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# THE SOLVENT EFFECT ON THE PHOTOREACTION OF TETRAPHENYLCYCLOPENTADIENONE

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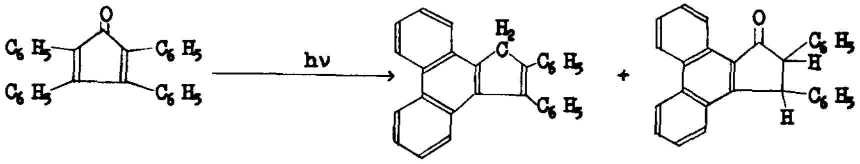
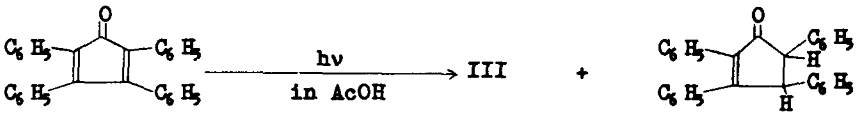
Tetraphenylcyclopentadienone (I) in solution was irradiated with ultraviolet light(1) under a slow stream of nitrogen. In methanol, isopropanol,(2) or *tert*-butanol, 2,3-diphenyl-*1H*-cyclopenta[*l*]phenanthrene (II) and 1-oxo-2,3-diphenyl-2,3-dihydro-*1H*-cyclopenta[*l*]phenanthrene (III) were obtained.



I II III

| | II | III |
|---|---|---|
| in MeOH | 12% | – |
| in *iso*-PrOH | 10% | 45% |
| in *tert*-BuOH | 17% | – |

On the other hand, in glacial acetic acid, irradiation of I produced 2,3,4,5-tetraphenyl-2-cyclopenten-1-one (IV), m.p. 178-180°, in 19% yield

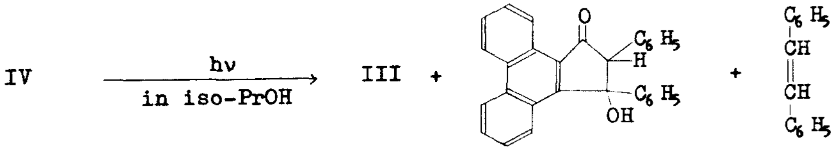


I IV

other than III in 40% yield. The structure of IV was confirmed by comparison with the authentic sample.(3)

However, no phenanthrene derivative was obtained in tetrahydrofuran or cyclohexane, and the starting material was recovered. Thus, the formation of *phenanthrene skeleton was observed only in protic solvents.*

A similar solvent effect was also observed in the photochemical transformation of compound IV. On irradiation with ultraviolet light for 7 hours, compound IV in isopropanol gave compound III (55% yield), 1-oxo-3-oxy-2,3-diphenyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene (V, 23% yield), and a small amount of stilbene.



V

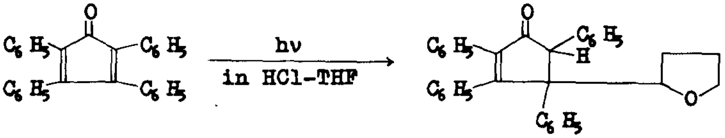
The molecular formula of compound V, m.p. 208-209°, was found to be $C_{29}H_{20}O_2$ based on elemental analysis and molecular weight.

Anal. Calcd. for $C_{29}H_{20}O_2$: C, 86.97; H, 5.03; Mol. Wt., 400. Found : C, 87.01; H, 5.13; Mol. Wt., 396 (in benzene by vapor pressure osmometer).

The infrared spectrum of compound V showed the bands of carbonyl and hydroxy group at 1688 and 3400 cm$^{-1}$, respectively. The ultraviolet spectrum had maxima at 244.5 mμ (log$\varepsilon$=4.5), 252 (sh) (4.4), 266 (4.4), 287 (4.0), and 323 (4.0). The nmr spectrum exhibited sharp singlets at $\tau$ 4.84 (1 hydrogen) and $\tau$ 6.83 (1 hydrogen), and complex multiplets at $\tau$ 0.7-0.8 (1 hydrogen), $\tau$ 1.4-1.5 (2 hydrogens), $\tau$ 2.3-2.55 (5 hydrogens), and $\tau$ 2.7-3.5 (10 hydrogens). These spectra showed the presence of a phenanthrene skeleton.(4,5) The structure of compound V was also confirmed by the fact that V was dehydrated by heating with sodium bisulfate to form 1-oxo-2,3-diphenyl-1H-cyclopenta[l]phenanthrene.

However, these photochemical transformations of compound IV were not observed in tetrahydrofuran or cyclohexane in the same conditions.

These solvent effects in the compound I or IV suggest that protic solvent or proton might be necessary for the formation of the phenanthrene skeleton. In order to ascertain which of the two plays an important role, protic solvent or proton itself, a solution of compound I in tetrahydrofuran containing hydrochloric acid was irradiated with ultraviolet light for 2.5 hours. The red color of the solution faded during the irradiation. The resulted products were worked up in the usual manner and submitted to alumina column chromatography. There was obtained a white crystalline material VI in 65% yield and a tarry material, which did not contain the phenanthrene skeleton so far as the ultraviolet spectra indicated.(4)



I

VI

The molecular formula for the compound VI, m.p. 194-195° (from benzene-ethanol), was found to be $C_{33}H_{28}O_2$ based on elemental analysis and molecular weight.

Anal. Calcd. for $C_{33}H_{28}O_2$ : C, 86.81; H, 6.18; Mol. Wt., 457. Found : C, 86.50; H, 6.15; Mol. Wt., 433 (in benzene by vapor pressure osmometer).

The ultraviolet spectrum of VI did not indicate the presence of a phenanthrene skeleton(4) and was quite similar to that of IV. The infrared spectrum of VI(6) was also almost similar to that of compound IV except a C-O stretching absorption appeared at 1062 $cm^{-1}$ in the compound VI. These data indicate that compound VI is 2,3,4,5-tetraphenyl-4-tetrahydrofurfuryl-2-cyclopenten-1-one. Moreover, the nmr spectrum(7) was consistent with the structure of VI.(8)

From the above results, it is clear that in the presence of hydrochloric acid, the cis-stilbene skeleton in I did not cyclize to the phenanthrene skeleton, but the addition of tetrahydrofuran solvent to I occurred.

In conclusion, the formation of the phenanthrene skeleton could not be activated by proton itself but by protic solvent. A further mechanistic investigation of these transformations is now in progress.

## REFERENCES

(1) A 500W high-pressure mercury arc (Eikosha Co., Ltd., Oyodo-ku, Osaka, Japan, model PlH-500S) was used.

(2) N. Toshima and I. Moritani, Tetrahedron Letters, in press.

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

(4) For ultraviolet spectra of phenanthrenes, see H. H. Jaffé and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, p. 323. John Wiley and Sons, Inc., New York, N. Y., (1962).

(5) For nmr spectra characteristic for phenanthrene skeleton, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, p. 250. McGraw-Hill, New York, N. Y., (1959).

(6) Strong peaks were observed at 1692, 1631, and 1062 $cm^{-1}$ in the infrared spectrum (nujol mull).

(7) Nmr spectrum exhibited a sharp singlet at $\tau$5.35 (1 hydrogen), and complex multiplets at $\tau$6.06-6.6 (3 hydrogens) and at $\tau$7.6-8.8 (4 hydrogens) other than aromatic protons (20 hydrogens).

(8) Indeed, the chemical shift of C-5 proton of authentic compound IV is $\tau$5.56 and that of $\alpha$- and $\beta$-protons of tetrahydrofuran(9), $\tau$6.25 and $\tau$8.15, respectively.

(9) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Vol. **1**, No. 77. Varian Associates, Palo Alto, California, (1962).