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学位論文題目	

Studies on the preparations of organophosphorus compounds from triphenylphosphine oxide
(トリフェニルホスフィンオキシドを用いる有機リン化合物の合成に関する研究)

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論文の要旨

Mr. Jian-Qiu Zhang's thesis described his achievements gained in studies on the development of new methods for the preparation of organophosphorus compounds from triphenylphosphine oxide. Organophosphine oxides $R_3P(O)$ are useful in flame-retardants, pharmaceuticals, extractants, and synthetic chemistry. The traditional synthesis of phosphine oxides mainly depended on the substitution reactions of phosphoryl chlorides $R_2P(O)Cl$ with organometal reagents RM (M = MgX or Li), but the processes were associated with heavy pollution and harsh reaction conditions. Triphenylphosphine oxide $Ph_3P(O)$, as a main byproduct from the Wittig reactions for producing vitamins in the industry, is generated tens of thousands of tons each year. Majority of $Ph_3P(O)$ has been discarded as waste because of the chemical stability and low added value. Therefore, dealing with the waste problem of $Ph_3P(O)$ by converting it to other valuable organophosphorus compounds is of great significance in the academia and industry.

In the thesis, the applicant studied a series of new methods for the conversion of triphenylphosphine oxide. By using the resource-abundant and cheap sodium (sodium finely dispersed in paraffin oil with μm-scale sizes, hereafter abbreviated as SD), $Ph_3P(O)$ could be employed as a starting material to efficiently and selectively produce four kinds of organophosphorus intermediates–sodium diphenylphosphinite (Ph_2PONa), sodium diphenylphosphide (Ph_2PNa), sodium 5H-benzo[b]-phosphindol-5-olate (3) (Ar_2PONa) and sodium benzo[b]phosphindol-5-ide (Ar_2PNa) through selective P-C, P-O and C-H bond cleavage, and the corresponding phosphine oxides and phosphines were obtained in good to excellent yield by treating with aliphatic or aromatic electrophiles RX. The SD-mediated P-C bond cleavage also occurred in other tertiary phosphine oxides $R_3P(O)$ besides $Ph_3P(O)$. In addition, the utilization of intermediate $Ph_2P(ONa)$ was further investigated that it could be facially converted to $Ph_2P(O)H$ which was subsequently transformed to

acylphosphine oxides $Ph_2P(O)$-C(O)R or chlorophosphine Ph_2PCl by adjusting the reaction conditions.

Firstly, the applicant disclosed the selective conversion of $Ph_3P(O)$ to three reactive organophosphorus intermediates—sodium diphenylphosphinite, sodium 5H-benzo [b]phosphindol-5-olate and sodium benzo[b]phosphindol-5-ide—that efficiently give the corresponding organophosphorus derivatives in good yields. By using SD, intermediate $Ph_2P(ONa)$ was produced exclusively within a few minutes, no side products could be detected at all. The obtained intermediate $Ph_2P(ONa)$ had good applications for the preparations of $Ph_2P(O)H$ (widely employed as a versatile starting material), $Ph_2P(O)C(O)Mes$ (well known as an important photoinitiator in polymerization) and diphenyl(alkyl)phosphine oxides. By treating $Ph_3P(O)$ with phenyl sodium (PhNa) in situ generated from PhCl with SD in hexane, a five-membered cyclic intermediate sodium 5H-benzo [b]phosphindol-5-olate $Ar_2P(ONa)$ was selective achieved to be the main product. Continual addition of SD to sodium 5H-benzo [b]phosphindol-5-olate $Ar_2P(ONa)$ resulted to the formation of sodium benzo[b]phosphindol-5-ide Ar_2PNa *via* a reduction process, these two intermediates were readily converted to the corresponding dibenzophosphole oxides $Ar_2P(O)R$ and dibenzophospholes Ar_2PR in good yields by quenching with aliphatic halides.

Then, the applicant further studied the generality of P-C bond cleavage of phosphine oxides by sodium, several important problems left in the last study were solved. First, the SD-mediated P-C bond cleavage was smoothly extended to the reaction of other pentavalent phosphine oxides $R_3P(O)$, and the selectivity of P-alkyl bond and P-aryl bond by SD was also investigated. And the result showed that P-Ph bond was prior to be broken by SD, P-O bond was easier to be broken then P-Ph bond. On the other hand, among the three alkali metals M (M = Li, Na and K) investigated, sodium exhibited the best efficacy and selectivity for converting triphenylphosphine oxide $Ph_3P(O)$ to diphenylphosphinite $Ph_2P(OM)$ while the reaction with lithium or potassium resulted to many by-products. In addition, the destiny of co-generated PhNa from the reaction of $Ph_3P(O)$ with Na was disclosed, sodium vinylate was the main base finally generated from the reaction of PhNa with THF, it was noteworthy that this sodium vinylate showed low reactivity to alkyl halides, thus hardly affecting the quenching reactions of the sodium phosphinite $R_2P(ONa)$ with alkyl halides. Last, the scope of $Ph_2P(ONa)$ reacting with alkyl halides and aryl halides (catalyzed by a Pd catalyst) was examined. The mechanism of P-C bond cleavage by Na was discussed.

As mentioned above, five-membered cyclic sodium 5H-benzo [b]phosphindol-5-olate $Ar_2P(ONa)$ could be readily reduced to sodium benzo[b]phosphindol-5-ide Ar_2PNa by SD. In the third section, the applicant wondered whether the corresponding sodium diphenylphosphide Ph_2PNa would be also generated from $Ph_2P(ONa)$ which was easily obtained from $Ph_3P(O)$. Therefore, by introducing trimethylsilyl chloride (TMSCl), the pentavalent phosphoryl compounds $R_3P(O)$ such as triphenylphosphine oxides, secondary phosphine oxides etc., were readily converted to the corresponding $R_2P(OTMS)$ intermediates, that could further react efficiently with an electrophile R'X or with a nucleophile R'Li to produce the corresponding trivalent phosphines R_2PR'. Chiral phosphines could also be obtained stereospecifically by this strategy.

Finally, the applicant disclosed that, by using diphenylphosphine oxide $Ph_2P(O)H$ as starting material that could be efficiently prepared from $Ph_3P(O)$ in large scale, two highly valuable industrial products, acylphosphine oxides and chlorophosphines was readily synthesized, respectively. In the presence of trimethylsilyl chloride (Me_3SiCl), $Ph_2P(O)H$ as well as other secondary phosphine oxides $R_2P(O)H$ reacted with acyl chlorides R'C(O)Cl to give acylphosphine oxides $R_2P(O)C(O)R'$ in high yields. Interestingly, the reactions proceeded smoothly catalyzed by trichloromethyl silane ($MeSiCl_3$). On the other hand, direct treatment of $Ph_2P(O)H$ with acetyl chloride (MeC(O)Cl) facially gave rise to chlorodiphenylphosphine (Ph_2PCl), the strategy could also be applicable to other secondary phosphine oxides $R_2P(O)H$ and delivering the corresponding phosphine chlorides R_2PCl in high yields.

審　査　の　要　旨

〔批評〕

The applicant comprehensively studied the transformations of the industry waste triphenylphosphine oxide, in which a series of valuable organophosphorus compounds including those pentavalent phosphorus compounds such as diphenylphosphine oxide, diphenyl(alkyl)phosphine oxides, diphenyl(aryl)phosphine oxides, dibenzophosphole oxides as well as those trivalent phosphorus compounds like diphenyl(alkyl)phosphines, diphenyl chloride and dibenzophospholes, were efficiently and selectively synthesized by using triphenylphosphine oxide as starting material. The systematical studies in this thesis not only solve the long-time waste problem of triphenylphosphine oxide, but also provide a series of new approaches toward organophosphorus compounds that are tediously accessed by the classical methods. The applicant cited the backgrounds of the study correctly, conducted the researches logically, and analyzed the results reliably, as evidenced by his seven papers published in renowned international journals.

〔最終試験結果〕

The final examination committee conducted a meeting as a final examination on July 14, 2021. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

〔結論〕

Based on the results of the above-mentioned dissertation defense and final examination, the final examination committee approved that the applicant is qualified to be awarded Doctor of Philosophy in Science.