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REDUCTIVE HALOGENATION OF EPOXIDES INDUCED BY HALOSILANES AND 1,1,3,3-TETRAMETHYLDISILOXANE (TMDS)[1]

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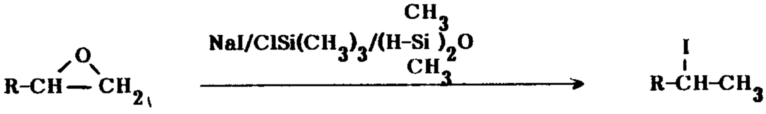
Summary: Synthesis of alkyl halides from epoxides and halosilanes together with silicon hydrides is briefly described.

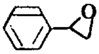
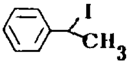
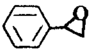
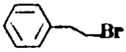
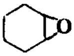
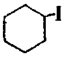
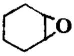
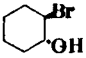
Several studies have revealed that halotrimethylsilanes react with epoxides to form beta--silyloxyalkylhalides under mild conditions[2]. Recent papers showed the preparation of allylic alcohols from epoxides and iodotrimethylsilane[2a] or trimethylsilyl trifluoromethanesulfonate[2d]. Denis and Krief[3a] have described the formation of olefins from epoxides and iodotrimethylsilane together with triethylamine, and Fry et al.[3b] have reported the reduction of epoxides to hydrocarbons by means of triethylsilane and boron trifluoride. We describe in this paper a new application of halosilanes for the direct synthesis of alkyl halides from epoxides and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agent.



The experimental procedure is exemplified as follows: a mixture of cyclohexane oxide (1.01ml, 10mmol), sodium iodide (2.00g, 1.33mmol) and trimethylchlorosilane (1.92ml, 15mmol) in ahnydrous acetonitrile (10ml) is stirred at 5-10ºC for 2-3min. 1,1,3,3-tetremethyldisiloxane (1.79ml, 10mmol) is then added and the mixture is refluxed for 30min. The remaining siloxane products are destroyed by adding 45% hydrofluoric acid (2.0ml) and refluxing for 5min. On completion, the reaction mixture is taken up in dichloromethane (30ml) and washed with water (20ml), 1N NaHSO$_3$ (10ml) and water again. Dring (Na$_2$SO$_4$) and evaporation of the solvents gives crude cyclohexyl iodide, which is purified by distillation (1.58g, 75%). b.p: 180-183ºC (lit. b.p: 179ºC/760torr)[4]. ^{1}H-NMR (CCl$_4$) δ ppm: 1.41 (m, 6H, CH$_2$), 1.92 (m, 4H, $\underline{\mathrm{CH}}_2$-CH) , 4.14 (m, 1H, CH).

Some examples are listed in the Table. Exceptionally, under these conditions, epoxypropane (entry 5) gives propene as only reaction product. On the other hand, it is noteworthy that the use of lithium bromide instead of sodium iodide gives the corresponding bromohydrines (entry 4) as only reaction products after prolonged reflux. However, we have found that the use of trifluoroacetic acid as solvent allowed the selective formation of the expected alkyl bromides (entry 2). This new reaction appears to provide the most general and convenient route to alkyl halides from epoxides[5]. Further investigations to explore the scope of the method are in progress in our laboratory.

Table. Reductive halogenation of epoxides.

Entry	Substrate	Salt	Time	Product(s)	Yield[a] (%)	m.p. or b.p/torr
1		**NaI**	45m		76	80-84/0.15
2		**LiBr**	15m		69	220-225/760
3		**NaI**	30m		75	180-183/760
4		**LiBr**	7h		93	195-200/760
5		**NaI**	6h		100	—
6		**NaI**	20m	 (57%)  (43%)	80[b]	1110-115/16 (dec.)

a) Yield of isolated pure products, the purity as determined by glc and tlc analysis, was $\geqslant$ 97%.

b) Conversion determined by glc analysis.

REFERENCES AND NOTES

1.- Considered as Reagents and Synthetic Methods 44. This work was supported by the Hezkuntza Saila of Eusko Jaurlaritza (Basque Governement) and Wacker-Chemie GMBH (München, Germany) with gifts of chlorotrimethylsilane and 1,1,3,3-tetramethyldisiloxane reagents.

2.- a) G.A. Olah, S.C. Narang, **Tetrahedron** , 38, 2225 (1982). b) G.C. Andrews, T.C. Crawford, L.G. Contillo Jr., **Tetrahedron Lett.**, 22, 3803 (1981) and references cited therein. c) H.R. Kricheldorf, G. Mörber, W. Regel, **Synthesis**, 383 (1981). d) S. Murata, M. Suzuki, R. Noyori, **J. Am. Chem. Soc.** 101, 2738 (1979).

3.-a) J.N. Denis, R. Mgnane, M. Van Eenoo, A. Krief, **Nouv. J. Chim.**, 3, 705 (1979). b) J.L. Fry, T.J. Mraz, **Tetrahedron Lett.**, 849 (1979).

4.-Z. Rappoport, "Organic Compounds Identification", 3rd Edn. C.R.C. press, Cleveland, 1977, p.60.

5.-In addition, alkenes were formed in high yields when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the crude reaction mixture; e.g. crude hydroiodinated 1,3,3-trimethyl-2-oxabicyclo[2.2.2] octane (cineole) (entry 6) afforded a mixture of  (53%) and  (47%) in 87% overall yield.

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