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# exo-2,3-EPOXYNORBORN-5-ENE

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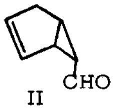
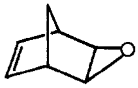
The conversion of norbornadiene (I) into bicyclo[3.1.0]hex-2-ene-endo-6-carboxaldehyde (II) by peracid oxidation has been described recently (1,2).

I



II



III

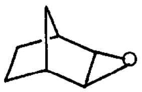
IV

The formation of II can be rationalized either as a consequence of the formation of the expected exo-epoxide III, followed by acid-catalyzed rearrangement, or by a more direct rearrangement mechanism involving participation of the second double bond during the peracid attack (1). We now wish to report evidence for the former mechanism.

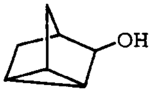
The concerted mechanism, in which positive charge in the transition state is distributed over several positions, might be expected to be characterized by an increased reactivity for I compared with norbornene (IV) itself. On the other hand, initial formation of the epoxide III from I might be expected to proceed at a rate comparable to that of the epoxidation of IV, after allowing for a small inductive deceleration and the statistical effect of having two double bonds. The rates of epoxidation of I and IV were examined in chloroform solution at $0.5^{\circ}$ using m-chloroperbenzoic acid, and were found to be comparable ($k_2 =$ 4.45 mole$^{-1}$ min.$^{-1}$ for I, 4.22 mole$^{-1}$ min.$^{-1}$ for IV). This observation gave renewed incentive to attempt the isolation of III itself from a more carefully controlled oxidation reaction.

In an experiment in which a methylene chloride solution of I over anhydrous potassium carbonate was treated below 5° with commercial 40% peracetic acid solution saturated with anhydrous potassium acetate, a crude product was obtained in approximately 70% yield, based on the peracetic acid. This material showed not only the expected infrared absorption peaks for the aldehyde II, but also intense absorption at 11.75μ characteristic of an epoxide (3). A proton magnetic resonance spectrum of this crude reaction product indicated the presence of only about 7% of aldehyde II. Distillation of this material (38-40°/12 mm.) gave two difficultly separable fractions, an initial partly crystalline one, followed by a liquid (4). The complete purification of this new, crystalline product was not possible, since it is converted into II with ease. However, a sample (20% yield) melting at 50-56° could be obtained simply by pressing the impure material between layers of filter paper. In the infrared (see fig. 1), this material retained carbonyl absorption (5.92μ), corresponding to contamination by II, of only moderate intensity, along with the very strong epoxide absorption (11.75μ) expected for III. The proton magnetic resonance spectrum of this solid material (see fig. 2) seemed to indicate contamination by approximately 5% of aldehyde. The following assignments were made: two olefinic protons at $\tau$3.61 (triplet, J = 1.9 cps), two epoxide protons at $\tau$6.79 (singlet), two bridgehead hydrogens at $\tau$7.16 (unresolved multiplet), and a typical AB pattern for the two bridge protons at $\tau$8.38 and 8.82 (J = 8.2 cps) (5). This material gave analytical figures in accord with expectations (calculated for $C_7H_8O$: C, 77.75; H, 7.46. Found: C, 77.63; H, 7.29).

The isomerization of III to II was observed as the partially purified epoxide III was allowed to stand at room temperature both in chloroform solution and without solvent. The gradual increase of intensity of the carbonyl absorption in the infrared spectrum (5.92μ) was accompanied by the disappearance of the 11.75μ band. Even after six days, however, some epoxide was still present. Shaking III in methylene chloride with dilute sulfuric acid solution at room temperature for ten minutes resulted in more deep-seated changes, as evidenced by the appearance of hydroxyl absorption in the infrared spectrum of the product as well as disappearance of the epoxide band. This transformation may be analogous to the acid-catalyzed ring opening of exo-2,3-epoxynorbornane (V) to a mixture of diols (6).



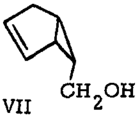
V

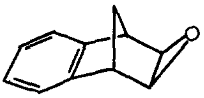


VI

The exo-configuration of the unsaturated epoxide (III) was demonstrated when 400 mg. of III was hydrogenated over 10% palladium-charcoal in ethyl acetate at atmospheric pressure. The oily product was sublimed to yield 305 mg. (75%) of colorless, crystalline exo-2,3-epoxynorbornane (V), identified by infrared spectral comparison with an authentic sample. In a further experiment, 500 mg. of V (from the hydrogenation of III) was treated with lithium diethylamide (7) to yield 240 mg. (48%), after sublimation, of colorless, crystalline nortricyclanol (VI), m.p. and mixture m.p. with authentic nortricyclanol 107-109° (lit. 108-109°) (8). The infrared spectra of VI obtained by the lithium diethylamide treatment of V and of authentic nortricyclanol were superimposable.

In further attempts to examine the chemistry of III, a freshly prepared sample (400 mg.) of epoxide was reduced with lithium aluminum hydride. The crude reaction mixture was examined by gas chromatography on a 10% Carbowax-20M (6' x 1/8") column at 135° revealing two components: a minor one (less than 5%) (3.3 min.) and the major one (6.1 min.). The major component was identified as endo-6-hydroxymethylbicyclo[3.1.0]-hex-2-ene (VII) by gas chromatographic comparison and by the superimposability of its infrared spectrum with that of an authentic sample. The previously unknown VII, b.p. 115-116°/55 mm., (Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.01. Found: C, 76.30; H, 9.17), was prepared by lithium aluminum hydride reduction of the aldehyde II. The initially unexpected course of the hydride reduction is not without precedent, since this reagent is known to bring about acid-catalyzed rearrangement during the reduction of the benznorbornadiene oxide VIII (9).


VII


VIII

It may be noted in conclusion that the unstable, crystalline substance shown in this work to be III is clearly different from the liquid "*endo*-2,3-epoxynorborn-5-ene" (IX), obtained from the peracetimidic acid oxidation of I (2). Thus, the proton magnetic resonance spectrum of III is clearly different from that of a sample of epoxide prepared as described by Lumb and Whitham. The formation of a small amount of *endo* epoxide (IX) along with III would not be at all unreasonable, however, since other examples of *endo* addition to a norbornene double bond are known (10). A simple explanation of Lumb and Whitham's results might be that under their reaction conditions III and IX are both formed, and that III rearranges preferentially to II, leaving the isomeric epoxide behind.

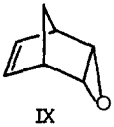

IX

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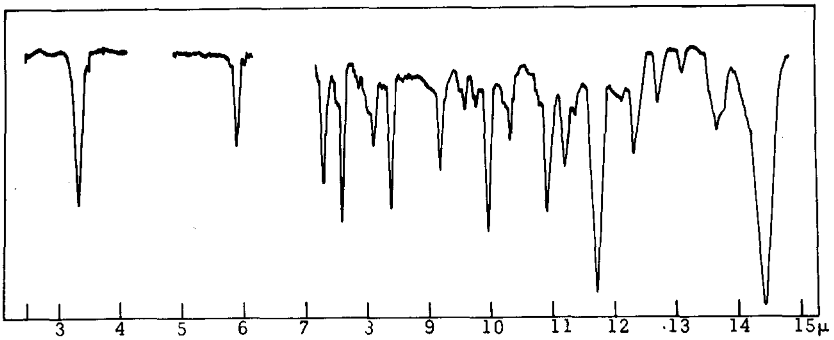
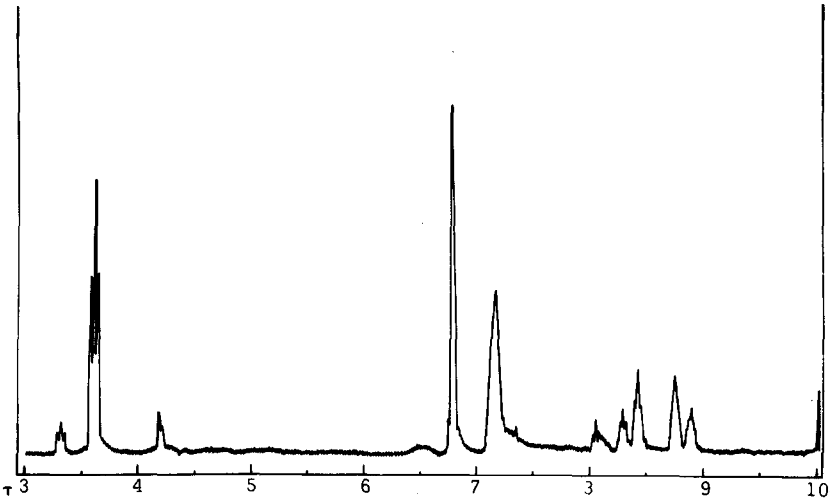
FIG. 1



Infrared spectrum of III (m.p. 50-56°) in carbon disulfide

FIG. 2



Proton magnetic resonance of III (m.p. 50-56°) in carbon tetrachloride