The Generation and Trapping of an Optically Active Free Radical in the Absence of a Cage. The Mechanism of Dissolving Metal Reduction of Alkyl Halides

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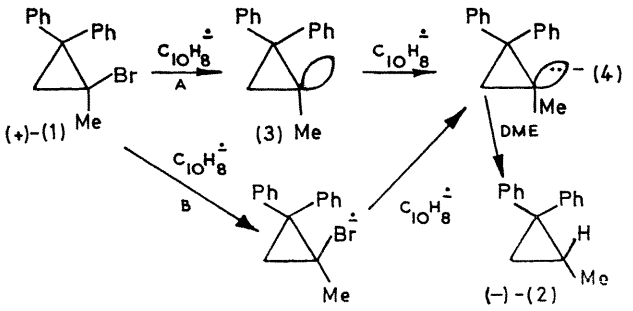
ALTHOUGH optically active radicals have been generated and trapped in cage reactions,[1] the general consequence of the generation of a radical site at the chiral centre of a molecule containing a single asymmetric centre in the absence of cage trapping is racemisation.[2] We report evidence that confirms[1b] that cyclopropyl radicals exist at least transiently as non-planar entities capable of being trapped prior to attaining C_s geometry, and, that the non-cage trapping of an optically-active free radical can lead to optically active products.



DME = 1,2-dimethoxyethane

Reduction of presumably optically pure (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane[3] (1) {$[\alpha]_D^{23}$ + 107 ± 2° (*c* 1·38, $CHCl_3$); lit.[3] $[\alpha]^{21\cdot3}$ + 107·1 ± 2·2° (*c* 1·034, $CHCl_3$)} with sodium dihydronaphtylide in dimethoxyethane (0·5 M) yields 29% optically pure (−)-(*R*)-1-methyl-2,2-diphenylcyclopropane (2) {$[\alpha]_D^{23}$ − 37·1° (*c* 9·68, $CHCl_3$); lit.[4] $[\alpha]_D^{26}$ − 127 ± 2° (*c* 0·388, $CHCl_3$)} with net retention of configuration.

The reaction of sodium dihydronaphthylide with alkyl halides has been shown[5] to proceed *via* dissociative electron capture (Path A) to yield an alkyl free radical (3) which is subsequently converted into a carbanion (4) by electron transfer from naphthylide ion. The latter reaction is probably diffusion controlled.[5] The rate of protonation of the anion (4) is unimportant since this species is known to be configurationally stable.[3,6] Protonation of the anion by solvent[3] leads to (−)-(2). We believe that the mechanism of the present reduction is Path A, *i.e.* the reaction involves the optically active free radical (3), and probably does not involve a partitioning between Paths A and B in which the result of Path A is racemisation and that of Path B is retention.

The radical trapping reaction must have a rate equal to or greater than the inversion frequency of the cyclopropyl radical[7] (10^8—10^{10} sec.$^{-1}$); evidently such is the case in electron transfer.

On the basis of net retention of configuration at the chiral centre in the reduction of (−)-(*R*)-3-chloro-3,7-dimethyloctane to (+)-(*S*)-2,6-dimethyloctane by alkali metals in liquid ammonia it has been concluded[8] that the reduction proceeds *via* two electron addition to the intact halide (mechanistically similar to Path B, or by termolecular reaction) prior to fission of the carbon–halogen bond. The present result indicates that electron addition to an intermediate free radical can be fast enough to complete favorably with inversion of the radical, *i.e.* the radical can be trapped by electron addition prior to inversion followed by diffusion-controlled (in the case of ammonia) protonation to give products of retained configuration. In the light of the known configurational stability of the cyclopropyl anion[3] and the configurational lability of the cyclopropyl radical[9] the results[10] of the reduction of optically active cyclopropyl halides with metal–ammonia solutions are best explained as proceeding *via*-Path A; all dissolving-metal reductions (metal–ammonia and radical anion) of alkyl halides probably proceed *via* this mechanism.

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