Tetrahedron Letters No. 13, pp. 1067-1070, 1970. Pergamon Press. Printed in Great Britain.

SOLVOLYSIS OF DERIVATIVES OF TRICYCLO $(3.3.0.0^{3,7})$ OCTAN-2-OL[1]

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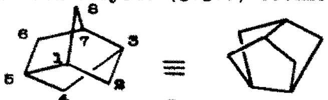
(Received in USA 9 February 1970; received in UK for publication 17 February 1970)

Tricyclo $(3.3.0.0^{3,7})$ octane (1) occupies an important position in the realm of polycyclic ring systems owing to the unique arrangement of the carbon atoms such that the smallest rings are all five-membered. The molecule may be viewed as a severely twisted norbornane derivative or as a constrained cisoid bicyclo (3.3.0) octane. Our interest in this system germinated from earlier studies[2] on the behavior of the isomeric tricyclo $(3.2.1.0^{3,6})$ octyl system 2 and has been kindled by recent studies with homologous C_9 and C_{10} analogs.[3] The specific objectives of this research were directed at a study of the generation and behavior of cationic intermediates at the methylene bridge in 1.



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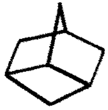

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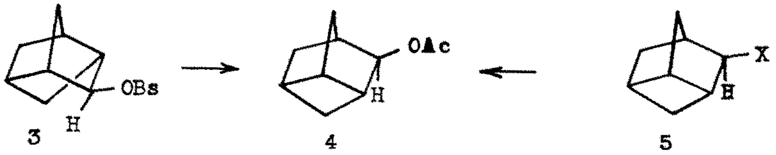
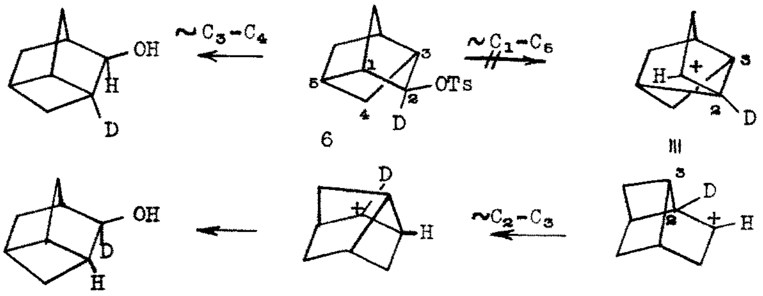
For these purposes, the p-bromobenzenesulfonate derivative 3 was prepared from the known[4] alcohol and subjected to acetolysis in the presence of excess sodium acetate. This reaction proceeded cleanly with the formation of acetate 4, the same product obtained earlier[2] from the acetolysis of 5-OTs.

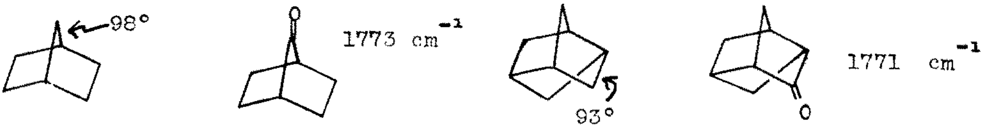


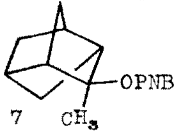
Two possible mechanistic pathways were considered for the rearrangement 3→4: (a) direct migration of the C_3- C_4 bond; (b) migration of the C_1- C_5 bond followed by migration of the C_2- C_3 bond. It was possible to rule out the operation of the two-step process from a consideration of the results of solvolysis of the deuterium analog 6.[5] The finding that the deuterated alcohol isolated from this reaction showed (nmr) one proton in the O-C-H region is inconsistent with the double migration process (see below).



Rate constants[6] for the acetolysis of 3 at 53.08 ± 0.07° were found to drift downward with time until a steady first order rate was attained at <u>ca</u>. 28% reaction. The calculated rate constant ($1.30 \times 10^{-5}\mathrm{sec}^{-1}$) beyond this point corresponded closely with that calculated[2] for the rate of acetolysis of 5-OBs under these conditions ($1.4 \times 10^{-5}\ \mathrm{sec}^{-1}$). Apparently, internal return with isomerization[7] competes with direct acetolysis in this system. Further evidence on this point was obtained by continuously monitoring the reaction by nmr. The rate of disappearance of 3 was clearly faster than the rate of appearance of 4. Furthermore, new peaks appeared which were attributable to 5-OBs. With this in mind, it was possible to analyze[7] the titrimetric data from the early stages of the reaction and to obtain values for the rate constant for direct acetolysis ($1.71 \times 10^{-4}\ \mathrm{sec}^{-1}$) and for isomerization ($8.51 \times 10^{-4}\ \mathrm{sec}^{-1}$).

It was of interest to estimate the driving force for this unusual rearrangement which, formally, involves contraction of a five to a four-membered ring. As a model system for rate comparisons, the analogous 7-norbornyl derivative appeared to be well-suited owing to the close correspondence of both the tetrahedral and trigonal geometries about the reaction centers. In the first approximation, a rate enhancement of 10^7 ($10^{-4}/10^{-11}$) may be calculated.[8] That this type of analysis has some creditability may be seen from the results with the tertiary derivative 7.[9] Hydrolysis of the latter in 80% aqueous acetone (14 hr. at 135°) in the presence of excess sodium bicarbonate, conditions under which the unrearranged alcohol 9 was stable, produced a new alcohol





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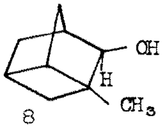

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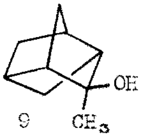

9

(>95%) to which structure 8 is assigned.[10] Thus, the driving force for rearrangement is sufficient to overcome the additional cationic stabilization provided by the methyl group. Since typical "methyl effects" in non-rearranging systems range[11] from 10^7 to 10^4, the estimated anchimeric assistance appears reasonable.

The extraordinary behavior of these tricyclo $(3.3.0.0^{3,7})$ octyl systems must be a manifestation of an inherently highly strained molecule. We would like to propose that only part of the driving force for these rearrangements is derived from bond angle strain relief at the reactive center (C_2). In addition, it appears that the geometry at the distal methylene group (C_6) is likewise favorably altered during rearrangement. We hope to explore more fully this type of "remote control" and to examine other substituent effects on these rearrangements.

Acknowledgments: We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We also acknowledge useful discussions with Professor P. K. Freeman.

1. R.R. Sauers, K. Kelly and B. Sickles, Abstracts 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, ORGN 74.
2. R. R. Sauers, R.A. Parent, and S.B. Damle, J. Am. Chem. Soc., **88**, 2257 (1966).
3. H. W. Whitlock, Jr. and M.W. Siefken, ibid, **90**, 4929 (1968); M. Nomura, P. von R. Schleyer, and A.A. Arz, ibid, **89**, 3657 (1967); A. Nickon, G.D. Pandit, and R.O. Williams, Tetrahedron Letters, 2851 (1967).
4. R.R. Sauers, W. Schinski, and M.M. Mason, ibid, 79 (1969). The brosylate had m.p. 45.5-47°.
5. The deuterio alcohol was prepared by reduction of tricyclo $(3.3.0.0^{3,7})$ octan-2-one with 98% sodium borodeuteride in isopropanol. The ketone was obtained from the alcohol[4] by chromic acid oxidation and had m.p. 106-110°; $\lambda_{max}^{CCl_4}$ 1771 cm^{-1} (weighted average).
6. S. Winstein, E. Grunwald, and L. Ingraham, J. Am. Chem. Soc., **70**, 821 (1948).
7. W. G. Young, S. Winstein, and H.L. Goering, ibid, **73**, 1958 (1951).
8. The data of H. Tanida, S. Ikegami, and H. Ishitobi, ibid, **89**, 2928 (1967) was used to calculate the acetolysis rate of 7-norbornyl brosylate at 53°. Calculation of the unassisted rate constant by the method of P. von R. Schleyer, ibid, **86**, 1854 (1964) gave similar results.
9. Alcohol 9 was prepared by the action of methylmagnesium iodide on the ketone,[5] m.p. 55.5-57°; δ 1.28 (singlet, CH_3); p-nitrobenzoate, m.p. 86-88°.
10. This structural assignment is supported by the appearance in the nmr spectrum of singlets

for both the methyl group (δ 1.00) and the carbinol proton (δ 3.60). The carbinol proton in the unsubstituted analog[2] also appears as a singlet (δ 3.7).

11. The high value referred to pertains to the 7-norbornyl system[8]; for other systems see K.L. Servis, S. Borčić, and D.E. Sunko, *Tetrahedron*, **24**, 1247 (1968) and H.C. Brown and M. - H. Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).