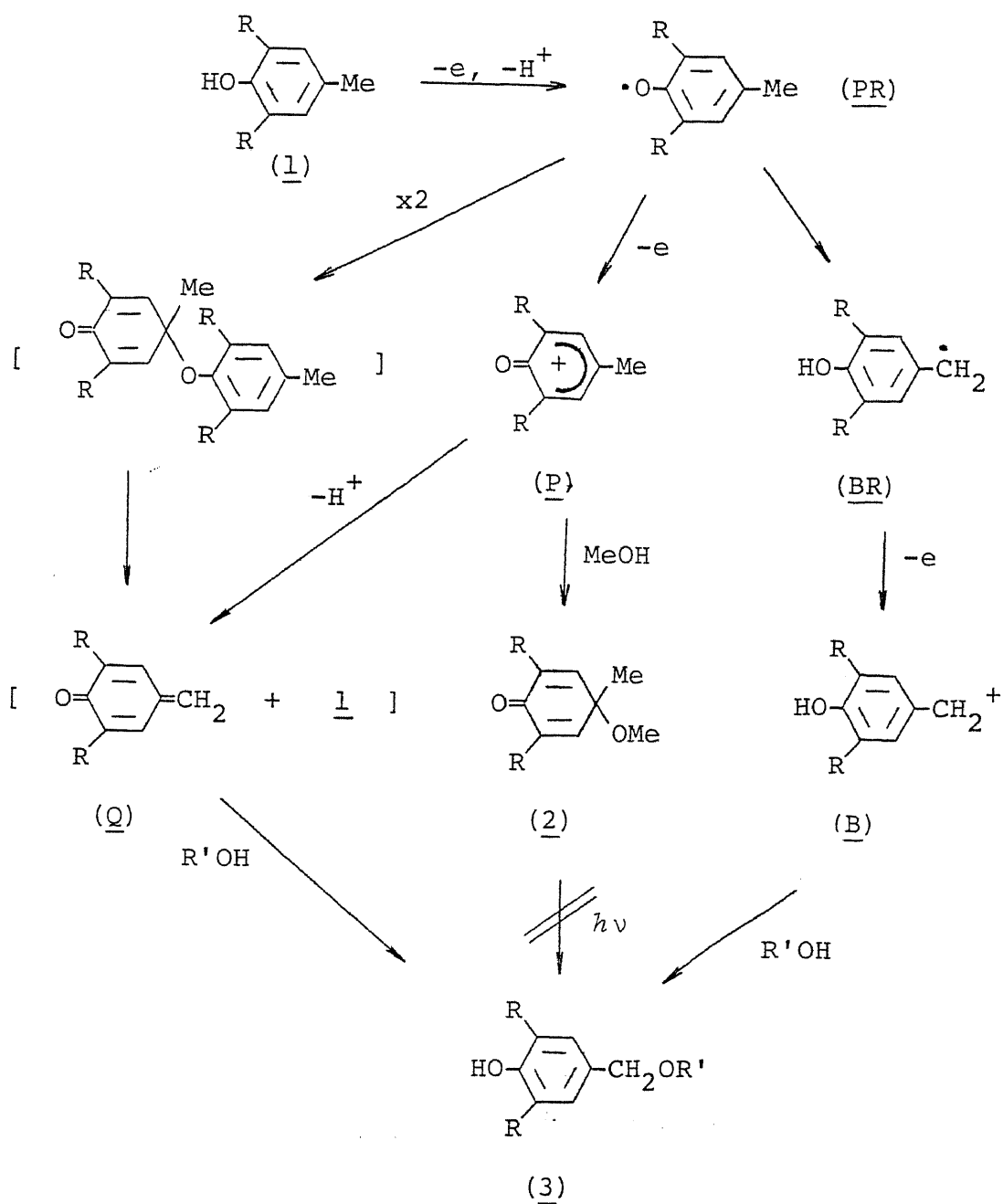
previously.^{5a,b)}

Possible Mechanism.

In the photochemical electron transfer, the production of 3 strongly suggests that 3 would be produced from the benzyl cations (B) or the quinonemethide (Q) as intermediates through their reaction with alcohols. These intermediates could be formed as depicted in Scheme. Thus, the phenoxonium ions (P), if they result, might rearrange into B or Q, and the phenoxy radicals (PR) might rearrange to benzyl radicals (BR), which are subsequently oxidized to B; PR may undergo dimerization followed by cleavage of the dimer to Q.²⁾

Taking account of the fact that the anodic oxidation of phenol ethers in methanol leads to the nuclear and sidechain methoxylations,⁹⁾ and that oxidation of 1 with manganese dioxide or lead dioxide in methanol causes the sidechain methoxylation¹⁾ but that with hexacyanoferrate(III) causes the nuclear methoxylation,⁴⁾ the present results suggest that the reaction course of the alkoxylation of phenols would be controlled by how the hydroxyl groups of phenols or oxygen functions in the intermediates interact with various metallic ions or electrodes, and/or by the difference between

Scheme



the rate of the dimerization of PR followed by cleavage of the dimer and that of the second electron transfer to give the phenoxonium ions (P).

EXPERIMENTAL

Photochemical Electron Transfer of Phenols (1) with Fe(III) salt.

As a typical run, a solution of 1a (2 g, 9 mmol) in methanol (300 cm³) containing iron(III) perchlorate hexahydrate (9 g, 20 mmol) was irradiated under a nitrogen stream at room temperature with a 160-W low pressure mercury lamp (Riko UVL-160LA) for 10 h. The reaction mixture was diluted with water (400 cm³) and extracted with dichloromethane (100 cm³ x 2). The organic layer was washed with water and dried (Na₂SO₄). After evaporation of the solvent, the residue was subjected to flash-column chromatography on silica gel to give 3a (0.69 g, 34 %), m.p. 99-100 °C (lit.⁵) 98-100 °C), and 4a (0.11 g, 5 %), m.p. 189.5-191 °C (lit.¹⁰) 189 °C). The organic layer was analyzed by GLPC to determine the product yield (Table 2).

Similar irradiation of 1a in ethanol and 2-propanol gave 2,6-di-*t*-butyl-4-ethoxymethylphenol (3a')¹⁰ and 2,6-di-*t*-butyl-4-isopropoxymethylphenol (3a''),¹⁰ respectively.

A solution of 1b (2 g, 15 mmol) in methanol (300 cm³) was irradiated similarly in the presence of Fe(ClO₄)₃·6H₂O (14 g, 30 mmol) for 18 h. The usual work-up and flash-column chromatography on silica gel of the reaction mixture gave a colorless crystalline product (0.6 g, 30 %), which was identified as 4-methoxymethyl-2,6-dimethylphenol according to the following physical data; m.p. 46-48 °C; IR(neat): 3350 cm⁻¹, ν_{O-H}, 1250-1040 cm⁻¹, ν_{C-O}; ¹H-NMR (CDCl₃): δ 2.20 (s, 6H, 2Me), 3.32 (s, 3H, MeO), 4.28 (s, 2H, CH₂O), 4.80 (s, 1H, OH), 6.88 (s, 2H, aromatic H); ¹³C-NMR(CDCl₃): δ 151.9 (s), 129.3 (s), 128.5 (d), 123.3 (s), 74.7 (t), 57.6 (q), 15.9 (q); MS: m/e 166 (M⁺, 53 %), 135 (100 %); Found: C, 72.22; H, 8.51 %; Calcd for C₁₀H₁₄O₂: C, 72.25; H, 8.48 %.

Anodic Oxidation of 2,4,6-trimethylphenol.

In a typical run, 1b (2 g, 15 mmol) was dissolved in methanol (120 cm³) containing sodium perchlorate (7.5 g, 61 mmol) and subjected to constant-current electrolysis [1 A (0.8-2.1 V)] at a platinum plate with many holes as an anode

(approximate area, 60 cm²) with a graphite rod (diameter, 1 cm; length 8 cm) as a cathode and SCE as a reference electrode under argon atmosphere at room temperature. After ca. 2.5 h, the electrolysis was interrupted and water (200 cm³) was added to the reaction mixture. The solution was extracted with CH₂Cl₂ (80 cm³ x 2). The organic layer was dried with anhydrous Na₂SO₄. Evaporation of CH₂Cl₂ and flash-column chromatographic separation of the residue gave 2b (1.37 g, 56 %), m.p. 44-46 °C (lit.³) 43-44 °C) and 2,6-dimethylbenzoquinone 5 (65 mg, 4 %).

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CHAPTER 5

PHOTOLYSIS OF CHLOROBENZENE.

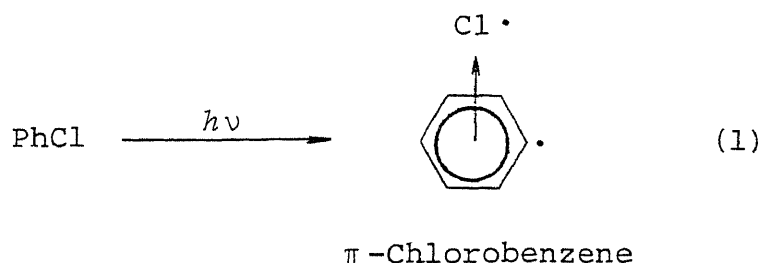
PHENYLATION OF CHLOROBENZENE WITH ANOMALOUS ORIENTATION

SUMMARY

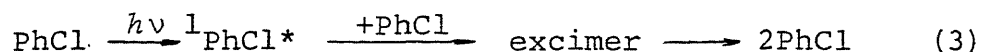
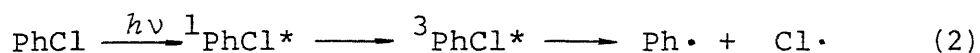
Photolysis of chlorobenzene as neat and in concentrated solutions gives a mixture of o-, m-, and p-chlorobiphenyls in an anomalous ratio, with the highest ratio of the p-isomer. However, on dilution with solvent, the isomer ratio tends to approach the normal ratio as obtained from the usual phenylation of chlorobenzene with the highest ratio of the o-isomer. A mechanism is proposed in which a triplet excimer of chlorobenzene arising in concentrated solutions favours the production of the p-isomer.

INTRODUCTION

Although photolyses of iodobenzene and bromobenzene are known to generate phenyl radicals,¹⁾ photolysis of chlorobenzene had not actively been investigated until Lemal and coworkers postulated a π -complexed pair of a chlorine atom and a phenyl radical (called π -chlorobenzene) to account for their unexpected observation that irradiation of dilute solutions of chlorobenzene in cyclohexane gave significant amounts of chlorocyclohexane (53 %), (eq. 1).²⁾

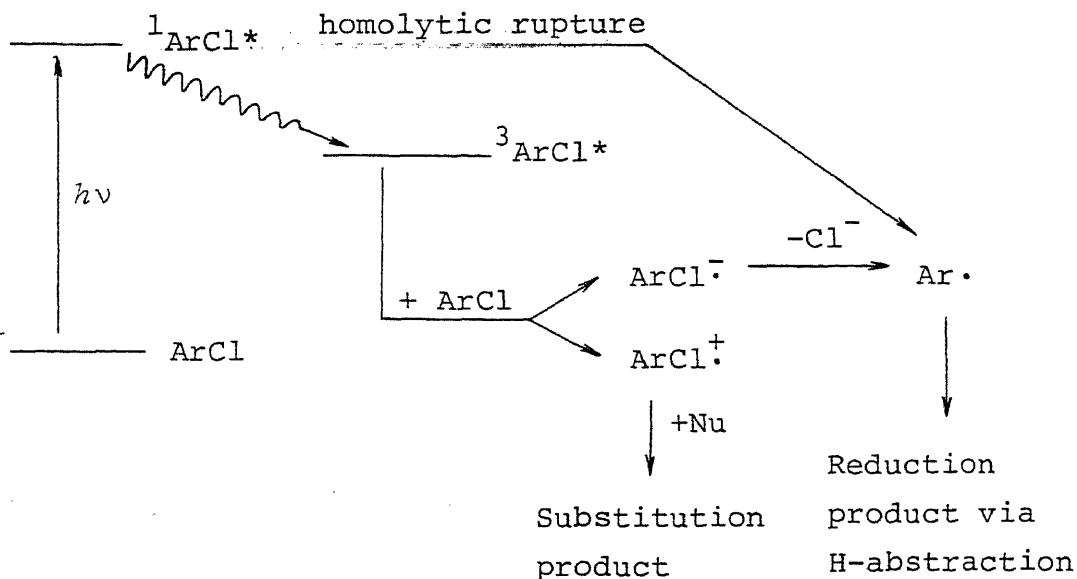


Since their work much attention has been paid to the mechanism for the photolytic cleavage of the carbon-chlorine bond in chlorobenzene.²⁻⁵⁾ Arnold and Wong explained Lemal's result in terms of a simple homolytic cleavage of the carbon-chlorine bond of the excited chlorobenzene.³⁾ Bunce and co-workers proposed that irradiation of chlorobenzene leads cleavage from the triplet state and its singlet excimer, if produced in higher concentrations of chlorobenzene, deactivates without undergoing the cleavage in contrast with 1-chloronaphthalene which dissociates through the excimer,⁴⁾ (eq. 2,3)



Recently, Soumillion and De Wolf reported that photolysis of chloroaromatic compounds in methanol proceeds through electron transfer from their triplets to ground-state molecules to generate their ion radicals which react with the solvent (Scheme 1).⁵⁾ This chapter shows my findings that photolysis of chlorobenzene results in phenylation of chlorobenzene with an orientation different from the usual phenylations, which indicates that the photolysis will take place through the interaction of the excited chlorobenzene molecules with the ground-state chlorobenzene molecules.

Scheme 1



RESULTS AND DISCUSSION

Irradiation of neat chlorobenzene (6 cm^3) in a quartz vessel with a 160-W low pressure mercury lamp under nitrogen atmosphere at room temperature for 5 h afforded o-, m-, and p-chlorobiphenyls as main products (nearly 0.1 mmol) in a ratio of 25 : 30 : 45 accompanied by a small amount of biphenyl.

As Table 1 indicates, the above ratio of the chlorobiphenyl isomers clearly differs from the "normal" ratio obtained from reactions of chlorobenzene with phenyl radicals generated from their well-known sources such as photolyses of iodobenzene¹⁾ and dibenzoyl peroxide,⁶⁾ and thermolysis of dibenzoyl peroxide,⁷⁾ which most favor the formation of the o-isomer.

Control experiments by irradiating the respective chlorobiphenyl isomers rule out the possibility that these isomers would photoisomerize to each other and show biphenyl arises from prolonged irradiation of o-chlorobiphenyl. Furthermore, the isomer ratio was not practically changed in the presence or absence of radical scavengers like oxygen, phenol, or 2,6-di-t-butyl-4-methylphenol.

Irradiation was carried out for different concentrations of chlorobenzene in 1,1,2-trichlorotrifluoroethane (200 cm^3) with a 400-W high pressure mercury lamp for 10 h and typical results for duplicate or triplicate runs are summarized in

Table 1. Typical Results for Phenylation of Chlorobenzene

Radical Source (mol/dm ³)	Distribution of Chlorobiphenyl	Isomers (%)		
		o-	m-	p-
PhCl photolysis (neat)		25	30	45
PhI photolysis (3.86)		59	26	15
(PhCO ₂) ₂ Photolysis (0.06)		55	28	17
(PhCO ₂) ₂ thermolysis(0.05)		57	27	16

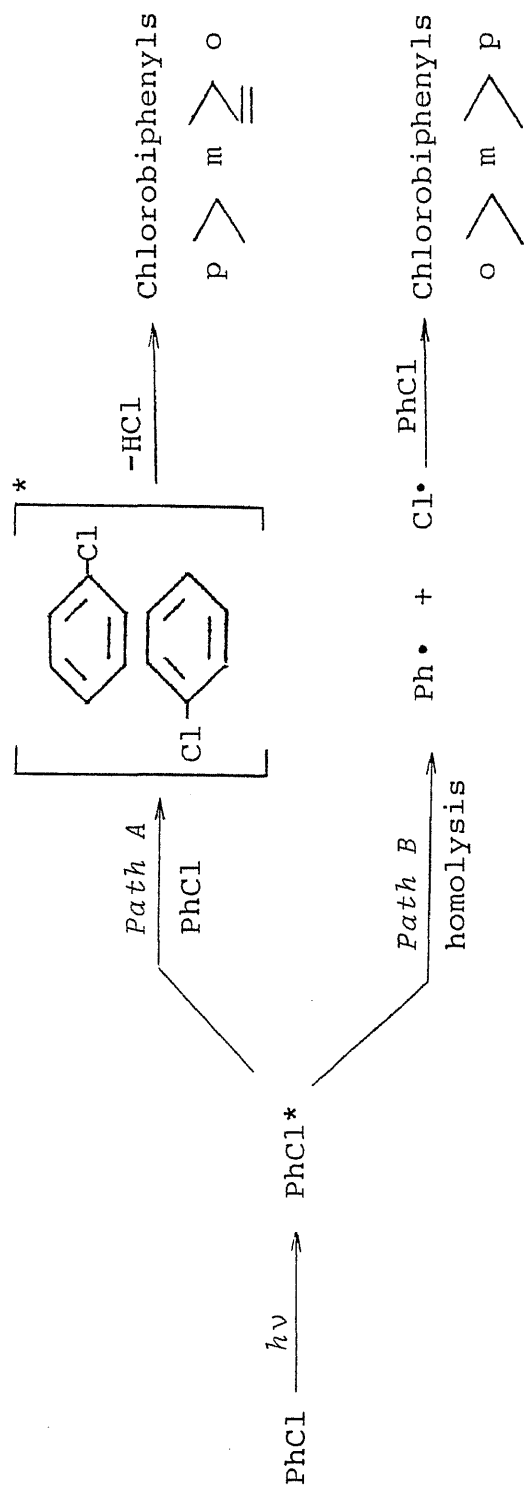
Table 2. Chlorobenzene in more than $5 \times 10^{-1} \text{ mol/dm}^3$ concentration gave the isomeric chlorobiphenyls in a similar ratio to that from the neat substrate, in the highest ratio of the p-isomer. However, decrease in chlorobenzene concentration altered the isomer ratio to give the highest ratio of the o-isomer approaching to the "normal" value.

These results suggest that in dilute solutions free phenyl radicals generated from photolysis of chlorobenzene act on chlorobenzene to give the normal ratio of isomeric chlorobiphenyls; on the other hand, in concentrated solutions the excited chlorobenzene would interact with ground-state chlorobenzene with a configuration favorable for affording the p-isomer after the cleavage of the C-Cl bond. In view of the report on a triplet excimer of chlorobenzene,⁸⁾ it is reasonable to suppose that this is responsible for the formation of p-chlorobiphenyl, while in dilute solutions the excited chlorobenzene molecules will undergo cleavage into phenyl radicals before their encounter with the ground-state molecules.

Table 2. Photolysis of Chlorobenzene in $\text{CCl}_2\text{FCClF}_2$ (200 cm^3)
with a 400-W high pressure mercury lamp (10 h)

Concentration of PhCl (mol/dm^3)	Product Distribution (%)			Yield (mmol)	
	Ph ₂	Chlorobiphenyl			
		o-	m-		p-
5×10^{-1}	2	34	25	39	0.2
5×10^{-2}	—	41	33	26	0.02
5×10^{-3}	—	51	25	25	0.002

Scheme 2



EXPERIMENTAL

Identification and quantitative analyses of all products were performed by a Hitachi 163 gas chromatograph with a flame ionization detector, using a 2 m column of PEG-20M (10 %). Irradiations were carried out with a 160-W low pressure mercury lamp (Riko UVL-160LA) and 400-W and 1-kW high pressure mercury lamps (Riko UVL-400HA and Ushio ML-1000W). Mass spectra were determined with a Hitachi RMU-6MC mass spectrometer.

Materials.

Chlorobenzene, iodobenzene, phenol, 2,6-di-t-butyl-4-methylphenol, dibenzoyl peroxide, 1,1,2-trichlorotrifluoroethane, and 2-hexanone were commercial samples from Wako Pure Chemical Industries or Nakarai Chemicals. Three kinds of chlorobiphenyl isomers were prepared according to literature.⁹⁾

Phenylation of Chlorobenzene.

a) Direct Irradiation of Neat Chlorobenzene.

Neat chlorobenzene (6 cm^3 , 59 mmol) was irradiated in a quartz vessel with a 160-W low pressure mercury lamp

under nitrogen atmosphere at room temperature for 5 h to afford o-, m-, and p-chlorobiphenyls in a ratio of 25 : 30 : 45 accompanied by a small amount of biphenyl. The structural assignment of these compounds were made by GC/mass and GLPC in comparison with the authentic samples.

b) Phenylation of Chlorobenzene by Photolysis of Iodobenzene.

A solution of iodobenzene (3 cm^3 , 27 mmol) in chlorobenzene (7 cm^3 , 69 mmol) in a Pyrex tube was irradiated with a 1-kW high pressure mercury lamp under nitrogen atmosphere at room temperature for 11 h. After treatment of the reaction solution with a 5 % aqueous solution of sodium thiosulfate, the isomer ratio of chlorobiphenyls was determined by GLPC analysis. The result is shown in Table 1.

c) Phenylation of Chlorobenzene by Photolysis of BPO.

A mixture of chlorobenzene (10 cm^3) and dibenzoyl peroxide (140 mg, 0.58 mmol) was irradiated in a Pyrex tube with the high pressure mercury lamp under nitrogen atmosphere at room temperature. After unreacted peroxide was decomposed by sodium iodide, the isomer ratio of chlorobiphenyls was determined by GLPC analysis. The result is shown in Table 1.

d) Phenylation of Chlorobenzene by Thermolysis of BPO.

Dibenzoyl peroxide (60 mg, 0.25 mmol) was heated in chlorobenzene (5 cm³) at 80-90 °C under nitrogen atmosphere for 5.5 h. The reaction solution was analyzed by GLPC. The result is shown in Table 1.

Photolysis of Chlorobenzene in the Presence of Radical Scavengers.

Chlorobenzene (3 cm³, 30 mmol) was photolyzed in the presence of phenol (525 mg, 5.6 mmol) or 2,6-di-t-butyl-4-methylphenol (100 mg, 0.45 mmol) in a quartz tube with a 160-W low pressure mercury lamp under nitrogen atmosphere at room temperature for 5 h. Similarly, chlorobenzene was photolyzed bubbling with oxygen. The results are summarized in Table 3.

Irradiation of Respective Chlorobiphenyl Isomers.

o-Chlorobiphenyl (60 mg, 0.3 mmol) was irradiated in benzene (5 cm³), cyclohexane (5 cm³), and the mixture solvent (5 cm³) of benzene and cyclohexane (3 : 2) in a quartz tube with a 160-W low pressure mercury lamp under

nitrogen atmosphere at room temperature for 5 h. The irradiated solution was analyzed by GLPC with a 2 m column of PEG-20M (10 %). Similar irradiations of m- and p-chlorobiphenyls (20 mg, 0.1 mmol) were carried out. These results are shown in Table 4.

Photolysis of Chlorobenzene in 1,1,2-Trichlorotrifluoroethane with a 400-W High Pressure Mercury Lamp.

Irradiations of chlorobenzene at different concentrations [11 g (100 mmol), 1.1 g (10 mmol), and 0.11 g (1 mmol)] were carried out in 1,1,2-trichlorotrifluoroethane (200 cm³) with a 400-W high pressure mercury lamp under nitrogen stream at room temperature for 10 h. Typical results for duplicate or triplicate runs are summarized in Table 2.

Quantum Yield for Production of Chlorobiphenyls with 313-nm Light.

Light intensity was measured using 2-hexanone actinometry.¹⁰⁾ A 2 mol/dm³ solution of chlorobenzene in CCl₂FCClF₂ was prepared and degassed by four freeze-pump-thaw cycles (2 x 10⁻¹ mmHg). The sample was irradiated

with a 1-kW high pressure mercury lamp, using a merry-go-round apparatus through a Pyrex filter and an aqueous solution including K_2CrO_4 (0.27 g/dm^3) and Na_2CO_3 (1 g/dm^3). The quantum yield for production of chlorobiphenyls estimated was corrected using the ratio of molar absorptivity of chlorobenzene and 2-hexanone, finally to be determined to be 1.8×10^{-4} .

Table 3. Photolysis of Chlorobenzene in the Presence of Radical Scavengers

Radical Scavenger	Distribution of Products (%)			
	Ph ₂	Chlorobiphenyls		
		o-	m-	p-
PhOH	12	31	27	30
2,6- ^t Bu ₂ - 4-MeC ₆ H ₂ OH	—	34	34	33
O ₂	1	31	33	35

Table 4. Irradiation of Respective Chlorobiphenyl Isomers

Irradiated Chlorobiphenyl	Solvent	Product (Relative Yield, %)			
		Ph ₂	Chlorobiphenyls		
			o-	m-	p-
o-isomer	PhH	10	90	-	-
	PhH-C ₆ H ₁₂	33	67	-	-
m-isomer	C ₆ H ₁₂	49	51	-	-
	PhH	trace	-	100	-
p-isomer	PhH-C ₆ H ₁₂	trace	-	100	-
	C ₆ H ₁₂	trace	-	100	-
p-isomer	PhH	trace	-	-	100
	PhH-C ₆ H ₁₂	trace	-	-	100
	C ₆ H ₁₂	trace	-	-	100

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ACKNOWLEDGEMENT

The author would record here his warmest acknowledgement to Professor Katsumi Tokumaru for his constant guidance and discussions throughout this investigation.

He wishes to thank to Associate Professor Hiroshi Kato and Hiroshi Tezuka of Shinshu University for their encouragement. Acknowledgement is made to the members of Professor Tokumaru's research group for their helpful discussions.



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December 1981