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The Reactions of Phenylmagnesium Halides with Seleninyl Chloride, Diphenyl Selenoxide, and Dibromodiphenylselenium

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Triphenylselenonium halides were readily prepared in good yields by the one-step reaction of seleninyl chloride with phenylmagnesium halides, followed by treatment with hydrogen halides. The yields of triphenylselenonium halides are markedly affected by the molar ratio of seleninyl chloride to the phenylmagnesium halides. In order to interpret the above results, some probable intermediates, such as diphenyl selenoxide, dibromodiphenylselenium, and diphenyl selenide, were investigated by allowing them to react with the phenylmagnesium halides. A pathway which consists of competitive and successive reactions is discussed.

Trimethylselenonium hydroxide ($(CH_3)_3Se^+OH^-$) is a very useful methylation reagent for carboxylic, thiol, and aromatic hydoroxyl groups.[1] Hampton[2] has reported on the use of diphenyliodonium chloride ($Ph_2I^+Cl^-$) for terminal phenylation. Triarylselenonium halides ($Ar_3Se^+X^-$), which may be expected as arylation reagents, could be prepared by a convenient one-step synthesis.[3] Strecker and Willing[4] have obtained only diphenyl selenide (Ph_2Se) and diphenyl (Ph_2) by the reaction of seleninyl chloride ($SeOCl_2$) with phenylmagnesium bromide (PhMgBr); they have not described the formation of selenonium salt. However, the addition of about three moles of arylmagnesium halides to one mole of $SeOCl_2$ afforded the corresponding triarylselenonium salts, together with Ph_2Se and Ph_2.[3] This method is useful for the preparation of selenonium salts, since the usual methods require several steps.[5,6]

In order to clarify the formation path of triphenylselenonium halides ($Ph_3Se^+X^-$), the reaction of phenylmagnesium halides (PhMgX) with such probable intermediates as diphenyl selenoxide (Ph_2SeO), dibromodiphenylselenium (Ph_2SeBr_2), and diphenyl selenide (Ph_2Se) were investigated.

Results and Discussion

Reaction of PhMgX with $SeOCl_2$. After the addition of 3.5-fold mole of various PhMgX's to $SeOCl_2$ in THF or ether, the solution was maintained at the reflux temperature for 2 h.[7] The hydrolysis of the reaction mixtures with aqueous hydrobromic acid (HBr *ca.* 1 mol dm^{-3}) gave $Ph_3Se^+X^-$, Ph_2Se, and Ph_2, as is shown in Table 1. It is of interest that $Ph_3Se^+Br^-$ appeared in the reaction of $SeOCl_2$ with the PhMgCl was afforded by the treatment of the resulting reaction mixtures with HBr. In the case of PhMgI, $Ph_3Se^+I^-$ was produced, even though the mixtures were similarly treated with HBr.[8]

The reaction with PhMgCl, followed by treatment with HBr, gave $Ph_3Se^+Br^-$ in a 56% yield, but the yield of selenonium salt in the same reaction in the presence of $MgBr_2$ fell to 39%, which is comparable to the yield of the reaction with PhMgBr,[9] as is shown in Table 1. These findings indicate the occurrence of halogen exchange in the reaction system during the period of reaction and the treatment with HBr. It is considered that the lower yield of selenonium salt in the reaction with PhMgBr results from the formation of more reactive, but less selective, $SeOBr_2$ by halogen exchange between $SeOCl_2$ and the resulting $MgBr_2$ during the reaction. The considerable lowering in the yield in the case of PhMgI is thought to be due to the decomposition of the unstable $SeOI_2$.[10]

These results indicate that the seleninyl halides ($SeOX_2$) generated by halogen exchange react with three moles of PhMgX to give triphenylselenonium halogenomagnesium oxide ($Ph_3Se^+OMgX^-$), which then affords $Ph_3Se^+X^-$ upon subsequent hydrolysis with HBr.

The product distributions of $Ph_3Se^+Br^-$, Ph_2Se, and Ph_2 varied with the ratio of PhMgX to $SeOCl_2$. Figure 1 shows a typical curve for the yield of each product obtained by the addition of PhMgBr to $SeOCl_2$ in ether. The production of Ph_2SeBr_2 was at its maximum at the molar ratio of 1.5; thereafter, it decreased rapidly to zero at the ratio of 2.5, in contrast to the increase in Ph_2Se and Ph_2. The amount of selenonium salt increased gradually with the increase in PhMgBr until the molar ratio of 3.5. At more than 3.5, a rapid decrease in the selenonium salt led to the formation of Ph_2Se and Ph_2. Thus, the present reaction is considered to be a complicated successive reaction.

Reaction of PhMgBr with Ph_2SeBr_2. A solution of PhMgBr in ether was added to equimolar amounts of Ph_2SeBr_2, and then the mixture was worked-up as above. The selenonium salt which was expected as the primary product was not obtained at all, but

Table 1. Addition of PhMgX to a solution of $SeOCl_2$[a]
(Followed by HBr work-up)

X PhMgX	MgX_2	Yield[b]/mmol		
		$Ph_3Se^+Br^-$	Ph_2Se	Ph_2[c]
Cl	—	16.9(56.2)	11.7(39.0)	4.2(14.3)
Br	—	11.2(37.3)	14.9(49.5)	7.9(26.3)
I[d]	—	0.8(2.5)[e]	10.6(35.2)	9.9(33.1)
Cl	$MgCl_2$	16.4(54.5)	12.1(40.2)	5.4(18.1)
Cl	$MgBr_2$	11.7(39.0)	15.1(50.5)	9.6(32.0)

a) PhMgX (105 mmol) was added to a solution of $SeOCl_2$ (30 mmol) in THF (100 ml). b) Yields given in parentheses indicate the mol% based on $SeOCl_2$. c) Formation from Ph_4Se was assumed. d) Ether was used as the solvent. e) $Ph_3Se^+I^-$.

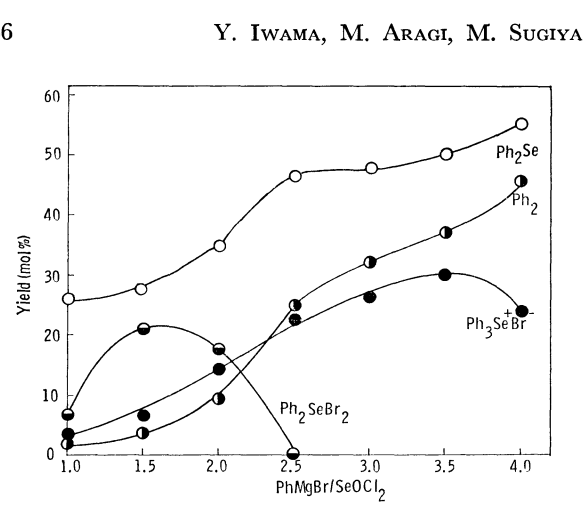

Fig. 1. Dependence of the yield of each product on the molar ratio of PhMgBr to $SeOCl_2$.

equimolar amounts of Ph_2Se and Ph_2 were.[11] This fact shows that Ph_2SeBr_2 reacts with PhMgBr to give, probably, an unstable tetraphenylselenium (Ph_4Se), which then immediately decomposed to Ph_2Se and Ph_2. It was found that Ph_2SeBr_2 is not connected with the production of selenonium salt.

On the other hand, no product was furnished by the reaction of Ph_2Se with PhMgBr.

Reaction of PhMgBr with Ph_2SeO. Ph_2SeO could not be isolated in the reaction of $SeOCl_2$ with PhMgBr, but it appeared to be one of the most probable intermediates. Wildi[12] has reported the production of triphenylsulfonium bromide ($Ph_3S^+Br^-$) by the reaction of diphenyl sulfoxide (Ph_2SO) with PhMgBr.

The reaction of Ph_2SeO with PhMgBr, followed by hydrolysis with HBr, gave $Ph_3Se^+Br^-$, Ph_2Se, and Ph_2 in yields of 25, 63, and 10% respectively. It seems that selenonium salt was produced through triphenylselenonium bromomagnesium oxide (Ph_3Se^+-$OMgBr^-$) according to the following equation.

$$Ph_2SeO + PhMgBr \longrightarrow Ph_3Se^+OMgBr^-$$

$$Ph_3Se^+OMgBr^- + HBr \longrightarrow Ph_3Se^+Br^- + MgBr(OH)$$

Some of the $Ph_3Se^+OMgBr^-$ reacts further with PhMgBr to afford Ph_2Se and Ph_2 *via* Ph_4Se:

$$Ph_3Se^+OMgBr^- + PhMgBr \longrightarrow Ph_4Se + (MgBr)_2O$$

$$Ph_4Se \longrightarrow Ph_2Se + Ph_2$$

However, the significant formation of Ph_2Se can not be interpreted by considering only the above reaction. It may be supposed that Ph_2Se is produced by the elimination of oxygen from Ph_2SeO, which is liable to be reduced, but the detailed process has not been ascertained.[13]

Consequently, the reaction proceeds first through halogen exchange between $SeOCl_2$ and PhMgX, as well as, the MgX_2 which is generated during the period of reaction, and the resulting $SeOX_2$ reacts with PhMgBr to give Ph_2SeO and Ph_2SeBr_2. Selenonium salts are chiefly derived from Ph_2SeO, and Ph_2Se and Ph_2, from Ph_2SeBr_2. From these results, it seems reasonable that the maximum yield of selenonium salts is at the molar ratio of PhMgX to $SeOCl_2$ of 3.5, and that the reaction proceeds through competitive and successive paths which are complicated by halogen exchange.

Experimental

The melting points, determined on a Yanagimoto micromelting-point apparatus (MP-J3), are uncorrected. The IR spectra were obtained with a Shimadzu IR-27G spectrophotometer. The mass spectra were measured with a JEOL JMS-01SG apparatus. The general procedure for the reaction of PhMgX with $SeOCl_2$ was the same as in a previous paper.[3] The yields of $Ph_3Se^+X^-$ and Ph_2Se, based on the $SeOCl_2$ used, and of Ph_2 were estimated and considered to result from the decomposition of Ph_4Se to Ph_2Se and Ph_2.

Reaction of PhMgCl with $SeOCl_2$ in the Presence of $MgBr_2$. Anhydrous $MgBr_2$ (5.5 g, 30 mmol) was added to a solution of $SeOCl_2$ (5.0 g, 30 mmol) in THF (100 ml). The mixture gradually became brownish and was then allowed to react with PhMgCl (105 mmol) in THF under reflux for 2 h. After the THF had been evaporated *in vacuo*, the mixture was hydrolyzed with HBr (*ca.* 1 mol dm^{-3}) and extracted with benzene; the remaining aqueous solution was further extracted with chloroform. The benzene extract was dried over sodium sulfate, and the benzene was evaporated *in vacuo*. The residue was distilled under reduced pressure to give Ph_2 (1.5 g; 32%) and Ph_2Se (3.6 g; 50.5%).

Ph_2: mp 69—70 °C; IR 3055, 3025, 1473, 1423, 902, 725, 690 cm^{-1}. These values were identical with those of an authentic sample.

Ph_2Se: bp 106 °C/2 mmHg; IR 3060, 1575, 1475, 1440, 1000, 735 cm^{-1}; MS *m/e* 234 (M^+), 154 (M^+-Se). Found: C, 61.77; H, 4.42%. Calcd for $C_{12}H_{10}Se$; C, 61.81; H, 4.32%.

The chloroform extract afforded $Ph_3Se^+Br^-$ (4.6 g; 37%) upon recrystallization from chloroform–acetone(1:5): mp 236 °C decomposed; IR 3050, 1580, 1430, 990, 765, 745, 734 cm^{-1}; MS *m/e* 234 (M^+-PhBr), 157 (M^+-Ph_2). Found; C, 55.32; H, 3.79%. Calcd for $C_{18}H_{15}SeBr$: C, 55.42; H, 3.88%.

Reaction of PhMgBr with Ph_2SeBr_2. $SeOCl_2$ (5.0 g; 30 mmol) was added to PhMgBr (45 mmol) in ether (100 ml), and the mixture was stirred under reflux for 1 h. After the removal of the ether, the reaction mixtures were treated with HBr (*ca.* 1 mol dm^{-3}), and then crude Ph_2SeBr_2 was precipitated. The crystals were collected and recrystallized from ether to afford Ph_2SeBr_2 (2.4 g; 21.6%): mp 147.5 °C decomposed; IR 1600, 1460, 1150, 990, 738, 681 cm^{-1}. Found: C, 36.62; H, 2.61%. Calcd for $C_{12}H_{10}Br_2Se$: C, 36.67; H, 2.57%.

Ph_2SeBr_2 (12.3 g; 31 mmol) was added to a solution of PhMgBr (31 mmol) in ether (50 ml) at 34 °C, and the mixture was hydrolyzed with HBr (*ca.* 1 mol dm^{-3}) and extracted with benzene and then with chloroform. Ph_2Se (3.5 g; 47.9%), Ph_2 (1.9 g; 42.4%), and unreacted Ph_2SeBr_2 (4.9 g; 40%) were obtained from the benzene extracts. From the chloroform extract, though, no product was obtained.

Reaction of PhMgBr with Ph_2SeO. Ph_2SeO was prepared by the method of Rheinboldt.[14] PhMgBr (60 mmol) was added, drop by drop, over a period of 1 h at 34 °C to an equimolar amount of Ph_2SeO (60 mmol) in ether (50 ml). After the addition, the ether was removed and the residue was hydrolyzed with HBr (*ca.* 1 mol dm^{-3}), and then extracted with benzene and subsequently with chloroform, as has been described above. From the extracts, Ph_2Se (6.2 g; 63.5%), $Ph_3Se^+Br^-$ (5.9 g; 25.2%), and Ph_2 (0.86 g; 10.0%) were afforded.

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6) "Organic Selenium Compound: their Chemistry and Biology," ed by D. L. Klayman and W. H. Gunther, John Wiley & Sons, N. Y. (1973), p. 173.

7) In the opposite addition of $SeOCl_2$ to PhMgX, almost no $Ph_3Se^+X^-$ was formed, but Ph_2Se and Ph_2 were.

8) Anion exchange in selenonium salts is possible using either the solubility differences between these salts or by taking advantage of the insolubility of certain metal salts: "Selenium," ed by R. A. Zingaro and W. C. Cooper, Van Nostrand Reinhold, N. Y. (1974), p. 507.

9) The addition of $MgBr_2$ to $SeOCl_2$ in THF led to a rapid color change indicating the formation of $SeOBr_2$.

10) The deposition of metallic selenium and the liberation of iodine are observed; $SeOI_2$ may be decomposed according to the following equation:

$$2SeOI_2 \longrightarrow SeO_2 + Se + 2I_2.$$

11) About 40% of the starting material, Ph_2SeBr_2, was recovered.

12) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Am. Chem. Soc.*, **73**, 1965 (1951).

13) In the reaction of PhSeO with PhMgBr, benzene is detected by gas chromatography in the light fraction of the resulting mixture, and the resinous residue obtained after the distillation shows a typical ^{13}C-NMR spectrum of polyphenylene. Thus, the direct reduction of Ph_2SeO may take place through the following radical reaction:

$$Ph_2SeO + 2PhMgX \longrightarrow Ph_2Se + 2Ph\cdot + (MgX)_2O,$$

$$n\mathrm{Ph}\cdot \longrightarrow \text{benzene} + \text{polyphenylene}.$$

14) H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.*, **69**, 664 (1947).