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REACTIONS OF DEHYDROBENZENE II. 7,8-BENZOBICYCLO-[4.2.1]NONA-2,4,7-TRIEN-9-ONE; A 1,6-CYCLOADDITION PRODUCT OF DEHYDROBENZENE

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In a previous communication, we described the first example of 1,6-cycloaddition reaction of dehydrobenzene(1). In this communication we report another example of this type of reaction.

In 1967, Ciabattoni, Crowley and Kende described the isolation of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (I) from the reaction mixture of tropone and benzyne (2). We examined this reaction to search for 1,6-cycloaddition product(s) of dehydrobenzene and isolated, in addition to the main product I, an isomer having a novel ring system, 7,8-benzobicyclo[4.2.1]nona-2,4,7-trien-9-one (II), as follows.

Decomposition of benzenediazonium-o-carboxylate (prepared from 13.5 gr. of anthranilic acid) was carried out by heating it in dioxane (250 ml.) in the presence of tropone (15.9 gr.) for four hours at 50°. After careful chromatographic separation (silicic acid/ benzene) we isolated a colourless crystalline product A (500 mg.) mp. 82-82.5° together with the compound I (6.32 gr.). The analytical data and molecular weight determination of compound A are consistent with the molecular formula $C_{13}H_{10}O$. Its spectral data are as follows; λ_{max}^{EtOH} mμ (log.ε) 220(4.01 end absorption), 262(3.43 infl.), 270(3.55), 277(3.51), 320(2.57); $\nu_{max}^{CCl_4}$ cm^{-1} 3037^{sh}, 3035, 2960, 1766, 1472, 1216, 1167. As shown by the IR spectrum it contained a 5-membered cyclic keto group, giving a 2,4-dinitrophenylhydrazone, $C_{19}H_{14}O_4N_4$, mp. 226-226.5°, λ_{max}^{EtOH} 361.5

mμ (log.ε 4.03).

The nmr spectrum of A taken in $CDCl_3$ showed the presence of 4 aromatic, 4 olefinic and 2 aliphatic protons (vide infra). Catalytic hydrogenation of compound A gave an oily tetrahydro derivative (VII), $C_{13}H_{14}O$, which had a characteristic UV absorption of indanone-2 (λ_{max}^{EtOH} mμ (log.ε) 263.5(3.48), 270 (3.62), 276(3.64)), a C=O streching band at 1758 cm^{-1}(CCl_4) in IR spectrum, and an aromatic protons singlet at 7.2(4H), a bridge-head protons multiplet at 3.47(2H) and complex multiplets at 0.7-2.5(8H) in nmr spectrum (δ^{CCl_4} in ppm.). It formed 2,4-dinitrophenylhydrazone, $C_{19}H_{18}O_4N_4$, mp. 162-162.5°, λ_{max}^{EtOH} 362 mμ (log.ε 4.30).

Consideration of the structures of the starting materials along with the presence of a five membered cyclic keto group in the product, proposes the structures II-V for compound A, of which III is eliminated by the examination of the nmr proton ratio, IV and V by UV spectrum. The most reasonable structure II (3) is supported by its nmr spectrum and the decoupling experiment (Fig. 1). Aromatic 4 protons appeared in AA'BB' type and remainning protons consisted of AA'BB'XX' pattern, which was revealed by irradiation at the position of the bridge-head protons (X part) in an AA'BB' type. These data are consistent with the symmetrical structure (4). The coupling constant of the bridge-head proton to the adjacent olefinic proton was 7 cps which was in accordance with the data given for similarly coupling protons in compound (IX) and (X) (7 and 6 cps, respectively)(5,6).

Recently, Friedman reported a facile conversion of benzobicyclo[2.2.2]-octatriene (XII) to benzocyclooctatetraene (XIII) by UV irradiation in cyclohexane solution (7). Compound XIII being assumed to be stable under this condition, we photolyzed compound A in a hexane solution using a low pressure mercury lamp under external ice cooling. After 30 minutes the UV spectrum of the solution showed a new maximum at 232.5 mμ with gas evolution. Isolation of the product gave colourless crystals mp. 48-49°, in 85% yield. The IR and UV spectra of the crystals were completely identical with those reported for benzocyclooctatetraene by Wittig (8).

The mass spectrum of compound A was quite interesting. The locations and intensities of peaks below m/e 155 were quite similar to the spectrum of XIII. That is, compound A decomposes exclusively to XIII and carbon monoxide in the spectrometer under the condition applied. This fact together with the photochemical transformation also supports the structure II for compound A. The compound A may be formed directly by 1,6-cycloaddition reaction of dehydrobenzene to tropone and not by the thermal rearrangement of compound I (9).

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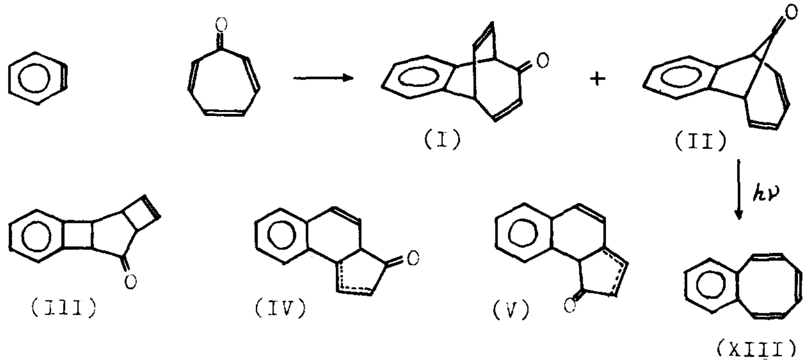


(I) (II) (III) (IV) (V) (XIII)

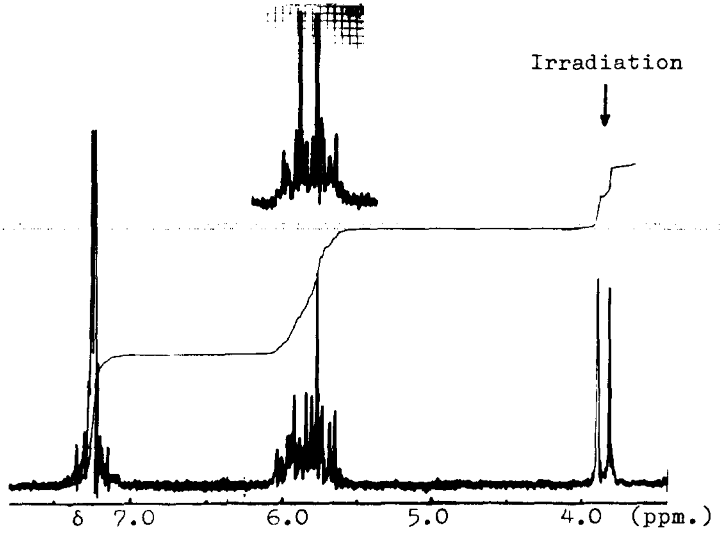
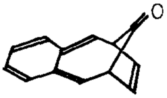
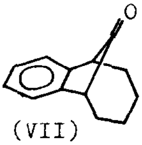
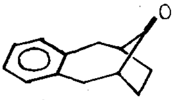
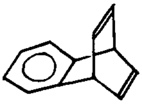


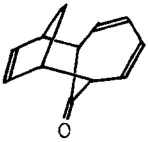
Fig.1 nmr spectrum of compound A (100 Mc. in $CDCl_3$)


(VI)


(VII)


(VIII)


(XII)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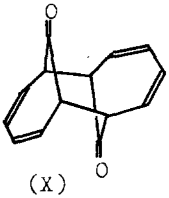
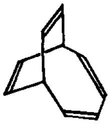

(X)


(XI)

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2. J.Ciabattoni, J.E.Crowley and A.S.Kende, J. Am. Chem. Soc., 89, 2778 (1967).

3. The structure VI was also considered for compound A, but the nmr and UV data were rather unlikely for VI. Since the tetrahydro derivative VIII, which had been reported by G.Opitz and H.Mildenberger[Liebigs Ann. Chem., 650, 115 (1961)] and was synthesized independently from indanone-2 and N,N'-dinitroso-N,N'-diethoxycarbonyl-1,4-diaminobutane under the influence of potassium carbonate in ethanol, was not identical with the tetrahydro A, the structure VI was eliminated. Such an example of homologation is found in the literature [C.D.Gutsche and T.D.Smith, J. Am. Chem. Soc., 82, 4067 (1960)]. We are indebted to Miss E.Uchiyama of our laboratory for the synthesis.

4. Similar nmr pattern of diene protons of XI has been reported; M.Jones, Jr. and B.Fairless, Tetrahedron Letters, 4881 (1968).

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9. The compound A was not detected in the mixture from the thermal decomposition of I at 350°. Below 250°, I was quite stable.