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IRRADIATION OF THE cis,cis -CYCLODECA-1,6-DIENE SYSTEM

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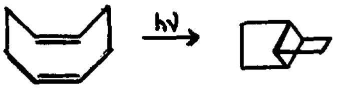
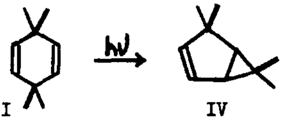
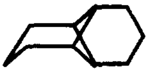
The photochemical reaction of cis,cis-cycloocta-1,5-diene (I) yielded the cross-bonded tricyclo $[3.3.0.0^{2,6}]$ octane (II) (1) and that of the cyclohexa-1,4-diene III led to the rearranged bicyclic product IV (2). We wish to report the photochemical reaction of the cis,cis-cyclodeca-1,6-diene system (3), (4). This follows the Woodward-Hoffmann rule (5) for the photochemical cycloaddition of two double bonds to yield cyclobutane VII, but not to the cross-bonded tricyclo $[4.4.0.0^{2,7}]$ decane system V (6), (7).



I II



III IV

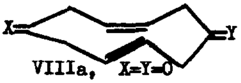


V

Irradiation (8) of 1 gr. of VIa in 130 ml benzene was carried out at room temperature under N_2 atmosphere. Thin layer chromatography indicated the completion of the reaction within 2 hours.

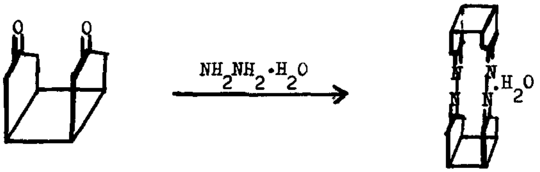
VIa, X=Y=O
b, X=O, Y=$(OCH_3)_2$
c, X=Y=$(OCH_3)_2$

VIIa, X=Y=O
b, X=O, Y=$(OCH_3)_2$
c, X=Y=$(OCH_3)_2$



VIIIa, X=Y=O
b, X=O, Y=$(OCH_3)_2$

Two major products, isomeric with the starting material, were isolated by column chromatography on Florisil. The less polar compound isolated (mp 73-4°, 25-30%) was shown to be cis,trans-cyclodeca-3,8-diene-1,6-dione (VIIIa). [ν^{KBr}_{max} 1699, 982 and 706 cm^{-1}; nmr ($CDCl_3$) δ 5.90 (2H, multiplet, trans olefinic protons), 5.60 (2H, triplet, cis olefinic protons) and 3.60 - 3.12 (8H, multiplet, allylic and α-carbonyl protons)]. Further confirmation of this structure was made by the catalytic reduction, using Adam's catalyst, to cyclodeca-1,6-dione, mp 98-9° (9). The more polar product (mp 133-4°, 45-50%) was shown to be the dione VIIa [ν^{KBr}_{max} 1725 cm^{-1}, $\nu^{CHCl_3}_{max}$ 1727 cm^{-1}; nmr δ 2.75 (4H, singlet, cyclobutane protons) and 2.60-2.45 (8H, multiplet, α-carbonyl protons, disappear upon exchange with deuterium). The *cis,syn,cis* structure of VIIa (10) was also chemically proved by reacting with hydrazine hydrate in 1:1 ratio to give IX (11). [mp > 290° (dec.); ν^{KBr}_{max} 1655 cm^{-1} (C=N)].



VIIa IX

The monoketone VIb also reacts in the same manner as VIa giving VIIIb (mp 72-3°, 30%), ν^{KBr}_{max} 1719, 980 and 697 cm^{-1}, nmr δ 5.50 (4H, multiplet), 3.27 (6H, singlet), 3.65-2.35 (8H) and VIIb [bp (bath temperature) 70°/0.5 mm, 40%], ν^{neat}_{max} 1730, 1111 and 1047 cm^{-1}, nmr δ 3.25 (3H, singlet), 3.18 (3H, singlet), 2.96-1.70 (12H).

Since VIc has no absorption in the UV (12), (13), acetone was used as sensitizer to give VIIc (mp 56-7°, 65%), ν^{KBr}_{max} 1089, 1049 and 869 cm^{-1}, nmr δ 3.22 (6H, singlet), 3.15 (6H, singlet), 2.38 (4H, broad singlet, cyclobutane protons), 2.10-1.64 (8H).

Both VIIb and VIIc are hydrolyzed, in quantitative yield, to VIIa.

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10. Stereochemical considerations of the cycloaddition are being investigated.
11. Satisfactory elemental analysis was obtained, as well as correct mass-spectrum with parent peak at 320 for the dimer (The H_2O molecule could not be detected).
12. There is a maximum at about 210 mμ (ε ~ 2000).
13. Irradiation in benzene for 9 hours gives unchanged starting material.