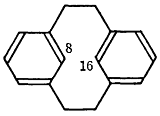
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2858—2859 (1971)

Photolytic Cyclodehydrogenation Reactions of [2.2]Metacyclophane by Means of Aryl Ketones and Alkoxyl and Thiyl Radicals[1]

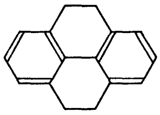
Takeo Sato, Kozaburo Nishiyama, Shigeru Shimada, and Kazuo Hata
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo

(Received March 12, 1971)

The irradiation of [2.2]metacyclophane (I) in benzene or cyclohexane solutions containing iodine through a quartz vessel led to a transannular dehydrogenation reaction to give 4,5,9,10-tetrahydropyrene (II) as the major product.[2,3] As a result of subsequent dehydrogenation processes occurring at a slower rate, the reaction mixture contained 4,5-dihydropyrene (III) and pyrene (IV).[3] Several alkyl derivatives of I were similarly converted into the corresponding 4,5,9,10-tetrahydropyrenes.[4]



I



II

The quantum yield of the initial dehydrogenation step for I was found to be 0.006.[3] The reaction mechanism was suggested to involve the photoexcitation of charge-transfer complex between I and iodine followed by dehydroiodination.[3] The formation and dissociation constants of the charge-transfer complexes involving I were studied spectroscopically.[5,6]

Oxygen is less effective as oxidant. The irradiation of an aerated solution of I in benzene using a high-pressure lamp produced only trace amounts of II and III after 45 hr.[7]

From mechanistic view, we wished to know whether photocyclodehydrogenation was possible with oxidants other than iodine or oxygen.[8] In this paper we will describe the attempts using aryl ketones, di-*t*-butyl peroxide (DTBP), and dibenzyl disulfide.

A benzene solution of I in the presence of a threefold excess of benzophenone was irradiated under a nitrogen current using a 100-W low-pressure lamp for 25 hr. A 41% yield of II together with further dehydrogenation products were produced (Table 1). Formation of pinacol during the reaction was noticed.

Similar results were obtained by irradiation with a 1-kW high-pressure lamp using a quartz vessel though the conversion was less complete. 4,4′-Dimethoxybenzophenone was also found to bring about the dehydrogenation reaction, while acetophenone, desoxybenzoin and fluorenone were less effective.[9]

The results are surprising since the abstraction of aryl hydrogens instead of benzylic ones is just the reverse of what is to be expected. The photoreduction of benzophenone is known to occur only with good hydrogen donors but never with aromatic hydrogens.[10] In the present case, the loss of aryl hydrogens at $C_{8,16}$ occurred more rapidly than the following aromatization steps leading to III and IV.

No cyclodehydrogenation with benzophenone took place when the reaction was carried out in a Pyrex vessel, where the excitation of only the carbonyl compound was possible since shorter wavelength regions required for I (λ_{max} 266 nm) were cut by a filter.

Cyclodehydrogenation with benzophenone was effectively quenched by naphthalene (E_T=61 kcal/mol) or by triphenylene (E_T=67 kcal/mol) (Table 1).[7]

These results suggest that direct photoexcitation of both the substrate and the aryl ketone is necessary for transannular reaction and no energy transfer from the aryl ketone to I occurs. If a triplet state of I is to be

---

[1] Photo-Aryl Coupling and Related Reactions. IX. Part VIII: T. Sato and T. Morita, This Bulletin, in press.

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

[3] T. Sato, M. Wakabayashi, S. Hayashi, and K. Hata, *ibid.*, **42**, 773 (1969).

[4] T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, **24**, 5557 (1968); H. Shizuka, K. Sorimachi, T. Morita, K. Nishiyama, and T. Sato, This Bulletin, **44**, 1983 (1971). Other dimethyl- and tetramethyl[2.2]metacyclophanes were similarly cyclodehydrogenated (unpublished results).

[5] S. Hayashi and T. Sato, *Nippon Kagaku Zasshi*, **91**, 950 (1970).

[6] S. Hayashi and T. Sato, unpublished results.

[7] The cyclodehydrogenation reaction of I was noticed with aerated and degassed solutions [Y. Takayama, K. Sorimachi, H. Shizuka, and T. Morita, Abstracts of Papers, the 23rd Annual Meeting of the Chemical Society of Japan, April, 1970 (Tokyo)]. The reaction rate appears to be lower compared with the case in which iodine is used.

[8] *p*-Benzoquinone was found to be effective for the conversion of I to II.[6]

[9] As a control experiment a benzene solution of I was irradiated for 45 hr under nitrogen. Only trace amounts (less than 1%) of II and III were detected.

[10] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York (1965), p. 137.

TABLE 1. PHOTOCYCLODEHYDROGENATION OF [2.2]METACYCLOPHANE (I) WITH ARYL KETONES

Aryl ketone	$\rangle$C=O/I	Additive	Irrad. time, hr	Filter	Product, %			
					II	III	IV	Recovery
Benzophenone	3		25	Vycor[b]	41	13	4	42
Benzophenone	3		44	quartz	24	9	3	64
Benzophenone	2		44.5	quartz	8	2	0	90
Benzophenone	2		45	Pyrex	0	0	0	100
Benzophenone	2	naphthalene	44.5	quartz	trace	trace	0	100
Benzpphenone	2	triphenylene	45	quartz	0	0	0	100
Benzophenone	2	acetophenone	45	quartz	trace	0	0	100
4,4′-Dimethoxybenzophenone	2		45	quartz	15	0	0	85
Acetophenone	2		45	quartz	3	trace	0	97
Desoxybenzoin	2		44	quartz	3	trace	0	97

a) Dilute benzene solutions of I (4×10^{-3} M) containing appropriate aryl ketones were irradiated with a 1-kW high-pressure lamp. The reaction mixture was analyzed by gas chromatography using 1 m XE-60 silicone gum rubber on Chromosorb W column. The yields are shown in product ratios.

b) A 100-W low-pressure lamp was used as the light source.

involved, E_T must be higher than that of benzophenone, namely, 69 kcal/mol. We propose that the reaction proceed through an excited singlet state since the iodine-induced reaction is not quenched by oxygen. Recently, Takayama, Sorimachi, Shizuka, and Morita[7] suggested a singlet-state mechanism for the photoreaction of I on basis of quenching experiments and emission spectra measurements.

The results with benzophenone led us to examine the photoreactions of I toward alkoxy and thiyl radicals. Whereas no reaction occurred when I was reacted with *t*-butoxy radicals generated by the thermal decomposition of DTBP at 140°C, the irradiation of a benzene solution of I containing DTBP under nitrogen produced II (7.4%), III (2.3%), and IV (trace). *t*-Butoxy radicals are believed not to abstract hydrogens on an aromatic ring.

The photolysis of a benzene solution containing I and dibenzyl disulfide also gave II (10.8%), III (6.1%), and IV (trace).

The inertness of the methylene groups in I toward radical attack can be ascribed to steric restrictions, rigidity of the molecule and bond angle deformation, which restrict usual charge stabilization associated with a benzylic radical. Tendency of I to undergo transannular reactions is explained by large angle and bond-distance changes. An enhanced reactivity of the aryl hydrogens upon photoexcitation appears to be explainable only by postulating an intermediate that possesses a transannular bonding between C_8 and C_{16} positions.

Experimental

Photolysis of I with Aryl Ketones. The results are summarized in Table 1. For quenching experiments three-molar equivalent of an additive was employed. A typical example is shown below.

A solution of 25.4 mg (0.12 mmol) of I and 68.7 mg (0.38 mmol) of benzophenone in 30 m*l* of benzene was irradiated under nitrogen using a 100-W low-pressure lamp for 25 hr. By gas chromatographical analysis using 1 m XE-60 on Chromosorb W column II (41%), III (13%), and IV (4%) were identified by comparing retention times with those of authentic materials.

Photolysis of I with DTBP. Irradiation of a benzene solution (30 m*l*) of 30.0 mg (0.14 mmol) of I and 57.3 mg (0.39 mmol) of DTBP contained in a quartz vessel using a 1-kW high-pressure lamp for 45 hr under nitrogen produced II (7.4%), III (2.3%), and IV (trace) as analyzed by gas chromatography.

Photolysis I with Dibenzyl Disulfide. Irradiation of a benzene solution (30 m*l*) of 26.0 mg (0.13 mmol) of I and 93.3 mg (0.38 mmol) of dibenzyl disulfide as above gave II (10.8%), III (6.1%), and IV (trace). The rest of the material was recoverable as I.