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INTRAMOLECULAR PHOTOCYCLIZATION OF CIS, CIS- AND TRANS, TRANS-CYCLODECA-1,6-DIENE TO ANTI TRICYCLO$\left[5.3.0.0^{2,6}\right]$DECANE.

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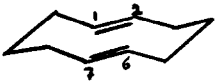
The transannular photocyclization of the cis,cis-cyclodeca-1,6-dienes to the tricyclo$\left[5.3.0.0^{2,6}\right]$decane (1) may be explained due to the proximity in space of the two double bonds in the "hammock" conformation I (2). Hence, in an intramolecular photocyclization of the isomeric trans,trans,cyclodeca-1,6-diene, both chair conformation IIa and the twisted conformation IIb must be considered. An inspection of Dreiding models indicated that the distances between C_1-C_7 and C_2-C_6 in I are 1.8 Å, while in IIa these distances are 2.8 Å and in IIb the distances between C_1-C_6 and C_2-C_7 are 1.0 Å.

I,R= H_2, XII,R = 0

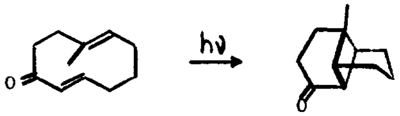


IIa

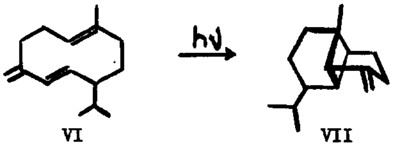
IIb

III

In similar systems, probably via conformation IIb, a few examples of photochemical crossbond formation have been reported in recent years. These are the conversions of cycloocta-1,5-diene to tricyclo$\left[3.3.0.0^{2,6}\right]$octane (III) (3), IV to V (4) and VI to VII (5).

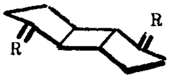


IV V



VI VII

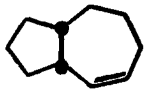
These observations have made it desirable to investigate the nature of photocyclization of I and II. Irradiation (6a) of II (7) in pentane-acetone gave a single product (m^+ 136), collected by preparative GLC (33% DC-550 on chromosorb W column), in almost quantitative yield (8a). Its NMR, IR and retention time in GLC were identical with those of anti tricyclo$\left[5.3.0.0^{2,6}\right]$decane (VIII), prepared by Wolf-Kishner reduction of anti tricyclo$\left[5.3.0.0^{2,6}\right]$deca-3,8 diene (IX) (9) and different from the NMR and IR spectra of the synisomer X (10).



VIII,R = H_2, IX,R = 0

X

XIII



XIV

It is interesting to note that irradiation (6a) of I (7) also gave VIII (8b) as the only intramolecular product. No intermediate could be detected by GLC during the irradiation. This suggests that the cis,cis isomer slowly isomerizes to the cis,trans (XI) and/or trans,trans isomer which, in turn, rapidly undergoes intramolecular photocyclization to VIII.

The rate of cyclization (6b) of II was found to be 20 times faster than I; whereas, under the same reaction conditions, the conversion of XII to XIII (11) was 1.5 times faster than that of II to VIII. In the absence of a sensitizer, in Pyrex vessel, II was slowly photocyclized to VIII (25 times slower than in the presence of the sensitizer), while I remained unchanged.

From the mentioned results, it cannot be concluded whether VIII is obtained from the singlet or the triplet excited state of II. The direct irradiation of I and II in shorter wavelengths is now under investigation.

The rate of photocyclization of II to VIII is almost the same in 8 different solvents.

Thermal cyclization of I and II, which is not allowed by W.H. Rules (12) to be concerted, was reported (13) to give bicyclo[5.3.0]decene-2 (XIV) as major and the anti tricyclodecane VIII and the syn isomer X as minor products, through radical reaction.

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6. a) All irradiations were carried out on the "Merry go round" apparatuse, using a 450 watt-Hanovia lamp in a pyrex well and 1 ml. test tubes placed 5 cm from the lamp. All solutions were 6.6 mmole (0.9% w/v) diene in a mixture of solvent and acetone in ratio of 3:1. Thereaction was over in about 1 hour. b) The concentration was 14.7 mmole (2% w/v).
7. We would like to thank Dr. P.Heimbach from Max Planck Institute, Germany, and Dr. J.R.Olechowski of Columbian Carbon Co., Lake Charles, Louisiana, USA, for the gift of the compounds.
8. a) An unknown minor component is slowly accumulated if irradiation is continued for more than 1-1,5 hours. This may be the 1:1 dimer of the hydrocarbon and acetone formed by an hydrogen abstraction reaction. b) a small amount of volatile products is formed of which one seems to be $CH_3COCH_2CH_2COCH_3$, the others believed to be derived from acetone and the solvent. A third component, in higher yield, which is similar to that obtained as in the case of the trans,trans-diene, is also accumulated.
9. P.E.Eaton, J.Amer. Chem. Soc., 84, 2344 (1962)
10. We would like to thank Dr. Von W.R.Roth of the Institute of Organic Chemistry, Köln University, Germany, for the IR and NMR spectra of VIII and X.
11. Many chemical reactions of tricyclo[5.3.0.0^{2,6}]deca-4,9-dione (XIII) and physical measurements such as dipole moment and Raman spectrum are not compatible with the anti structure of XIII unless it is a twisted and distorted molecule. Preliminary X-ray measurements of XIII do not show a centrosymmetric compound.
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