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THE REACTIONS OF DIBENZYLSELENONIUM YLIDE, IMIDE, AND SELENOXIDE WITH TRIPHENYLPHOSPHINE

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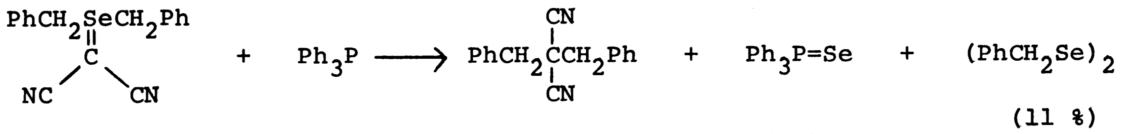
The reactions of dibenzylselenonium dicyanomethylide or cyanomethoxycarbonylmethylide with triphenylphosphine at room temperature gave 2-benzyl-2-cyano-3-phenylpropanenitrile or methyl 2-benzyl-2-cyano-3-phenylpropanoate by deselenization and the addition of acetic acid into the reaction system changed the reaction mode, yielding mainly dibenzyl diselenide. Meanwhile, the corresponding selenonium imide and selenoxide afforded dibenzyl selenide.

The chemistry of selenium compounds such as selenonium ylides1) and imides,2) and selenoxides3) have attracted attention in recent years, but reactions of those compounds have not been scrutinized to clarify the rather peculiar behaviors of selenium compounds as compared with those of the corresponding sulfur analogs.4)

In the present study we examined the reactions of a series of selenium compounds, i.e., dibenzyl selenoxide, selenonium imide, and selenonium ylide, with triphenylphosphine and a comparison of products thus obtained was made.

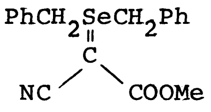
A mixture of 489 mg(1.5 mmol) of dibenzylselenonium dicyanomethylide(I) and 393 mg(1.5 mmol) of triphenylphosphine in 10 ml of CH_2Cl_2 was stirred at room temperature for 12 hours. The solvent was evaporated in vacuo, and then chromatographic separation of the resulting residue gave 446 mg(87 %) of triphenylphosphine selenide(II, mp 186-187°C)5) and 2-benzyl-2-cyano-3-phenylpropanenitrile(III, 53 %, mp 129-130°C)6) along with a small amount of dibenzyl diselenide(mp 87-89°C), but no dibenzyl selenide.



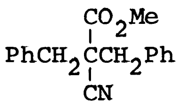
$$PhCH_2\underset{\underset{NC\quad CN}{\overset{\|}{C}}}{Se}CH_2Ph + Ph_3P \longrightarrow PhCH_2\overset{CN}{\underset{CN}{C}}CH_2Ph + Ph_3P{=}Se + (PhCH_2Se)_2$$

(I) (III) (II) (11 %)

Similar treatment of dibenzylselenonium cyanomethoxycarbonylmethylide(IV) with an equimolar amount of triphenylphosphine afforded methyl 2-benzyl-2-cyano-3-phenylpropanoate(V,mp 77-78°C),7) triphenylphosphine selenide, and dibenzyl diselenide in 29, 49, and 28 % isolated yields, respectively.



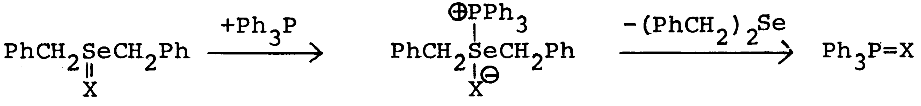
(IV)



$\mathrm{PhCH_2\overset{CO_2Me}{\underset{CN}{C}}CH_2Ph}$

(V)

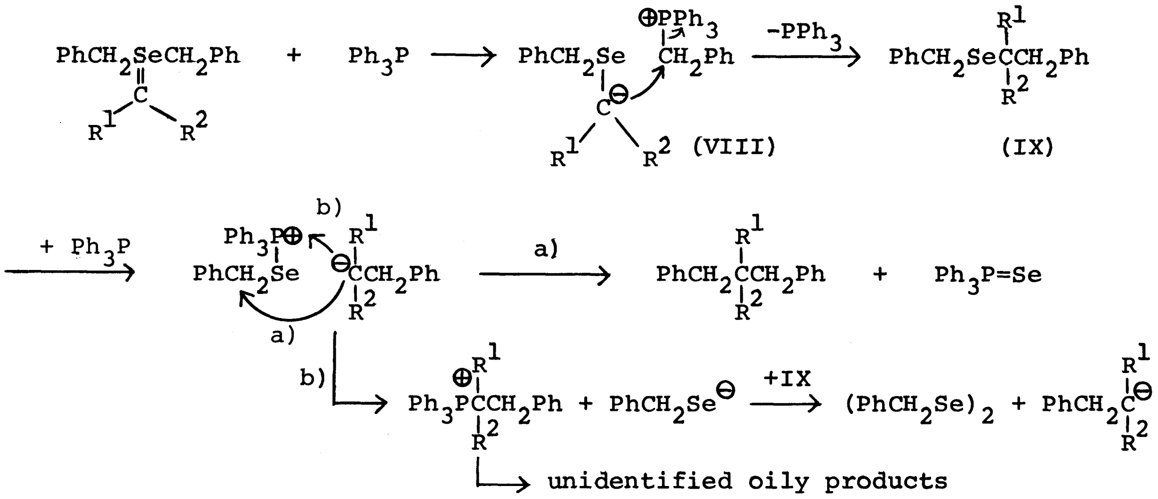
In contrast, the reaction of dibenzylselenonium N-tosylimide with triphenylphosphine at room temperature for 24 hours led preferentially to the formation of dibenzyl selenide(81 %) and triphenyl N-tosylphosphimine(54 %, mp 185-186°C), accompanied by a trace of phosphine selenide(6 %). The isolation of the phosphine selenide indicates clearly that the selenonium imide also undergoes deselenization but as a minor process. Meanwhile, the reaction of dibenzyl selenoxide or even less reactive diphenyl selenoxide with triphenylphosphine was found to be much more facile than wuold be expected from those of sulfoxides4) and was completed within one minute at room temperature, quantitatively yielding dibenzyl selenide and triphenylphosphine oxide, but no deselenization products. Therefore, the reactivity order for the reduction into dibenzyl selenide is selenoxide > selenonium imide > selenonium ylide.



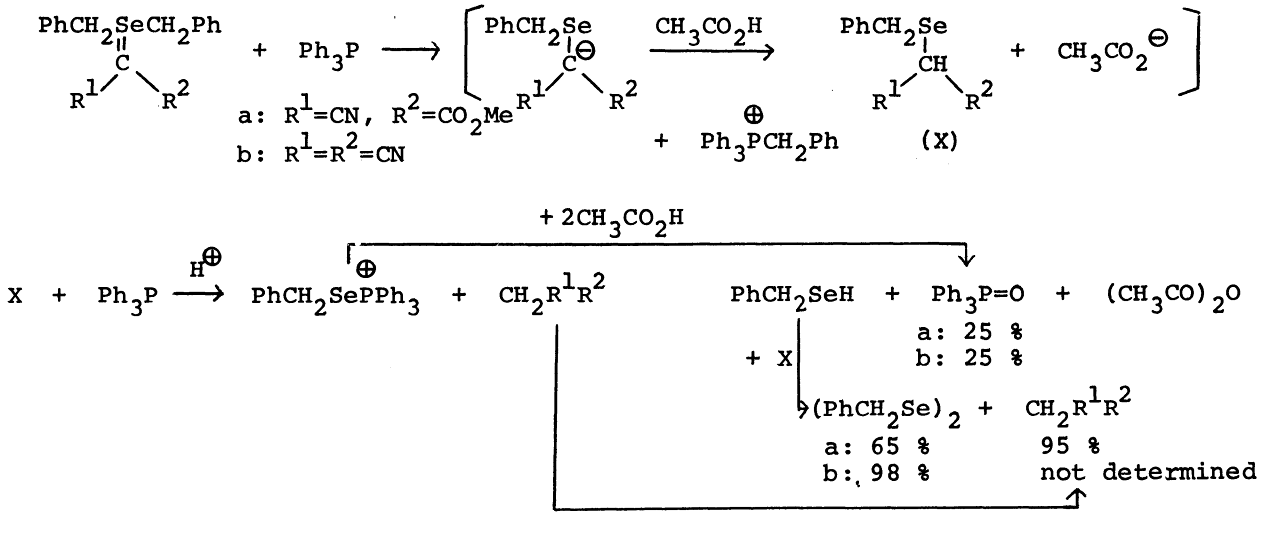
$$\mathrm{PhCH_2\underset{X}{\overset{\|}{Se}}CH_2Ph \xrightarrow{+Ph_3P} PhCH_2\overset{\oplus PPh_3}{\underset{X^{\ominus}}{Se}}CH_2Ph \xrightarrow{-(PhCH_2)_2Se} Ph_3P{=}X}$$

(X=O, NTs) (VI) (VII)

The remarkable difference in the reaction mode between the selenonium ylide and imide or selenoxide is now being examined. However, it would be argued that the formations of hypervalent intermediates(VI)8) and/or final oxidized products(VII) are much easier in the reactions of the latters than that of the former and hence the reaction of the ylide proceeds by an initial attack of phosphine on the benzylic carbon rather than on the tetravalent selenium. In fact, it was reported that in the reaction of phenyl benzyl N-tosylsulfilimide with halide anion in DMF the halide anion initially attacks the benzylic carbon atom to form the rearranged key intermediate, i.e., S-phenyl-N-benzyl-N-tosylsulfenamide, which collapses to the final products.9) Thus, the mechanism for the deselenization would best be rationalized as involving an initial S_N2 attack by phosphine on the benzylic carbon, subsequently leading, through the ion-pair (VIII), to IX, followed by a nucleophilic attack of phosphine on the divalent selenium of IX,[10] eventually affording observed products, as outlined below.



Meanwhile, addition of acetic acid or water into the reaction system led to a change in product distributions and reaction modes, yielding dibenzyl diselenide, the corresponding active methylene compound and phosphine oxide. The formations of these products could be explicable in terms of the reaction sequence including the initial attack of phosphine on the benzylic carbon atom, as depicted below.[11]



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References and Notes

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5) Found: C, 63.33; H, 4.70%. Calcd for $C_{18}H_{15}PSe$: C, 63.36; H, 4.43%.

6) Found: C, 82.93; H, 5.69; N, 11.83%. Calcd for $C_{17}H_{14}N_2$: C, 82.60; H, 5.65; N, 11.41%. NMR($CDCl_3$): δ 7.55(s, 10H), 3.35(s, 4H) ppm.

7) Found: C, 77.46; H, 6.27; N, 4.88%. Calcd for $C_{18}H_{17}O_2N$: C, 77.39; H, 6.14; N; 5.01%. NMR($CDCl_3$): δ 7.35(s, 10H), 3.60(s, 3H), 3.30(dd, 4H) ppm. IR(KBr): 2250 cm^{-1} ($C\equiv N$).

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10) A reaction relevant to this stage was reported in the literature.

$$\mathrm{RSeCN} + \mathrm{Ph_3P} \longrightarrow \mathrm{RCN} + \mathrm{Ph_3P{=}Se}$$

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11) Yields(%) of dibenzyl diselenide and phosphine oxide were calculated based on material balances of selenium and phosphorus atoms, respectively.

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