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Photochemical Oxidations of 4,5,9,10-Tetrahydropyrenes

Haruo Shizuka, Kenji Sorimachi, Toshifumi Morita, Kozaburo Nishiyama,[1] and Takeo Sato[1]
Department of Chemistry, Gunma University, Kiryu, Gunma

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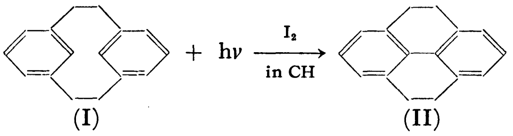
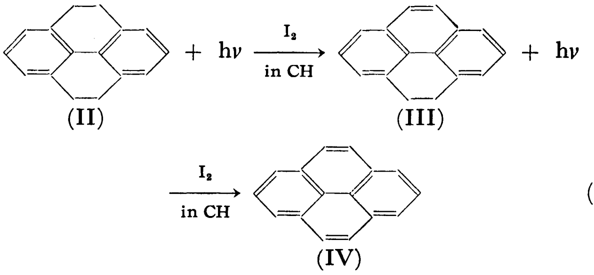
It is known that the photocyclizations of [2.2]-metacyclophanes in the presence of iodine yield 4,5,9,10-tetrahydropyrenes (Eq. (1)).[2-4] The further photochemical dehydrogenation of 4,5,9,10-tetrahydropyrene (II), induced by iodine, has been suggested;[5] the dehydrogenation products were 4,5-dihydropyrene (III) and pyrene (IV), as is shown in Eq. (2), where CH denotes cyclohexane.



(1)



(2)

In the present work, the photolyses of II and 2,7-dimethyl-4,5,9,10-tetrahydropyrene (V) in aerated and degassed cyclohexane solutions have been carried out.

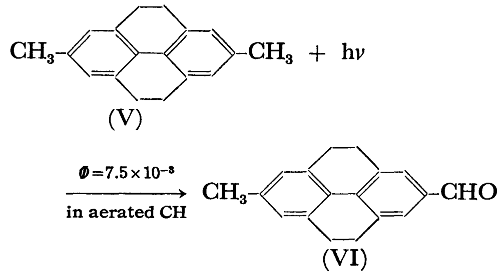
Experimental

The experimental procedure was almost the same as that previously described.[6] The II and V used in this work were prepared by the photocyclization of [2.2]metacyclophanes[2-4] and were purified by column chromatography (Al_2O_3) and by repeated recrystallizations. The photoproducts were separated by thin-layer chromatography and column chromatography (Al_2O_3 and *n*-hexane were used), and were purified by recrystallization.

The identifications were performed by means of NMR, UV, mp, and elemental analyses. A low-pressure marcury lamp, equipped with a Vycor glass filter, was used as the 2537Å radiation source. Actionometry was carried out using a ferric oxalate solution.[7] The solution was thoroughly degassed on a high-vacuum line by the freeze-pump-thaw technique.

Results and Discussion

It was found that the photoproduct of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (V) in aerated cyclohexane was a different type from that of 4,5,9,10-tetrahydropyrene (II); the photooxidation of V gave a new type of product, 2-methyl-4,5,9,10-tetrahydropyrene-7-carbaldehyde (VI, mp 137—140°C), which resulted from the oxidation of the methyl group substituted at the 7 position of V by the UV irradiation (Eq. (3)), and in the case of II, 4,5-dihydropyrene (III) and pyrene (IV) were obtained as the photoproducts (Eq. (4)).



(3)

$$\mathrm{II} + h\nu \xrightarrow[\text{in aerated CH}]{\Phi=9.2\times10^{-4}} \mathrm{III} + h\nu \xrightarrow[\text{in aerated CH}]{\Phi=6.5\times10^{-4}} \mathrm{IV} \qquad (4)$$

A 2,7-dimethyl substituent had a very large effect on the photochemical oxidation of 4,5,9,10-tetrahydropyrenes. In addition to the main product, VI, traces of 2,7-dimethyl-4,5-dihydropyrene and 2,7-dimethyl-

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[1] Department of Chemistry, Tokyo Metropolitan University, Setagaya-ku, Tokyo.

[2] T. Sato, E. Yamada, Y. Okamura, T. Amada, and K. Hata, This Bulletin, **38**, 1225 (1965).

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

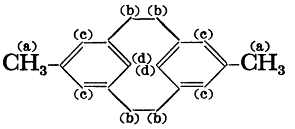
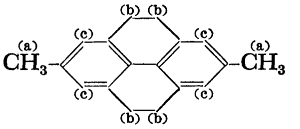
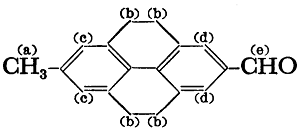
[4] T. Sato, M. Wakabayashi, S. Hayashi, and K. Hata, This Bulletin, **42**, 773 (1969).

[5] T. Sato, K. Nishiyama, S. Shimada, and K. Hata, Paper presented at the Symposium on Organic Free-Radical Reactions, Oct., 1969 (Osaka).

[6] *E. g.*, H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968); H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *J. Amer. Chem Soc.*, **92**, 7270 (1970).

[7] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A. 235,** 518 (1956).

Table 1. The assignments of the NMR spectra of 5,13-dimethyl[2.2]metacyclophane-related compounds dissolved in CCl_4

No.	Substance	Assignment δ
A		a, 2.33 (6H) b, 1.95, 2.08, 2.89, 3.02 (8H) c, 6.75 (4H) d, 4.05 (2H)
B	 (V)	a, 2.24 (6H) b, 2.73 (8H) c, 6.74 (4H)
C	 (VI)	a, 2.32 (3H) b, 2.88 (8H) c, 6.84 (2H) d, 7.50 (2H) e, 9.89 (1H)

pyrene were also detected by column chromatography. None of the products described above were obtained in the degassed system.

The NMR spectral data of 5,13-dimethyl [2.2]-metacyclophane-related compounds are listed in Table 1; they are similar to those of I and II reported by Sato *et al.*[8,9] The IR spectrum of the photoproduct (VI) showed the characteristic absorption band (at 1685 cm^{-1}) of the carbonyl group. Furthermore, the results of elemental analyses of the product supported these assignments.

The UV spectrum of the aerated cyclohexane solution of V changed upon irradiation with a 2537 Å light. The absorption band (286 nm, $\varepsilon = 2.18 \times 10^4$) of V decreased, and new maxima of VI appeared at 321 ($\varepsilon = 2.95 \times 10^4$) and 337 nm ($\varepsilon = 2.98 \times 10^4$), with two isosbestic points at 260 and 303 nm. The UV spectral change showed that V was transformed into VI by the photochemical oxidation in the presence of oxygen. The quantum yield ($\phi = 7.5 \times 10^{-3}$) for the VI formation from V was larger than that ($\phi = 9.2 \times 10^{-4}$) of II, as is shown in Eqs. (3) and (4).

Finally, it can be said that the hydrogens of the methyl group in V are more reactive to photooxidation than those of the ethylene group in the molecule. A mechanistic study concerning the photochemistry of [2.2]-metacyclophanes and their derivatives is in progress.

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[8] T. Sato, S. Akabori, M. Kainosho, and K. Hata, This Bulletin, **41**, 218 (1968).

[9] M. Fujimoto, T. Sato, and K. Hata, *ibid.*, **40**, 600 (1967).