Preparation of Alkyl Bromides from the corresponding Alcohols and Me_2SBr_2

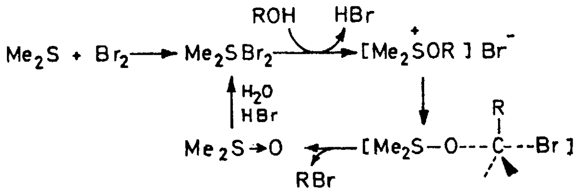
By Naomichi Furukawa, Teruhiko Inoue, Tetsuo Aida, and Shigeru Oae*

(*Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshiku, Osaka, Japan*)

Summary On treating various alcohols with dimethylbromosulphonium bromide the corresponding bromide is obtained in high yield, the reaction proceeding mainly through an inversion process.

We report the preparation of alkyl bromides from the corresponding alcohols and dimethylbromosulphonium bromide,[1] (DMBS). DMBS was dissolved in an excess of various alcohols and in each case the mixture was heated at *ca.* 80 °C for 4—5 h. The bromides were separated by standard methods and identified by spectral data and g.l.c. analysis. Yields† were as follows: R (% yield); Bu^n (73·2); Bu^s (57·2); Bu^t (37·5); n-C_5H_{11} (78·4); n-$Me(CH_2)_{11}$ (78·5); cyclopropylmethyl (77·7).

The results suggest that DMBS acts as a mild reductive brominating agent for alcohols. When optically active (+)-s-octyl alcohol $[\alpha]_D$ +9·40 was treated with DMBS, (−)-s-octyl bromide was obtained in 70% yield, $[\alpha]_D$ −25·14 (optical yield 91%).[2] This suggests that the reaction proceeds mainly through an inversion mechanism at the reaction centre. Corey[3] *et al.* have reported that dimethylchloro (or bromo) sulphonium salts can convert alcohols into the corresponding halides at −25 °C with high selectivity, but we could not detect any Me_2SO which might have arisen from the decomposition of the intermediate sulphoxonium salt.[4] However, in the presence of water even a trace amount of HBr can catalyse the reduction of Me_2SO to Me_2S and Br_2,[5] and bromosulphonium bromide may be prepared from sulphoxide and HBr.[6] We therefore assume that the Me_2SO formed is converted into DMBS again by HBr and propose the reaction mechanism shown in the Scheme.



Scheme

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† The yields were calculated from the following stoicheiometric equation: $(CH_3)_2SBr_2 + 2ROH \rightarrow (CH_3)_2SO + 2RBr + H_2O$. In the case of cyclopropylmethyl alcohol the reaction was carried out at 40 °C.

[1] Dimethylbromosulphonium bromide (DMBS) (orange crystals dec. 81—82 °C) is readily prepared from dimethyl sulphide and Br_2. It can be stored for several weeks at room temperature in the absence of light and moisture. *Cf.* F. Bobery, G. Winter, and G. R. Schultze, *Chem. Ber.*, 1965, **89**, 1160; H. Böhme and E. Boll, *Z. Anorg. Allg. Chem.*, 1957, **290**, 17.

[2] Optical activities of the alcohol and the bromide in the literature are $[\alpha]^{17}_D$ +9·9° (in ethanol) and −34·2° (in ethanol) respectively. Thus, calculated value of the inversion process is 91·6%. See C. H. Suueh and C. S. Marvel, *J. Amer. Chem. Soc.*, 1928, **50**, 855; J. Kenyon, *Org. Synth.* Coll. vol. I, 1956, 418.

[3] E. J. Corey, C. U. Kim, and M. Takada, *Tetrahedron Letters*, 1972, 4339.

[4] C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, 1969, **91**, 5398.

[5] N. Furukawa, T. Aida, and S. Oae, unpublished results.

[6] T. Zincke and W. Frohneberg, *Chem. Ber.*, 1909, **42**, 2721.