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A CONVENIENT SYNTHESIS OF PHENYL SELENOCYANATE

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Treatment of benzeneselenenyl chloride with trimethylsilyl cyanide in various organic solvents provided phenyl selenocyanate in virtually quantitative yield. The reaction presents a very simple preparation of the useful selenenylation agent.

Organic synthesis using organoselenium compounds is of current interest because of the facilities of transformations of these compounds to effect selective functional group interconversion.1) Among them, phenyl selenocyanate (1) occupies a unique position; it is used successfully for selective conversion of primary2) and secondary2),3) alcohols into corresponding selenides *via* S_n2 mechanism3) and aldehydes4) and carboxylic acids5) are converted into cyanoselenides and selenocarboxylate in high yields, respectively(Eq. 1-3). More recently, a high-yield copper-catalyzed oxyselenenylation of olefins using 1 has been reported.6)

$$\mathrm{ROH} \xrightarrow{\mathrm{PhSeCN}\ (1)} \mathrm{RSePh} \qquad (1)$$

$$\mathrm{RCHO} \longrightarrow \mathrm{RCH(CN)SePh} \qquad (2)$$

$$\mathrm{RCOOH} \longrightarrow \mathrm{RCOSePh} \qquad (3)$$

Current method for the preparation of 1 employs diazo reaction.7) This requires two consecutive steps and tedious purification procedure(ethereal extraction and fractional distillation) which presents a nuisance not only because of unpleasant odor of 18) but also because of the fatal low yield of the reaction. Herein we report a very simple synthesis of 1, which provides 1 in virtually quantitative yield.

As shown in eq. 4, treatment of benzeneselenenyl chloride9) with 20% excess trimethylsilyl cyanide10) in dry tetrahydrofuran or in dry dichloromethane at room temperature for 5 to 10 min afforded a 96% yield of 1 after evaporation of solvent and the trimethylsilyl chloride produced.11) The

$$\mathrm{PhSeCl} \quad + \quad (\mathrm{CH_3})_3\mathrm{SiCN} \longrightarrow \mathrm{PhSeCN} \quad + \quad (\mathrm{CH_3})_3\mathrm{SiCl} \qquad (4)$$

phenyl selenocyanate thus obtained as a light yellow oil12) is sufficiently pure for most practical purposes as shown by thin layer chromatographic analysis.13) This new method is particularly attractive for small-scale laboratory operations. Experimental details are as following:

Synthesis of Phenyl Selenocyanate: A solution of benzeneselenenyl chloride(212 mg, 1.11 mmol)[9)] in dry THF(distilled from sodium diphenylketyl under argon, 2 ml) was added dropwise over 3 min to a solution of trimethylsilyl cyanide(131 mg, 1.33 mmol)[10)] in dry THF(2 ml) with stirring at room temperature under argon. After addition, the mixture was stirred for 10 min and the system was evacuated to remove all volatile components, leaving 194 mg of practically pure phenyl selenocyanate (1) as a light yellow oil(96% yield); bp 104 °C/ 4 torr(lit[7)] bp 118 °C/11 torr); IR(liquid film) 3312(w), 2120(m, CN), 1564 (m), 1470(s), 1431(s) cm^{-1}; ^{1}H-NMR($CDCl_3$) δ=7.39(multiplet, 5H); ^{13}C-NMR($CDCl_3$) δ=132.7(d), 130.4(d), 129.7(d), 121.8(s), 101.4(s). If analytically pure 1 is desired, silica-gel column chromatography eluting with a hexane-dichloromethane(2:1) mixture or simple distillation under reduced pressure using Kugel-rohr is recommended.

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10) Prepared from trimethylsilyl chloride and silver cyanide; D.A. Evans, G.L. Carrol, and L.K. Truesdal, J. Org. Chem., 39, 914(1974). This reagent is commercially available from Aldrich Chem. Co.,New Jersey, U.S.A. More economical syntheses of this reagent appeared recently in; a) J.K. Rasmussen and S.M. Heilman, Synthesis, 1979, 523; b) S. Hünig and G. Wehner, ibid, 1979, 522.
11) The reaction in acetonitrile at room temperature was extremely fast and afforded slightly less clean product mixture. In this case the temperature had to be lowered to -20 °C in order to minimize side reactions.
12) Compound 1 was identified by comparison of spectral data(IR and NMR) and physical constants(bp and TLC) with those of an authentic sample prepared according to reference 7.
13) The only minor impurity(less than 4%) was identified as diphenyl diselenide by TLC and IR spectral comparison with an authentic sample.

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