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STEREOCHEMISTRY OF TRIFLUOROACETOLYSIS OF 2-PHENYLETHYL BROSYLATE

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Nordlander has recently reported[2] an appreciable rate enhancement in the solvolysis of 2-phenylethyl tosylate, relative to ethyl tosylate, in trifluoroacetic acid (rate ratio 3040). This was cited as the first unambiguous piece of kinetic evidence for phenyl participation, and he attributed the enhancement to direct formation of the ethylenephenonium ion. In support of this interpretation, they found complete scrambling of chain label after one half-life, whereas unreacted brosylate showed only 5% isotope redistribution.

We have recently performed the relevant stereochemical studies and find that *trifluoroacetolysis occurs with complete retention of configuration.*

threo-2-Phenylethanol-1,2-d_2, prepared by catalytic deuterogenation of pure *trans-β*-acetoxystyrene, was converted to the brosylate by standard procedures. Treatment of the *threo*-brosylate with lithium chloride in acetone affords *erythro*-2-chloroethylbenzene-1,2-d_2. Since the *erythro* and *threo* isomers of the chloride show different coupling constants, $J_{erythro} \neq J_{threo}$, each gives rise to a distinct AB pattern, and a mixture of the two shows two superimposed AB patterns. The integrated intensity of the appropriate lines is then a measure of the relative amount of each isomer. Such analysis of the *erythro*-chloride prepared above demonstrated a maximum of about 2% *threo*-chloride[3].

threo-$C_6H_5CHDCHDOBs$ was solvolyzed for 8.0 hrs. at 72°C (ca. 9 half-lives) under those conditions used by Nordlander. The resulting trifluoroacetate was hydrogenolyzed by lithium aluminum hydride and converted into brosylate, (74% yield overall of pure brosylate) m.p. 60.0-60.5, thence to chloride. Examination by nmr showed this to be *erythro*-chloride whose stereochemical purity is experimentally indistinguishable from that prepared from the original *threo*-brosylate. Therefore, the solvolysis has proceeded with complete retention of configuration to within the experimental limits of the method (estimated ±2%)[4].

The phenonium ion interpretation of solvolysis seems to demand that all products resulting via phenonium ion have retained configuration.[5] Therefore, our results can be interpreted as providing support for this hypothesis. If Nordlander's observation of rate enhancement be taken as diagnostic of participation then the alternative interpretation[6] of rapidly equilibrating open ions seems not to be valid. Although the postulate[7] of rapidly equilibrating, unsymmetrical π-bridged ions might account for participation it is not obvious that they, or any other type of unsymmetrically bridged species, would predict *a priori* the observed stereochemical course.

The stereochemical results of solvolysis under other conditions, performed as part of a continuing attempt to distinguish between the alternative hypotheses, will be reported shortly.

REFERENCES

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(2) J. E. Nordlander and W. G. Deadman, *Tetrahedron Letters*, 000(1967). We thank Dr. Nordlander for communicating his results prior to publication.

(3) Mass spectral analysis of the alcohol shows minor amounts of d_1 and d_3 species. However, these are present in sufficient quantities to give rise to observable resonances in the region of interest. Furthermore, the chlorides examined contained 3% of unidentified impurities according to vpc examination. These may also contribute to the uncertainty in the measurements reported. Suitable control experiments with *threo*-chloride might reduce uncertainty below 2%, but the required pure material is not yet available.

(4) Since the scrambling results demonstrate (probably internal) return our results also demonstrate that this occurs with retention of configuration.

(5) For a review of arguments *pro* phenonium ion see D. J. Cram, *J. Am. Chem Soc.*, **86**, 3767 (1964).

(6) For a review of arguments *pro* equilibrating ions see H. C. Brown, K. J. Morgan and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).

(7) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, ibid., **89**, 370 (1967).