[Contribution from the Chemical Laboratories of the Polytechnic Institute of Brooklyn]

The Photoöxidation of Tetracyclone

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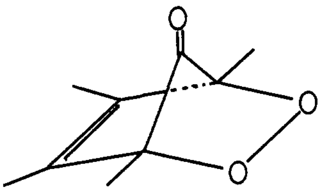
Received June 18, 1956

The photoöxidation of tetracyclone in benzene affords *cis*- and *trans*-dibenzoylstilbene, tetraphenyl-2-pyrone, and carbon monoxide. Identification of carbon monoxide along with the dibenzoylstilbenes lends support to tetraphenyl-2,3-dioxa-7-oxo[2,2,1]-bicyclohept-5-ene as an intermediate.

INTRODUCTION

In a study of the absorption spectrum of the tetracyclone (2,3,4,5-tetraphenylcyclopentadienone) and related compounds, it was noticed that its absorption characteristics changed upon standing in solution.[3] When irradiated with ultraviolet light, the purple color of the solution eventually became yellow. Evaporation of the solvent and purification of the residue yielded *trans*-dibenzoylstilbene. The present investigation was undertaken to study this reaction more extensively. In particular, it was of interest to determine whether additional evidence could be obtained to substantiate a proposed course of reaction which involves 1,4-addition of oxygen to the dienic system to give an intermediate photooxide I, which, upon, decomposition, would yield dibenzoylstilbene[4] (see attached drawing). This hypothesis required the elimination of carbon monoxide as a by-product. Photoöxides of configuration similar to I have been described.[5,6]



I

After a substantial part of this work had been completed, Dufraisse and co-workers reported[7,8] that they had obtained from the photolysis of tetracyclone, carried out under unspecified conditions, *cis*-dibenzoylstilbene in contradistinction to the earlier work. Dufraisse's work also suggested that, similarly to the photoöxides of pentaärylcyclopentadienols, the photoöxide I might cleave to give tetraphenylfuran and carbon dioxide. The present study therefore was also concerned with the clarification of the nature of additional products of the reaction.

EXPERIMENTAL[9]

IRRADIATION OF TETRACYCLONE

Apparatus. The light source was a 500-watt quartz mercury vapor ultraviolet lamp Type 74-20, Analytic Model, manufactured by the Hanovia Chemical and Manufacturing Company, Newark, N. J.

Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer recording spectrophotometer, Model 21. Ultraviolet spectra were taken in cyclohexane solution using a Cary recording spectrophotometer, Model 11.

Three types of reaction vessels were used: (1) a 315-ml. capacity Pyrex tube of 32 mm. diameter, equipped with a two-way stopcock; (2) a Vycor tube of 475 ml. capacity and 38 mm. diameter, equipped with a two-way pressure-type stockcock and a thermometer well to allow temperature readings of the solution; (3) a 195-ml. capacity quartz tube of 38 mm. diameter, the ends of which had been closed with watch glasses, using "High-Pyseal" as cement. Two holes in the walls kept the vessel open to the atmosphere. In some cases, a manometer was connected to the Pyrex or Vycor vessel by means of Tygon tubing.

Cooling of the reaction vessels, by means of a 10-inch electric fan, kept the temperature at approximately 35°.

Procedure. A solution of 0.50 g. (1.3×10^{-3} mole) of tetracyclone in 50 ml. of *m*-xylene was irradiated in the closed Pyrex tube at 8 inches from the source of light until the purple-red color of tetracyclone had nearly disappeared, which required five days. A sample of the gas above the solution then was withdrawn into an evacuated infrared gas analysis cell, and the cell contents were brought to atmospheric pressure using prepurified nitrogen. Spectroscopic analysis showed the presence of 1.4×10^{-3} mole of carbon monoxide and 0.25×10^{-3} mole of carbon dioxide.

The solution then was chromatographed, using activated alumina F 20, made by the Aluminum Ore Company of East St. Louis, Ill. Benzene, then a benzene-acetone mixture and finally acetone was used for elution, the progress of which was followed by visual observation aided by filtered ultraviolet light. After evaporation of the solvent, the residues from the various fractions were examined in the infrared and combined where necessary. In addition to 43 mg. of unreacted tetracyclone, the following were obtained:

A: 36 mg. of a white solid, m.p. 229.7–231.6°. The infrared spectrum showed the following bands in μ:

6.02(s), 6.26(m), 6.32(m), 6.69(m), 7.45(w), 7.62(m), 7.96(s), 8.12(s), 8.50(w), 8.52(m), 8.60(m), 9.23(m),

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(1) From the thesis submitted by N. M. B. to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

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(3) S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 900 (1953).

(4) W. Dilthey, S. Henkels, and M. Leonhard, *J. prakt. Chem.*, **151**, 97 (1938).

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(7) C. Dufraisse, A. Etienne, and J. Aubry, *Bull. soc. chim. France*, **21**, 1201 (1954).

(8) C. Dufraisse, A. Etienne, and J. Aubry, *Compt. rend.*, **239**, 1170 (1954).

(9) All melting points are corrected.

9.30(m), 9.52(m), 9.68(w), 9.76(m), 9.98(w), 10.25(w), 10.67(w), 10.80(w), 11.56(w), 12.30(m), 13.09(s), 13.30(s), 14.18(s), 14.40(s), 14.65(s), 15.18(m).

Ultraviolet absorption: λ_{max} 252 mμ, E_{max} 35,200.

B: A solid, which upon recrystallization from xylene-hexane mixture gave 10 mg. of yellow flakes, m.p. 163.5–164.0°, carbonyl absorption at 5.83 μ, and which analyzed: C, 87.10; H, 5.41. (Calculated for $C_{29}H_{20}O_2$: C, 86.98; H, 5.03.)

C: 12 mg. of a white solid, m.p. 212.6–213.0° (ethanol). The principal bands in the infrared spectrum, in μ are:

6.02(s), 6.24(m), 6.30(m), 6.70(w), 7.55(m), 7.69(m), 7.90(s), 8.08(m), 8.36(w), 8.47(m), 8.58(w), 9.11(w), 9.30(w), 9.60(w), 9.72(w), 9.82(m), 10.00(w), 10.89(m), 11.70(w), 11.88(w), 12.12(m), 12.42(w) 12.97(s), 13.42(m), 13.62(s), 14.12(s), 14.39(s), 14.64(m), 14.85(w), 15.55(m).

Ultraviolet absorption: λ_{max} 252 mμ, E_{max} 28,700. Extraction of the column with hot glacial acetic removed a yellow fraction tenaciously held by the alumina, but its purification was unsuccessful.

Substitution of reagent grade aluminum hydroxide, activated by heating for 8 hours at 400°, for the F-20 alumina together with the use of xylene alone as eluant gave similar results, except that the separation of the various fractions appeared to be neater, and that compound "C" was not found.

When the irradiation of 2.00 g. of tetracyclone in 100 ml. of benzene was carried out in the quartz reactor, 14 days were required to effect decoloration (to yellow) of the solution, probably because of the smaller area illuminated. Filtration of the solution gave 150 mg. of "A", m.p. 230.7–231.5°. Chromatography of the filtrate on F-20 alumina yielded only two identifiable fractions: 60 mg. of tetracyclone and 162 mg. of A, m.p. 231.2–232.5°. The major portion of the product consisted of dark brown tars, with carbonyl absorptions at 5.70–5.72, 5.82–5.88, and 6.03–6.07 μ. The fraction absorbing at about 5.85 μ, which had been extracted from the column with glacial acetic acid, was found to be nearly completely soluble in cold 5% sodium hydroxide, from which it could be reprecipitated by the addition of mineral acid with the carbonyl absorption changing to 5.77 μ.

Decoloration of the tetracyclone solution (0.50 g. in 75 ml. of benzene) in the Vycor tube required 7 to 12 days. It was noted that a partial vacuum eventually formed if the vessel was kept closed. Gas analysis revealed the presence of 9.7×10^{-4} mole of carbon monoxide and 1.3×10^{-4} mole of carbon dioxide. Evaporation of the solvent gave a yellow-brown oil from which only 13 mg. of "A" could be isolated by crystallization. Thus, chromatography is preferred as a method for working up the reaction product.

Bubbling air through the reaction mixture or the addition of methylene blue[6] did not noticeably affect the rate of reaction.

Irradiation of solid tetracyclone for 14 days caused no significant change, m.p. 218–220°.

RESULTS

Identification of products. The melting points, ultraviolet absorption characteristics, and carbonyl absorption of "A" and "C" indicated that these were respectively the *trans*- and *cis*-isomers of dibenzoylstilbene.[3,10] Comparison of spectra in the infrared revealed that there were significant differences, however, between the absorption characteristics of "A" and "C" and those reported for the dibenzoylstilbenes.

cis-Dibenzoylstilbene was synthesized by a known route, from benzoin to tetraphenylfuran in 20% yield,[11] followed by nitric acid oxidation of the latter[12] in 85% yield, m. p 210.0–210.8°. The ultraviolet and infrared spectra of the product were in agreement with those obtained with "C".[13] A mixture melting point with "C" was not depressed.

cis-Dibenzoylstilbene was isomerized using 0.5 *N* ethanolic potassium hydroxide at reflux for 21 hrs.,[15] m.p. 230.3–230.6°; no depression on admixture with "A." The infrared spectrum was likewise in agreement with that obtained for "A".

It thus appears that fractions "A" and "C" are *trans*- and *cis*-dibenzoylstilbene, respectively, and that the previous assignments of infrared spectra are in error.[10] The maximum yields were 16% for the *trans*- and 2.4% for the *cis*-isomer.

Fraction "B" was insoluble in cold 5% sodium hydroxide. The melting point and the ultimate analysis indicated this compound to be tetraphenyl-2-pyrone. Confirmation of the identity of the compound was obtained by comparison of its infrared spectrum with that of an authentic sample.[16] Pütter and Dilthey have given its melting point as 166–167°.[17] The yield was therefore 1.9%.

A mixture melting point of "B" with a sample of 2,3,4,5-tetraphenylcyclopent-2-enone, m.p. 163.2–164.4°, gave a 40° depression in melting point. Infrared spectra also showed important differences.[18]

IRRADIATION OF CARBON MONOXIDE AND CARBON DIOXIDE

Carbon monoxide, 1.3×10^{-3} mole, was irradiated in the presence of 75 ml. of benzene in the closed Vycor tube, the initial pressure inside the vessel being brought to atmospheric with air. After seven days, the ratio of CO:CO_2 was 6:1. The relative amounts of the gases in this blank experiment, therefore, closely approximated the ratio of carbon monoxide to carbon dioxide found after irradiation of tetracyclone. When the same experiment was repeated with carbon dioxide, only a trace of carbon monoxide could be detected. Supporting this observation are the known facts that carbon monoxide oxidizes to carbon dioxide upon irradiation in air,[19] and that carbon dioxide and air alone under irradiation are converted to an equilibrium mixture in a static system with the ratio CO:CO_2::0.02:1.0.[20] This low ratio of carbon dioxide and the earlier observations preclude the formation of carbon monoxide in the quantities obtained from carbon dioxide.

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(11) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 662 (1890).

(12) K. Bernhauer, P. Müller, and F. Neiser, *J. prakt. Chem.*, **145**, 301 (1936).

(13) Comparison was also made with a sample of *cis*-dibenzoylstilbene graciously supplied by Professor P. Yates of Harvard University, which had been obtained from oxidation reactions of tetracyclone.[14] The absorption characteristics of this sample matched those of C.

(14) P. Yates and G. H. Stout, *J. Am. Chem. Soc.*, **76**, 5110 (1954).

(15) N. Zinin, *Ber.*, **8**, 695 (1875).

(16) We are indebted to Professor P. Yates for suggesting this comparison and for supplying the spectral characteristics of the pyrone which he had prepared by acid treatment of the monoacetate of 2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-enone.[14]

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(18) The infrared spectrum obtained for this compound was at variance in some respects with that published by N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Am. Chem. Soc.*, **75**, 2283 (1953). The strong bands we found were observed at 5.92, 6.16, 6.22, 6.68, 7.41, 8.67, 13.25, 13.95, 14.40μ. Except for the wavelengths, the appearance of the spectra was identical.

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IRRADIATION OF *cis*- AND *trans*-DIBENZOYLSTILBENE

A 1.3×10^{-4} *molar* solution of *cis*-dibenzoylstilbene in cyclohexane was irradiated in a Pyrex flask. After six hours, new peaks had appeared at 233, 277, 297, 306, 318, 339, and 357 mμ. These peaks, together with the original at 252 mμ, became less intense upon further irradiation with eventual disappearance of nearly all absorption in the range.

Similar results were obtained with an $8.9 \times {}^{-5}$ *molar* solution of *trans*-dibenzoylstilbene. The same new peaks were observed as with the *cis*-isomer.

Infrared examination of carbon tetrachloride solutions of the products showed the absence of carbonyl absorption at 6.02 μ. Instead, a band had appeared at 5.63 μ. It is apparent that extensive decomposition of the stilbenes had taken place upon irradiation.

DISCUSSION

The discovery of carbon monoxide as a product of the reaction and in an amount nearly equivalent to the tetracyclone used suggests that the proposed course of the reaction *via* the photoöxide I may indeed be valid. Since it was shown that the carbon dioxide most likely formed as a secondary product from carbon monoxide and air under the conditions used, it is believed that any mechanism which postulates the formation of carbon dioxide as a product, such as the one proposed by Dufraisse for pentaarylcyclopentadienols, does not apply in this case.

The presence of *cis*- and *trans*-dibenzoylstilbene has also been confirmed. Hitherto, only one of the isomers had been obtained by each set of investigators. In the present investigation, both isomers were isolated, although the *cis*-isomer was found only in some of the experiments, and then in very low yield. The formation of *trans*-dibenzoylstilbene in preference to the *cis*-isomer which would be expected from the steric structure of I can be explained as resulting either from light-induced isomerization of the first-formed *cis*-isomer, or from thermodynamic stabilization of an activated intermediate in the *cis*-configuration, formed by cleavage of the postulated photoöxide.

The discovery of tetraphenyl-2-pyrone in this reaction parallels the earlier finding of a similar pyrone as a product obtained upon prolonged irradiation of phencyclone 2,5-diphenyl-3,4-(2,2′-biphenylene)cyclopentadienone in the presence of air.[4] Its formation might be the result of a side-reaction with ozone,[21] since this gas can be obtained by the action of ultraviolet radiation on air.[22]

The tars, which were by far the major product, most likely originated by photolysis of dibenzoylstilbene, or by side-reactions involving the solvent.[23] It is considered significant that the highest yield of *trans*-dibenzoylstilbene was obtained under conditions which caused its partial precipitation from solution, thus making it unavailable for further reaction.

Acknowledgment. The authors wish to thank the American Cyanamid Company for permission to use their facilities for this work. Thanks are also due to personnel at the Stamford Laboratories, in particular Mr. N. B. Colthup for valuable help with the infrared spectra, Mr. S. E. Polchlopek for the gas analyses, Dr. H. C. Hirt and Mr. J. G. Koren, for the ultraviolet spectra, and Mrs. P. A. Altieri for the microanalyses.

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(23) For a discussion of radical-induced reactions of substituted benzenes, see D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 6 (1955).