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Photoreaction of Tetraphenylcyclopentadienone

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When tetraphenylcyclopentadienone in 2-propanol was irradiated with ultraviolet light under a slow steam of nitrogen, 2, 3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene and 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene were obtained in 10% and 45% yields respectively. That is, a *cis*-stilbene skeleton cyclized oxidatively to a phenanthrene, while the carbonyl group was reduced to methylene, or olefin, to paraffin. In this reaction, a protic solvent was observed to be favorable. In contrast to this, tetraphenylcyclopentadiene gave no similar cyclized products under the same conditions. The mechanism of this photoreaction is proposed.

Recently, the photoreaction of various cross-conjugated ketones, especially of 2, 5-cyclohexadienones,[1,2] has been investigated. However, there have been few studies of the photoreaction of full conjugated cyclic ketones. Only the decarbonylation of cyclopropenone[3] and the intramolecular cyclization of tropones[1] to form bicyclo[3, 2, 0]heptadienones have been reported. In the present paper, the photoreaction of five-membered cross-conjugated cyclic ketone will be investigated.

Tetraphenylcyclopentadienone (I) in 2-propanol was irradiated under a slow stream of nitrogen. 2, 3-Diphenyl-1*H*-cyclopenta[*l*]phenanthrene (II) and 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta-[*l*]phenanthrene (III) were thus obtained in 10% and 45% yields respectively. The structures were assigned on the basis of the spectroscopic properties.

The molecular formula for compound II (mp 183.0—183.8°C) was found to be $C_{29}H_{20}$. Its ultraviolet spectrum has absorptions characteristic of 9, 10-disubstituted phenanthrenes,[4] while its NMR spectrum shows a complex multiplet at τ 1.18—1.33 assigned to 4, 5-protons of the phenanthrene skeleton.[5] The presence of methylene was demonstrated by a study of the infrared and NMR spectrum. From these data, compound II was identified as 2, 3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene.

The molecular formula for compound III (mp 179.0—180.4°C) was found to be $C_{29}H_{20}O$. The presence of a C=O stretching frequency at

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[1] O. L. Chapman, "Advances in Photochemistry," Vol. I, ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y. (1963), p. 323.

[2] a) H. E. Zimmerman, *ibid.*, Vol. I, (1963), p. 183; b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **48**, 4527 (1962); c) P. J. Kropp, *Tetrahedron*, **21**, 2183 (1965); d) D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **88**, 1722 (1966).

[3] a) C. W. Bird and J. Hudec, *Chem. Ind.* (*London*); **1959**, 570; b) G. Quinkert, K. Opitz, W. W. Wiersdorff and J. Weinlich, *Tetrahedron Letters*, **1963**, 1863.

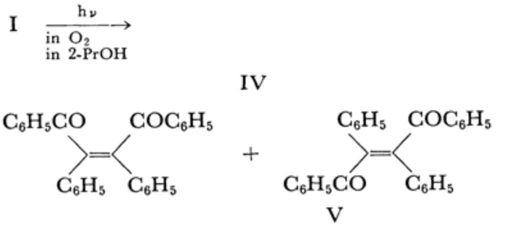
[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy, " John Wiley and Sons, New York, N. Y. (1962), p. 323.

[5] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y. (1959), p. 250.

1691 cm^{-1} in the infrared spectrum suggests that III is a five-membered cyclic ketone with a conjugated double bond. The ultraviolet[4] and NMR[5] spectra showed the presence of a phenanthrene skeleton. Moreover, III exhibited NMR signals at τ 5.08 and τ 6.26 coupled with each other. Thus, the compound III was identified as 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene.[6]

It is clear that the *cis*-stilbene skeleton of I cyclized oxidatively to the phenanthrene, while the carbonyl group was reduced to the methylene, or olefin, to paraffin. This photochemical transformation occurred in a stream of nitrogen. However, Wood *et al.*[8] found that substituted *trans*-stilbenes gave the corresponding phenanthrene derivatives on irradiation in the presence of iodine-oxygen. Therefore, it is important to investigate also the effect of oxygen on this reaction.

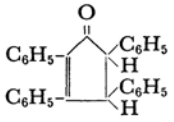
The solution of I in 2-propanol was irradiated with ultraviolet light under a slow stream of oxygen. The red color of the solution disappeared in 2.5 hr. The resulting products were *cis*- and *trans*-dibenzoylstilbene (IV and V), in 17% and 18% yields respectively.[9] The ultraviolet spectrum of each eluent of alumina-column chromatography showed the absence of the phenanthrene skeleton.[4] These facts indicate that the photocyclization reaction from I under nitrogen is not due to contamination by the oxygen of the reaction system.



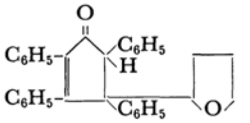
IV

V

The solvent effect on this photoreaction was also investigated. When methanol or *t*-butanol was used instead of 2-propanol, the irradiation of I gave the cyclized product, II, in a 12% or a 17% yield respectively. In glacial acetic acid, the cyclized product, III, was obtained in a 40% yield, besides the reduced product, 2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one (VI), in a 19% yield. The structure of VI was identified by comparison with an authentic sample.[10]



VI

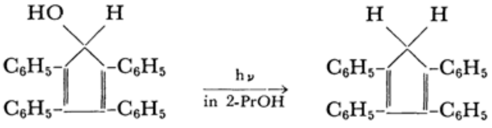


VII

On the contrary, in tetrahydrofuran or cyclohexane, the starting substance, I, was recovered after a similar irradiation. When irradiation was continued, the red color of I gradually faded. The only products obtained were *cis*- and *trans*-dibenzoylstilbene (IV and V)[11]. The absence of products with a phenanthrene skeleton[12] was established by a study of the ultraviolet spectra. Therefore, the photocyclization to phenanthrene derivatives occurs only in protic solvents. The photoreaction of I in tetrahydrofuran was carried out in the presence of hydrochloric acid as a proton source. Instead of cyclized products, there was obtained an addition product of tetrahydrofuran VII in a 65% yield. The structure of VII (mp 194—195°C) was identified as 4-tetrahydrofur-2′-yl-2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one on the basis of its spectroscopic properties (see Experimental Section).

These findings on the solvent effect indicate that the most important factor in the photoreaction of I is not the higher concentration of protons itself, but the presence of the protic solvent.

The effect of structure on the photocyclization was also investigated. On the irradiation of 2, 3, 4, 5 - tetraphenyl - 2, 4 - cyclopentadien - 1 - ol (VIII), 1, 2, 3, 4-tetraphenyl-1, 3-cyclopentadiene (IX) was easily obtained in a 36% yield.



VIII

IX

The structure of IX was identified by comparison with an authentic sample.[13] The ultraviolet spectra of the remaining tarry substances showed the absence of products with a phenanthrene skeleton. That is, the photocyclization occurred in compound I, but not in compound VIII. In addition, the irradiation of the hydrocarbon IX[13] gave no cyclized products, and the starting material was recovered.

It has been reported that the irradiation of stilbenes gives phenanthrene derivatives in the

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6) The structure was also confirmed by the fact that III was obtained on the irradiation of VI.[7]

7) I. Moritani and N. Toshima, *Tetrahedron Letters*, **1967**, 467.

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

9) N. M. Bikales and E. I. Becker, *ibid.*, **21**, 1405 (1956).

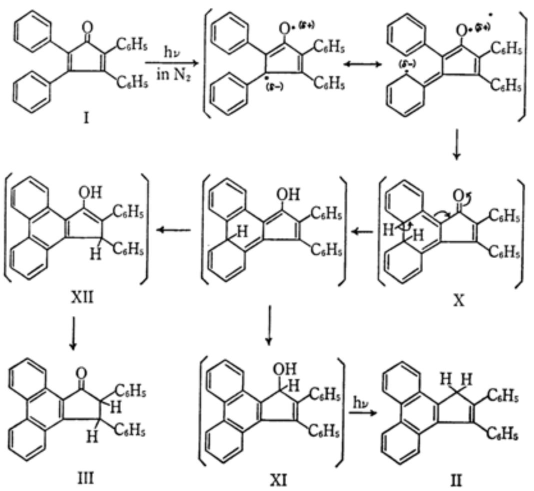
10) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, *J. Am. Chem. Soc.*, **75**, 2283 (1953).

11) Apparently, the formation of IV and V was due to the contamination by oxygen in the reaction system, which has been described above.

12) This is consistent with the fact[8] that the irradiation of acetylstilbene in cyclohexane gave no phenanthrene derivative in the presence of an oxidizing agent.

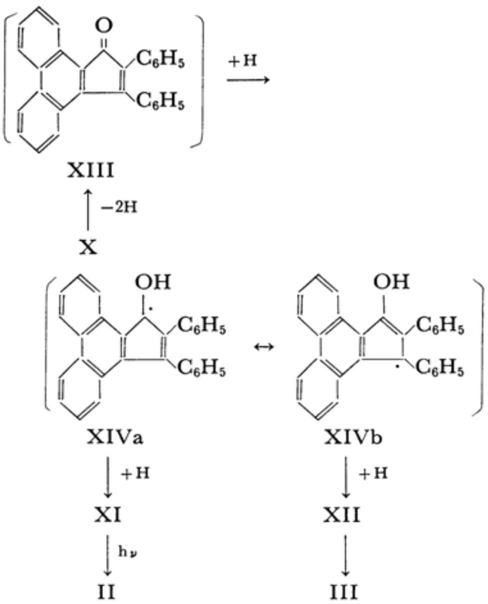
13) F. C. Leariff, T. A. Mannel, F. Johnson, L. U. Matternas and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).

presence of oxidizing agents.[8,14] A similar photocyclization was also observed with azobenzene in strong acid.[15-17] In both photocyclizations, the excited state initially formed has been proposed to be a $\pi-\pi^*$ singlet.[14] However, the present findings on the solvent effect suggest that the photocyclization of I to the dihydrophenanthrene intermediate X does not occur through a $\pi-\pi^*$ singlet, but probably through a $n-\pi^*$ singlet state, as is shown in Scheme I.[2,18,19]



Scheme I

Dehydrogenation from dihydrophenanthrene intermediate X would afford II and III as products. Therefore, two interpretations for this dehydrogenation are possible. One is an intramolecular proton shift by tautomerism, as is shown in Scheme I. The intermediate XI could not be isolated. However, the compound II might be formed from XI, since the irradiation of VIII gave IX. Another interpretation of the dehydrogenation is a direct hydrogen-atom abstraction by a photoexcited carbonyl group.[20,21] Thus, an oxygen atom of a carbonyl group of ketone XIII[23] abstracts a hydrogen atom from the dihydrophenanthrene intermediate X.[20] A ketyl radical, XIVa (or XIVb) may abstract one more hydrogen atom to afford II (or III) (see Scheme II).



Scheme II

Although the former course can be expected to produce the photocyclization of I in an acidic medium, no cyclized products were obtained. Furthermore, the formation of VI from I in acetic acid could not be interpreted in terms of a tautomerism mechanism (the former course). Therefore, all of these experimental results support the latter course.

Experimental[24]

Irradiation of Tetraphenylcyclopentadienone (I) in the Absence of Oxygen. *A. In 2-Propanol.* A solution of 2.0 g of I[25] in 1.1 *l* of 2-propanol, agitated by the bubbling of nitrogen gas, was irradiated with an internal, water-cooled high-pressure mercury arc lamp (Eikosha Co., Ltd., Oyodo-ku, Osaka, model

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[14] a) W. M. Moore, D. D. Morgen and F. R. Stermitz, *ibid.*, **85**, 829 (1963); b) F. B. Mallory, C. S. Wood and J. T. Gordon, *ibid.*, **86**, 3094 (1964).

[15] a) G. E. Lewis, *Tetrahedron Letters*, **1960**, 12 (1960); b) G. E. Lewis, *J. Org. Chem.*, **25**, 2193 (1960).

[16] G. M. Badger, R. J. Drewer and G. E. Lewis, *Australian J. Chem.*, **16**, 1042 (1963).

[17] a) P. Hugelshofer, J. Kalvoda and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960); b) G. M. Badger, C. P. Joshua and G. E. Lewis, *Tetrahedron Letters*, **1964**, 3711.

[18] J. Sidman, *Chem. Revs.*, **58**, 689 (1958).

[19] a) E. J. Corey, J. D. Bass, R. Le Machieu and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); b) H. Morrison, H. Curtis and T. McDowell, *ibid.*, **88**, 5415 (1966).

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

[21] Moreover, thermally-excited tetraphenylcyclopentadienone (I) seems to have the ability to abstract hydrogens.[22]

[22] a) B. A. Arbuzov, L. A. Shapshinskaya and G. A. Prytkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2084 (1962); b) E. McNelis, *J. Org. Chem.*, **30**, 4324 (1965).

[23] Ketone XIII might be formed by dehydrogenation from the dihydrophenanthrene intermediate X, although XIII could not be isolated in this reaction.

[24] The melting points are uncorrected. The infrared spectra were obtained with a Hitachi ESI-S2 infrared spectrophotometer. The ultraviolet spectra were recorded with a Hitachi EPS-2 recording spectrophotometer. The NMR spectra were obtained with a JNM-4H-100 apparatus. Tetramethylsilane was used as an internal standard. Molecular weights were determined with a Michrolab vapor-pressure osmometer, model 301 A, in a benzene solution.

[25] J. R. Johnson and O. Grummitt, "Organic Syntheses," Coll. Vol. III, p. 806 (1955).

P1H-500S, 500 watt). After about 7 hr, the red color of the solution faded completely. The solvent was then removed. The residue dissolved in a minimum amount of benzene was chromatographed on a column of 60 g of activated alumina, after which the column was eluted with 1 *l* of petroleum ether (bp 45—60°C). The eluent, in 100-m*l* fractions, was concentrated and dried *in vacuo*. The first fraction contained 0.2 g of 2, 3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene (II), mp 183.0—183.8°C (from cyclohexane).

Found: C, 94.41; H, 5.72%; mol wt, 361. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47%; mol wt, 368.5.

Compound II, isolated in a 10% yield, shows IR absorptions (haxachlorobutadiene mull) at 2915, 2855 and 1454 cm^{-1} typical of methylene. The UV spectrum in cyclohexane has maxima at 215 mμ (log ε 4.7), 224 (4.7), 250 (sh) (4.7), 257 (4.8), 271 (sh) (4.3), 280 (4.1), 291 (4.2), 303 (4.3), 323 (2.7), 330 (2.7), 338 (3.0), 346 (2.7), and 355 (3.1). The NMR spectrum in CCl_4 has complex multiplets at τ 1.18—1.33 (2 H) and τ 2.35—2.63 (6 H), and singlets at τ 2.82 (10 H) and τ 5.43 (2 H).

Fractions 2 and 3 contained 0.91 g of 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (III), mp 179.0—180.4°C (from benzene-cyclohexane).

Found: C, 90.81; H, 5.35%; mol wt, 390. Calcd for $C_{29}H_{20}O$: C, 90.59; H, 5.24%; mol wt, 384.5.

Compound III, isolated in a 45% yield, shows UV maxima (in cyclohexane) at 216 mμ (log ε 5.1), 243 (5.0), 251 (sh) (5.0), 259 (sh) (5.0), 266 (sh) (5.0), 284.5 (4.6), 301 (sh) (4.4), 314 (4.4), 322 (4.3), 342 (3.8), and 359 (3.6). The NMR spectrum in CCl_4 has complex multiplets at τ 0.56—0.7 (1 H), τ 1.3—1.5 (2 H), τ 2.25—2.55 (5 H) and τ 2.6—3.1 (10 H), and doublets at τ 5.08 (1 H) and τ 6.26 (1 H) (J=2.5 cps).

The remaining substances were tarry materials.

B. In Glacial Acetic Acid. A solution of 2.0 g of I[25] in 550 m*l* of glacial acetic acid was irradiated for 130 min as has been described in A. The solvent was removed *in vacuo*, and the residue was chromatographed on a column of 60 g of alumina. The column was eluted with 1 *l* of benzene. Each 50-m*l* eluent was concentrated and dried *in vacuo* to afford 0.2 g (10%) of the starting material I, 0.81 g (40%) of 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (III), and 0.38 g (19%) of 2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one (VI), mp 158—160°C and mixed mp 159—161°C.[10] Further elution with ether and methanol gave only tarry materials.

C. In the Solution of Hydrochloric Acid in Tetrahydrofuran. Two grams of I[25] were dissolved in a solution of concentrated hydrochloric acid (2 m*l*) in 550 m*l* of absolute tetrahydrofuran, after which this solution of I was irradiated for 2.5 hr as has been described above. After most of the solvent had been evaporated, the residual solution was poured into water. The organic layer was extracted with ether, the ethereal solution was washed with water and dried over anhydrous calcium chloride, and the solvent was removed. The residue was chromatographed on a column of 60 g of alumina, after which the column was eluted with 500 m*l* of benzene. Each 20-m*l* eluent was concentrated and dried *in vacuo* to afford 1.5 g of 4-tetrahydrofur-2′-yl-2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one (VII), mp 194—195°C (from benzene-cyclohexane).

Found: C, 86.50; H, 6.15%; mol wt, 433. Calcd for $C_{33}H_{28}O_2$: C, 86.81; H, 6.18%; mol wt, 457.

Compound VII, formed in a 65% yield, shows strong IR absorptions (Nujol mull), at 1692, 1631 and 1062 cm^{-1}, which were very similar to those of compound VI except for the C–O stretching absorption at 1062 cm^{-1}. The carbonyl stretching frequency at 1692 cm^{-1} is characteristic of a five-membered cyclic ketone with a conjugated double bond. The UV spectrum in ethanol is also similar to that of VI and has maxima at 224 mμ (sh) (log ε 4.6), 240 (sh) (4.4) and 298 (4.2). The NMR spectrum exhibits a sharp singlet at τ 5.35 (1 H), and complex multiplets at τ 6.06—6.6 (3 H) and τ 7.6—8.8 (4H) other than aromatic protons (20 H). These chemical shifts are consistent with the structure of VII. In fact, the chemical shift of the C-5 proton of the authentic compound, VI[10], is τ 5.56, while those of the α- and β-protons of tetrahydrofuran are τ 6.25 and τ 8.15 respectively.[26]

Irradiation of Tetraphenylcyclopentadienone (I) in the Presence of Oxygen. A solution of 2.0 g of I[25] in 1.1 *l* of 2-propanol was irradiated with a slow stream of oxygen for 100 min as has been described above. The resulting products were worked up in the usual manner, and chromatographed on a column of 60 g of alumina. The column was then eluted with 1 *l* of benzene, and the eluent was concentrated and dried *in vacuo*. The resulting solid contained 0.36 g (18%) of *trans*-dibenzoylstilbene (V), mp 230.0—231.5°C (lit.[9] mp 229.7—231.6°C). The eluent with 1 *l* of ether gave 0.35 g (17%) of *cis*-dibenzoylstilbene (IV), mp 212.5—213.0°C (lit.[9] mp 212.6—213.0°C).

2, 3, 4, 5-Tetraphenyl-2, 4-cyclopentadien-1-ol (VIII). Compound VIII was prepared by the reduction of I according to the method reported by Sonntag *et al.*[10] Upon exposure to light and air, VIII darkened rapidly.[10] Therefore, the crude crystalline material (from a rather large amount of acetone) was dried over potassium hydroxide and anhydrous calcium chloride, and subjected to irradiation. This substance did not contain IX, whose absence was ascertained by a study of the IR spectrum.

Irradiation of 2, 3, 4, 5-Tetraphenyl-2, 4-cyclopentadien-1-ol (VIII). A solution of 0.6 g of VIII in 550 m*l* of 2-propanol was irradiated for 4.5 hr as has been described above. The reaction was followed by means of the UV spectra of aliquots. The products were worked up in the usual manner, and were chromatographed on a column of 20 g of alumina. The column was eluted with 500 m*l* of benzene. The eluent, in 20-m*l* fractions, was concentrated and dried *in vacuo*. Fractions 2 and 3 contained 0.22 g (36%) of 1, 2, 3, 4-tetraphenyl-1, 3-cyclopentadiene (IX), mp 178°C (lit.[13] mp 182—184°C), undepressed upon admixture with an authentic sample.[13]

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[26] N. S. Bhacca, L. F. Johnson and J. N. Shoolery, "NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, California (1962), No. 77.