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ALKYLHALIDES SYNTHESIS FROM SELENOXIDES
A NEW HOMOLOGIZATION PROCESS

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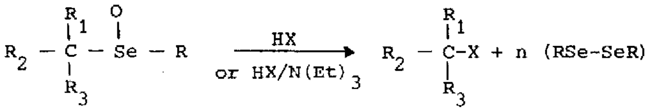
In connection with our interest in the transformation of selenium containing molecules to alkylhalides [4], we report the conversion of selenoxides to alkylhalides as described in scheme I

SCHEME I

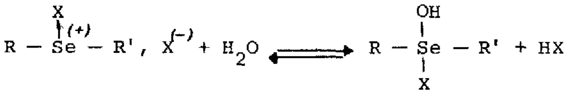


$R_2-\overset{R_1}{\underset{R_3}{C}}-\overset{O}{Se}-R \xrightarrow[\text{or } HX/N(Et)_3]{HX} R_2-\overset{R_1}{\underset{R_3}{C}}-X + n\,(RSe\text{-}SeR)$

3 4

$R_1 = C_6H_5$ or CH_3 X = Br or Cl

To our knowledge no such transformation has been described in the litterature. Nevertheless there are already several reports [2,3] on the equilibrium of dimethyl selenide dihalides 1 with dimethyl selenide hydroxy-halide 2 in the presence of water. This suggests then that the reaction described in scheme I may be closely related [4] to the transformation of a selenide to the corresponding alkylhalide, through the dihalide, which is reported in the accompanying paper.



$R-\overset{X}{\overset{\uparrow(+)}{Se}}-R',\ X^{(-)} + H_2O \rightleftarrows R-\underset{X}{\overset{OH}{Se}}-R' + HX$

1 2

Thus selenoxides, (obtained from the corresponding selenide and ozone in CH_2Cl_2 - 78°C)[8] are transformed to alkylhalides (scheme I - table I) when treated with an excess of gazeous hydrochloric or hydrobromic acid in methylene chloride. Under these conditions, apart from the benzyl phenyl selenoxide, the reactions are very slow at room temperature and give only low alkylhalide yield (Method A).[5]

Selenoxides treated in the same way but in the presence of triethylamine produce halides much easier and in higher yield (Method B).[5] However, an acidic reaction medium is required even in the presence of triethyl amine (Method B).

TABLE I

R_1	R_2	R_3	R	X	Method (*)	Yield in 4 %
C_6H_5	H	H	C_6H_5	Cl	A(1.5hr)	high
C_6H_5	H	H	C_6H_5	Br	A(10mn)	97
nC_9H_{19}	CH_3	H	CH_3	Br	A(7hrs)[a]	63
					B(18hrs)	77
nC_9H_{19}	CH_3	H	C_6H_5	Br	B(2.5hrs)	94
				Cl	B(6.5hrs)	64[b]
nC_6H_{13}	nC_6H_{13}	H	CH_3	Br	B(5hrs)	54[c]
		C_6H_{13}	CH_3	Br	B(1.5hrs)	75[d]

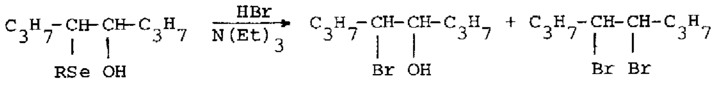
* refers to the reaction time at room temperature, unless otherwise stated

a) reaction conducted at 50°C. b) olefins are also formed in 16% yield

c) olefins are also formed in 34% yield d) olefins are obtained by HBr elimination during the TLC purification (SiO_2 Merck in 75% yield)

In general alkyl bromides are obtained faster and in higher yield than alkyl chlorides; phenyl selenoxides (R :C_6H_5) react easier and give a higher yield than do the methyl analogs (R :CH_3) and finally primary n-alkylhalides are produced but in very poor yield (less than 10%) (Method A or B). In some cases a small amount of olefins is formed.

When β-hydroxy selenides 5 are reacted under the above conditions (HBr/NEt_3), vicinal dibromide are obtained in fair yield along with a few percent bromohydrins 6.Dibromide probably arises from the substitution of the hydroxyl group in 6 in such acidic media.

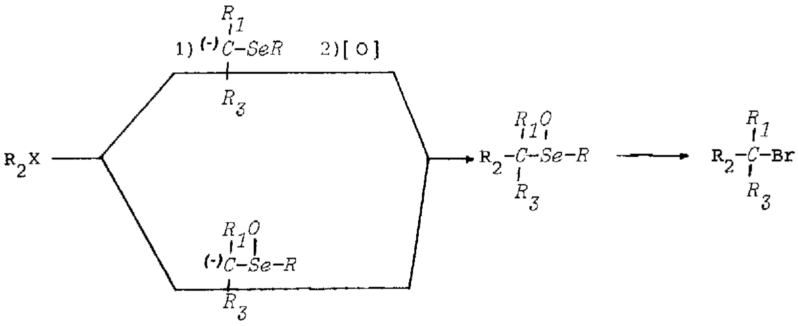


$$C_3H_7-\underset{RSe}{CH}-\underset{OH}{CH}-C_3H_7 \xrightarrow[N(Et)_3]{HBr} C_3H_7-\underset{Br}{CH}-\underset{OH}{CH}-C_3H_7 + C_3H_7-\underset{Br}{CH}-\underset{Br}{CH}-C_3H_7$$

5	6	7
R : CH_3	11	47
R : C_6H_5	0	83

As selenoxides can be synthesized directly from an alkylhalide and an α-selenoxicarbanion[6] (route 1) or in the two step process from the same alkylhalide and an α-selenocarbanion[7] followed by oxidation of the resulting selenide[8,9] (route 2);the scheme II offers two new methods of homologization of alkylhalide.

SCHEME II



X = Br, I

Work is now in progress to comprehend [10] the mechanism of selenoxide transformation as well as the role of the amine in this process.

References

1) The authors are grateful for a fellowship to M. Sevrin from I.R.S.I.A. (Belgium) - Institut pour la Recherche Scientifique dans l'Industrie et l'Agriculture - this work will be included in the Ph.D. Thesis of M. Sevrin.

2) See for example, W.R. Gaythwaite, J. Kenyon and H. Phillips, J. Chem. Soc., 2287 (1928)

   In the case of sulfur analogs, see C.M. Hull and J.W. Bargar, J. Org. Chem., 3152 (1975)

3) R. Paetzold, U. Lindner, G. Bochmann and P. Reich, Z. Anorg. Allg. Chem., 350, 295 (1967)

4) M. Sevrin, W. Dumont, L. Hevesi and A. Krief,accommpanying paper.

5) Synthesis of alkylhalide from selenoxide - *Typical experiment*

   Method B : dichloromethane solution (5 ml) of 312 mg (10^{-3}M) of 2-decylphenylselenide is ozonized at -78°C for 2 minutes . Gazeous HBr is bubbled in the cold solution of the obtained selenoxide for 30 seconds. Triethylamine (200 mg) is then added and the resulting solution is allowed to reach room temperature. At the end of the reaction (2.5 hrs) water (20 ml) is added and the mixture is extracted with ether. The ethereal solution is washed with thiosulfate, saturated sodium chloride, dried and evaporated. The crude product mixture (340 mg) is purified by PLC (petrolether elution) to yield 220 mg (94 %) of 2-bromo-decane.

   Method A : same experiment than in Method B except that addition of triethylamine is omitted and the reaction is much slower.

6) H.J. Reich and S.K. Shah, J. Amer. Chem. Soc., 97,3250 (1975)

7) D. Van Ende, W. Dumont and A. Krief, Ang. Chem. Int. Ed., 14, 700 (1975)

8) H. Reich and S.K. Shah, J. Amer. Chem. Soc., 97, 3250 (1975)- ref.17

9) L. Hevesi and A. Krief, Angew. Chem. in press

10) We were not able to isolate products arising from a Pummerer rearrangement.