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The Reaction of Benzeneseleninic Acid with Olefins in Acetic Acid. A New Method of Acetoxyselenation

Noritaka Miyoshi, Yoshitsugu Takai, Shinji Murai, and Noboru Sonoda*
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

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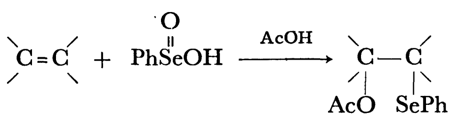
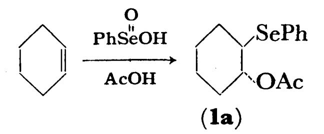
Synopsis. The reaction of benzeneseleninic acid with olefins in acetic acid gave 2-acetoxyalkyl phenyl selenides in good yields.

During the course of studies on oxyselenation,[1,2] a new and convenient method was found for the synthesis of 2-acetoxyalkyl phenyl selenides by use of benzeneseleninic acid.[3] The acetoxyselenation was carried out



(1)

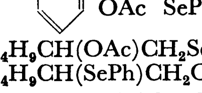
by heating in acetic acid an equimolar mixture of olefin and benzeneseleninic acid, prepared from diphenyl diselenide by the procedure of Ayrey *et al.*[4] Acetoxyselenated products, 2-acetoxyalkyl phenyl selenides (**1**), were easily isolated by distillation under reduced pressure in good yields. The results of acetoxyselenation of cyclohexene, styrene, 1-hexene, and 1-octene are given in Table 1. The structure of (**1**) was determined by spectroscopic methods and elemental analyses. The reaction of cyclohexene with benzeneseleninic acid in acetic acid at 80 °C gave *trans*-2-acetoxycyclohexyl phenyl selenide (**1a**) as the sole product (Eq. 2). In the acetoxyselenation of styrene, addition of the phenylseleno group occurred selectively at the terminal methylene carbon atom to give 2-acetoxy-2-phenylethyl phenyl selenide (**1b**), whereas a similar reaction of aliphatic terminal olefin such as 1-hexene or 1-octene gave two isomers, the primary selenide as a major product and the secondary selenide as shown below.

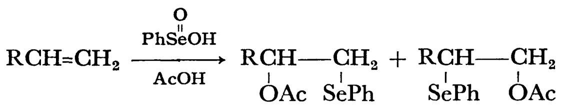


(**1a**)

(2)

Table 1. Reaction of benzeneseleninic acid with olefins in acetic acid

Olefin	Acetoxyselenated product (**1**)		Yield (%)
Cyclohexene	 **1a**		81
Styrene	 **1b**		80
1-Hexene	n-$C_4H_9CH(OAc)CH_2SePh$ **1c** n-$C_4H_9CH(SePh)CH_2OAc$ **1d**	[82:18]	87
1-Octene	n-$C_6H_{13}CH(OAc)CH_2SePh$ **1e** n-$C_6H_{13}CH(SePh)CH_2OAc$ **1f**	[86:14]	86



$$RCH{=}CH_2 \xrightarrow[\text{AcOH}]{\text{PhSeOH}} \underset{\text{OAc}}{RCH}{-}\underset{\text{SePh}}{CH_2} + \underset{\text{SePh}}{RCH}{-}\underset{\text{OAc}}{CH_2} \quad (3)$$

$R = n$-C_4H_9, n-C_6H_{13}

It is likely that the attack of phenylselenenyl acetate (PhSeOAc)[5] to olefinic double bond takes place judging from the cationic mode of addition of phenylseleno group observed in the present acetoxyselenation. The destiny of the oxygen atom which was originally bonded to the selenium atom of the seleninic acid is not clear. However, evolution of a considerable amount of carbon dioxide (one fifth moles per one mole of the seleninic acid used) was observed in all cases. Oxidation of the solvent seems likely to take place concurrently.

Considerable interest has developed in the chemistry of selenoxide,[6] the syn elimination of phenyl selenoxide having recently been found to be a convenient and high-yield method for the preparation of various olefinic compounds.[7] The present oxyselenation may provide a useful procedure for the preparation of the precursor of an allyl acetate[8] from olefin.

Experimental

Materials. Commercial olefins (styrene, 1-hexene and 1-octene) were purified by distillation before use. Cyclohexene was prepared by the dehydration of cyclohexanol.[9] Benzeneseleninic acid was prepared from diphenyl diselenide according to the procedure of Ayrey *et al.*[4]

Apparatus. IR spectra were measured with a Shimalzu Model IR-27C grating infrared spectrometer, proton NMR spectra with a JEOL Model JNM-3H-60 and JNM-PS-100 using tetrachloromethane as a solvent and tetramethylsilane (TMS) as an internal standard, and mass spectra with a Hitachi Model RM-60 mass spectrometer operating at 70 eV.

Reaction of Cyclohexene with Benzeneseleninic Acid. A solution of cyclohexene(10 mmol, 0.82g) and benzeneseleninic acid(10 mmol, 1.90 g) in acetic acid (30 ml) was heated at 80 °C for 24 h under stirring. After completion of the reaction, evaporation of acetic acid gave a dark orange oil, which was purified by distillation to give 2-acetoxycyclohexyl phenyl selenide(**1a**, 2.41 g, 81%), bp 137—138 °C/1 Torr; Found: 56.52; H, 6.26%. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10%. IR (neat), 1740 cm^{-1} ($\nu_{C=O}$). MS *m/e*, 298 (M$^+$), 238 (M$^+$−AcOH). NMR (100 MHz) δ 1.92 (3H, s, OC(=O)C$\underline{H}_3$), 1.36—2.06 (8H, m, ring methylene), 3.12 (1H, d-t, J=4.1 and 9.2 Hz, C$\underline{H}$SePh), 4.72 (1H, d-t, J=4.1 and 9.2 Hz, C$\underline{H}$OAc), 7.15—7.40 (3H, m, phenyl), 7.40—7.56 (2H, m, phenyl).

Reaction of Styrene with Benzeneseleninic Acid. A solution of styrene (10 mmol, 1.04 g) and benzeneseleninic acid (10 mmol, 1.90 g) in acetic acid (30 ml) was heated at 80° for 24 h under stirring. Removal of the solvent gave a dark orange oil, which was purified by distillation to give 2-acetoxy-2-phenylethyl phenyl selenide (**1b**, 2.56 g, 80%), bp 166—167 °C/0.5

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* To whom correspondence should be addressed.

Torr; Found: C, 59.89; H, 5.19%. Calcd for $C_{16}H_{16}O_2Se$: C, 60.19; H, 5.05%. IR (neat), 1748 cm^{-1}. MS *m/e* 320 (M^+), 260 (M^+-AcOH). NMR (60 MHz) δ 1.96 (3H, s, $OC(=O)C\underline{H}_3$), 3.16 (1H, d-d, $J=6$ Hz, $C\underline{H}_2SePh$), 3.22 (1H, d, $J=7.5$ Hz, $C\underline{H}_2SePh$), 5.83 (1H, d-d, $J=6$ and 7.5 Hz, $C\underline{H}OAc$), 7.14—7.55 (10H, m, phenyl).

Reaction of 1-Hexene with Benzeneseleninic Acid. A solution of 1-hexene (10 mmol, 0.84 g) and benzeneseleninic Acid (10 mmol, 1.90 g) in acetic acid (30 ml) was heated at 80 °C for 24 h under stirring. Removal of the solvent by distillation gave a dark orange oil, which was distilled under reduced pressure to give a mixture of isomeric acetoxyselenated products (2.60 g) [Table 1], bp 122—134 °C/0.6 Torr; MS *m/e* 300 (M^+), 240 (M^+-AcOH). Found: C, 55.92; H, 6.75%. Calcd for $C_{14}H_{20}O_2Se$: C, 56.19; H, 6.74%. The NMR spectrum of the distillate showed the presence of two isomers. 2-Acetoxyhexyl phenyl selenide (**1c**) was isolated by repeated distillation of the mixture. Attempts to isolate **1d** were unsuccessful. NMR (CCl_4) of **1c**; δ 1.92 (3H, s, $OC(=O)C\underline{H}_3$), 0.70—0.90 (9H, m, n-$C_4\underline{H}_9$), 2.99 (2H, d, $J=6$ Hz, $C\underline{H}_2SePh$), 4.90—5.15 (1H, quintet centered at δ 4.93, $J=6$ Hz, $C\underline{H}OAc$). 2-(Phenylseleno)hexyl acetate (**1d**) was characterized by analysis of the NMR spectrum of a mixture of **1c** and **1d**. The methine (CHSePh) and methylene (CH_2-OAc) signals of **1d** were observed at δ 3.32—3.60 (m, 1H) and δ 4.00—4.40 (m, 2H), respectively. The amount of **1d** in the mixture of two isomers was estimated from the NMR spectrum of the mixture by comparison of the integrated peak area of methylene of **1c** (d, δ 2.99, $C\underline{H}_2SePh$) with that of **1d** (m, δ 4.00—4.40, $C\underline{H}_2OAc$). The NMR spectrum of the mixture of two isomers (**1c** and **1d**) showed the ratio of **1c**: **1d** to be 82: 18.

Reaction of 1-Octene with Benzeneseleninic Acid. A solution of 1-octene (10 mmol, 1.02 g) and benzeneseleninic acid (10 mmol, 1.90 g) in acetic acid (30 ml) was heated at 80 °C for 24 h under stirring. Removal of the solvent by distillation gave a dark orange oil, which was distilled under reduced pressure to give a mixture of isomeric acetoxyselenated products (2.82 g) [Table 1], bp 135—148 °C/0.8 Torr; MS *m/e* 328 (M^+), 268 (M^+-AcOH). Found: C, 58.54; H, 7.67%. Calcd for $C_{16}H_{24}O_2Se$: C, 58.71; H, 7.39%. The NMR spectrum of the distillate showed the presence of two isomers. 2-Acetoxyoctyl phenyl selenide (**1e**) was isolated by repeated distillation of the mixture. Attempts to isolate **1f** were unsuccessful. NMR (CCl_4) of **1e**; δ 1.93 (3H, s, $OC(=O)C\underline{H}_3$), 0.90—2.15 (13H, m, n-C_6H_{13}), 2.98 (2H, d, $J=6$ Hz, $C\underline{H}_2SePH$), 4.70—5.15 (1H, quintet centered at δ 4.92, $C\underline{H}OAc$), 7.11—7.50 (5H, m, phenyl). 2-(Phenylseleno)octyl acetate (**1f**) was characterized on the basis of the NMR spectrum of a mixture of **1e** and **1f**. The methine ($C\underline{H}SePh$) and methylene ($C\underline{H}_2$-OAc) signals of **1f** were observed at δ 3.30—3.70 (m, 1H) and δ 4.00—4.40 (m, 2H), respectively. The amount of **1f** in the mixture of two isomers was estimated from the NMR spectrum of the mixture by comparison of the integrated peak area of methylene of **1e** (d, δ 2.98, $C\underline{H}_2SePh$) with that of **1f** (m, δ 4.00—4.40, $C\underline{H}_2OAc$). The NMR spectrum of the mixture of two isomers (**1e** and **1f**) showed the ratio of **1e**: **1f** to be 86: 14.

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