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Photo-Aryl Coupling and Related Reactions. III. The Transannular Dehydrogenation of [2.2]Metacyclophane Induced by Iodine[1]

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The ultraviolet irradiation of [2.2]metacyclophane (I) with iodine in a cyclohexane solution was shown to afford 4,5,9,10-tetrahydropyrene (II), which, on further dehydrogenation, was led to 4,5-dihydropyrene and pyrene. The transannular reaction leading to II occurred much more rapidly than the subsequent dehydrogenation reactions. Thus II was obtainable in an optimum yield of 62% by the irradiation of I in the presence of an equimolar amount of iodine and an excess of sodium bicarbonate. By ESR and UV spectral studies, 253.7 mμ light was found to be responsible for the transannular reaction.

The origin of pyrene (IV) in coal tar was once questioned and was attributed to *m*-xylene, assuming the intermediacy of either 2,2′,6,6′-tetramethylbiphenyl or [2.2]metacyclophane (I).[2] Baker and his co-workers[3] have realized the conversion of I to IV in a 60% yield by the action of palladium charcoal. They also showed hexahydropyrene was obtainable from I by treating it with aluminum chloride. As a related observation, we confirmed smooth conversion of I to 4,5,9,10-tetrahydropyrene (II) by the action of ferric chloride.[4]

Both ionic and homolytic pathways are shown to effect the transannular reaction of I. Thus, electrophilic substitution reactions, such as nitration[5,6] or halogenation reaction[5,7,8] afforded II or its 2-substituted derivatives. Noteworthy is the isolation of II, 4, 5-dihydropyrene (III) and IV from the nitration reaction mixture using benzoyl nitrate.[6] In this case both electrophilic and radical reactions are occurring as competing processes. Photochemical conversion of I to IV was first realized by Lindsay and his co-workers[9] who treated I with bromine under ultraviolet irradiation. We observed that irradiation of I with nitrosyl chloride afforded II in a good yield.[4]


I


II


III


IV

Apart from curiosity in the origin of IV in nature, those reactions involving transannular dehydrogenation or cycloisomerization step are of considerable interest as regards the reaction mechanism and synthetic utility. Whereas some mechanistic studies on the transannular reactions initiated by electrophiles are available,[5,6,8,10,11] only limited studies have been carried out on the photochemical behavior of I.[7,9,12] Our earlier findings that the photo-aryl coupling of I induced by iodine afforded a good yield of II,[7] urged us to study the reaction further in order to find out the optimum reaction conditions and to obtain mechanistic evidence.

The photochemistry of I was examined under selected conditions using a 1-kW high-pressure mercury arc lamp. A cyclohexane solution (0.83×10^{-2} M) contained in a quartz tube was irradiated externally for 20hr under oxygen or nitrogen current. The reaction mixture was analyzed by column chromatography on alumina and the products were characterized by spectroscopic methods or by a direct comparison with the authentic samples. The results are summarized in Table 1.

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[1] Part II: T. Sato, S. Shimada and K. Hata, This Bulletin, **42**, 766 (1969).

[2] W. Baker, J. F. W. McOmie and J. M. Norman, *Chem. & Ind.*, **1950**, 77.

[3] W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, **1951**, 1114.

[4] Unpublished results.

[5] N. L. Allinger, M. A. DaRooge and R. B. Hermann, *J. Am. Chem. Soc.*, **83**, 1974 (1961).

[6] M. Fujimoto, T. Sato and K. Hata, This Bulletin, **40**, 600 (1967).

[7] T. Sato, E. Yamada, Y. Okamura, T. Amada and K. Hata, *ibid.*, **38**, 1049 (1965).

[8] T. Sato, M. Wakabayashi, Y. Okamura, T. Amada and K. Hata, *ibid.*, **40**, 2363 (1967).

[9] W. S. Lindsay, P. Stokes, L. G. Humber and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

[10] N. L. Allinger, B. J. Gordon, S.-E. Hu and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).

[11] *Cf.* R. W. Griffin, Jr., and R. A. Coburn, *J. Am. Chem. Soc.*, **89**, 4638 (1967).

[12] For other attempts of ultraviolet irradiation of I, see R. W. Griffin, Jr., *Chem. Revs.*, **63**, 45 (1963).

TABLE 1. THE PHOTOCHEMICAL REACTIONS OF [2.2]METACYCLOPHANE (I) AND 4,5,9,10-TETRAHYDROPYRENE (II)[a]

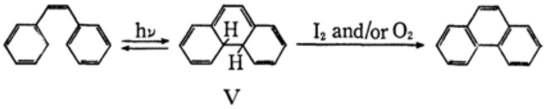
No.	Compound, mmol		Iodine mmol	Sodium bicarbonate mmol	Products, %			
					I	II	III	IV
1[b]	I	0.25			100			
2	I	0.25	0.01		17	37	8.2	trace
3	I	0.25	0.25			15	22.4	29.2
4	I	0.25	0.25	0.3		21	28.8	27.4
5	I	0.25	0.125	0.5		38.2	15.0	24.0
6	I	0.25	0.125	0.5[d]		58.4	30.0	10.2
7[b]	I	0.25	0.25	8.3		62.0	26.7	11.3
8[b,c]	I	0.25	0.25	8.3		51.4	48.6	
9	II	0.50	0.25	1.2		54.3	28.2	8.3

a) A cyclohexane solution (30 ml) contained in a quartz tube was irradiated externally with a 1-kW high-pressure mercury are lamp for 20 hr. Except for No. 1, which was carried out under oxygen, all photolysis reactions were performed under a current of nitrogen.
b) Yields are expressed in a product ratio.
c) Ultraviolet irradiation was continued for 40 hr.
d) Instead of sodium bicarbonate, sodium carbonate was used.

First, it was found that oxygen was not effective as the oxidant for the transannular dehydrogenation reaction (No. 1). The rest of the photolyses were thus performed under nitrogen. Addition of a small amount of iodine, however, was shown to lead to the formation of II and III together with a trace amount of IV (No. 2). Higher rate of conversion to pyrene was achieved by the irradiation with an equimolar amount of iodine. In this case the yield of pyrene reached 29.2% (No. 3).

As will be discussed in detail later, the initial product of the reaction is assumed to be II, of which further dehydrogenation may be responsible for the formation of III and IV. This was clearly confirmed by carrying out similar photolysis studies on II itself (No. 9). The compound was found to afford 36.5% of dehydrogenation products. Examination of the effect of base revealed that the presence of an excess of sodium bicarbonate retarded further transformation of II. Thus as high as a 62% yield of II was achieved (No. 7). The fact that only a small amount of iodine is enough to effect the reaction to a significant extent (No. 2) indicates that iodine is regenerated[13] from hydrogen iodide, which is formed in the photolytic dehydrogenation processes. Use of an equimolar amount of iodine and trapping of generated hydrogen iodide thus made this reaction highly specific one.

The photochemical transformation of *cis*-stilbene to phenanthrene[13,14] has been extensively studied and has been extended to the syntheses of phenanthrene derivatives,[15] triphenylenes,[1,16,17] polycondensed ring compounds including phenanthrene system[18–20] and heterocyclic analogs.[21,22] The reaction mechanism has been elucidated beyond doubt by trapping the intermediate compound 4a,4b-dihydrophenanthrene (V), by carrying out ultraviolet irradiation of stilbene solutions in the absence of oxygen.[14,23,24] Oxidation of V with oxygen, iodine, or more effectively with the mixture of these two as the dark reaction was assumed to be the final stage of the reaction. Atomic sulfur generated from *cis*-stilbene sulfide was also found to be effective as an oxidant.[25]



V

It is apparent that no such mechanism formulated above is conceivable for the metacyclophane case,

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[13] F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

[14] F. R. Stermitz in O. L. Chapman ed. "Organic Photochemistry," Vol. 1, Mercel Dekker, Inc., New York (1967), p. 249.

[15] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

[16] N. Kharasch, T. G. Alston, H. B. Lewis and W. Wolf, *Chem. Commun.*, **1965**, 242.

[17] T. Sato, Y. Goto and K. Hata, This Bulletin, **40**, 1994 (1967).

[18] M. Scholz, M. Mühlstädt and F. Dietz, *Tetrahedron Letters.*, **1967**, 665.

[19] W. Carruthers, *J. Chem. Soc.*, (*C*), **1967**, 1525.

[20] M. F.-Barbieux, J. Nasielski and K. H. Martin, *Tetrahedron Letters*, **1967**, 743.

[21] R. M. Kellogg, M. B. Groen and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

[22] C. E. Loader and C. J. Timmons, *J. Chem. Soc.*, (*C*), **1967**, 1677.

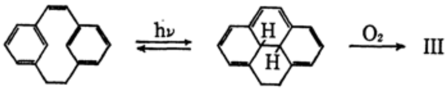
[23] W. M. Moore, D. D. Morgan and F. R. Stermitz, *J. Am. Chem. Soc.*, **85**, 829 (1963).

[24] K. A. Muskat and E. Fischer, *J. Chem. Soc.*, (*B*), **1967**, 663.

[25] T. Sato, Y. Goto, T. Tohyama, S. Hayashi and K. Hata, This Bulletin, **40**, 2975 (1967).

since the two benzene rings in this compound are not in conjugation. Moreover, the fact that oxygen is not effective for cycliaztion suggested that the photo-aryl coupling of I proceeded through an entirely different mechanism from that of *cis*-stilbene-phenanthrene cases.

Recently, Blaschke and Boekelheide[26] prepared [2.2]metacyclophan-1-ene (IV) and observed a photochemical equilibrium (VI$\rightleftarrows$VII). They have



VI VII

noticed that VII is extremely sensitive to oxygen and is easily convertible to III by its presence. The cyclization step in this case is thus similar to the stilbene type and different from ours.

Kinetic studies[27] have revealed that the dehydrogenation reaction of ethylene bridge occurs much more slowly compared with the transannular cyclization step. This permits us to treat the latter process separately from the competing reactions in the initial stage of the reaction. Therefore our effort was concentrated to define the nature of the transannular reaction step.

An ESR signal appeared when a deaerated cyclohexane solution of I containing iodine was irradiated with unfiltered light of a high-pressure mercury lamp at room temperature. The signal was observed as a single line spectrum with a band width of 23 gauss. When, however, I or iodine alone was irradiated under similar conditions no such signal was observable. These facts indicated that a fairly stable radical species was formed by the irradiation of I in the presence of iodine.

It was also found that only 253.7 mμ light was responsible for the formation of the radical intermediate as revealed by the ESR studies using light with various wavelengths. This specificity was further confirmed by the UV spectra measurements under irradiation. The spectral changes under irradiation with 253.7 mμ light are shown in Fig. 1. The appearance of peaks characteristic of II occurring at 260, 268, 280, 292, 320 and 335 mμ after about 3.5hr clearly demonstrated the formation of II. At the same time, if an equimolar or more of iodine was present, the absorbance of the iodine band at 525 mμ showed a marked decrease with the progress of the reaction as shown in Fig. 1. No changes in the spectrum occurred by the irradiation with other lines. From these experiments, it was confirmed that the reaction was initiated by the light of 253.7 mμ and that the excitation of a long wave band of iodine was not effective to bring about the cyclization.

Several mechanisms are conceivable for the facile transannular reaction of I. In view of the appearance of a rather stable radical intermediate, abstraction of 8,16-hydrogen occurred most probably in a stepwise manner. Excited I could react with iodine to give a cation radical or analogous species, of which further dehydrogenation would lead to II.

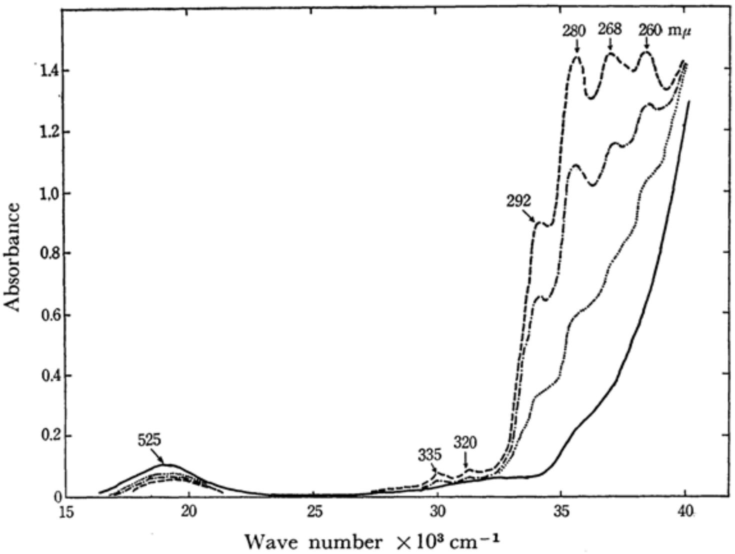


Fig. 1. Change of the absorption spectra of [2.2]metacyclophane (1.3×10^{-4} M) and iodine (0.3×10^{-3} M) in a cyclohexane solution upon irradiation for 69 (……), 205 (-·-·-) and 330 min (----). The spectrum of the original solution is also shown (——).

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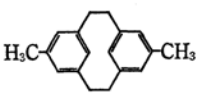
[26] H. Blaschke and V. Boekelheide, *J. Am. Chem. Soc.*, **89**, 2747 (1967).

[27] Details of the kinetic studies will be reported elsewhere by one of the authors (S. H.).

Excitation of iodine at the short wave band might also lead to a similar pathway. Since a mixture of I and iodine in cyclohexane showed a weak charge-transfer band at 280 mμ, excitiation of the complex could also be the initial step of the reaction. On the other hand, the participation of σ-complex would not be likely when one considers the instability of the iodinated aromatic compounds toward irradiation,[1,28] thus our original scheme[7] became unattractive. Although the data at hand strongly suggested the participation of iodine in the initial stage of the reaction, the choice among the absorbing species could not be achieved. The quantum yield of this reaction was found to be 0.016[27] with unfiltered light.

Obviously the cyclization is facilitated by the proximity of two benzene rings which are separated only by 2.689 Å.[29] As expected no reaction occurred when bibenzyl, an open-chain model of I, was irradiated under the conditions described above. The driving force of the reaction might be sought in the highly strained nature of the metacyclophane structure which is relieved by going into bicyclic.

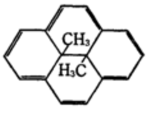
5,13-Dimethyl[2.2]metacyclophane (VIII) has been shown to react similarly to give 2,7-dimethyl-4,5,9,10-tetrahydropyrene (IX).[30] The occurrence of the transannular reaction with the metacyclophane derivative, of which 5- and 13-positions are blocked by methyl groups, also excludes the possibility of the participation of the σ-complex.



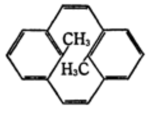
VIII

IX

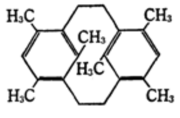
Boekelheide and his co-workers[31] have observed a photochemical equilibrium between *trans*-15,16-dimethyldihydropyrene (X) and 8,16-dimethyl-[2.2]metacyclophane-1,9-diene (XI). It appeared to be of interest to attempt the photocyclization reaction with 8,16-dimethyl derivative such as XII. The hexamethyl[2.2]metacyclophane has, however, been recovered unchanged by the photolysis experiments carried out as above.[30]



X



XI



XII

Experimental

Light Sources. For preparative experiments, a 1-kW high-pressure mercury arc lamp, Wako HBC-1000, was used. Cyclohexane solutions were irradiated externally in a quartz tube under the selected conditions by being immersed in a water bucket which housed the light source. Cooling was achieved by running water.

For the measurements of the ESR and UV spectra under irradiation a 100-W Toshiba SHL-100 UV lamp was used. The specific lines were selected by using a combination of glass filters (Toshiba and Hoya filters; UV-D25, UV-29, UV-DlC, V-Y48) and nickel sulfate solution (100 g/300 m*l*).

Spectra Measurements. UV spectra were recorded with Shimadzu RS autorecording spectrophotometer or Hitachi EPU-2 spectrophotometer. ESR spectra were recorded with Japan Electron Optics Co., X-band, ESR instrument model JES-3B type. Deaerated cyclohexane solutions were used for the measurements.

The Photolysis of [2.2]Metacyclophane (I). As a typical example, details of experiment No. 7 are given below. A mixture of 50 mg (0.25 mmol) of I, 63 mg (0.25 mmol) of iodine and 70 mg (8.3 mmol) of sodium bicarbonate in 30 m*l* of cyclohexane was irradiated for 20 hr under a nitrogen current. After the reaction was over, the mixture was successively washed with water, sodium thiosulfate solution and water. After drying over magnesium sulfate, the solution was concentrated. By column chromatography on alumina using *n*-hexane as an eluent, there were isolated three fractions, which consisted of 62.0% of II, mp 138°C, 26.7% of III, mp 132°C, and 11.3% of IV, mp 150°C (in the order of elution from the column). They were characterized by NMR and IR spectra and also by a direct comparison with the authentic materials.[6]

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[28] W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

[29] C. J. Brown, *J. Chem. Soc.*, **1953**, 3278.

[30] T. Sato, S. Akabori, N. Muto and K. Hata, *Tetrahedron*, **24**, 5557 (1968).

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