Tetrahedron Letters No.4, pp. 357-360, 1967. Pergamon Press Ltd. Printed in Great Britain.

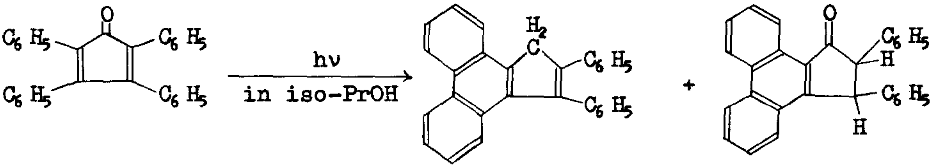
AN UNUSUAL PHOTOCHEMICAL TRANSFORMATION OF TETRAPHENYLCYCLOPENTADIENONE

Naoki Toshima and Ichiro Moritani(1)

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Machikaneyama, Toyonaka, Osaka, Japan

(Received 17 October 1966; in revised form 2 November 1966)

Interestingly, on irradiation with ultraviolet light, tetraphenylcyclopentadienone(2) (I) underwent an unusual transformation into 2,3-diphenyl-1*H*-cyclopenta〔*l*〕phenanthrene (II) and 1-oxo-2,3-diphenyl-2,3-dihydro-1*H*-cyclopenta〔*l*〕phenanthrene(III). Namely the *cis*-stilbene skeleton in I cyclized oxidatively to the phenanthrene, while the carbonyl group was reduced to a methylene to form a hydrocarbon II, or the double bond was hydrogenated to give a saturated compound III.



I II III

Tetraphenylcyclopentadienone(1) was dissolved in isopropanol and the solution, under reflux, was irradiated, under a slow stream of nitrogen, with ultraviolet light(3) for 7 hours. The red color of the solution gradually faded during the irradiation and finally a colorless solution was obtained. The solvent was removed and the residue was subjected to column chromatography on activated alumina. There were obtained two crystalline materials, II and

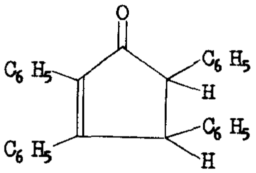
III, in 10% and 45% yield, respectively.

The molecular formula for compound II, m.p. 183.0-183.8°, was found to be $C_{29}H_{20}$ based on analytical results and molecular weight determination.

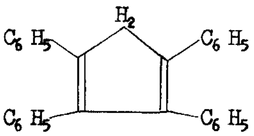
Anal. Calcd. for $C_{29}H_{20}$: C, 94.53; H, 5.47; Mol. Wt., 368.5. Found : C, 94.41; H, 5.72; Mol. Wt., 361 (in benzene by Vapour Pressure Osmometer). Unexpectedly compound II was shown to be a hydrocarbon. Absence of a carbonyl group was clearly demonstrated by the infrared spectrum and absence of reactions with carbonyl reagents, and the presence of a methylene group in II was indicated by the infrared(4) and nmr(5) spectra. The ultraviolet spectrum showed the presence of a 9,10-disubstituted phenanthrene structure in II(6). The presence of a phenanthrene skeleton was also evident from the nmr spectrum.(7) Thus compound II is identified as 2,3-diphenyl-1H-cyclopenta[1]-phenanthrene.

The product III, m.p. 179.0-180.4°, was identified as 1-oxo-2,3-diphenyl-2,3-dihydro-1H-cyclopenta[1]phenanthrene by the following observations. The material III was found to be a ketone having a formula of $C_{29}H_{20}O$.

Anal. Calcd. for $C_{29}H_{20}O$: C, 90.59; H, 5.24; Mol. Wt., 384.5. Found : C, 90.81; H, 5.35; Mol. Wt., 390 (in benzene by Vapor Pressure Osmometer). A carbonyl stretching frequency of III at 1691 cm.$^{-1}$ suggests that compound III compries a structure of a five-membered cyclic ketone conjugated with a double bond. The ultraviolet and nmr spectra clearly indicates that the material III contains a phenanthrene skeleton. Moreover, in the nmr spectrum compound III exhibits two doublet signals at 5.08τ(1 hydrogen, J=2.5 cps.) and at 6.26τ(1 hydrogen, J=2.5 cps.) besides eighteen aromatic protons, indicating that compound III has two non-olefinic protons located next to an unsaturated group. Indeed, authentic trans-2,3,4,5-tetraphenyl-2-cyclopenten-1-one(8)(IV) also exhibits two doublets at 5.56τ and 6.48τ with a coupling constant of 2.5 cps.

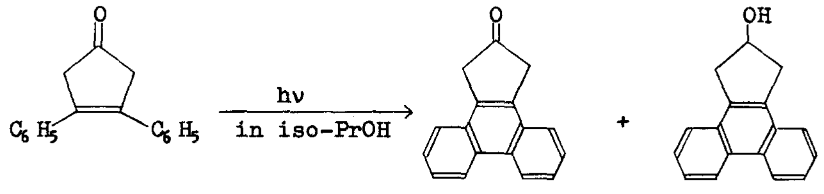


IV



V

Contrary to the above observations, compound of a similar structure but lacking a carbonyl group, namely 1,2,3,4-tetraphenylcyclopentadiene(V), did not give a product containing phenanthrene skeleton. Apparently, the phenanthrene formation was achieved only when the parent material contained a carbonyl group. Another example of the cyclization was observed in the transformation of 3,4-diphenyl-3-cyclopentene-1-one(9)(VI) to 2-oxo-2,3-dihydro-*1H*-cyclopenta[*l*]phenanthrene(VII) and 2-oxy-derivative VIII.(10)



VI VII VIII

The oxidative cyclization of *cis*-stilbene to phenanthrene is well known to occur in the presence of an oxidizing agent, such as iodine or oxygen.(11) In the present case, however, it is clear that the phenanthrene derivatives were formed in the absence of such an oxidizing agent. Indeed, when the isopropanol solution of I was irradiated in the presence of oxygen, the reaction products obtained were *cis*- and *trans*-dibenzoylstilbene (17% and 18% yield, respectively),(12) and the material having a phenanthrene skelton, such as II and III, could not be detected in the reaction product. Consequently it is evident that the formation of a phenanthrene skeleton is not due to the contamination with oxygen of the reaction system. The formation of compounds II and III from I, and of VIII from VI, indicates that the cyclization might be achieved at the expense of the reduction in the carbonyl group. A mechanistic investigation of these interesting transformations is now in progress.

REFERENCES

(1) All correspondence should be addressed to I. M.

(2) J. R. Johnson and O. Grummitt, *Organic Syntheses*, Coll. Vol. **3**, p. 806. (1955).

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

(4) Infrared peaks (as a hexachlorobutadiene mull) were observed at 2915, 2855, and 1454 $cm.^{-1}$

(5) The nmr spectrum (in CCl_4) showed a sharp singlet at 5.425τ (2 hydrogens).

(6) Ultraviolet maxima (in ethanol) were present at 215 mμ ($\log\varepsilon$=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), 355 (3.1). The spectrum is chracteristic of 9,10-disubstituted phenanthrene; 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).

(7) The nmr spectra (CCl_4) showed signals at 1.18~1.33τ (2 hydrogens) and 2.35~2.63τ (6 hydrogens) characteristic of phenanthrene derivatives; 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).

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

(9) E. J. Corey and H. Uda, *ibid.*, **85**, 1788 (1963).

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

(11) (a) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964); and literatures cited therein; (b) A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, 88, 3759 (1966).

(12) For a similar observation, see N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).