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THE CYCLIZATION OF EPOXYOLEFINS, III.

THE FORMATION OF BRIDGED SYSTEMS[1]

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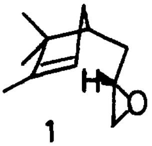
Previous attempts to prepare bridged bicyclic compounds by the cyclization of epoxyolefins have been unsuccessful[3,4]. We wish to report here, however, the conversion of the epoxyolefins 1a,b to a number of bi- and tricyclic compounds.



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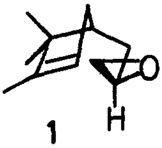

1

A mixture* of the diastereoisomeric epoxides was prepared by treatment of α-campholene aldehyde[3] with trimethylsulfoxonium methylide[5]. From the subsequent reaction of 1a,b with 1 molar equivalent of stannic chloride in benzene at room temperature there were obtained four products. Three of these materials were purified by g.l.c. and identified as the tricyclic ethers 2 and 3 and 2-formylbornane[6], 4. The fourth component appears to be a carbonyl compound which has

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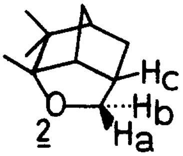
*Although no separation of 1a and 1b has been accomplished, the mixture is assumed to be 1:1 since the asymmetric center of α-campholene aldehyde should have little or no stereochemical effect on the formation of the new epoxide center.

not yet been obtained in sufficient purity to identify. Gas chromatographic analysis of the crude reaction mixture showed these compounds to be formed in the following relative percentages; 16% of 2, 19% of 3, 49% of 4 and 16% of the unidentified material. The absolute yield of products was found to 90% from g.l.c. measurements using borneol as an internal standard.



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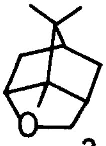

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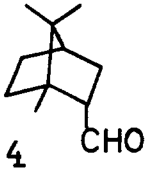
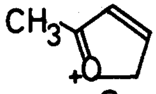
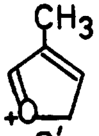


4

The structural assignments of 2, 3, and 4 are based on the following spectral data[7]. The "camphene" skeleton of 2 was shown by the appearance in its NMR spectrum of three singlets at 0.81, 0.90 and 1.09 p.p.m. relative to tetramethylsilane corresponding to the two geminal methyl groups and the methyl next to oxygen respectively. In addition, the methylene protons of the ether bridge are seen as basically an AB quartet centered at 3.5 and 3.8 ppm (J = 7 c.p.s.). The proton (Ha) corresponding to the lower field portion of the AB system is further split into a pair of doublets (J = 4 c.p.s.) by the bridgehead hydrogen Hc. In contrast, Hb forming an angle of almost 90 with Hc appears only as the higher field doublet of the AB pattern. The second tricyclic ether 3 is clearly a bornane derivative since its NMR spectrum closely resembles that of borneol. The methylene protons of the ether bridge again appear as basically an AB pattern. The mass spectra of both ethers display a fragment at m/e 83 as the base peak. High resolution measurements show the composition of these ions to be $C_5H_7O^+$ corresponding to the structures a and a'. A possible pathway for their formation is illustrated below for the production of a from 2.


a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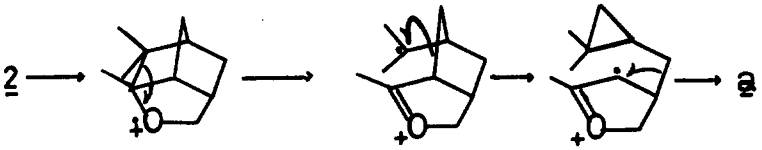
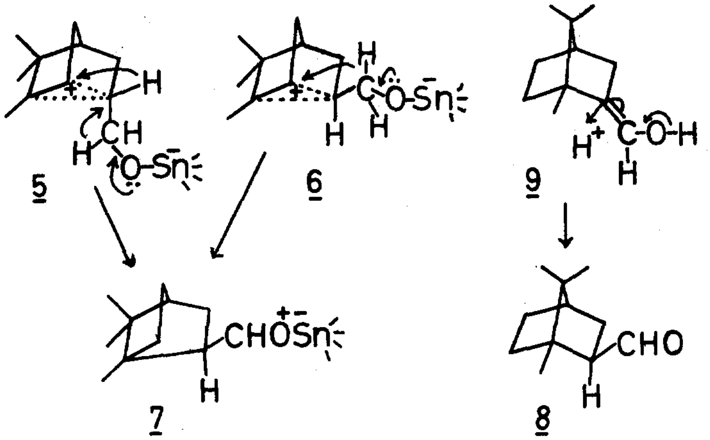


The third product, 2-formylbornane was again identified from its NMR and mass spectra and was shown to be principally the endo isomer. Oxidation of the aldehyde with m-chloroperbenzoic acid gave a mixture of alcohols consisting of 8% isoborneol and 92% borneol.

It is interesting to note that the predominant skeletal type found in these products is the bornane structure. The similarity of this system to the cyclopentenyl ethyl sulfonate systems studied by Bartlett[8] suggests that the intervention of bridged ions may most readily explain this result. Accordingly, the diastereomeric epoxides 1a,b would be expected to yield the electronically equivalent, tertiary, secondary ions represented by 5 and 6. As shown below the production of two tricyclic ethers is apparently a function of the geometry of the oxymethylene substitutent; 5 yielding 2, and 6 leading to 3. In contrast, the major product, endo-2-formylbornane must arise from both diastereoisomers since the total yield of the bornane skeleton is greater than 50%. Approximately half of this aldehydehyde may be produced by transfer of a hydride from the oxymethylene group as in 6 to 7. The remainder, however, must arise from a 2,6 hydride migration, 5 to 7, a particularly favorable process here since it entails the conversion of a tertiary, secondary bridged ion to a tertiary, tertiary one[8]. The latter, then, as shown below would also lead specifically to the endo aldehyde. The small amount of exo aldehyde 8 produced may result from the formation of some of the enol 9 followed by irreversible endo-protonation on work up of the reaction mixture with water.



When the cyclization was carried out in 85% phosphoric acid only two products, the tricyclic ethers 2 and 3, were obtained in a ratio of approximately 1:1. The lack of aldehydic products in this medium may be a function of the greater nucleophilicity of an hydroxyl group compared to oxygen bound to tin.

References

1. We wish to thank the National Institutes of Health for support of this work on Public Health Service Grant GM 11728-01.
2. (a) NASA Pre-doctoral Research Fellow, (b) Coca-Cola Pre-doctoral Research Fellow.
3. D. J. Goldsmith and C. J. Cheer, J. Org. Chem., 30, 2264 (1965).
4. Unpublished observations of R. C. Joines.
5. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1353 (1965).
6. J. A. Berson, and C. J. Olsen, J. Am. Chem. Soc., 84, 3178 (1962).
7. The NMR spectra were determined by Mr. H. B. Evans of this laboratory with a Varian A-60 spectrometer. Both the high and low resolution mass spectra were determined by D. J. G. in the laboratory of Professor Carl Djerassi, Stanford University, using an AEI MS-9 Spectrometer. All elemental analyses (combustion and/or high resolution mass spectrometry) corresponded to the expected formulations.
8. P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, J. Am. Chem. Soc., 87, 1288 (1965) and succeeding papers.