The Photochemical Transannular Reaction of [2.2]Metacyclophane

By Takeo SATO, Ei-ichi YAMADA, Yoshio OKAMURA, Teruo AMADA
and Kazuo HATA

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A recent report[1] describing the occurrence of a photochemical equilibrium between *trans*-15, 16-dimethyldihydropyrene and its valence tautomer with a metacyclophane structure has prompted us to submit our findings on the photochemical transannular reaction of [2.2]-metacyclophane (I), which leads to 4, 5, 9, 10-tetrahydropyrene (II), in a preliminary form.

The irradiation of compound I, which had been prepared in a 45% yield by a modification of the method of Müller and Röscheisen[2] using a high dilution condition, was carried out in a quartz vessel placed in a circulating-water jacket housing a 1000 W. mercury arc lamp (Wako Denki Co., HBC-1000). Under a current of nitrogen, a mixture of 53.5 mg. (0.257 mmol.) of compound I, 68.1 mg. (0.268 mmol.) of iodine, and 700 mg. (excess) of sodium bicarbonate in 40 ml. of cyclohexane was irradiated for 44 hr.; it gave 45.5 mg. of colorless plates, m.p. 135—136°C (from methanol-ethanol), the NMR spectra of which in carbon disulfide showed only two singlets at 3.05 (6H) and 7.20 τ (8H). The disappearance of the characteristic peak of compound I at 5.77 τ (C_8 and C_{16} protons) indicated that the transannular reaction occurred. The compound was shown to be 4, 5, 9, 10-tetrahydropyrene (II) by its identical infrared spectra and by a mixed melting point determination with an authentic specimen, m. p. 137—138°C. The yield reached 85.9%. A series of experiments confirmed that the formation of compound II in a somewhat lower yield was also possible by the irradiation of compound I and iodine in cyclohexane, *n*-hexane or ethanol under nitrogen as well as under oxygen. Compound I itself, however, was shown to be quite stable toward irradiation, and it could be recovered

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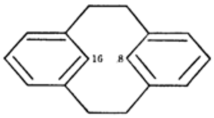
[1] H.-R. Blattmann, D. Menche, E. Heilbronner, R. J. Molyneux and V. Boekelheide, *J. Am. Chem. Soc.*, **87**, 130 (1965).

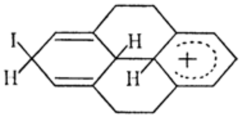
[2] E. Müller and G. Röscheisen, *Chem. Ber.*, **90**, 543 (1957).

in a 56% yield after irradiation for 20 hr. under oxygen.

It is assumed that the mechanism of this reaction is different from that of the related photochemical cyclization,[3] the formation of phenanthrenes from *cis*-stilbenes in the presence of a suitable oxidant (molecular oxygen or iodine), since the mechanism that has been formulated[3] requires the presence of the conjugated system. Further, the fact that the formation of II was best achieved by the reaction with one mole equivalent of iodine in the presence of the base suggested the participation of iodine to give iodinated radicals as the intermediate, followed by transannular reaction and dehydroiodination. Moreover, the driving force of this cyclization step may be sought in the unique features of the meta-cyclophane structure, namely, the proximity of C_8 and C_{16} atoms and the presence of a highly strained ten-membered ring system, which is relieved by going into bicyclic. Thus no reaction occurred when bibenzyl, the open-chain model of compound I, was irradiated under the conditions described above.



(I)



(III)

The attempted iodination reaction of compound I with iodine and silver perchlorate in ether was also shown to give compound II in a 60% yield. Apparently the first step of this reaction is the electrophilic substitution by the iodonium ion, accompanied by the transannular reaction, giving an intermediate III.[4] Compound II is formed by a loss of the proton, followed by dehydroiodination.

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo

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[3] F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964), and the literature cited therein.

[4] N. L. Allinger, M. A. Da Rooge and R. B. Hermann, ibid., **83**, 1974 (1961).