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THERMAL REARRANGEMENT OF PENTACYCLO[6.5.0.0^{2,4}.0^{3,7}.0^{10,13}]TRIDECA-5,11-DIENE, THE PHOTOCHEMICAL 1,3-ADDUCT OF BENZENE TO BICYCLO[3.2.0]HEPTA-2,6-DIENE.

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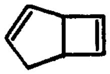
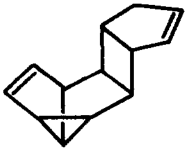
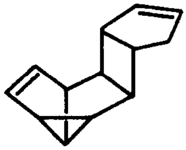
It has been shown elsewhere[1] that the major product (30% yield) of the photochemical addition of benzene to bicyclo[3.2.0]hepta-2,6-diene (I) consists of the isomers IIa and b which are the 1,3-adducts of benzene to the cyclobutene ring in I. As was expected,[2,3] 1,3-addition favored the more strained of the two olefinic groups in I. The minor product (15%) from this reaction also consisted of two isomers in nearly equal amounts which, based on the evidence already presented[1] were identified to be the 1,3-photoadducts of benzene to the cyclopentene ring in I. No information on the stereochemistry of the adducts was available at that time but it has since been found[4] that the 1,3-addition of benzene to cyclopentene itself is preferentially (10:1) endo-oriented. It is reasonable to infer that this stereochemistry prevails in the addition to I as well. The cyclobutene ring in these adducts may be pointed away from the rest of the molecule in order to minimize steric hindrance. The exact orientation of the cyclobutene ring is not crucial to the results that are presented here. IIIa and b would be reasonable representations of these adducts.[5]



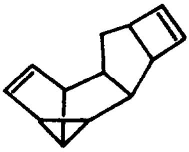
I



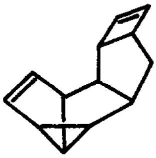
IIa



IIb



IIIa

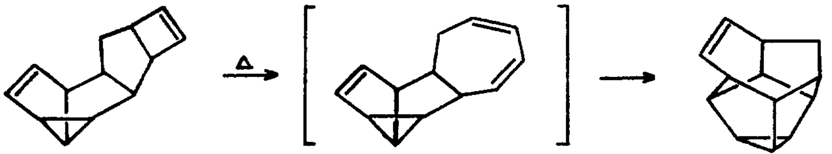


IIIb

Pyrolysis of the mixture of IIIa and b was carried out in a static system in the vapor phase in sealed Pyrex bulbs. The half-life for decomposition was less than 10 min. at 300° The products were analyzed by gas chromatography on a UCON-550X column (8') at 155°. In addition to materials formed by fragmentation (e.g. benzene) which were not further analyzed, there was one isomeric compound (Mol. wt. by mass spectrum: 170. Anal. Calcd. for $C_{13}H_{14}$: C, 91.73; H, 8.29. Found: C, 91.42; H, 8.19.) m.p. 67.0° formed in 50% yield. Its infrared spectrum showed the presence of olefinic absorption (1625 cm^{-1}) but was otherwise unexceptional.

Its ultraviolet spectrum (solv.: pentane) showed only end absorption ($\varepsilon_{210} = 3700$; $\varepsilon_{220} = 1545$). There was a shoulder at 204 nm. Its proton magnetic resonance spectrum at 60 MHz[6] consisted of two olefinic absorptions at δ 5.70 and 6.35 while the remaining twelve protons formed a complex pattern from δ 1.0 to 3.0. The presence of only one double bond in the molecule was verified by the proton-decoupled C_{13} resonance spectrum. Of the fourteen separate lines that were observed, two which occurred at 1000 and 720 Hz downfield from CCl_4 could be attributed to olefinic carbons. The dozen lines from the remaining carbons were in the narrow region from 830 to 1510 Hz upfield from CCl_4.

The analytical data are compatible with the presence of one olefinic group only if the compound is hexacyclic. This is remarkable because the precursor to this product (IIIa or b or both) was pentacyclic. A reasonable expectation on pyrolyzing IIIa or b is that the cyclobutene ring will undergo valence isomerization to a conjugated diene. In bicyclo[3.2.0]heptene-6, this reaction occurs at an appreciable rate only at about 300°.[7] The triene that will be formed from IIIa or b by valence isomerization may undergo an internal Diels-Alder addition to give the hexacyclic product on hand. The possibility that any of the new rings that are formed during the pyrolysis can be 3- or 4- membered seems unlikely. Therefore a reasonable hypothetical structure for the product is V and its mode of formation from IIIa can be as follows:

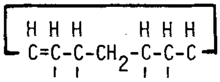


IIIa IV V (1)

The corresponding transformation from IIIb would lead to a product with a new cyclobutane ring. This possibility was therefore rejected.

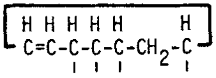
Confirmatory evidence for the structure of V was obtained from the 220 MHz proton magnetic resonance spectra (Fig. 1) of the compound and its hexadeuterioanalog (VI) which was made from perdeuteriobenzene and I.

A comparison of the two spectra shows that the resonances of the olefinic protons as well as of the two protons at 381 and 325 Hz (frequencies measured downfield from TMS) are completely unchanged on partial deuteration. The latter two, which form an AB pair with a mutual coupling of 12.5 Hz presumably belong to a methylene group which does not adjoin either of the olefinic protons since there is no coupling between the two pairs. The resonance at 540 Hz due to three protons is seen to change its coupling pattern on partial deuteration of the molecule and therefore must belong to protons located on carbons which are linked to the benzene moiety. This is probably true of the eighth proton resonance at 455 Hz as well, although its pattern is partly obscured in the spectrum of V. It follows that the seven carbons from the original cycloheptatriene molecule are arranged as in A or B:



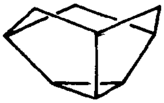
$\underset{|}{\overset{H}{C}}=\underset{|}{\overset{H}{C}}-\overset{H}{C}-CH_2-\underset{|}{\overset{H}{C}}-\underset{|}{\overset{H}{C}}-\overset{H}{C}$

A

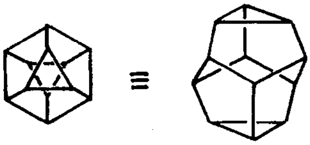


$\overset{H}{C}=\overset{H}{C}-\underset{|}{\overset{H}{C}}-\underset{|}{\overset{H}{C}}-\underset{|}{\overset{H}{C}}-CH_2-\underset{|}{\overset{H}{C}}$

B



VII



VIII

In either case, two new points of attachment to the benzene carbons have appeared during the rearrangement.

The six protons which originally belonged to the benzene ring fall into two narrow ranges of frequencies indicating a high degree of order in this part of the molecule. In particular, the strongly coupled resonances due to a set of three protons at ca 430 Hz (farthest upfield with the exception of the -CH_2- protons) suggests that they may be located on a cyclopropyl ring. The disappearance of the vinylcyclopropane chromophore that was present in IIIa and b, during the thermal rearrangement (as shown by the absence of a UV maximum at ca 220 nm) indicates that the two new bonds to the C_7 part may have occurred at these olefinic carbons. These considerations along with partial structure A give rise to the overall structure V. The same reasoning along with the partial structure B would give a total structure with both cyclopropane and cyclobutane rings - an unattractive possibility for a product formed at 300°.

V incorporates the hitherto unknown tetracyclononane VII in it and also offers an attractive route to the symmetric $C_{12}H_{12}$ cage compound, VIII.

ACKNOWLEDGMENT

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2. R. Srinivasan, IBM J. Res. Dev., 15, 34 (1971).
3. R. Srinivasan, J. Phys. Chem., 76, 15 (1972).
4. R. Srinivasan and V. Y. Merritt, unpublished work.

5. The title compound is IIIa. The isomer IIIb would be pentacyclo[6.5.0.0^{2,4}.0^{3,7}.0^{9,12}]-trideca-5,10-diene.
6. Both 60 and 220 MHz nmr spectra as well as the C_{13} spectra were run in CCl_4 solution with TMS as the internal reference. The instruments used were a JEOL Co. Minimar, a Varian HR-220 and a Bruker HFX-10 spectrometer. The latter was operated by the Consortium at the Rockefeller University in New York.
7. G. R. Branton, H. M. Frey, D. C. Montague and I. D. R. Stevens, Trans. Faraday Soc., 62, 659 (1966).

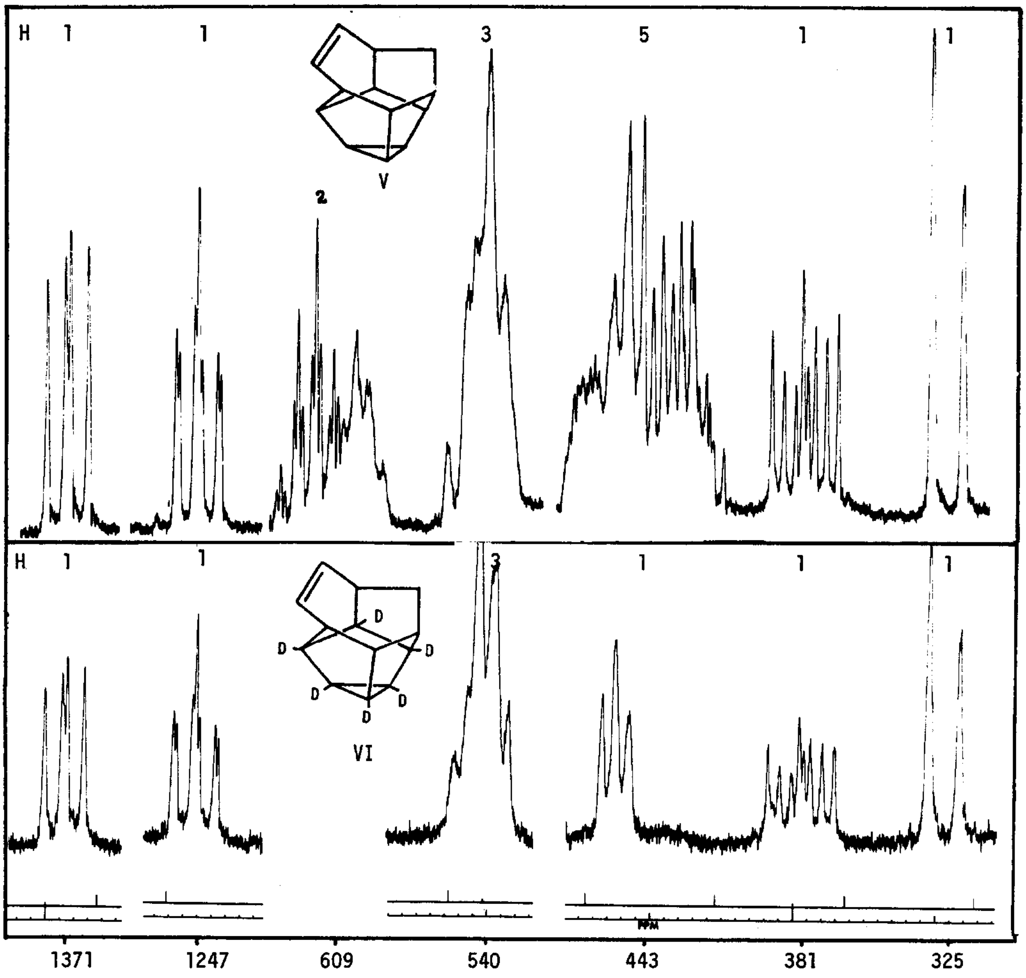

Figure 1. Proton Magnetic Resonance Spectra at 220 MHz