The Mechanism of the Reduction of Alkyl Halides with Sodium Borohydride in Dimethyl Sulphoxide

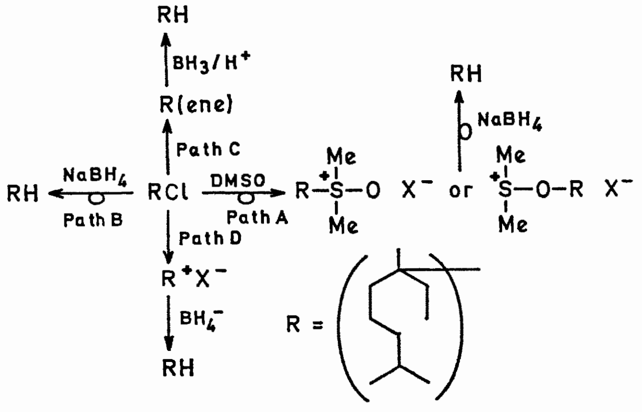
By JOHN JACOBUS

(*Department of Chemistry, Clemson University, Clemson, South Carolina* 29631)

Summary The reduction of optically active tertiary alkyl halides with sodium borohydride in dimethyl sulphoxide proceeds with racemization, presumably *via* an elimination–addition mechanism.

THE reduction of alkyl halides to hydrocarbons by sodium borohydride in dimethyl sulphoxide (DMSO) has recently been reported.[1] Four possible mechanisms for this reduction are shown in the Scheme: reaction of the halide with DMSO to yield either an oxysulphonium or sulphoxonium salt followed by reduction (Path A), direct S_N2 displacement (Path B), elimination–reduction (Path C), or S_N1 solvolysis and reduction (Path D).

Reduction of an optically active tertiary halide allows a choice of the most probable path. Path A should yield hydrocarbon of retained configuration,† path B of inverted configuration, and paths C or D racemic product.



SCHEME

Reduction of (—)-(*R*)-3-chloro-3,7-dimethyloctane[2,3] (**1**), α_D^{23} —0·47 ± 0·04° (neat, *l* 1), in DMSO with 8 equiv. of $NaBH_4$ at 100° for 18 hr. afforded racemic 2,6-dimethyloctane, α_D^{23} 0·00 ± 0·02° (neat, *l* 1).

Either Path C or D is consistent with the observed stereochemistry. A choice in favour of C as the preferred mechanism is based on the following observations: the reduction proceeds slowly at 85° with only *ca.* 10% reduction occurring in 18 hr. Recovered (**1**) from this reaction has α_D^{23} — 0·43 ± 0·03° (neat, *l* 1), indicating that racemization does not occur before reduction. Attempted distillation of the crude reduction product from a reaction conducted at 100° for 18 hr. afforded a mixture of C_{10} olefins as the major product; however, treatment of the crude product with valeric acid under reflux for 2 hr. followed by normal isolation and distillation afforded 2,6-dimethyloctane (**2**), indicating the intermediacy of organoboron species which pyrolyse to olefins on attempted distillation at atmospheric pressure and which are hydrolysed to the corresponding hydrocarbon by acid treatment. The n.m.r. spectrum of the crude product is essentially identical to that of (**2**), indicating that normal *anti*-Markovnikov addition of BH_3 to the intermediate olefin(s) has occurred.

The stereochemical results of the present reaction preclude its use for the correlation of configuration of alkyl halides and hydrocarbons. Elimination reactions of tertiary halides in the presence of lithium aluminium hydride have previously been reported;[4] however, under the same conditions secondary halides are reduced with inversion of configuration.[5]

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† Provided that the sulphonium intermediate is optically stable.

[1] (a) R. O. Hutchins, D. Hoke, J. Keogh, and D. Koharski, *Tetrahedron Letters*, 1969, 3495; (b) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, 1969, **34**, 3923.

[2] Prepared from tetrahydrolinalool, $[\alpha]_D^{23}$ —0·56 ± 0·02° (neat, *l* 1) by the method of P. E. Verkade, K. S. DeVries, and B. M. Wepster, *Rec. Trav. chim.*, 1964, **83**, 367.

[3] The absolute configuration of tetrahydrolinalool (3,7-dimethyloctan-3-ol) was assigned by R. H. Cornforth, J. W. Cornforth, and V. Prelog, *Annalen*, 1960, **634**, 197. The corresponding chloride is presumably formed with inversion of configuration [(—)-(*S*)-ol→(—)-(*R*)-chloride] (ref. 2).

[4] L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 1675.

[5] E. L. Eliel, *J. Amer. Chem. Soc.*, 1949, **71**, 3970.