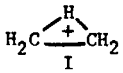
Tetrahedron Letters No.13, pp 1241 - 1244, 1972. Pergamon Press. Printed in Great Britain.

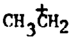
HYDROGEN-BRIDGING IN THE 2-BUTYL CATION

J.J. Dannenberg, D.H. Weinwurzel, K. Dill and B.J. Goldberg
Hunter College of the City University of New York
695 Park Ave., New York, New York 10021

(Received in USA 14 February 1972; received in UK for publication 21 February 1972)

There has been substantial recent interest, both theoretical and experimental, in the structure of simple carbonium ions, in particular, the ethyl cation. Whereas semi-empirical INDO[1] and NDDO[2] calculations predict a hydrogen-bridged structure for cation, I, <u>ab initio</u> calculations[2,3,4] as well as extended Huckel calculations[6], predict a structure more similar to the open cation, II. The experimental evidence on the structure of the


I


$CH_3\overset{+}{C}H_2$
II

ethyl cation has, likewise, been somewhat inconclusive. Roberts and Yancey[6], who generated the C^{14} labelled cation by action of HNO_2 on the ethylamine observed only 2% rearrangement, while Myhre and Evans[7], who generated the 1,1-dideuteroethyl cation by action of fluorosulfuric acid on ethylosylate, observed 42% rearrangement. The large difference in the experimental observations might well be attributed to interaction of the cation with the different media. Since ethyl cation is a particularly unstable species, one might expect it to be exceedingly sensitive to change in medium.

The 2-butyl cation is intrinsically more stable than the ethyl cation and affords the possibility of forming a symmetrically bridged species. N.m.r. studies in SbF_5-HSO_3F [8] and SO_2ClF-SbF_5 [9] suggest that the 2-butyl cation exists as a rapidly equilibrating mixture of its two degenerate non-bridged structures in these media. Also, acetolysis of C^{14} labeled 2-butyl tosylate afforded only 9% rearranged product[10]. Nevertheless, the recent reports of solvolyses in the extremely non-nucleophilic solvent, trifluoroacetic acid[12], prompted us to investigate the trifluoroacetolysis of a suitably labeled 2-butyl tosylate, III, in the hope of observing a hydrogen-bridged intermediate. 1,1,1,2-tetradeutero-2-butyl tosylate, III, was chosen for this purpose, as the bridged cation, IV, should form a 1:1 mixture of products V and VI, whereas rapidly equilibrating 2-butyl cations should form a mixture of V,VI, VII, and VIII. If the cation neither bridges nor equilibrates, only V should be formed. Products V-VIII are easily distinguishable in the n.m.r. by the methyl resonances of the protons on the 1 and 4 positions. In unlabeled 2-butyl derivatives, the proton resonances on carbon 1 appear as a doublet and those on carbon 4 as a triplet at somewhat higher field. In, V, the doublet from position 1 should be lacking while in VI the triplet from position 4 should be lacking. In VII the resonance corresponding to the triplet at position 4 in the unlabeled derivative should appear as a doublet, while in VIII resonance corresponding to the doublet at position 1 should appear as a singlet.

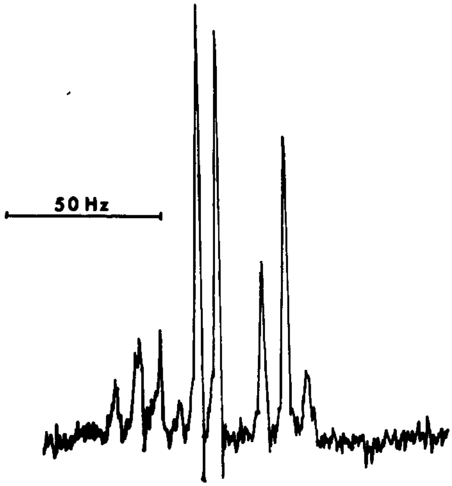


Figure 1: N.m.r. spectrum (60 MHz) of the methyl region of the trifluoroacetolysis product of unlabeled 2-butyl tosylate.

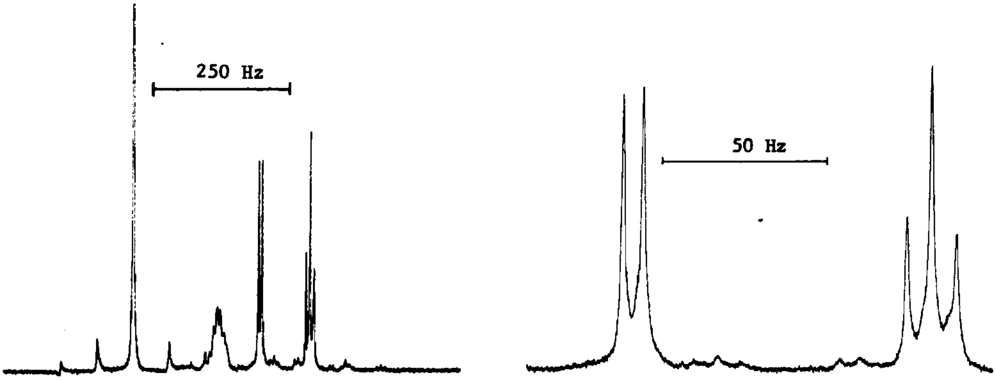
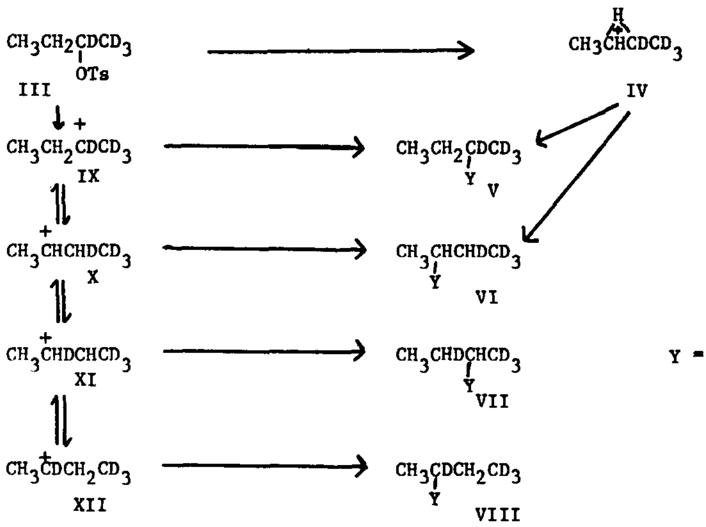


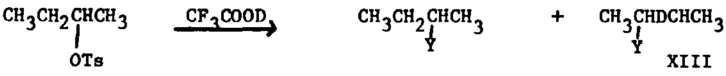
Figure 2: N.m.r. spectra (220 MHz) of the upfield portion of the trifluoroacetolysis products of III. The small peaks between the doublet and triplet in the expanded scale spectrum (right) are spinning side bands, as can be seen from the condensed scale spectrum (left). The sharp singlet in the left hand spectrum (methyl group of TsOH) has been cut to ca. 1/3 its height to conserve space.



Y = trifluoroacetate

The spectra of figure 2 illustrate the results of the trifluoroacetylsis of III. The product mixture has the triplet and the doublet in a 1.08:1 ratio indicating equal formation of V and VI. If the ratio of V to VI be the result of equilibration of the open carbonium ions, IX-XII, the carbonium ion must live several hydrogen-transfer half-lives. The β -deuterium isotope effect, k_H/k_D for hydride transfer in the ethyl cation is 2.4[7]. If the same isotope effect is applicable to the 2-butyl cation, only slightly more than 1 half-life would be necessary for the formation of 5% VII. Integration of the spectra using a Dupont Model 310 curve resolver indicates little singlet (2±1%) between the doublet peaks and little doublet (4±1%) between the peaks of the triplet, thus demonstrating the relative absence of VII.and VIII. Careful integration of the 220 MHz spectra of the solvolysis products of III indicated no loss of deuterium.

To test the possibility that the bulk of the trifluoroacetolysis proceeds via an elimination-addition mechanism, 2-butyl tosylate (0.5M) was solvolyzed in CF_3COOD(96%D). A similar elimination-addition mechanism was reported for the H_2SO_4 solvolysis of n-propyl tosylate[12]. The trifluoroacetolysis of 2-butyl tosylate, however, yielded only 24%(n.m.r.)



$$\underset{OTs}{CH_3CH_2\underset{|}{C}HCH_3} \xrightarrow{CF_3COOD} CH_3CH_2\underset{Y}{\underset{|}{C}}HCH_3 + \underset{XIII}{CH_3\underset{Y}{\underset{|}{C}}HDCHCH_3}$$

Y=trifluoroacetate

of the deuterated trifluoroacetate, XIII. This result cannot be explained by preferential addition of the 4% CF_3COOH to 2-butene as the kinetic isotope effect $k_{CF_3COOH}/k_{CF_3COOD}$ for this addition has been observed to be 4.4.[15] Elimination-addition, therefore cannot be the major reaction path.

The evidence, therefore, leads us to conclude that a significant amount of the cationic intermediate in the trifluoroacetolysis of 2-butyl tosylate is hydrogen-bridged as depicted in IV. A study of the potential energy surface of the 2-butyl cation using the INDO method yields results in accord with these experiments.[14] These calculations are somewhat questionable in the light of the recent demonstration that the CNDO method favors small ring systems.[15]

The tosylate, III was prepared by action of ethyl magnesium bromide upon perdeuteroacetaldehyde, followed by treatment of the intermediate tetradeutero-2-butanol with toluenesulfonyl chloride in pyridine. The structures of the tetradeutero-2-butanol and tosylate were verified by n.m.r. The trifluoroacetolysis were performed at 37° in the n.m.r. probe.

The authors are indebted to Professor W.A. Gibbons and Mr. P. Zeigler of Rockefeller University for the 220 MHz n.m.r. spectra and to Dr. C. Angell of Union Carbide for use of the Curve resolver.

References

1. J.J. Dannenberg and T.D. Berke, Abstracts, 158th National Meeting of the American Chemical Society, New York, N.Y., September, 1969, No. PHYS. 163.
2. R. Sustmann, J.E. Williams, M.J.S. Dewar, L.C. Allen and P.v.R. Schleyer, *J. Am.Chem Soc.*, 91, 5350,(1969).
3. G.V. Pfeiffer and J.G. Jewett, J. Am. Chem. Soc., 92, 2143(1970).
4. J.E. Williams, Jr., V. Buss, L.C. Allen, P.v.R. Schleyer, W.A. Latham, W.J. Hehre and J.A. Pople, *J. Am. Chem. Soc.*, 92, 214 (1970).
5. R. Hoffman, *J. Chem. Phys.*, 40, 2480 (1964).
6. J.D. Roberts, and J.A. Yancey, *J. Am. Chem. Soc.*, 74, 5943(1952).
7. P.C. Myhre and E. Evans, *J. Am. Chem. Soc.*, 91,5641, 1969.
8. M. Saunders, E.C. Hagen and J. Rosenfeld, *J. Am. Chem. Soc.*, 90, 6882,(1968).
9. G.A. Olah and A.M. White, *J. Am. Chem. Soc.*, 91, 5801(1969).
10. J.D. Roberts, W. Bennett, R.E. McMahon and E.W. Holroyo, Jr., *J. Am. Chem. Soc.*, 74, 4283,(1952).
11. a) J.E. Nordlander and W.J. Kelly, J. Am. Chem. Soc., 91, 996(1969) , b) A. Diaz and S. Winstein, *J. Am. Chem. Soc.*, 91, 4300 (1969) and references cited therein.
12. P.C. Myhre and K.S. Brown, *J. Am. Chem. Soc.*, 91, 5639 (1969)
13. J.J. Dannenberg, and M.O. Longas, unpublished results.
14. J.J. Dannenberg, T.D. Berke, *Theoretica Chimica Acta*, in press.
15. E.I. Snyder, *J. Am. Chem. Soc.*, 92, 7529 (1970).