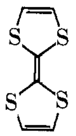

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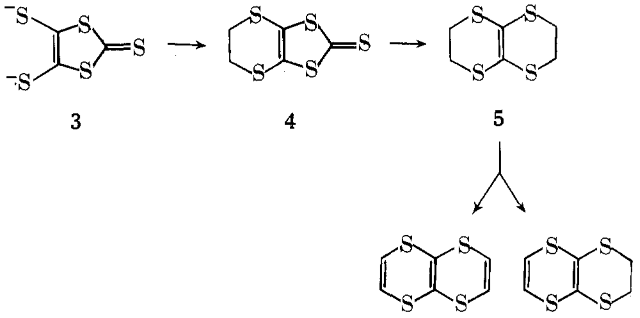

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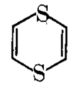

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oxidative behavior is directly provided by polarographic measurements. Whereas **1** is reversibly oxidized with values of 0.006 V and 0.385 V for $E_{1/2}{}^1$ and $E_{1/2}{}^2$, **2** is oxidized with corresponding values of 0.561 V and 0.965 V, where the second oxidation step occurs irreversibly.[5] This lack of relative ease to oxidize **2** hinders its use as a donor cation in highly conducting organic metals.

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References and Notes

(1) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).

(2) The more cumbersome systematic name of **2** is 1,4-dithiino[2,3-*b*]-1,4-dithiin. Satisfactory elemental analyses were obtained for compounds **2**, **4**, **5**, and **6**.

(3) S. Wawzonek and S. M. Heilmann, *J. Org. Chem.*, **39**, 511 (1974).

(4) W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. M. Curtis, and W. L. Lipscomb, *J. Am. Chem. Soc.*, **76**, 4957 (1954).

(5) Measured in CH_3CN with tetraethylammonium perchlorate (0.05 M) added vs. Ag/Ag^+ (0.1 N in CH_3CN) with a glassy carbon electrode (GCE) as the working electrode.

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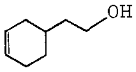
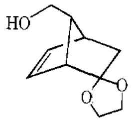
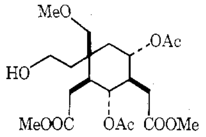
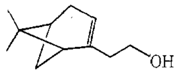
Organoselenium Chemistry. A Facile One-Step Synthesis of Alkyl Aryl Selenides from Alcohols

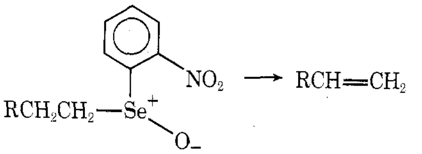
Summary: Treatment of alcohols with aryl selenocyanates in either tetrahydrofuran or pyridine containing tributylphosphine results in high yields of alkyl aryl selenides.

Sir: Substituents on the β and/or γ carbons of primary alkyl phenyl selenoxides result in low yields of terminal olefins. Recently it was demonstrated[1,2] that primary alkyl *o*-nitrophenyl selenoxides undergo facile elimination with formation of terminal olefins in high yield (eq 1). For example, the *o*-nitrophenyl selenoxide derived from cyclohexylmethanol provides a twofold increase in the yield of *exo*-methylenecyclohexane as compared to the corresponding phenyl selenoxide.[1] *o*-Nitrophenyl selenoxides are generated by oxidation of the corresponding alkyl *o*-nitrophenyl selenides which are prepared by displacement of alkyl tosylates, mesylates, or halides with the corresponding selenium anion (eq 2). The *o*-nitrophenyl selenium anion is generated by treatment of *o*-nitrophenyl selenocyanate with sodium borohydride in either absolute ethanol[1] or dimethylformamide[2b] (eq 2). We wish to describe in this communication the direct one-step conversion of alcohols to alkyl aryl selenides (eq 3).

Table I. Conversion of Alcohols to Alkyl *o*-Nitrophenyl Selenides

Compound	% yield of selenide[a–c] in pyridine	% yield of selenide[a–c] in THF
1-Dodecanol	92	94
1-Heptanol	85	
3-Hexyn-1-ol	93	88
Benzyl alcohol	97	93
Cyclohexylmethanol	99	88
	98	95
	91	90
		91
	98	85
2-Propanol	93	
Cyclooctanol		63

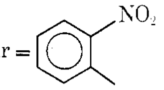
[a] All compounds were fully characterized by spectral methods. [b] Yields reported are for isolated, chromatographically pure substances. [c] All reactions were performed at room temperature in the presence of the indicated solvent.



(1)

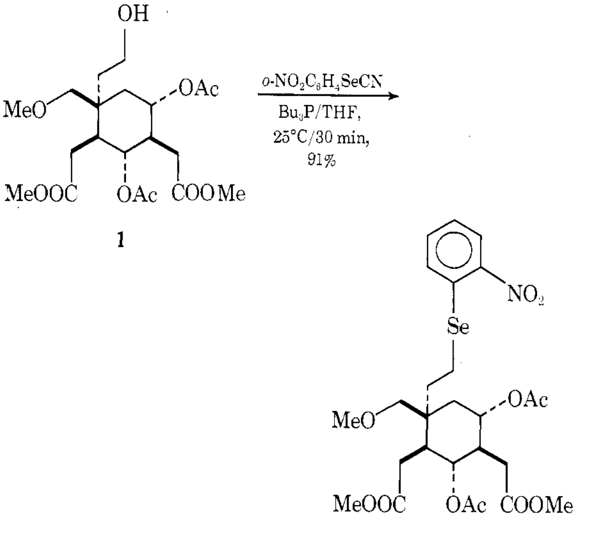
$$ArSeCN \xrightarrow[\text{EtOH or DMF}]{BH_4^-} [ArSe^-] \xrightarrow{RCH_2X} ArSeCH_2R \xrightarrow[\text{THF}]{H_2O_2} ArSe^+(O^-)CH_2R \quad (2)$$

Ar =



$$RCH_2OH \xrightarrow[\text{THF or pyridine}]{ArSeCN/Bu_3P} RCH_2SeAr \quad (3)$$

Treatment of a variety of primary alcohols with *o*-nitrophenyl selenocyanate[3] in tetrahydrofuran or pyridine at room temperature in the presence of tri-*n*-butylphosphine results in very high yields of primary alkyl selenides (see Table I). The method obviates the necessity of preforming the mesylate, tosylate, or halide and avoids the use of borohydride in ethanol or dimethylformamide to generate the selenium anion. The method is best illustrated by the conversion of the highly functionalized primary alcohol 1 to selenide **2** (eq 4) which results in a 91% yield of chromatographically pure material. It should be pointed out that the two-step procedure involving mesylation and displacement by selenium proceeds at best in only 77% yield.



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2

(4)

The one-step conversion of alcohols to selenides by the above method was not successful with di-*o*-nitrophenyl diselenide,[4] diphenyl diselenide, or phenylselenenyl chloride. A reaction however does take place with phenyl selenocyanate. For example, treatment of dodecanol with phenyl selenocyanate[5] (1.2 equiv) in tetrahydrofuran containing tri-*n*-butylphosphine (1.2 equiv) resulted in a 92% yield of dodecyl phenyl selenide (eq 5).

$$CH_3(CH_2)_{10}CH_2OH \xrightarrow[\text{THF}]{\text{PhSeCN/Bu}_3\text{P}} CH_3(CH_2)_{10}CH_2SePh \qquad (5)$$

The reaction of secondary alcohols with *o*-nitrophenyl selenocyanate to give secondary alkyl selenides can be performed in reasonable yield as illustrated in Table I for 2-propanol and cyclooctanol. Phenyl selenocyanate can be employed for the conversion of secondary alcohols to alkyl phenyl selenides; e.g., 2-propanol was converted in 85% yield to isopropyl phenyl selenide.

The above reactions can be rationalized as indicated in eq 6–8 by formation of a selenophosphonium salt which reacts with the alcohol providing an oxaphosphonium salt. Reaction of the aryl selenium anion with the oxaphosphonium species provides the corresponding alkyl aryl selenide plus tributylphosphine oxide. We cannot at this time rule out the intermediacy of $Bu_3P^+CN\ ArSe^-$.

$$ArSeCN + Bu_3P \rightarrow ArSe\overset{+}{P}Bu_3\ CN^- \qquad (6)$$

$$ArSe\overset{+}{P}Bu_3\ CN^- + RCH_2OH \rightarrow RCH_2O\overset{+}{P}Bu_3 + HCN + ArSe^- \qquad (7)$$

$$RCH_2O\overset{+}{P}Bu_3 + ArSe^- \rightarrow RCH_2SeAr + Bu_3P{=}O \qquad (8)$$

The following experimental procedure indicates the simplicity of this convenient method. A solution of dodecanol (115 mg, 0.62 mmol) in 2.0 ml of tetrahydrofuran containing *o*-nitrophenyl selenocyanate (168 mg, 0.74 mmol) under nitrogen was treated dropwise with tri-*n*-butylphosphine (150 mg, 0.74 mmol) at room temperature. After the reaction was stirred for 30 min, the solvent was removed in vacuo. Chromatography of the residue on silica gel using hexane–ether (3:1) gave 214 mg (94%) of dodecyl *o*-nitrophenyl selenide as a yellow crystalline compound: mp 43–44 °C; ir ν_{CHCl_3} 1518, 1332 cm^{-1}; NMR δ_{CDCl_3} 0.88 (t, 3 H), 1.15–2.20 (m, 20 H), 2.91 (t, 2 H), 7.10–7.65 (m, 3 H), 8.27 (d, 1 H).

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(1) K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40**, 947 (1975).

(2) For application of the *o*-nitrophenyl selenoxide elimination to natural product synthesis, see (a) P. A. Grieco, Y. Masaki, and D. Boxler, *J. Am. Chem. Soc.*, **97**, 1597 (1975); (b) P. A. Grieco, J. A. Noguez, and Y. Masaki, *Tetrahedron Lett.*, 4213 (1975).

(3) H. Bauer, *Ber.*, **46**, 92 (1913).

(4) Di-*o*-nitrophenyl diselenide is prepared from *o*-nitrophenyl selenocyanate which is readily available in one step from *o*-nitroaniline according to the procedure of Bauer.[3]

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(6) Fellow of the Alfred P. Sloan Foundation, 1974–1976.

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