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MIGRATION OF THE METHYLENE BRIDGE DURING ACETOLYSIS OF A CYCLOPROPANATED ENDO-NORBORNYL BROSYLATE.

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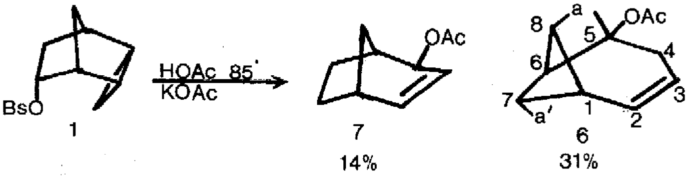
Although migration of the C_1-C_7 bond in reactions of endo nonbornane derivatives has been proposed to rationalize the products of a number of reactions,[1] only two examples of isolation of the fused cyclobutane product exist.[2] Both of these examples involve diazonium ion decompositions, a reaction known to give product compositions which may differ from those found in ordinary solvolysis reactions.[2b,3] We report here an example from an acetolysis.

Acetolysis of three of the tricyclo [3.2.1.$0^{2,4}$] octan-6-yl brosylates and nortricyclycarbinyl brosylate leads to products 2→5[4]. It is apparent that the acetolysis of the fourth isomer, 1, is unique, for acetolysis leads to the products indicated in Scheme I.

SCHEME I

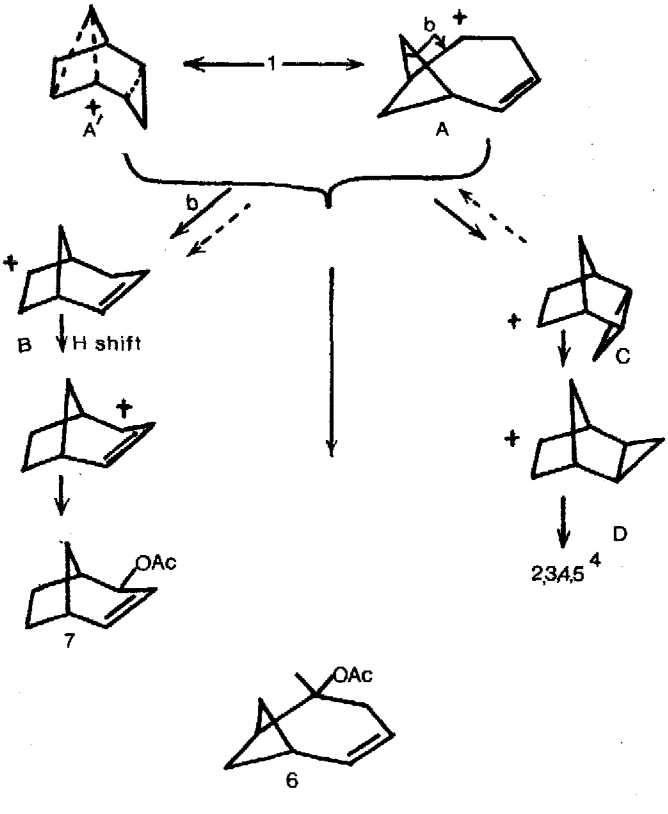


+ exo-exo tricyclo [3.2.1.$0^{2,4}$] octan-6-yl acetate (2, 17%), tricyclo [3.2.1.$0^{2,7}$] octan-4-yl acetate (5, 27%), 3-Nortricyclycarbinyl acetate (4, 1-2%), exo-bicyclo [3.2.1] oct-2-en-7-yl acetate (3, 10.5%) and 1.6% of unknown acetate.[5]

The structures of 2, 3, 4, 5, 7 were proved by comparison with authentic samples.[6] The structure of 6 rests on the following data; Mass spectral MW 166; ^{1}H NMR; δ 1.45 (q), J = 9.8 Hz, 6.5, 1H, 1.93 (s), 3H, 2.03 (m), J = 11, 6.5, 1H, 2.21 (two triplets), J = 11, 7, 1H, 2.4 (m), 1H, 2.5-2.65 (m), 4H, 5.12 (two triplets), J = 7, 7, 2.3; 1H, 5.43 (overlapping quartets), J = 11, 6, 4.5, 1H, 6.09 (m), J = 11, 6, 1H. The unique high field proton (δ 1.45) is characteristic of n·1·1 systems studied by Wiberg.[7]

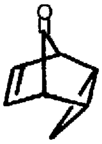
This quartet is assigned to the a or a' proton (J_{gem} = 9.8, J_{gem} 3·1·1 = 9.5) (J_W = 6.5, J_W 3·1·1 = 6). The large value for the W coupling (a-a') is in agreement with those for n·1·1 compounds.[7] All couplings agree with the presence of the $-\underset{H}{C}=\underset{H}{C}-CH_2-\underset{|}{C}H-OAC$ sequence. Decoupling of both bridgeheads and allylic hydrogens reduces the $-\underset{H}{C}-OAC$ proton resonance to a singlet. This verifies the four carbon unit and since the compound is bicyclic, unsaturated and does not contain a cyclopropane ring (^{13}C NMR) it must be a 4·1·1 compound.[8] The single frequency off resonance ^{13}C NMR also supports this assignment. ^{13}C NMR; δ 21.2 (q), 27.4 (t), 32 (t), 34·2·34·5 (t, d), 2C, 39.2 (d), 75.4 (d), 122.2 (d), 135.0 (d), 170.6 (s). The C_{13}-H coupling constants for the $-CH_2-$ and C-H protons on the cyclobutane ring are C_1, C_6, 139, 137, C_7, C_8, 144, 132. These large $^{13}C-^{1}H$ coupling constants are expected for cyclobutane rings.[9]

SCHEME II



Scheme II presents a simplified acetolysis pathway.[10,12] Since the endo-endo compound **1** is the only one of the four possible tricyclo [3.2.1.0^{2,4}] octan-6-yl brosylates that produce 6 and 7 it appears that the cyclopropane ring may be at least loosely involved in the ionization step. Whereas the nature of the interaction of the cyclopropane ring remains open ion **A'** represents an interesting possibility. This type of orbital interaction, represented in E, has been proposed before in the thermal decarbonylation of **8** and in related reactions.[13,14]

E



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Since the rate of acetolysis of **1** is the same as found for the exo-endo brosylate[4] it appears that if this interaction occurs it does not supply a large driving force for ionization.[15,16,17] However, it is clear that the cyclopropane ring supplies the energy for ring contraction whereas previous examples utilize the energy of diazonium ion decomposition.[2]

Acknowledgements

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References and Notes

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W. Huckel and H. Wolowski, Ber., 80, 39 (1947);
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(2) a. P. Yates and R.J. Crawford, J. Am. Chem. Soc., 88, 1561 (1966);
b. C.J. Collins et. al., J. Am. Chem. Soc., 89, 3940 (1967).

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(4) R.R. Sauers and J.A. Beisler, Tetrahedron Letters, 2181 (1964); K.B. Wiberg and G.R. Wenzinger, J. Org. Chem., 30, 2278 (1965); J.A. Berson et. al., J. Am. Chem. Soc., 91, 5601 (1969); J.A. Berson et. al., ibid. 91, 5594, (1969).

(5) The structure which best fits our present data is:

(6) The data for 5 is made less certain by the presence of a contaminant. However ^{13}C NMR of a $\sim$60, 40 mixture of 5 and 2 allows the C_{13} NMR of 5 to be deduced. The C_{13} NMR clearly indicates the cyclopropyl carbons and is consistent with the structure given.

(7) K.B. Wiberg and B. Andes Hess, J. Org. Chem., 31, 2250 (1966); and further spectra kindly supplied by Professor Wiberg.

(8) The 4·2·0 system is ruled out by the ^{1}H NMR.

(9) George C. Levy and Gordon L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley - Interscience, 1972.

(10) For simplicity all cations except A are drawn as classical, even if evidence to contrary exists. For example, there is reasonable evidence that D can be represented by [4,11]

(11) P.K. Freeman, D.M. Balls and J.N. Blazevich, J. Am. Chem. Soc., 92, 2051, (1970).

(12) It is possible that A, A' is formed in competition with C and two distinct pathways are involved in this solvolysis.

(13) M.A. Battiste, et. al., J. Am. Chem. Soc., 89, 5964 (1967).

(14) M.A. Battiste, J.M. Coxon and R. Edelman, Tetrahedron Letters, 45, 4577, (1972); M.A. Battiste and J. Mackiernan, Tetrahedron Letters, 40, 4095, (1972).

(15) It is very possible that acetolysis of 1 is sterically retarded and that indeed acceleration due to cyclopropyl participation is present but is swamped by such steric effects. This does not explain the facile conversion of A to other cations, however.

(16) For a review see; J.H. Farmer, Chem. Rev., 74, 315 (1974).

(17) It is possible that the classical ion produces 6, 7 by rearrangement. See dotted lines in Scheme II.