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SELENOCYANATION USING A COMBINED REAGENT OF TRIPHENYLPHOSPHINE AND SELENOCYANOGEN. A NEW AND SIMPLE SYNTHESIS OF ALKYL SELENOCYANATES AND SYMMETRICAL ALKYL DISELENIDES FROM ALCOHOLS

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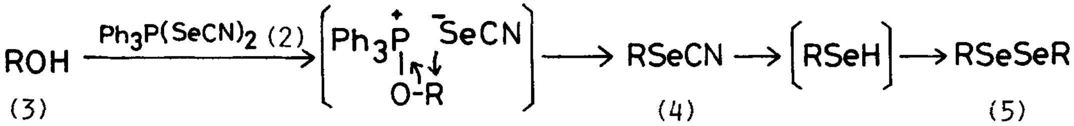
Summary: A novel reagent $Ph_3P(SeCN)_2$, easily prepared by adding an equimolar amount of triphenylphosphine to selenocyanogen solution in methylene chloride and tetrahydrofuran reacts below -60° with primary alcohols to produce directly the corresponding alkyl selenocyanates and alkyl diselenides in good yields. With secondary alcohols mixtures of selenocyanates and isoselenocyanates are obtained, while tertiary alcohols fail to react with the reagent.

The potential use of $Ph_3P(SCN)_2$ (1) as useful reagents has recently been demonstrated. Not only does (1) serve as reagents for thiocyanation or isothiocyanation of alcohols[1], carboxylic acids[1,2] and epoxides[3], but for thiocarbamoylation of amines[4] and cyanation of indoles[1]. We have now prepared the corresponding selenium reagent $Ph_3P(SeCN)_2$ (2) from triphenylphosphine and selenocyanogen and found that reaction of (2) with primary alcohols (3) provides a general one-pot method for preparing alkyl selenocyanates (4) and alkyl diselenides (5), which are versatile intermediates for the organoselenium compounds[5].



In a typical reaction, a solution of benzyl alcohol (3a, 2 mmole) in methylene chloride (10 ml) was added to freshly prepared (2) in THF—CH_2Cl_2 (ca. 3 mmole)[6,7] at -60°. The mixture was stirred for 4 hr at the same temperature, allowed to warm to room temperature. Concentration of the reaction mixture *in vacuo* followed by chromatography on Silica-gel (elution with benzene: n-hexane=1:1) gave benzyl selenocyanate (4a) in 86% yield. Instead of concentration, treatment of the reaction mixture with a solution of KOH-MeOH (5%, 10 ml) for 2 hr followed by neutralization with hydrogen chloride, and purification of the extract by column chromatography on Silica-gel (elution with n-hexane) gave benzyl diselenide (5a) in 90% yield[8]. In a similar manner, a number of other primary alcohols (3b-e) were directly converted to the corresponding alkyl selenocyanates (4b-e) and alkyl diselenides (5b-e). In contrast to the primary alcohols, the reagent reacted with secondary alcohols to give a mixture of selenocyanates and isoselenocyanates [e.g., cyclopentyl alcohol: cyclopentyl selenocyanate (66%) and cyclopentyl isoselenocyanate (13%), cyclooctyl alcohol: cyclooctyl selenocyanate (66%) and cyclooctyl isoselenocyanate (12%)], while it failed to react with tertiary alcohols.

Although many methods for alkyl selenocyanates (4)[9] and alkyl diselenides (5)[10] have been reported from the various compounds, the present one-pot method from alcohols (3) is the most simplified, mild and facile procedure, giving (4) and (5) in good yields.

Table

R	Yield(%)* of RSeCN(4)**	mp(from) or bp(mmHg)***	Lit.	Yield(%)* of RSeSeR(5)**	mp(from) or bp(mmHg)***	Lit.
a) $C_6H_5CH_2$	86	70-71° (n-hexane)	71.5°[9g]	90	91.5-93° (EtOH)	92°[10e]
b) p-$ClC_6H_4CH_2$	76	55-57° (n-hexane)	—	72	76.5-77.5° (EtOH)	76°[10e]
c) p-$CH_3OC_6H_4CH_2$	81	55-56° (n-hexane)	—	69	71-72.5° (EtOH)	72°[10e]
d) $CH_3(CH_2)_5$	61	120-125°(15)	114°(13)[9c]	62	150-155°(7)	148°(11)[10e]
e) $CH_3(CH_2)_9$	51	105-110°(0.3)	97-98°(0.2)[9c]	76	185-193°(0.26)	13-14°[8a]

* Yields (%) are based on the alcohols (3) used.
** All products gave satisfactory spectral and physical data.
*** Bath temperatures are provided.

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