Solvolysis of Chiral [1-$^2H_1$]Neopentyl Toluene-*p*-Sulphonate

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THE stereochemistry of carbonium ions derived from the neopentyl system is of interest. The deoxidation reaction of [1-$^2H_1$]neopentyl alcohol[1] and the nitrous acid deamination of [1-$^2H_1$]neopentylamine[2] have been studied, but the simple solvolytic behaviour of the optically active neopentyl system is not known. We report preliminary results on the solvolysis of chiral [1-$^2H_1$]-neopentyl toluene-*p*-sulphonate. (*S*)-[1-$^2H_1$]Neopentyl alcohol (I, 20·3 g., acid phthalate: 0·82 deuterium atoms per molecule† and $[\alpha]_D^{28}$ $-0·95 \pm 0·04$, *c* 20, *l* 1 dm., acetone), prepared by asymmetric reduction of trimethylacetaldehyde by actively fermenting yeast,[3] was converted into (*S*)-[1-$^2H_1$]neopentyl toluene-*p*-sulphonate (II, 27 g., m.p. 45—46°, 0·82 deuterium atoms per molecule†) which showed no observable rotation between 300 and 589 mμ.‡ By using the conditions of Hoffmann[4] this toluene-*p*-sulphonate (0·041 moles) underwent solvolysis in absolute ethanol (20 ml.), to which 2,6-dimethylpyridine (0·047 moles) had been added, at 130° for 24 hours in a sealed tube. Distillation of the reaction mixture gave unreacted [1-$^2H_1$]neopentyl toluene-*p*-sulphonate (60%, 0·83 deuterium atoms per molecule†), 2,6-dimethylpyridinium toluene-*p*-sulphonate (38%)

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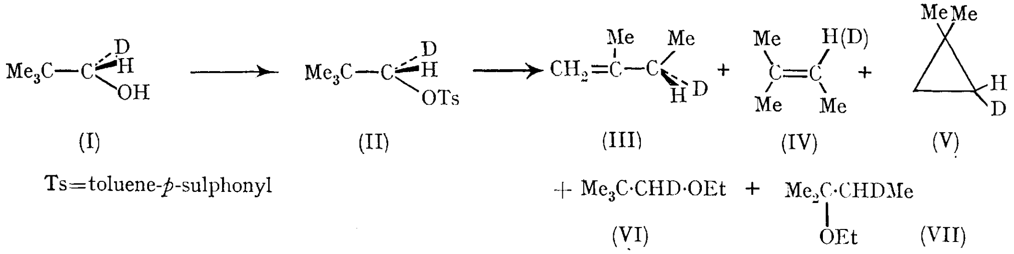
† Deuterium analysis by J. Nemeth, Urbana, Illinois.

‡ Assumed to be enantiomerically pure because the neopentyl alcohol from which it is prepared has been shown to be 99 ±1% enantiomerically pure (K. Mislow and M. R. Raban, *Tetrahedron Letters*, 1966, **33**, 3961) and racemization is unlikely during toluene-*p*-sulphonate formation.



(I) (II) (III) (IV) (V)

Ts=toluene-*p*-sulphonyl

(VI) (VII)

and an alcohol distillate (analysed by g.l.c.). The products were: 1,1-dimethyl[2-$^{2}\text{H}_{1}$]cyclopropane (V, 0·4%),§ (+)-(*S*)-2-methyl[3-$^{2}\text{H}_{1}$]but-1-ene (III, 30·0%), 2-methyl-[3-$^{2}\text{H}_{1}$]but-2-ene (VI, 30·4%), ethyl[1-$^{2}\text{H}_{1}$]neopentyl ether (VI, 8·6%), and 2-ethoxy-2-methyl[3-$^{2}\text{H}_{1}$]butane (VII, 30·8%). The distillates from this and similar solvolyses were subjected to preparative gas chromatography. Only traces of (V) were recovered and thus its deuterium content and rotation were not determined. The (+)-(*S*)-2-methyl[3-$^{2}\text{H}_{1}$]but-1-ene (III) had α_{D}^{20} + 0·25 + 0·02 (*l* 0·5 dm.) and 0·81 ± 0·01 deuterium atoms per molecule.¶ Correcting for the deuterium content and using a density[1] of d_{4}^{20} 0·6635, this corresponds to a specific rotation of $[\alpha]_{\text{D}}^{20}$ + 0·91 ± 0·07. The 2-methyl[3-$^{2}\text{H}_{1}$]but-3-ene (IV) had 0·60 ± 0·01 deuterium atoms per molecule¶ and the 2-ethoxy-2-methyl[3-$^{2}\text{H}_{1}$]butane (VII), α_{D}^{20} + 0·15 ± 0·02 (*l* = 0·5 dm.), had 0·77 deuterium atoms per molecule.† The ethyl [1-$^{2}\text{H}_{1}$]neopentyl ether (VI), showed a plain, positive o.r.d. curve.

The (+)-(*S*)-2-methyl[3-$^{2}\text{H}_{1}$]but-1-ene (III), produced by the rearrangement and elimination in this solvolysis, is 91 ± 7% pure, based upon the maximum rotation of $[\alpha]_{\text{D}}^{20}$ + 1·01° reported[1] for this olefin. The solvolysis reaction is therefore highly stereoselective, proceeding with 91 ± 7% inversion at the rearrangement terminus. This is similar to the inversion found previously in the deoxidation reaction of [1-$^{2}\text{H}_{1}$]neopentyl alcohol[1] and established by Guthrie[2] for the deamination reactions of [1-$^{2}\text{H}_{1}$]neopentylamine although our results were obtained under milder conditions of solvolysis in alcoholic medium.

We conclude that the rearrangement is highly concerted, but the extent to which the reaction may involve a carbonium ion which rearranges faster than it rotates[1,5] has not yet been ascertained. The determination of the optical purity and configuration of (VI), should give valuable information on this point.

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§ Percentage areas of peaks for components (III), (IV), (V), (VI), and (VII) were normalized on the basis of standard mixtures. The solvolyses were carried to *ca.* 40% completion to avoid racemization of products.

¶ Determined by mass spectroscopy using 70 ev ionization potential.

[1] W. A. Sanderson and H. S. Mosher, *J. Amer. Chem. Soc.*, 1966, **88**, 4185.
[2] R. D. Guthrie, *J. Amer. Chem. Soc.*, 1967, **89**, 6718.
[3] V. A. Althouse, K. Ueda, and H. S. Mosher, *J. Amer. Chem. Soc.*, 1960, **82**, 5938.
[4] G. M. Fraser and H. M. R. Hoffmann, *Chem. Comm.*, 1967, 561.
[5] See B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, 1957, **79**, 6160.