

THE REACTION OF DIORGANYL DISELENIDES AND DITELLURIDES WITH ORGANIC MERCURY COMPOUNDS. A CONVENIENT METHOD FOR THE SYNTHESIS OF UNSYMMETRICAL ORGANIC SELENIDES AND TELLURIDES

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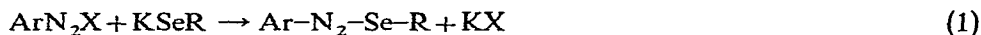
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SUMMARY

The reaction of diphenyl diselenide with di-n-butylmercury in dioxane at refluxing temperature gave n-butyl phenyl selenide (80% yield) and metallic mercury. When the same reaction was carried out at room temperature, n-butyl phenyl selenide and bis(phenylseleno)mercury were obtained. This reaction furnished a convenient method for the preparation of several organic selenides as well as tellurides.

INTRODUCTION

Several methods for preparation of alkyl aryl selenides have been reported. Those most commonly used include the reaction of diazonium salts with a potassium alkaneselenolate [eqns. (1) and (2)], the reaction of an alkyl halide with sodium arylselenolate and the reaction of an aryl selenium monohalide with a Grignard reagent^{1,2}.



Only a few alkyl aryl tellurides have been reported in the literature. They were synthesized using methods similar to those used in the preparation of organic selenides². However, the nucleophilic reaction of the telluride anions with suitable alkyl halides may be a preferable one-step method for the preparation of unsymmetric organic tellurides, such as in the preparation of selenides³. But, this method has not been reported and may not be suitable for the preparations of isoalkyl and tertiary alkyl derivatives *i.e.*, the yields are generally very poor. Moreover, the selenide and telluride anions are readily oxidized in air to the corresponding diselenides and ditellurides.

It has been reported that diaryl diselenides readily form bis(arylseleno)-mercury compounds (Ar-Se-Hg-Se-Ar) in quantitative yield on treatment with metallic mercury at room temperature⁴. We have found that diphenyl selenide reacted readily with dialkylmercury compounds to produce an alkyl phenyl selenide and

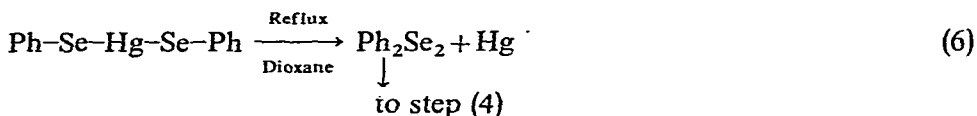
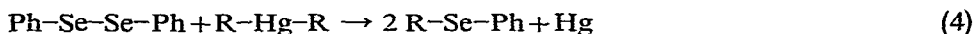


metallic mercury. Diphenyl ditelluride also reacted with dialkylmercury compounds to give alkyl phenyl tellurides. These findings have led to a convenient general method for the synthesis of unsymmetrical organic selenides as well as tellurides. This method is especially suitable for laboratory-scale preparations because the required starting materials are generally stable at room temperature and can be stored for long periods. Some of those compounds also are commercially available.

RESULTS AND DISCUSSION

The preparation of alkyl aryl selenides involved the addition of a dialkylmercury compound in dioxane to an equimolar amount of diphenyl diselenide in dioxane. The mixture was refluxed under a nitrogen atmosphere for several hours. The metallic mercury formed was pipetted out from the reaction system and the solvent was distilled off. The alkyl phenyl selenide thus produced was distilled under reduced pressure.

The reaction was found to proceed even at room temperature. However, in this case, the products were the alkyl phenyl selenide and bis(phenylseleno)mercury [eqns. (4)–(6)]. The mercury compound was stable at room temperature, but decomposed to the parent diselenide and metallic mercury in refluxing dioxane. Thus at reflux, complete conversion of the diselenide to alkyl aryl selenide is achieved



The reaction was applied to the synthesis of a number of organic selenides. The results are summarized in Table 1.

When an organic selenide containing a weak carbon-to-selenium bond was used as the starting material, the C-Se bond was broken and mercuric selenide was

TABLE 1
PREPARATION OF ORGANIC SELENIDES

Product	Reactants	Yield (%)	B.p. [°C(mm)]
n-C ₄ H ₉ SePh	PhSeSePh + (n-C ₄ H ₉) ₂ Hg	80	85 (3) ^a
i-C ₃ H ₇ SePh	PhSeSePh + (i-C ₃ H ₇) ₂ Hg	74	63 (3) ^b
C ₆ H ₅ CH ₂ SePh	PhSeSePh + (C ₆ H ₅ CH ₂) ₂ Hg	72	155 (7) ^c
n-C ₄ H ₉ SeCH ₂ C ₆ H ₅	(n-C ₄ H ₉ Se) ₂ + (C ₆ H ₅ CH ₂) ₂ Hg	70	76 (2) ^d
(C ₆ H ₅ CH ₂) ₂ Se	(C ₆ H ₅ CH ₂ Se) ₂ + (C ₆ H ₅ CH ₂) ₂ Hg	45	

^a Reported⁵: b.p. 105° (5 mm). ^b Ref. 6. ^c Reported⁷: b.p. 201° (15 mm). ^d M.p. 43°; reported⁸: m.p. 45°.

TABLE 2

PREPARATION OF ORGANIC TELLURIDES

Product	Reactants	Yield (%)	B.p. [$^{\circ}\text{C}$ (mm)]
$n\text{-C}_4\text{H}_9\text{TePh}$	$\text{PhTeTePh} + (n\text{-C}_4\text{H}_9)_2\text{Hg}$	75	115 (7)
$i\text{-C}_3\text{H}_7\text{TePh}$	$\text{PhTeTePh} + (i\text{-C}_3\text{H}_7)_2\text{Hg}$	79	83 (7)
$\text{C}_6\text{H}_5\text{CH}_2\text{TePh}$	$\text{PhTeTePh} + (\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}$	^a	

^a The compound was unstable even at room temperature. Other aryl benzyl tellurides, *i.e.*, benzyl *p*-methoxyphenyl telluride, were reported⁹ to be unstable.

produced along with the organic selenide. Thus, when dibenzyl diselenide was allowed to react with dibenzylmercury, dibenzyl selenide was obtained in poor yield and a large amount of dark mercuric selenide precipitated from the solution. The reaction also was not suitable for the preparation of aryl selenides. For example, the reaction between diphenyl diselenide and diphenylmercury did not proceed, even in refluxing dioxane solution. This may be due to the strength of the C–Hg bond in diphenylmercury.

This synthetic procedure was also applied to the preparation of the organic tellurides which are listed in Table 2.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of nitrogen in three-necked flasks of appropriate size equipped with reflux condenser, drying tube, and a magnetic stirring assembly. An oil bath was used for external heating. IR spectra were recorded using a Perkin–Elmer Model 457 spectrometer, and NMR spectra on a Varian Associates A-60 spectrometer, using tetramethylsilane as internal standard. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory. The identification of most products was corroborated by IR and NMR spectral measurements.

Alkyl and aryl diselenides were prepared by the air oxidation in alkaline solution of the corresponding selenols¹. Diphenyl ditelluride was synthesized by the air oxidation of benzenetellurol, which was prepared via the decomposition (by water) of the reaction product of phenylmagnesium bromide with an equimolar amount of tellurium powder in ethyl ether¹⁰. The benzenetellurol was not isolated and directly oxidized in air to diphenyl ditelluride. The ditelluride, yield 60% based on the bromobenzene used, was recrystallized from ethanol, m.p. 61–62 $^{\circ}$, dark orange needles. The organic mercury compounds were obtained from commercial sources and purified by distillation or by recrystallization. Dioxane was purified by distillation and stored over sodium wire.

Reactions of organic diselenides and ditellurides with diorganomercury compounds

A typical procedure for the reaction of a diselenide or ditelluride with organic mercury compounds is as follows: To a solution of 3.1 g (~ 0.01 mole) of PhSeSePh in 15 ml of dioxane at room temperature was added slowly, with stirring, 3.1 g (~ 0.01 mole), $(n\text{-C}_4\text{H}_9)_2\text{Hg}$ in 10 ml of dioxane. After completion of the addition

(30–40 min), the mixture was heated at reflux temperature for 3 h. Metallic mercury was produced. The reaction mixture was allowed to cool to room temperature and then the mercury was pipetted out. After the dioxane was distilled off, the product, $n\text{-C}_4\text{H}_9\text{SePh}$ (3.2 g, yield 80%) was distilled at $85^\circ/3$ mm (lit.⁴ $105^\circ/5$ mm). When this reaction was carried out at room temperature for 5 h, $n\text{-C}_4\text{H}_9\text{SePh}$, 2.5 g, was obtained. The residue from the distillation was treated with tetrahydrofuran and pure $(\text{PhSe})_2\text{Hg}$ (2.2 g) was obtained from the solution by recrystallization, m.p. $152\text{--}153^\circ$ (lit. 152°)¹¹. (Found: C, 28.57; H, 2.25; Hg, 38.46; Se, 31.40. $(\text{C}_6\text{H}_5\text{Se})_2\text{Hg}$ calcd.: C, 28.14; H, 1.96; Hg, 39.06; Se, 30.86%.)

The elemental analyses of new compounds are listed in Table 3.

TABLE 3
ELEMENTAL ANALYSES

Formula	Calcd. (%)				Found (%)			
	C	H	Se	Te	C	H	Se	Te
$i\text{-C}_3\text{H}_7\text{SePh}$	53.80	6.09	40.10		53.21	5.80	40.70	
$n\text{-C}_4\text{H}_9\text{SeCH}_2\text{C}_6\text{H}_5$	58.14	7.04	34.80		57.56	6.90	35.20	
$i\text{-C}_3\text{H}_7\text{TePh}$	43.61	4.85		51.53	43.20	4.50		51.70
$n\text{-C}_4\text{H}_9\text{TePh}$	45.87	5.35		48.77	45.28	5.08		49.20

Reactions of organic diselenides and ditellurides with Mercury. Decomposition of bis(organo)seleno- and bis(organo)telluro)mercury

To a solution of 2.0 g (~ 0.007 mole) of PhSeSePh in 20 ml of dioxane was added 2.0 g metallic mercury. The solution was vigorously shaken under nitrogen

TABLE 4
NMR SPECTRA OF DIORGANOSELENIDES AND -TELLURIDES IN CCl_4

Compounds	Chemical shift (τ)	
	Alkyl protons	Aryl protons
$n\text{-C}_4\text{H}_9\text{SePh}$	7.18 (t, 2H), J 15 Hz 8.15–8.90 (m, 4H) 9.05 (d, 3H), J 13 Hz	2.47–2.70 (m, 2H) 2.75–2.98 (m, 3H)
$i\text{-C}_3\text{H}_7\text{SePh}$	6.39–6.92 (m, 1H) 8.62 (d, 6H), J 13 Hz	2.33–2.66 (m, 2H) 2.70–2.92 (m, 3H)
$\text{C}_6\text{H}_5\text{CH}_2\text{SePh}$	6.00 (s, 2H)	2.50–3.00 (m, 10H)
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Se}$	6.44 (s, 4H)	2.87 (s, 10H)
$n\text{-C}_4\text{H}_9\text{SeCH}_2\text{C}_6\text{H}_5$	5.75 (s, 2H) 7.62 (t, 2H), J 15 Hz 8.30–8.87 (m, 4H) 9.15 (d, 3H), J 12 Hz	2.80 (s, 5H)
$n\text{-C}_4\text{H}_9\text{TePh}$	7.15 (t, 2H), J 15 Hz 7.95–8.87 (m, 4H) 9.08 (d, 3H), J 10 Hz	2.08–2.42 (m, 2H) 2.76–2.92 (m, 3H)
$i\text{-C}_3\text{H}_7\text{TePh}$	6.45–6.92 (m, 1H) 8.70 (d, 6H), J 13 Hz	2.39–2.59 (m, 2H) 2.73–2.95 (m, 3H)

atmosphere for 30 min. A pale yellow solid, $(\text{PhSe})_2\text{Hg}$, 2.9 g (85% yield) was precipitated from the solution. The reaction also proceeded in benzene or toluene.

Bis(phenyltelluro)mercury, 2.5 g (83% yield), was also prepared from diphenyl ditelluride, 2.0 g (0.005 moles), with metallic mercury, 2.0 g, in 20 ml benzene. (Found: C, 23.93; H, 2.02; Hg, 33.04; Te, 40.88. $(\text{C}_6\text{H}_5\text{Te})_2\text{Hg}$ calcd.: C, 23.63; H, 1.64; Hg, 32.83; Te, 41.89%.)

Bis(phenylseleno)mercury, 2.0 g was added into 20 ml dioxane. The compound dissolved completely at the reflux temperature. The solution was refluxed under a nitrogen atmosphere. Metallic mercury was produced slowly. After 2 h, 0.3 g (40% yield) of metallic mercury was isolated. Similar results were also observed for $(\text{PhTe})_2\text{-Hg}$ (62% yield of mercury).

The NMR spectra of the organic selenides and tellurides prepared are summarized in Table 4.

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