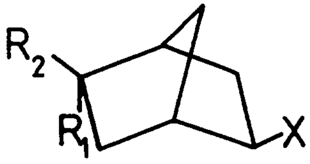
Tetrahedron Letters No.49, pp. 4363-4366, 1970. Pergamon Press. Printed in Great Britain.

THE PREPARATION AND ACETOLYSES OF 5-DEUTERIATED *EXO*-NORBORNYL BROSYLATES

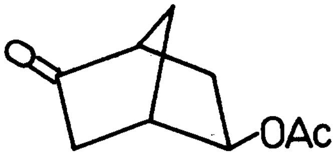
N. H. Werstiuk, R. R. MacDonald[1], R. W. Ouwehand[1],
W. L. Chan[1], F. P. Cappelli[2], J. G. Ballard[2],
R. E. Young[2], R. E Massey[2] and G Timmins,
Department of Chemistry, McMaster University,
Hamilton, Ontario, Canada.

(Received in USA 21 August 1970; received in UK for publication 21 September 1970)

α, β and γ deuterium isotope effects have been used extensively to probe the nature of the norbornyl cation[3(a)-3(i)] generated solvolytically. Of special interest has been the work of Murr et al.[3(c)] and Borčić et al.[3(d)] which showed that the isotope effects for the *exo*-norbornyl-6-d- and *endo*-norbornyl-6-d-brosylates are 1.10 and 1.00, respectively. We have prepared and solvolyzed the *exo*-norbornyl-5-d- and *exo*-norbornyl-5,5-d_2 brosylates (1a and 1b) to check for (a) non-bonded effects[4] due to deuterium and (b) stabilization of the norbornonium ion via hyperconjugation to the C-5 hydrogens. To calibrate the results *exo*-norbornyl-6-*endo*-d-brosylate was also prepared and solvolyzed. We report the results of the study in this communication (Table 1).



1a, R_1 = D, R_2 = H, X = OBs
b, R_1 = D, R_2 = D, X = OBs
c, R_1 = D, R_2 = H, X = OH
d, R_1 = D, R_2 = D, X = OH
e, R_1 = H, R_2 = D, X = OH



2

Table 1. Data for Acetolyses of Norbornyl Brosylates at 24.90 ± 0.02°

Compound	k_H/k_D[a] (HOAc-KOAc)
endo-5-d-	1.01 ± 0.01[b]
endo-5-*exo*-5-d_2	0.99 ± 0.01[c]
endo-6-d-	1.11 ± 0.01[d]

[a] Determined by monitoring the protium and deuterium compounds simultaneously in the same thermostatted spectrophotometric compartment (C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964)) and corrected for incomplete deuteration.

[b] An average of four runs; 95.1% d_1, 4.9% d_0 species as determined mass spectrometrically at 10 eV on the norcamphor.

[c] An average of four runs; 91.6% d_2, 6.4% d_1 and 2.0% d_0 species.

[d] An average of two runs; 81.2% d_1 and 18.8% d_0 species.

The syntheses of the **1a** and **1b** began with the reduction of **2**[5] with $NaBD_4$ in EtOH to a 85:15 mixture of the *exo*-norbornyl-5-*endo*-hydroxy-5-*exo*-d- and 5-*endo*-d-5-*exo*-hydroxy acetates. The hydroxyacetate mixture was converted to the mixture of the brosylates (m.p. 79-81°) with brosyl chloride in pyridine. **1c** was obtained in one step from the brosylate acetate mixture by using $LiAH_4$ in refluxing ether to accomplish the displacement of the brosylate[6] and the reduction of the acetate. When $LiAlD_4$ was used **1d** was obtained. To prepare **1e** reductions with $NaBH_4$ and $LiAlD_4$ would be required. **1c** and **1d**, isolated by preparative gas chromatography, were $>$99% pure and $\geq$99% stereochemical pure *exo*.

A new and novel route to *exo*-norborneol-6-*endo*-d[3(c)] was used. We found that the addition of DOAc to 3-bromo- and 3-chloro-nortricyclene yields deuteriobromoacetates and chloroacetates, respectively.[7] Reduction of the deuteriobromoacetates with $LiAH_4$ in ether and the deuteriochloroacetates with sodium in isopropanol gave, in each case, *exo*-norborneol-6-*endo*-d 85-90% stereochemically pure *endo* at C-6 as estimated by a comparison of the fingerprint region in the infrared spectrum to that of an authentic sample.[8]

Since the change in the non-bonded interactions[4,9] (contributing to the ground state energy) should essentially be identical when a deuteron replaces a C-5-exo-H or a C-6-exo-H (likewise the endo-Hs) within the eclipsed butane structure as viewed along the C-5, C-6 bond, the results in Table 1 show that (a) the non-bonded interactions of deuterium at C-5 and C-6[14] and (b) hyperconjugation to the C-5 protons are not important in the solvolyses of 2-X-norbornyl systems. The latter removes the possibility that loss of hyperconjugative stabilization *via* the C-5 hydrogens contributes significantly to the rate retardation observed by Greever et al.[13] in the solvolyses of norbornyl-5-keto-brosylates. The results also provide the first experimental evidence that hydrogen (deuteron) shifts followed by internal return to brosylate contribute negligibly to the isotope effects as predicted by Murr et al.(3c) This work has also provided a general route to previously unknown norbornyl-5-d systems and an alternative more direct route to *exo*-norborneol-6-*endo*-d.

REFERENCES

1. McMaster Undergraduate Summer Student, 1968-1969.
2. McMaster Undergraduate Student, 1969-1970.
3. (a) S. Borčić, V. Belanic-Lipovac and D. E. Sunko, *Croat. Chem. Acta.*, **33**, 35 (1961);
   (b) C. C. Lee and E. W. Wong, *J. Amer. Chem. Soc.*, **86**, 2753 (1964);
   (c) B. L. Murr, A. Nickon, T. Swartz and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 1730 (1967);
   (d) J. M. Jerkunica, S. Borcic and D. E. Sunko, *J. Amer. Chem. Soc.*, **89**, 1732 (1967);
   (e) J. M. Jerkunica, S. Borcic and D. E. Sunko, *Chem. Commun.*, 1302 (1967);
   (f) J. P. Schaefer, M. J. Dagani and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967);
   (g) H. L. Goering and K. Humski, *J. Amer. Chem. Soc.*, **91**, 4594 (1969).
   (h) B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, **92**, 3462 (1970);
   (i) B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, **92**, 3464 (1970).

The term non-bonded includes steric effects and the effects which contribute to the rotational barrier in ethane.

5. J. Meinwald, J. K. Crandall and P. G. Gassman, *Tetrahedron*, *18*, 815 (1962).
6. A. Nickon and J. H. Hammons, *J. Amer. Chem. Soc.*, *86*, 3322(1964).
7. Preliminary work on the opening of the tricyclenes has shown that the *syn* and *anti*-7-halo-*exo*-2-norbornyl acetates comprise 85-90% of the total reaction mixture. That the *exo*-norborneol-d is 90% stereochemically pure *endo* at C-6 gives information on the stereochemistry of the opening and pinpoints the bond which is attacked. Further work is presently being carried out on these and other systems.
8. Professor A. Nickon very kindly provided the spectra of the deuterionorborneols.
9. The effect of replacing one or two of the C-H bonds with C-D bonds is difficult to predict. That some effect could have been possible was seen from information available on the rotational barriers of various deuteriated ethanes (See ref. 10, 11, 12). Our study was further prompted by the report (ref. 3(a)) that the isotope effect for *exo*-norbornyl-5-*exo*-6-*exo*-d_2-brosylate is 1.06-1.07.
10. D. R. Lide, Jr., *J. Chem. Phys.*, *29*, 1426 (1958).
11. S. Weiss and G. E. Leroi, *J. Chem. Phys.*, *48*, 962 (1968).
12. W. H. Fink and L. C. Allen, *J. Chem. Phys.*, *46*, 2261 (1967).
13. J. C Greever and D. E. Gwynn, *Tet. Lets.*, *10*, 813 (1969)
14. The extra large γ isotope effects observed for the *exo*-norbornyl-6-d-brosylates must therefore result from a change in hybridization at C-6. See A. Streiwiser, R. H. Jagow, R. L. Fahey and S. Suzuki, *J. Amer. Chem. Soc.*, *80*, 2326 (1958) for some discussion on this concept.