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Photoreactions of Cyclopentenone Derivatives

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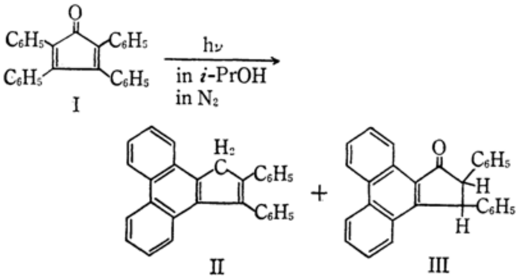
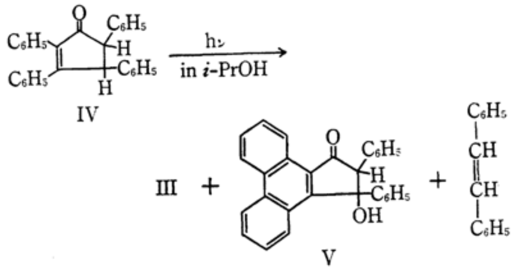
Photoreactions of conjugated or non-conjugated, five-membered, cyclic ketones were investigated. Irradiation of 2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one in 2-propanol with ultraviolet light under a slow stream of nitrogen or oxygen gave 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (55%) and 1-oxo-3-hydroxy-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (about 20%). Similar irradiation of 3, 4-diphenyl-3-cyclopenten-1-one under a nitrogen stream gave 2-oxo- and 2-hydroxy-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene in 33% and 11% yields respectively. In both cases, there was observed photocyclization of a *cis*-stilbene skeleton to a phenanthrene. However, on irradiation of 2, 2-dimethyl-3, 4-diphenyl-3-cyclopenten-1-one, there was obtained a decarbonylation product, 1, 1-dimethyl-1, 2-dihydrocyclobuta[*l*]phenanthrene. The reaction courses of these photoreactions are proposed.

Previously, we reported that irradiation of tetraphenylcyclopentadienone (I) in 2-propanol with ultraviolet light under a slow stream of nitrogen gave 2, 3-diphenyl-1 *H*-cyclopenta[*l*]phenanthrene (II) and 1-oxo-2, 3-diphenyl-2, 3-dihyro-1*H*-cyclopenta[*l*]phenanthrene (III).[1] It is proposed for this photochemical oxidation-reduction that I cyclizes to dihydrophenanthrene intermediate through *n*-π^* singlet state and then a photo-exited carbonyl group abstracts hydrogens from this intermediate to result in products. In order to ascertain this mechanism, the photoreaction of conjugated 2, 3, 4, 5-tetraphenyl-2-cyclopenten-1-one, non-conjugated 3, 4-diphenyl-3-cyclopenten-1-one and the related compounds was investigated in the present paper.



Results and Discussion

2, 3, 4, 5-Tetraphenyl-2-cyclopenten-1-one (IV)[2] in 2-propanol was irradiated under a slow stream of nitrogen for 7 hr. The reaction products were chromatographed on activated alumina. There were obtained 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (III, in 55% yield), 1-oxo-3-hydroxy-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenathrene (V, in 23% yield), and a small amount of stilbene.



The structure of compound III, mp 179.0—180.4°C, was identified by comparison with the authentic sample prepared by irradiation of compound I.[1] The structure of *trans*-stilbene was also confirmed by comparison with an authentic sample.[3]

The molecular formula for compound V, mp 208—209°C, was found to be $C_{29}H_{20}O_2$ on the basis of elemental analyses and the molecular weight. The strong absorptions at 1688 cm^{-1} and 3400 cm^{-1} in the infrared spectrum of V indicate the presence of a five-membered, cyclic ketone conjugated with a double bond,[4] and a hydroxyl

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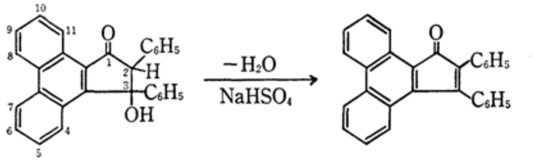
1) a) N. Toshima and I. Moritani, *Tetrahedron Letters*, **1967**, 357; b) I. Moritani and N. Toshima, *ibid.*, **1967**, 467; c) N. Toshima and I. Moritani, This Bulletin, in press,

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

3) R. L. Shrinder and A. Berger, "Organic Syntheses," Coll. Vol. III, p. 768 (1955).

4) In fact, the frequency of the carbonyl absorption of compound III or IV lies at 1691 cm^{-1} or at 1690 cm^{-1}.

group, respectively. The ultraviolet spectrum of V is quite similar to that of III. This fact shows that compound V has the similar chromophore to that of compound III.[5] The NMR spectrum exhibits complex multiplets at τ 0.7—0.8 (1H), τ 1.4—1.5 (2H), τ 2.3—2.55 (5H) and τ 2.7—3.5 (10H), and sharp singlets at τ 4.84 (1H) and τ 6.83 (1H). The signal at τ 0.7—0.8 was assigned to the proton at 11 position of compound V. This assignment was made on the basis of the deshielding effect of the carbonyl group.[6] The signal at τ 1.4—1.5 comes from 7 and 8 protons,[7] and the signal at τ 2.3—2.55 from other protons of a phenanthrene skeleton. These figures of τ value show the presence of a phenanthrene skeleton adjacent to a carbonyl group. The signal at τ 4.84 is due to a methine proton at 2 position.[8] Disappearance of the signal at τ 6.83 by addition of deuterium oxide indicates clearly that this signal comes from a hydroxyl proton. The structure of compound V was further confirmed by the fact that heating of V in xylene with sodium bisulfate gave 1-oxo-2, 3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene (VI).

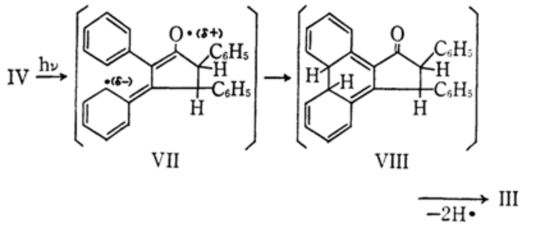


V VI

The molecular formula for compound VI, mp 275.8—276.2°C, was found to be $C_{29}H_{18}O$. The carbonyl stretching frequency at 1708 cm^{-1} in the infrared spectrum of VI is characteristic of a cross-conjugated, five-membered, cyclic ketone. In fact, compound I has a band at 1710 cm^{-1}. The ultraviolet spectrum of VI shows the similar absorption to that of I except those due to a phenanthrene skeleton. In fact, the maximum absorption at the longest wavelength appears at 508 mμ in compound I, while at 519 mμ in compound VI. All signals in the NMR spectrum were attributed to aromatic protons, and characteristic of a phenanthrene skeleton adjacent to a carbonyl group. On the basis of these results, the structure of VI was confirmed.

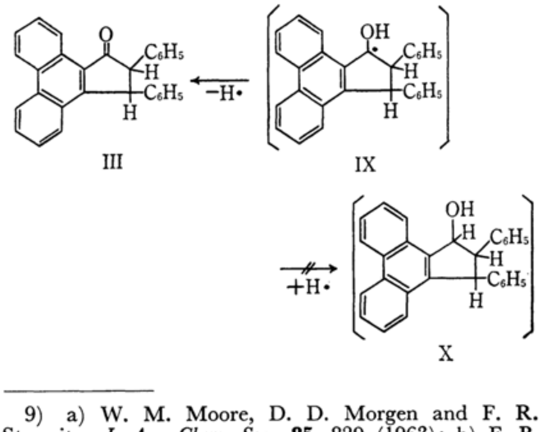
Photocyclization to form a phenanthrene skeleton[9] occurred in the photoreaction of IV as well as that of I. However, photoreaction of compound I involved reduction of a carbonyl group or a double bond, while, in the case of compound IV, the reduction was not observed.

Now, photoreaction of IV in cyclohexane was investigated in order to ascertain whether or not the photoreactivity of IV is different from that of I. When IV in cyclohexane was irradiated with ultraviolet light under a slow stream of nitrogen for 31 hr, 49% of the starting material IV was recovered. The reaction products contained ketone III (8%), *trans*-stilbene (7%), and tarry materials, the structure of which could not be identified. The rate of photoreaction of IV in cyclohexane was clearly slower than in 2-propanol.



VII VIII

The similar solvent effect was also observed in photoreaction of I as previously reported.[1] This similar solvent effect in IV and I fragilely suggests that the photoreaction of IV involves the similar scheme to that of I,[1] although the reaction products of IV are rather complex. Thus, irradiation of IV would give dihydrophenanthrene intermediate VIII through intermediate VII. Hydrogens of the dihydrophenanthrene skeleton of intermediate VIII might be abstracted by oxygen contained in nitrogen gas or by the photo-excited carbonyl group of another ketone, for instance III, and there



III IX

X

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5) For the ultraviolet spectrum of a phenanthrene derivative, see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y. (1962), p. 323.

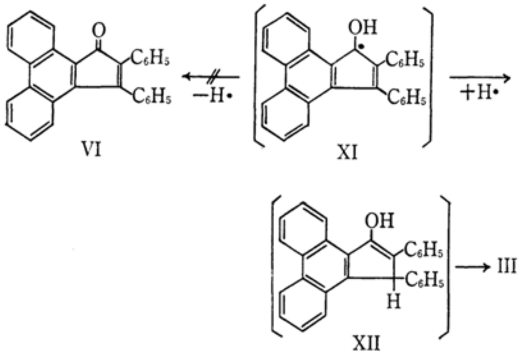
6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y. (1959), Chap. 7.

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

8) In fact, the chemical shifts of the protons in methine groups α and β to the carbonyl group in compound III are at τ 5.08 and τ 6.26 respectively.

9) a) W. M. Moore, D. D. Morgen and F. R. Stermitz, *J. Am. Chem. Soc.*, **85**, 829 (1963); b) F. B. Mallory, C. S. Wood and J. T. Gordon, *ibid.*, **86**, 3094 (1964); c) A. Padwa and R. Hartman, *ibid.*, **88**, 3759 (1966).

would be obtained ketone III from VIII. However, irradiation of compound IV gave the cyclized product involving no reduction of a carbonyl group. On the contrary, compound I was cyclized to result in the product which involved reduction of a carbonyl group. This fact could be explained by the stability of the product as follows. One hydrogen abstraction by a photo-excited carbonyl group of III from VIII would probably give a radical intermediate IX.10) This intermediate can give a ketone III by dehydrogenation, or alcohol X by hydrogen abstraction. The course of reaction of IX would be controlled by the stability of the product. Ketone III may be more stabilized than alcohol X by conjugation. Thus, irradiation of IV gave III, but not X. On the contrary, in the case of compound I, the ketyl radical intermediate XI would not give ketone VI by dehydrogenation, but enol XII by hydrogen abstraction, because the ketone VI had an unstable cyclopentadienone skeleton.11) Thus, irradiation of I gave III, but not VI.



It is well known that photocyclization of *cis*-stilbene to phenanthrene occurs only in the presence of oxidizing agent such as oxygen.9) The effect of oxygen on the photoreaction of IV was investigated. Compound IV in 2-propanol was irradiated under a slow stream of oxygen. The reaction was followed by ultraviolet spectra of aliquots, and was found to be completed by irradiation for only 3 hr. The products were similar to those under a nitrogen stream, and contained ketone III and keto-alcohol V in 54% and 18% yields respectively. On irradiation of IV in cyclohexane, 7 hr were sufficient for a half conversion of the starting compound IV under an oxygen stream, while 31 hr were necessary under a nitrogen stream. The reaction mixtures under an oxygen stream contained the recovered compound IV (51%) and ketone III (15%). The remainings were tarry materials and could not be identified. These results show that the photocyclization of IV is more accelerated in 2-propanol than in cyclohexane, and moreover, under an oxygen stream than under a nitrogen. The fact that the photocyclization is accelerated by the presence of oxygen exhibits that oxygen acts as a dehydrogenating agent in photoreaction of compound IV, while compound I reacts with oxygen to form dibenzoylstilbene.1)

The product V may be formed by reaction of III with oxygen contained in nitrogen gas through hydroperoxide derivative, although other explanations may be possible.

Then, the photocyclization in non-conjugated system was investigated. Irradiation of 3, 4-diphenyl-3-cyclopenten-1-one (XIII)12) in 2-propanol under a slow stream of nitrogen gave 2-oxo-2, 3-dihydro-1*H*-cyclopenta[*l*]phenathrene (XIV) and 2-hydroxy-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (XV) in 33% and 11% yields respectively. The structures of XIV13) and XV were identified by comparison with the authentic samples. The reaction path of this photochemical oxidation-reduction of compound XIII would be different from that of I or IV. The mechanism through π-π^* excitation that has been proposed in the case of *cis*-stilbene9a) can be applied to this photoreaction of XIII in spite of the presence of a carbonyl group. The formation of phenanthrene derivatives XIV and XV from XIII was observed not only in a protic solvent, 2-propanol, but also in an aprotic solvent, tetrahydrofuran, while the photocyclization of I was not observed in an aprotic solvent, tetrahydrofuran or cyclohexane. This solvent effect on the reaction of XIII is shown in Table 1.

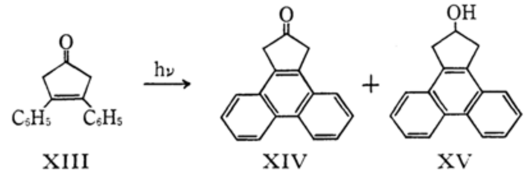


TABLE 1. THE SOLVENT EFFECT ON THE PHOTOREACTION OF XIII

Solvent	Yield, %		Ratio of yield XIV/XV
	XIV	XV	
Methanol	65	7	9.3
2-Propanol	33	11	3.0
Tetrahydrofuran	20	35	0.57

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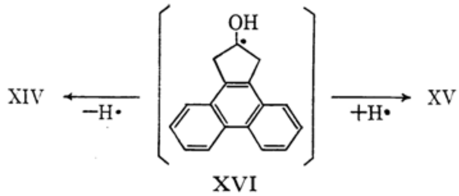
10) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1965), p. 142.

11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y. (1961), p. 271.

12) E. J. Corey and H. Uda, *J. Am. Chem. Soc.*, **85**, 1788 (1963).

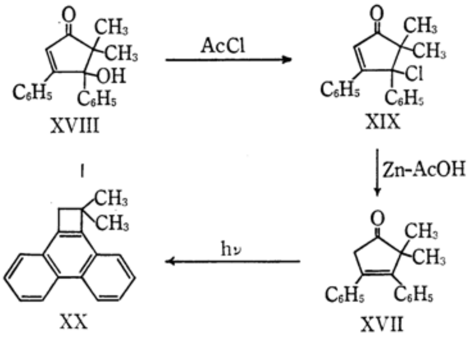
13) A. C. Cope and D. W. H. MacDowell, *ibid.*, **80**, 5513 (1958).

Two processes may be possible in formation of reduced product XV. One is the two 1, 5-proton-shifts after enolization of the corresponding dihydrophenanthrene intermediate.[1c] The other is a direct hydrogen abstraction with a photo-excited carbonyl group. If the reaction undergoes through the former process, XV should be obtained in the better yield in the acidic condition, because keto-enolization is well known to be acid-catalyzed. To ascertain whether this is the case or not, irradiation of XIII in tetrahydrofuran containing hydrochloric acid was attempted. The reaction mixtures were carefully chromatographed on activated alumina. However, compound XV could not be obtained, but only tarry materials. This result suggests that XV is not formed through the mechanism involving the tautomerization, but rather through a hydrogen abstraction with a photo-excited carbonyl group as that observed in the case of compound I.[1] Thus, further hydrogen abstraction of intermediate XVI would give alcohol XV and dehydrogenation would give ketone XIV. In fact, the more polar the solvent is, the larger the ratio of XIV to XV is, as shown in Table 1. Reasonable explanation for this result may be as follows. A strong polar solvent may surround the intermediate XVI by solvation and make difficult a further hydrogen abstraction to form alcohol XV.[14]



XVI

Irradiation of 3, 4-diphenyl-3-cyclopenten-1-one (XIII) gave cyclization-reduction product XV. However, when methyl groups were introduced into α-position to the carbonyl group, a different photoreaction occurred.



2, 2-Dimethyl-3, 4-diphenyl-3-cyclopenten-1-one (XVII) was synthesized from chloride XIX of 5, 5-dimethyl-3, 4-diphenyl-4-hydroxy-2-cyclopenten-1-one (XVIII).[15] The structure of XVII was ascertained by elemental analyses. molecular weight, and infrared, ultraviolet and nuclear magnetic resonance spectra. (See Experimental Section.)

On irradiation with ultraviolet light, XVII in 2-propanol gave 1, 1-dimethyl-1, 2-dihydrocyclobuta[*l*]phenanthrene (XX) in 34% yield.

The molecular formula for compound XX, mp 123—124°C, was found to be $C_{18}H_{16}$. The ultraviolet spectrum of XX shows the characteristic bands of 9, 10-disubstituted phenanthrene derivatives.[5] The NMR spectrum has complex multiplets at τ 1.3—1.5 and τ 2.25—2.6 assigned to aromatic protons of a phenanthrene skeleton,[7] and singlets at τ 6.85 (2H) and τ 8.3 (6H). These spectral data are in excellent agreement with the structure of XX. In fact, 1, 2-dihydrocyclobuta[*l*]phenanthrene (XXI), which prepared by photolysis of sodium salt of Δ^2-2, 3-diphenylcyclopropenecarboxaldehyde tosylhydrazone[16] or by irradiation of 9, 10-dimethylene-9, 10-dihydrophenanthrene,[17] has the similar spectral data. Thus, methylene protons of XXI appear at τ 6.55 in the NMR spectrum, and the reported ultraviolet spectrum of XXI is similar to that of XX.

The photodecarbonylation of ketone in vapor phase was observed.[18,19] However, there are a few reports on decarbonylation of ketone in liquid phase.[19,20] In the present case, two methyl groups were introduced at α-position to a carbonyl group led to the photodecarbonylation of compound XVIII. The similar result was reported in the irradiations of 2-indanone and 1-phenyl-2-indanone.[21] Thus, introduction of a phenyl group made easy the photodecarbonylation in this reaction, as well as that of a methyl group in the present photoreaction. In both cases, a methyl or a phenyl group could be considered to stabilize the radicals which would be formed by α-cleavage of the ketones.

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[14] Much larger ratio of yields in 2-propanol than in tetrahydrofuran would probably exclude the possibility that easiness of hydrogen-atom abstraction from solvent is related to this result.

[15] F. R. Japp and A. N. Meldrum, *J. Chem. Soc.*, **79**, 1024 (1901).

[16] S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965); **88**, 610 (1966).

[17] E. H. White, G. E. Maier, R. Graeve, U. Zirngibl and E. W. Friend, *ibid.*, **88**, 611 (1966); and the footnote 10.

[18] R. Srinivasan, "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. 83.

[19] O. L. Chapman, *ibid.*, p. 323.

[20] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers and G. F. Vesley, *J. Am. Chem. Soc.*, **87**, 2613 (1965).

[21] G. Quinkert, K. Opitz, W. W. Wiersdorff and J. Weinlich, *Tetrahedron Letters*, **1963**, 1863.

Experimental Section[22]

2, 3, 4, 5-Tetraphenyl-2-cyclopenten-1-one (IV). 2, 3, 4, 5-Tetraphenyl-2-cyclopenten-1-one (IV), mp 159.5—161°C (lit. mp 160—161°C), was prepared by reduction of tetraphenylcyclopentadienone (I)[23] with zinc amalgam by the method of Sonntag *et al.*[2]

Irradiation of 2, 3, 4, 5-Tetraphenyl-2-cyclopenten-1-one (IV). A solution of 2.0 g of IV in 1100 m*l* of anhydrous 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 P1H-500S, 500W). 2-Propanol began to reflux after 20-min irradiation. The reaction was followed by ultraviolet spectra of aliquots. After irradiation for 7 hr, 2-propanol was removed. The crystalline substance precipitated from the concentrated solution. Recrystallization from benzene-cyclohexane gave 0.7 g of III, mp 179.0—180.4°C. III was identified to be 1-oxo-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene by comparison with the sample prepared by irradiation of tetraphenylcyclopentadienone (I).[1] The mother liquor was concentrated and the residue was submitted to the column chromatography over 50 g of activated alumina. From the eluent with petroleum ether (bp 45—60°C)- 0.20 g of *trans*-stilbene, mp 120—122°C, was obtained. This structure was confirmed by comparison with the authentic sample[3] (lit. mp 123—124°C). From the eluent with benzene, 0.39 g of crystalline material III was obtained. The total yield of III was 1.09 g (55%).

From the eluent with ether, there was obtained 0.48 g (23%) of white crystalline 1-oxo-3-hydroxy-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (V), mp 208—209°C (from benzene—cyclohexane).

Found: C, 87.01; H, 5.13%; mol wt, 396. Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.03%; mol wt, 400.

The infrared spectrum (Nujol mull) of V has strong absorptions at 1688 cm^{-1} and 3400 cm^{-1}. The ultraviolet spectrum in ethanol shows maxima at 244.5 mμ (log ε 4.5), 252 (sh) (4.4), 266 (4.4), 287 (4.0), 323 (4.0) and 362 (3.4). The NMR spectrum in chloroform-d exhibits complex multiplets at τ 0.7—0.8 (1H), τ 1.4—1.5 (2H), τ 2.3—2.55 (5H) and τ 2.7—3.5 (10H)), and sharp singlets at τ 4.84 (1H) and τ 6.83 (1H). The signal at τ 6.83 disappears by addition of deuterium oxide.

Irradiations of ketone IV (2.0 g) under the other conditions were carried out in the same way. The yields were determined by separation with alumina column chromatography.

Dehydration of 1-Oxo-3-hydroxy-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (V).[24] A solution of 1-oxo-3-hydroxy-2, 3-diphenyl-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (V) (0.2 g, 0.5 mmol) in 20 m*l* of xylene was boiled with 1.5 g of sodium bisulfate. The reaction mixture turned red. After refluxing for 6 hr, the xylene solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated *in vacuo* and the residue was chromatographed on activated alumina. From the eluent with benzene, threre was obtained 40 mg (21%) of red needles, 1-oxo-2, 3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene (VI), mp 275.8—276.2°C (from benzene - petroleum ether).

Found: C, 91.18; H, 4.86%. Calcd for $C_{29}H_{18}O$: C, 91.07; H, 4.74%.

The infrared spectrum of VI exhibits C=O stretching frequency at 1708 cm^{-1}. The ultraviolet spectrum in cyclohexane has maxima at 212.5 mμ (log ε 4.5), 248.5 (4.6), 262 (4.6), 270 (sh) (4.5), 290 (sh)(4.1), 316 (4.0), 329 (4.1), 411 (3.0), 430 (3.0), and 519 (3.0). The NMR spectrum in carbon disulfide shows complex multiplets at τ 1.0—1.2 (1H), τ 1.4—1.6 (2H), and τ 2.4—3.1 (15H). From the eluent with ether, the starting material V was recovered.

3, 4-Diphenyl-3-cyclopenten-1-one (XIII). Reduction of 4-chloro-3, 4-diphenyl-2-cyclopenten-1-one in large amount of dry ether with zinc-acetic acid by the method of Corey and Uda[12] gave 3, 4-diphenyl-3-cyclopenten-1-one (XIII), mp 141.3—142.1°C (lit. mp 136—147°C), which showed all of the characteristic properties reported in the literature.

Irradiation of 3, 4-Diphenyl-3-cyclopenten-1-one (XIII). A solution of 2.0 g of XIII in 550 m*l* of 2-propanol was irradiated under a slow stream of nitrogen as described above. The reaction was followed by ultraviolet spectra of aliquots. After 14 hr, the solvent was removed and the residue was chromatographed on 80 g of activated alumina. From the eluent with benzene, there was obtained 0.65 g (33%) of crystalline 2-oxo-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (XIV), mp 215—217.5°C (from chloroform). The structure of XIV was identified by comparison with the authentic sample,[13] mp 215—219°C (from dioxane) (lit. mp 222.5—223.0°C). From the eluent with ether, there was obtained 0.22 g (11%) of 2-hydroxy-2, 3-dihydro-1*H*-cyclopenta[*l*]phenathrene (XV), mp 184.5—185.0°C (from benzene). The structure was identified by its failure to depress the melting point of the authentic sample independently synthesized described below.

Irradiation of XIII in methanol or tetrahydrofuran was carried out in a similar way. The yields of XIV and XV were confirmed by separation with column chromatography on activated alumina.

Preparation of 2-Hydroxy-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (XV). A mixture of 2-oxo-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (XIV) (46.4 mg, 0.2 mmol)[13] and sodium borohydride (42.8 mg, 1.1 mmol) in 30 m*l* of 2-propanol was boiled for 15 min. The reaction mixture was poured into water and organic substance was extracted with ether. The ether solution was washed with dilute hydrochloric acid solution and aqueous sodium chloride solution, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 44 mg (93%) of white crystalline 2-hydroxy-2, 3-dihydro-1*H*-cyclopenta[*l*]phenanthrene (XV), mp 185.0—186.0°C (from benzene).

Found: C, 86.96; H, 6.22%. Calcd for $C_{17}H_{14}O$:

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

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

[24] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 130 (1928).

C, 87.15; H, 6.02%

The infrared spectrum of XV (Nujol mull) has bands at 3320 cm^{-1}, 1044, 752, and 723. The ultraviolet spectrum in ethanol exhibits maxima at 213.5 mμ (log ε 4.0), 222.5 (3.9), 248 (4.1), 255.5 (4.2), 271.5 (3.7), 279 (3.6), 290 (3.4), 302 (3.5), 323 (2.2), 338 (2.3), and 355 (2.4).

Preparation of 5, 5-Dimethyl-3, 4-diphenyl-4-hydroxy-2-cyclopenten-1-one (XVIII). The method of Japp *et al.*[15] was modified in this preparation. Twenty-four grams (0.114 mol) of benzil[25] and 14.6 g (0.17 mol) of isopropyl methyl ketone were dissolved in 400 m*l* of ethanol with 1.6 g of potassium hydroxide. This solution was heated at 50°C for 30 hr. The reaction mixture was poured into water. The precipitate was collected by filtration and washed with a large amount of water and then a small amount of ethanol. There was obtained 20.9 g (65.8%) of yellow, crystalline 5, 5-dimethyl-3, 4-diphenyl-4 - hydroxy - 2 - cyclopenten-1-one (XVIII), which melted at 181.5—182.5°C (lit.[15] mp 181°C) after recrystallization from ethanol. The infrared spectrum of XVIII (Nujol mull) shows absorptions at 3450 cm^{-1} and 1685 cm^{-1}. The ultraviolet spectrum in ethanol exhibits maxima at 220 mμ (log ε 4.7) and 288 (4.5).

Preparation of 5, 5-Dimethyl-3, 4-diphenyl-4-chloro-2-cyclopenten-1-one (XIX). A mixture of 5, 5-dimethyl-3, 4-diphenyl-4-hydroxy-2- cyclopenten- 1-one (XVIII, 5.0 g) and freshly distilled acetyl chloride (30 m*l*) was gradually heated to 40—45°C with stirring. After 5—10 hr, the crystalline materials were dissolved into solution and the color of the solution turned green. Acetyl chloride and acetic acid were evaporated *in vacuo*. Recrystallization of the residual solid from benzene - petroleum ether (bp 45—60°C) gave 1.75 g (33%) of white crystalline 5, 5-dimethyl-3, 4-diphenyl-4-chloro-2-cyclopenten-1-one (XIX), mp 114—122°C. Hydroxy stretching frequency disappeared in the infrared spectrum of the crude XIX. This crude material was used in the next reaction without further purification because of its unstability.

Preparation of 2, 2-Dimethyl-3, 4-diphenyl-3-cyclopenten-1-one (XVII). A solution of crude 5, 5-dimethyl-3, 4-diphenyl-4-chloro-2-cyclopenten-1-one (XIX, 1.0 g) in 100 m*l* of ether was added with stirring to a mixture of 10 g of zinc dust, 2 m*l* of glacial acetic acid, and 100 m*l* of ether. After stirring at room temperature for 3 hr, inorganic substance was removed by filtration. The ether solution was washed with water, 5% aqueous sodium carbonate solution, and then aqueous sodium chloride solution. The ether solution was dried over anhydrous magnesium sulfate. Evaporation of ether gave 0.78 g (83%) of white, crystalline 2, 2-dimethyl-3, 4-diphenyl-3-cyclopenten-1-one (XVII), which melted at 94—95°C after recrystallization from benzene - petroleum ether (bp 45—60°C).

Found: C, 86.66; H, 6.93%; mol wt, 223. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%; mol wt, 262.

Compound XVII shows infrared absorption at 1755 cm^{-1} characteristic of a non-conjugated, five-membered cyclic ketone. The ultraviolet spectrum in ethanol has maxima at 225 mμ (sh)(log ε 4.1) and 260 (4.1). This spectrum is different from that of 2-cyclopentenone derivative XVIII, and shows that XVII is 3-cyclopentenone derivative. The structure of XVII was confirmed by NMR spectrum. The NMR spectrum of XVII has a complex multiplet at τ 2.6—3.2 (10H), and singlets at τ 6.26 (2H) and τ 8.86 (6H) characteristic of methylene protons adjacent to the carbonyl group and geminal dimethyl protons, respectively.

Irradiation of 2, 2-Dimethyl-3, 4-diphenyl-3-cyclopenten-1-one (XVII). A solution of 2, 2-dimethyl-3, 4-diphenyl-3-cyclopenten-1-one (XVII, 1.0 g) in 550 m*l* of 2-propanol was irradiated as described above. After a usual work-up, the tarry matrial was chromatographed on 30 g of activated alumina. From the eluent with cyclohexane, there was obtained 300 mg (34%) of white, crystalline 1, 1-dimethyl-1, 2-dihydrocyclobuta[*l*]phenanthrene (XX), which melted at 123—124°C after recrystallization from petroleum ether (bp 45—60°C).

Found: C, 93.42; H, 6.87%; mol wt, 226. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%; mol wt, 232.

The infrared spectrum of XX (hexachlorobutadiene mull) has bands at 2950, 755, and 725 cm^{-1}. The ultraviolet spectrum in ethanol shows maxima at 212.5 mμ (log ε 4.6), 222 (4.4), 248 (sh)(4.7), 255 (4.9), 271 (4.3), 279.5 (4.1), 290.5 (4.0), 303 (4.1), 325 (2.6), 341 (2.9), and 358 (2.9). The NMR spectrum in carbon tetrachloride exhibits complex multiplets at τ 1.3—1.5 (2H) and τ 2.25—2.6 (6H), and sharp singlets at τ 6.85 (2H) and τ 8.3 (6H). These data are in agreement with the structure.

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[25] H. T. Clarke and E. E. Dreger, "Organic Syntheses," Coll. Vol. I, p. 87 (1956).