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SYNTHETIC ROUTES TO α-SELENOACETALS, α-SELENONIO SULFIDES, α-SELENONIO ETHERS, α-SELENONIO AMINE AND α-SELENONIO SILANE.(1)

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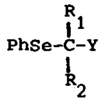
Compounds with the general formula I should be potent intermediates in organic synthesis; for instance C-Se bond cleavage (1, 2, 3, 4, 5, 6) in some of these compounds has been used for connective (7) synthesis of allyl alcohols (3, 4) or epoxides (5, 6). Nevertheless only a few routes to such compounds have been yet disclosed : 1 (2); 2 (1,4); 4 (8).

I 

$$\mathrm{PhSe{-}}\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{\mathrm{C}}}\mathrm{{-}Y}$$

1 Y = SeR

2 Y = SR

3 Y = OR

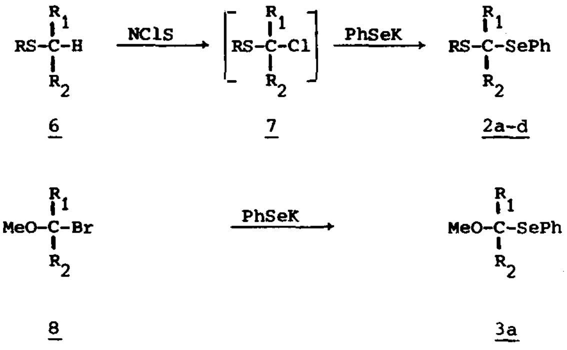
4 Y = NR_2

5 Y = $SiMe_3$

This communication reports new routes to selenoacetals 1, α-selenonio sulfides 2, and α-selenonio amines 4 as well as the first synthesis of α-selenonio ethers 3 and an α-selenonio silane 5. Among the possible pathways, we focus our attention on the five following synthons illustrated in schemes I, II, III, IV and V.

First we found that α-phenyl selenonio sulfides 2 and the α-phenyl selenonio ether 3a can be conveniently prepared by reacting the highly nucleophilic potassium selenophenate with α-chloro sulfide 7 or α-bromo ether 8 in ethanol, water or DMF (25°C, 1 → 12 hrs) (Scheme I).

Scheme I

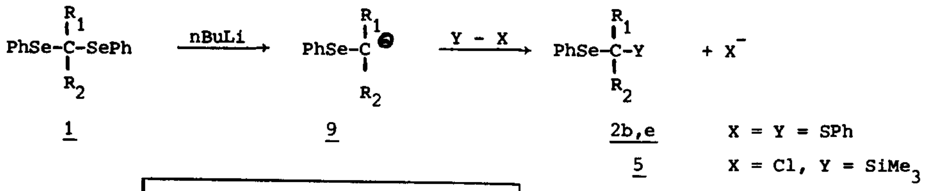


	R	R_1	R_2	Yield %	Solvent
2a	Ph	H	H	65	DMF
2b	Ph	H	CH_3	73	H_2O
				78	DMF
2c	Ph	CH_3	CH_3	50	DMF
2d	CH_3	H	H	76	C_2H_5OH
3a		H	H	80	C_2H_5OH

The α-chloro sulfides 7a, 7b and 7c were conveniently prepared from the corresponding sulfide 6 by action of N-chlorosuccinimide in carbon tetrachloride (9), however the α-chloro sulfide 7e (R_1=CH_3 , R_2=C_2H_5) cannot be prepared by this way (10).

We also successfully tried the route outlined in the scheme II, which takes advantage of the ready cleavage of selenoacetals 1 with N-Butyllithium (-78°C, THF, 1 hr) (3,4) leading to α-selenonio carbanions 9, which in turn can be trapped by diphenyl disulfide (4) to produce, α-selenonio sulfide 2 or by chlorotrimethyl silane to yield α-selenonio silane 5 (scheme II).

Scheme II

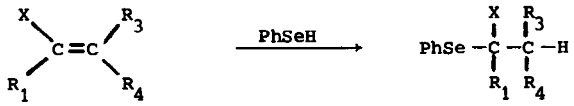


	R_1	R_2	yield %
2b	H	CH_3	55
2e	CH_3	C_2H_5	50
5	CH_3	CH_3	75

The α-phenyl selenonio sulfide 2e, which cannot be prepared according to scheme I (10), was readily obtained following this way.

We also found that the highly acidic selenophenol adds to a variety of nucleophilic double bonds (scheme III) : an α-selenonio sulfide 2f and α-selenonio ethers 3b,c, were obtained in high yield starting from the corresponding vinyl sulfide or vinyl ether.

Scheme III

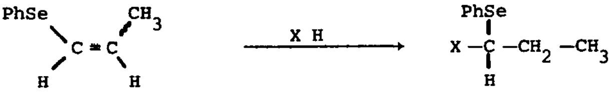


X = SR 2 ; X = OR 3.

	R_1	R_2	R_3	X	Yield %	Conditions
3b	H	H	$-CH_2(CH_2)_2-O-$		90	neat, p-toluene sulfonic acid as catalyst. 5mn. (exothermic)
3c	H	H	H	OC_2H_5	90	" " " "
2f	H	CH_3	H	SPh	75	neat, [BF_3 :etherate] as catalyst. 5 mn. (exothermic).

α-Selenonio sulfide 2f or selenoacetal 1d are produced in good yield by addition of thiophenol or selenophenol on vinyl phenyl selenide 10 (scheme IV). In this case the double bond of 10 is weakly nucleophilic and [BF_3: etherate] is needed as catalyst and the reaction is carried out at higher temperature (60° C, 15 hrs).

Scheme IV



10

X = PhS 2f (45 %) ; X = PhSe 1d (55 %)

Finally, NN-diethylaminoselenophenylmethylene 4a was obtained (38 % yield) by heating all together NN-diethylamine, selenophenol and paraformaldehyde (8) (scheme V). However it still remains to determine the scope of this reaction.

Scheme V

$$PhSeH + CH_2O + (C_2H_5)_2NH \longrightarrow PhSe{-}CH_2{-}N(C_2H_5)_2$$

4a

Work is actually in progress to generalize the reported reactions. In the following paper we describe some reactions of the mixed α-selenonio sulfide 2 and selenonio ether 3 as well as their use in organic synthesis.

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1) Preliminary report of part of this work was presented by the authors at the First I.U.P.A.C. Symposium on Organic Synthesis (F.I.C.O.S.) held at Louvain-La-Neuve (Belgium) August 1974.

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10) This compound was obtained during the first stage of the reaction along with starting material (NMR proof), then decomposed leading to several products.