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ACID-CATALYZED REARRANGEMENTS OF 7-OXYGENATED NORBORNENYL DERIVATIVES

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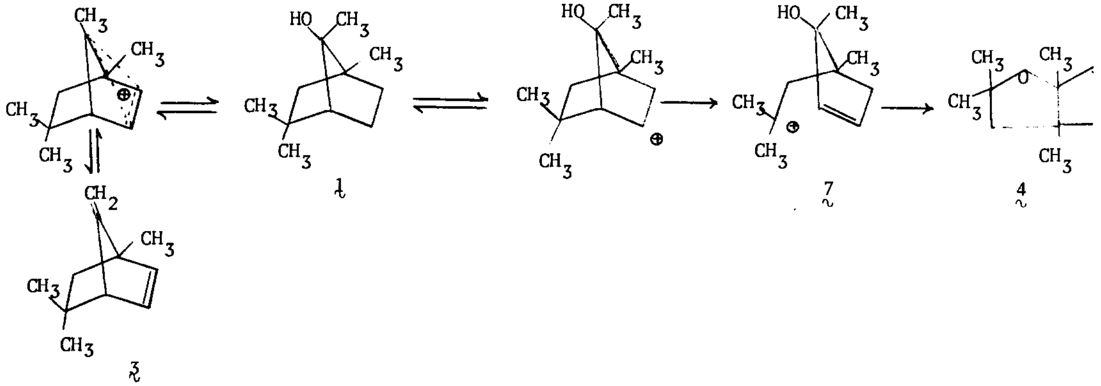
Recently, Gassman and coworkers described a number of studies[2] involving 7-oxygenated bicyclo[2.2.1]heptane systems. In each case unusual solvolytic behavior and rearrangement products were observed. For example, the tosylate of endo-7,7-dimethoxybicyclo[2.2.1]heptan-2-ol reacted *via* neighboring-group participation of the syn-7-methoxy substituent to yield an exo-2-methoxynorbornyl derivative. Both exo- and endo-2-tosyloxybicyclo[2.2.1]heptan-7-one ethylene glycol ketal reacted to yield a variety of products including a cyclohexene derivative arising from C_1-C_7 bond rupture (in the norbornyl skeleton). In none of the 7-oxygenated derivatives studied to date has a C_1-C_6 bond rupture been noted. In this communication we report the results of acid-catalyzed rearrangement reactions of anti-2,2,4,7-tetramethylbicyclo[2.2.1]hept-5-en-7-ol (1) and anti-2,2,4,6-tetramethylbicyclo[2.2.1]hept-5-en-7-ol (2), which give rise to products resulting from fragmentation of the C_1-C_6 and C_1-C_7 bonds, respectively.

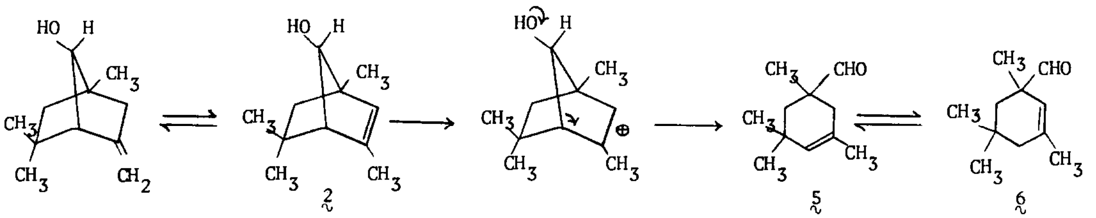
Compounds 1 and 2 were synthesized by acetolysis of the p-nitrobenzoate of endo-1,2,4,4-tetramethylbicyclo[3.2.0]hept-6-en-2-ol and exo-2,4,4,6-tetramethylbicyclo[3.2.0]hept-6-en-2-ol, respectively, with subsequent lithium aluminum hydride reduction of the corresponding anti-norbornenyl acetate.[3] Structural assignments of 1 and 2 were made on the basis of ir, nmr, and analytical data.

Acid-catalyzed rearrangement of 1 for 10 min. in refluxing aqueous acetic acid containing a catalytic amount of sulfuric acid resulted in the formation of 12% 3, 63% 4, 11% unidentified products, and 15% unreacted 1. When 3 was subjected to the same reaction conditions a mixture of 13% 3, 60% 4, 9% unidentified products, and 19% 1 was produced. A reaction scheme consistent with these observations is presented.



The structure assigned to 4 is based on mechanistic considerations and is consistent wi spectral data (as well as deuterium-labelling experiments). The nmr of 4 shows the methyl grou at δ1.03, 110 and 1.16 (12 H), the C_2 hydrogens as an AB quartet δ_B 1.73 and δ_A 1.82 (J_{AB} = 12 Hz), the C_8 hydrogens as an AB quartet with δ_B 2.08 and δ_A 2.34 (J_{AB} = 16 Hz) contain further splitting (J = 12 Hz), a one-hydrogen doublet at 5.44 (J = 6 Hz) containing fine splitt (J = 2 Hz), and a one-hydrogen doublet at 5.61 ppm (J = 6 Hz) containing fine splitting (J = ca. 1.5 Hz). The ir spectrum of 4 shows a sharp band at 3050 cm^{-1} (olefinic C-H), strong absorption at 1050-1200 (C-O), and a strong band at 735 (*cis*-disubstituted double bond). The u spectrum shows no maximum (ε_{210} 690) and is consistent with a disubstituted double bond.

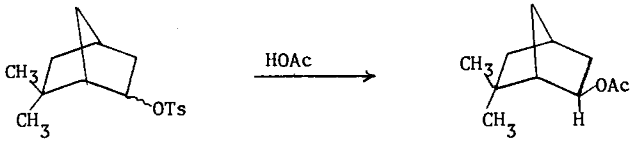
Acid-catalyzed rearrangement of 2 for 30 min. in refluxing aqueous acetic acid containi a catalytic amount of sulfuric acid resulted in the formation of 60% aldehyde 5 and 40% of its double bond isomer 6. A reaction scheme summarizing this reaction is indicated.

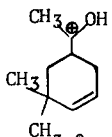


The structures of 5 and 6 were assigned on the basis of spectral and analytical data. nmr spectrum of 5 shows absorbances at δ0.85, 0.96, 0.98 (s, 9H, C-CH_3), 1.32 (d, 1H, J = 14 Hz HC$\underline{H}$), 1.82 (d, 1H, J = 14 Hz, HCH), 1.63 (d, 1H, J = 18 Hz, allylic $\underline{H}$CH), 217 (d, 1H, J = 18 Hz allylic HC$\underline{H}$), 1.63 (br s superimposed on preceding AB spectrum, 3H, C =C-$\underline{CH_3}$), 5.04 (br s, 1H, vinyl proton), and 9.36 ppm (s, 1H, -C$\underline{H}$O). The ir spectrum of 5 shows bands at 2780 cm^{-1}

(aldehyde CH) and 1715 (aldehyde C=O), and very weak absorption below 1300. The uv spectrum contains maxima at 274 nm (ε 56) and 266 (ε 56) and end absorption with ε_{210nm} 4330 (disubstituted double bond).

Of particular interest is the observation that rearrangements of 1 and 2 proceed with fragmentation of the C_1-C_6 bond in the case of 1 and of the C_1-C_7 bond in the case of 2. These two modes of reaction must reflect, at least in part, the fact that the carbonium ion produced upon reaction of 1 is secondary while that produced from 2 is tertiary. However, it should be noted that fragmentation of the C_1-C_6 bond in norbornyl systems devoid of oxygenated substituents[4] could not be detected. In view of these data it is surprising that 1 upon protonation opens to carbonium ion 7 rather than 8 which would be expected to be more stable. Possibly, carbonium ion 7 should be represented as a nonclassical ion[5] and the effect of the 7-oxygenated substituent is to alter the importance of the contributing resonance structures 9, 10, and 11 in such a way to make the contribution of 9 large enough for detection.

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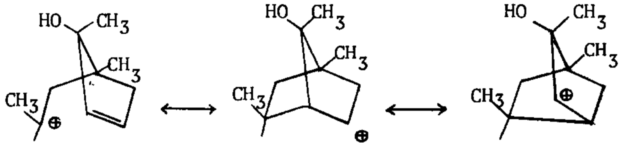
9 10 11

Further studies are in progress to more fully delineate the factors responsible for the different behavior of compounds 1 and 2.

REFERENCES

1. Author to whom inquiries should be addressed.
2. P. G. Gassman and J. L. Marshall, J. Amer. Chem. Soc., 88, 2822 (1966); P. G. Gassman and J. L. Marshall, Tetrahedron Lett., 2429, 2433 (1968); P. G. Gassman and J. G. Macmillan, J. Amer. Chem. Soc., 91, 5527 (1969).
3. Details of these reactions will be reported in a subsequent publication.
4. P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, J. Amer. Chem. Soc., 87, 375 (1965).
5. S. Winstein and D. S. Trifan, ibid., 74, 1147, 1154 (1952).