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CARBON-CARBON BOND FISSION IN CYCLOPROPANES III.*
THE ACID PROMOTED OPENING OF THE THREE-MEMBERED RING IN EXO-TRICYCLO[3.2.1.0^{2,4}]OCTANE

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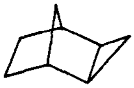
In our search for appropriate substrates which might be employed in a study of the mode of electrophilic attack of strained carbon-carbon bonds, we have investigated the acid promoted cleavage of the three-membered ring in exo-tricyclo[3.2.1.0^{2,4}]octane, I.



I

In this communication we report and discuss our preliminary results.

The treatment of I with glacial acetic acid, 0.07N in sulfuric acid, for fifty hours at room temperature produced a mixture of olefins (20%) and acetates (80%). The acetate component was shown by gas chromatographic analysis (Carbowax at 159°) to consist of five poorly resolved acetates. The acetates were converted by lithium aluminium hydride hydrogenolysis to a mixture of alcohols whose gas chromatogram, obtained by employing a 17% glycerol on Celite column at 103°, demonstrated the presence of six alcohols. The predominant alcohol was present in 44% of the alcohol fraction and its gas chromatographic retention time (peak 4, 45 min.) was identical with that of axial-2-bicyclo[3.2.1]octanol, II (R=H). The next most abundant

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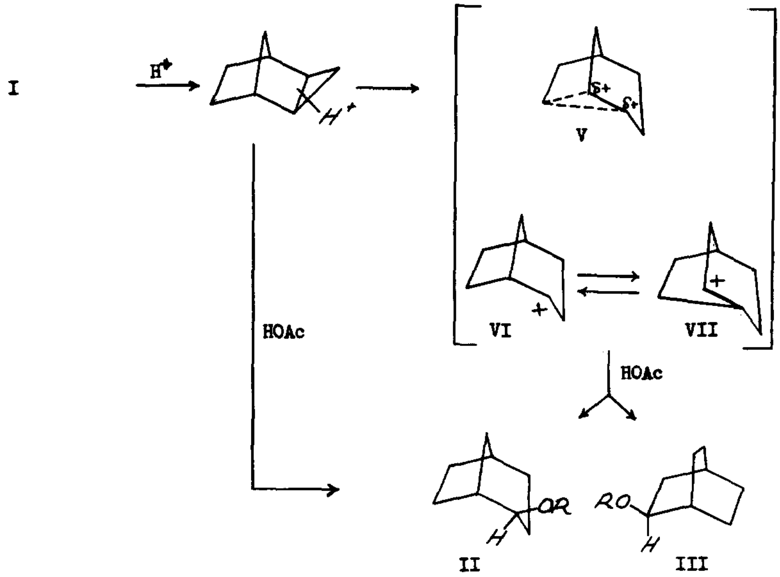

alcohol was present in 28% of the alcohol fraction and its retention time (peak 5, 50 min.) was identical with that of 2-bicyclo[2.2.2]octanol, III (R=H). The chromatogram also showed that three other alcohols (peaks 1, 2 and 3) were present in the sum of 28% of the alcohol fraction.

Conversion of the alcohol mixture to a mixture of p-nitrobenzoates and subsequent repeated recrystallization gave the p-nitrobenzoate of axial-2-bicyclo[3.2.1]octanol m.p. 98-98.5° (reported (1) 94-95°) which did not depress the melting point of authentic material.

The two major alcohols, along with an alcohol present in a trace quantity (peak 6, retention time 53 min. on glycerol on Celite at 103°), were cleanly separated together from a mixture of the other three alcohols (peaks 1, 2, 3) by preparative scale gas chromatography employing a silicone column. The latter mixture of three alcohols gave an infrared spectrum showing a hydroxyl band at 2.98μ and a methyl band at 7.27μ and on this basis was considered to be a mixture of the methylbicyclo[2.2.1]heptanols. This component of the total alcohol mixture was not further investigated. The mixture of three alcohols consisting of peaks 4, 5 and 6 gave an infrared spectrum which showed no methyl absorption in the region of 7.3μ but which did show bands at 9.15, 9.70, 10.20, 10.70, 11.05 and 11.80μ which are reported for 2-bicyclo[2.2.2]octanol (1) as well as the bands at 10.40 and 9.85μ which are found in the spectrum of *axial*-2-bicyclo[3.2.1]octanol (1,2). Only two (9.40 and 10.00μ) of the four strong bands reported (1,2) for *equatorial*-2-bicyclo[3.2.1]octanol, IV, could be detected and these were of diminished intensity compared to the other bands in this region. Oxidation of this partially separated mixture by the method of Brown and Garg (3) gave a ketone mixture which again exhibited no methyl absorption in the region of 7.3μ. Although this ketone mixture showed only a single peak on the gas chromatograms (employing 17% glycerol or Carbowax), the presence of more than one ketone was demonstrated through the conversion with lithium aluminium hydride to a mixture consisting of *axial*-2-bicyclo[3.2.1]octanol (14%), 2-bicyclo[2.2.2]octanol (39%), and an alcohol (47%) whose gas chromatographic retention time was identical with that of the alcohol in the ring-opening mixture present in a trace quantity. From these results it appeared that this last alcohol was being produced in the oxidation-reduction sequence at the expense of *axial*-2-bicyclo[3.2.1]octanol and must, therefore, be the *equatorial* isomer.

That the ring-opening mixture of alcohols represents almost completely the products formed directly from I rather than the products formed by equilibration or addition to olefin was demonstrated by the observation that neither II (R=Ac) nor III (R=Ac) gave more than 4% of isomeric acetates and that bicyclo[2.2.2]oct-2-ene gave 1% acetate while bicyclo[3.2.1]oct-2-ene gave less than 1% acetate under ring-opening conditions.

The predominance of non-Markovnikov opening in the addition of acetic acid to I can be explained on the basis of the polarization of the three-membered ring by the perturbing proton in the direction of the maximum relief of strain in the transition state. In view of the formation of both 2-bicyclo[2.2.2]octyl acetate and *axial*-2-bicyclo[3.2.1]octyl acetate, it appears that the ring-opening process proceeds in part by way of the non-classical carbonium ion V (1,4) or through the extremely rapidly inter-converting carbonium ions VI and VII (5). The formation of a non-classical carbonium ion intermediate in the acid-promoted cleavage of a strained bond has previously been invoked to account for the products obtained from the cleavage of the three-membered ring in nortricyclene (6).

The solvolysis and deamination of 2-bicyclo[3.2.1]octyl and 2-bicyclo-[2.2.2]octyl brosylates (4,5), tosylates and amines (1) produce mixtures of the isomeric bicycloöctanols which consist of 35-46% *axial*-2-bicyclo[3.2.1]-octanol and 65-54% 2-bicyclo[2.2.2]octanol. In the mixture of alcohols which originates from I, the *axial*-2-bicyclo[3.2.1]octanol has been found to make up 44% of the total alcohol mixture or 61% of the mixture of bicycloöctanols. If a liberal correction of 6% is subtracted to account for *axial*-2-bicyclo-[3.2.1]octanol which might be produced by isomerization of 2-bicyclo[2.2.2]-octyl acetate and addition to olefin, it is apparent that *axial*-2-bicyclo-[3.2.1]octanol is still the predominating bicycloöctanol arising from I. This observation strongly suggests that the acid-promoted addition of acetic acid to I might occur in some small measure by the direct nucleophilic solvent attack on a protonated or protonating I. The excessive formation of the *axial*-isomer indicates that this attack must occur with inversion of configuration.

The strained carbon-carbon bond in fused-ring compounds which is cleaved by an electrophilic reagent is usually the same bond cleaved in hydrogenolysis. Thus the bond external to the large rings in the bicyclo[n.1.0]alkanes (where n=3-5) is cleaved both in the hydrogenolysis (7,8,9) and in the reaction with an electrophilic reagent (10). Both the hydrogenolysis (11) or acid treatment (10) of the severely strained bicyclo[2.1.0]pentane results in rupture of the carbon-carbon bond common to both rings. However, the highly strained I and its derivatives undergo hydrogenolysis of the bond external to the large ring (12,13) to give methylbicyclo[2.2.1]heptanes but, as shown here, is attacked predominantly by a proton in such a manner as to cleave the bond common to the three-membered ring and the large ring. The explanation for the apparent anomalous behavior of I must lie in the difficulty of the *endo*-attack of I by the hydrogenation catalyst. Approach by catalyst from the more sterically hindered *endo*-direction is necessary in order to cleave what would appear to be the most strained carbon-carbon bond in I. On the other hand a proton, having smaller steric requirements, might be capable of *endo*-attack or perhaps attack in a manner analogous to that which occurs in electrophilic substitution with inversion (14). Work is now underway in an attempt to learn which of these two possible modes of electrophilic attack takes place.

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