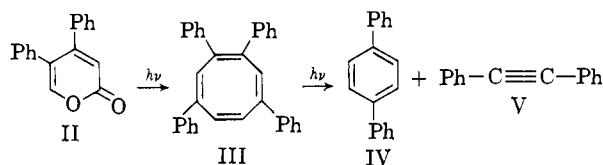


The three major products obtained from the photolysis of II were assigned structures III (1,2,4,7-tetraphenylcyclooctatetraene), IV (*p*-terphenyl), and V (diphenylacetylene).



The yields of these compounds are strongly affected by the length of the irradiation as shown in Table I. As II decreases, III appears and, more slowly, IV and V are formed. Continued irradiation gives mostly *p*-terphenyl and diphenylacetylene. The structures of III, IV, and V are based on the following observations. The infrared spectrum of III showed a weak band at 6.16μ attributed to the carbon-carbon double bond stretching frequency of the cyclooctatetraene ring.³ The intense ultraviolet absorption at $263 m\mu$ ($\log \epsilon$ 4.71) is in accord with structure III. The n.m.r. of III has a multiplet centered at τ 2.68, a singlet at 3.12, and a singlet at 3.39. The peak areas are in the ratio of 1:10:1. Elemental analysis and a molecular weight determination also support structure III. The infrared spectrum of this substance in a potassium bromide pellet was identical in every detail with that of an authentic sample of 1,2,4,7-tetraphenylcyclooctatetraene.⁴ *p*-Terphenyl and diphenylacetylene were identified by comparison of infrared and mixture melting point with that of an authentic sample.

The isolation of *p*-terphenyl and diphenylacetylene from the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (I) certainly represents an unusual photochemical transformation. The resolution of this complex photochemical sequence necessitates a description of the intermediates involved between starting material and product. Consideration of the product distribution as a function of time showed that this transformation may be resolved into a sequence of discrete photochemical reactions, as shown above.

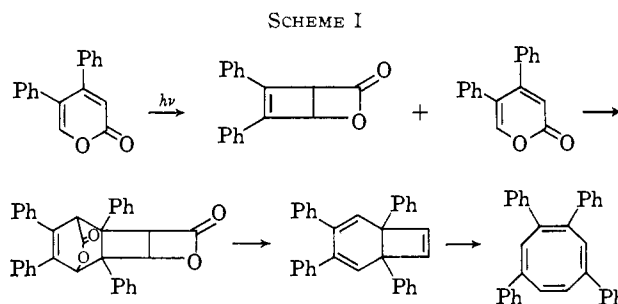
The light-induced rearrangement of 4,5-diphenyl-2-pyrone to 1,2,4,7-tetraphenylcyclooctatetraene represents the most complex step in the sequence outlined above. A recent report describing an internal photoaddition reaction of α -pyrone suggests a likely mechanism, however. Corey⁵ found that the low-temperature ultraviolet irradiation of 2-pyrone in ether afforded in almost quantitative yield a photoisomer to which a bicyclic β -lactone structure was assigned. The intermediacy of a bicyclic β -lactone suggests the sequence shown in Scheme I as a reasonable series of events in the formation of the cyclooctatetraene derivative.

Attempts to isolate the hypothetical bicyclic β -lactone by irradiation at low temperatures were unsuccessful. Irradiation of III in the solid state at -185° revealed no carbonyl band in its infrared spectrum at wave lengths shorter than 5.65μ . It is quite conceivable that this particular β -lactone is very photolabile itself, because of the presence of the stilbene chromophore, and reacts instantaneously with additional

(3) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964).

(4) A highly purified sample was kindly provided by Professor Emil H. White.

(5) E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964).



pyrone to give IV. Experiments designed to trap the β -lactone and further work on related 2-pyrone are in progress.

The final step in the sequence involves the known photochemical decomposition of 1,2,4,7-tetraphenylcyclooctatetraene (III).⁶ White has recently reported that the irradiation of III gave a complex mixture of compounds from which *p*-terphenyl and diphenylacetylene could be isolated in moderate yield.

Acknowledgment.—The authors wish to thank Professor E. H. White for supplying us with low temperature data and for his interest in the work. This work has been supported in part by the Petroleum Research Fund, administered by the American Chemical Society, through a Type G grant.

(6) E. H. White and R. L. Stern, *Tetrahedron Letters*, No. 4, 193 (1964).

(7) National Science Foundation Predoctoral Fellow, 1962–present.

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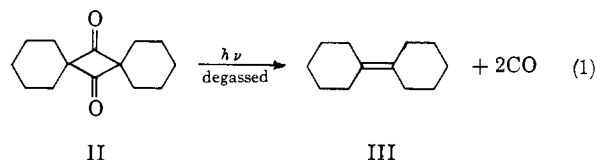
ALBERT PADWA
RICHARD HARTMAN⁷

RECEIVED JULY 24, 1964

Photochemistry of Tetrasubstituted 1,3-Cyclobutanediones. II. Effect of Oxygen¹

Sir:

Relevant to our recent studies¹ on the photochemistry of tetramethyl-1,3-cyclobutanedione (I) we have observed that photolysis² of dispiro[5.1.5.1]tetradecane-7,14-dione II in benzene and methylene chloride under degassed conditions leads to a 61% net yield of cyclohexylidene cyclohexane (III) accompanied by rapid evolution of carbon monoxide (eq. 1). III was identified by its melting point (53 – 54° , lit.³ 54 – 55°), and



by its n.m.r. spectrum consisting of two broad peaks at 1.5 p.p.m. (12 protons) and 2.2 p.p.m. (8 protons), the spectrum being virtually identical with that of exomethylene cyclohexane^{4a} except that III showed no proton resonance in the vinyl region.^{4b} In analyzing

(1) Part I: N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964).

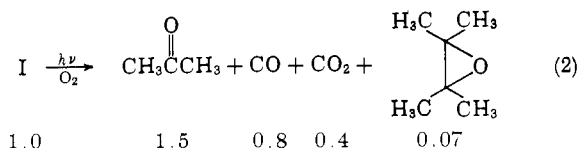
(2) Irradiations for product runs were carried out in a Hanovia 450w immersion reactor with a 3000 Å cut-off filter. A eudiometer was used to collect gases. A similar light source was employed for quantitative runs, but a special reaction vessel and sampling device was used which will be described in a subsequent paper.

(3) J. Jaques and C. Weidmann-Hattier, *Bull. soc. chim. France*, 1478 (1958).

(4) (a) Varian Associates, "High Resolution N.M.R. Catalogue," Vol. I, Spectrum No. 180. (b) All n.m.r. spectra were taken at 60 Mc. on a Varian A60 instrument. Solvent was carbon tetrachloride; tetramethylsilane was employed as an external standard.

the reaction mixture by gas chromatography it was observed that another compound, identified as cyclohexanone by its infrared and n.m.r. spectrum, began to form rapidly if the photolyzed solution remained open to the air. The olefin, however, remained constant in concentration as cyclohexanone formed. On the reasoning that if a cyclopropanone intermediate did intercede in the photoprocess (eq. 1) it might be highly reactive toward oxygen the photoreaction was repeated with a stream of oxygen passing continuously through the system. In this case, formation of the olefin III was completely inhibited, and cyclohexanone was formed in 43% net yield (based on 1 mole of II going to 2 moles of the ketone).

It was thus decided to reinvestigate the original member of the series, I, and study quantitatively the products of the photolysis of I in the presence and absence of oxygen in benzene solution. When photolyses were carried out under 540 mm. of oxygen and the reaction was followed simultaneously by mass spectroscopic and vapor chromatographic analysis, the products shown in eq. 2 (with approximate molar ratios) were obtained. However, when the reaction



was run under argon (340 mm.) with no oxygen present, the approximate stoichiometry listed in Table I was found at the times indicated.

TABLE I

I	$\frac{h\nu}{A}$	C_4H_8	CO	[IV]	Time, min.
1.0	0.8	1.5	0.14		60
1.0	0.4	1.6	0.7		12

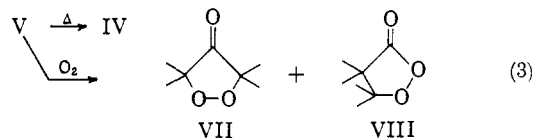
IV was obtained pure *via* preparative vapor chromatography and was shown to be isopropenyl isopropyl ketone by its n.m.r. spectrum, mass spectrum, and comparison of its infrared spectrum with that of an authentic sample prepared by the method of Smith.⁵ We have found that IV is stable to oxygen, and that it fails to form tetramethylethylene upon irradiation. Thus we conclude that a precursor of IV exists in the photolysis reaction mixture; this precursor reacts further under degassed conditions to form tetramethylethylene or in the presence of oxygen to form acetone and tetramethylethylene oxide. When oxygen was admitted to a partially photolyzed degassed solution of I, carbon monoxide, carbon dioxide, tetramethylethylene oxide, and acetone were formed, with oxygen being noticeably consumed. Analysis by vapor chromatography showed that acetone and tetramethylethylene oxide were formed in the same ratio as given in eq. 2, and, furthermore, in a total molar amount nearly equal to the amount of material which analyzed as IV which disappeared. From these and previous results^{1,6} we conclude that the precursor of IV is tetramethylcyclopropanone (V). This material exhibits the re-

markable property of being able to react as either a biradical with oxygen or as a dipolar species^{7,8} with hydroxylic solvents.^{1,9} Apparently, V is pyrolyzed during vapor chromatographic analysis to produce IV in virtually quantitative yield.

We have previously¹ postulated cyclopropanone intermediates to account for the products formed in the photolysis of I in hydroxylic solvents. Subsequent to our previous communication we have observed that the formation of the esters and keto ethers (analyzed by gas chromatography) increased if the irradiated solutions were allowed to stand in the dark.¹⁰ We now wish to report the isolation of the methyl hemiketal of tetramethylcyclopropanone, VI, formed in the photolysis of I in methanol, which decomposes to give the products previously reported.^{1,9,10}

When the reaction mixture from the photolysis of I in methanol at 0° was stripped of solvent, a crude unstable crystalline product (VI) was obtained in 70–75% yield. With difficulty the compound was purified by recrystallization. The mass spectrum¹¹ of VI shows a parent peak at $m/e = 144$ and relatively intense peaks corresponding to loss of CH₃, OH, H₂O, and CH₃O. The infrared spectrum shows hydroxyl absorption at 3370 cm.⁻¹ and bands due to various C–O–C and C–O–H vibrational modes (1220, 1145, 1110, 1090, and 1015 cm.⁻¹). The n.m.r. spectrum consists of singlets at 3.40 p.p.m. (1 proton), 2.95 p.p.m. (3 protons), and 0.70 p.p.m. (12 protons). The latter splits into a doublet in pyridine solution. These data, then, define VI as 1-methoxy-1-hydroxy-2,2,3,3-tetramethylcyclopropane (the methyl hemiketal of V).

Possible oxidation products of V might be the cyclic peroxides VII and VIII (eq. 3) which should be capable of cleaving smoothly to yield the observed products, possibly during gas chromatographic analysis.



Tetramethylethylene is unaffected by oxygen under the photolysis reaction conditions and therefore cannot be involved in the oxidation reactions. Presumably reaction pathways analogous to eq. 3 can account for the products observed in the photolytic oxidation of II.

The mass spectral cracking pattern of I may bear some relation to the photolysis of I. The mass spectrum shows, in addition to the parent peak, major peaks corresponding to $m/e = 70$, 84, and 112. These peaks have been tentatively assigned to the positive ions of dimethylketene, tetramethylethylene, and IV or V, respectively. The detailed mass spectra of I,

(7) A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620; 2625 (1962); *ibid.*, **82**, 4979 (1960), and references therein.

(8) R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963).

(9) In addition to the methyl and isopropyl 2,2,3-trimethylbutyrates formed by photolysis of I in the corresponding alcohols,¹ we have also isolated the keto ether 2,4-dimethyl-4-isopropoxy-3-pentanone from irradiation in isopropyl alcohol (identified by n.m.r., elemental analysis, and comparison with a sample synthesized by an alternate route). This latter compound corresponds to ionic ring opening at one of the quaternary carbons rather than at the carbonyl.

(10) G. W. Byers, M.A. Thesis, Wesleyan University, 1964.

(11) Mass spectra were obtained using a Consolidated 21-301C instrument.

(5) B. H. Smith, Jr., Ph.D. Dissertation, Emory University, 1951; *Dissertation Abstr.*, **19**, 2480 (1959).

(6) R. C. Cookson, J. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964).

II, and other 1,3-cyclobutanediones will be the subject of a future publication.

Acknowledgments.—It is a pleasure to acknowledge the generosity of Professor P. D. Bartlett for allowing us the use of his laboratories for some of the above experiments. We are also indebted to Dr. F. W. McLafferty of Dow Eastern Chemical Research Laboratory for helpful discussions concerning the mass spectra described herein, and to Dr. Kent C. Brannock of Tennessee Eastman for a sample of II. We thank the National Science Foundation (Grant GP2848) for financial support.

(12) National Science Foundation Postdoctoral Fellow, 1963–1964.

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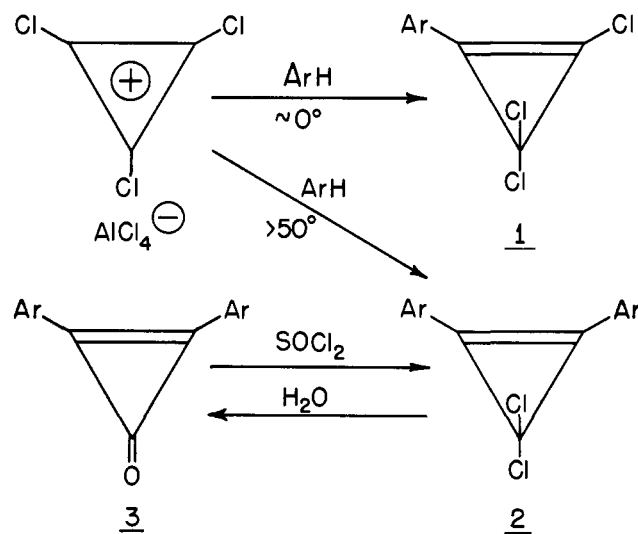
NICHOLAS J. TURRO¹²
DOUGLAS C. NECKERS

RECEIVED JULY 21, 1964

Diarylcyclopropenones via the Trichlorocyclopropenium Ion

Sir:

We have found that the trichlorocyclopropenium ion¹ reacts smoothly with benzene derivatives to provide either aryltrichlorocyclopropenes (1) or *gem*-dichlorodiarylcyclopropenes (2) depending on reaction conditions, and that the *gem*-dichlorodiarylcyclopropenes obtained can be readily interconverted with the corresponding diarylcyclopropenones (3). These reactions



provide additional evidence for the existence of halo- and mixed arylhalocyclopropenium ions and demonstrate the ability of these species to effect electrophilic aromatic substitution. Moreover, they provide an exceptionally convenient route to compounds of the types 1, 2, and 3.

The following experiments using trichlorocyclopropenium tetrachloroaluminate and fluorobenzene illustrate the synthetic methods employed and the properties of the products obtained. Momentary local warming of 12.1 g. (0.039 mole) of $C_3Cl_3^+AlCl_4^-$ in 10 ml. of fluorobenzene at 0° started a vigorous exothermic reaction which evolved much HCl. The solution

turned deep red. Immediate recooling caused the reaction to subside after 30 sec. On quenching the reaction mixture in ice-water the red color was discharged and 6.2 g. of a clear oil was obtained. This oil showed a single sharp v.p.c. peak at 135° on a silicone oil column and had an analysis corresponding to 1 (Ar = *p*-F-C₆H₄-) (0.026 mole, 67% yield). *Anal.* Calcd. for C₉H₄Cl₃F: C, 45.52; H, 1.70; Cl, 44.78; F, 8.00. Found: C, 45.34; H, 1.65; Cl, 44.76; F, 8.04. The F¹⁹ n.m.r. spectrum (10% v./v. in CCl₄) shows the triplet of triplets diagnostic of a *para*-substituted fluorobenzene.² The position of the central resonance at 10.0 p.p.m. downfield from fluorobenzene suggests the structure 1.³ The infrared spectrum (liquid film) shows strong bands at 1603, 1505, 1254, 1239, 1155, 1009, 841, 728, and 710 cm.⁻¹ in the NaCl region. On standing in air the oil hydrolyzes to give a *p*-fluorophenylchloroacrylic acid.

If the reaction between $C_3Cl_3^+AlCl_4^-$ and fluorobenzene is carried out at higher temperatures two phenyl groups can be attached to the cyclopropene nucleus. Thus when 3.9 g. (0.0125 mole) of $C_3Cl_3^+AlCl_4^-$ and 5.0 ml. of fluorobenzene were treated as above, and then warmed to 50°, HCl evolution began again and continued for 10 min. The solution gradually turned from red to brown. Quenching this material in ice-water produced a tan solid which was dried and repeatedly extracted with hot CCl₄. The solid obtained by evaporation of the combined extracts was treated with a small amount of 95% ethanol (see below) and then sublimed at 50 μ and 135° to provide 1.45 g. of colorless bis-*p*-fluorophenylcyclopropenone (3, Ar = *p*-F-C₆H₄-) (0.006 mole, 48% yield), m.p. 184–185°. *Anal.* Calcd. for C₁₅H₈F₂O: C, 74.38; H, 3.33; F, 15.69; O, 6.61. Found: C, 74.26; H, 3.44; F, 15.52; O, 6.78 (by difference). The F¹⁹ n.m.r. pattern of this compound also indicates *para*-fluoro substitution. The infrared spectrum (Nujol mull) of this compound shows strong bands at 1842 (C=O), 1632 (C=C), 1592, 1500, 1409, 1299, 1240, 1152, 1101, 834, and 759 cm.⁻¹ in the NaCl region.

Neither triarylcyclopropenium ion salts⁴ nor triarylcyclopropenes⁵ have been observed in any of the reactions we have carried out. Prolonged heating of solutions of $C_3Cl_3^+AlCl_4^-$ in benzene derivatives leads to extensive tarring.

If the treatment with aqueous ethanol in the work-up of the diphenylcyclopropenones is omitted, the corresponding *gem*-dichlorodiphenylcyclopropene (2) is a major side product. This suggests that 2 is actually the initial reaction product, and 3 arises by hydrolysis.⁶ Since separation of 2 and 3 is difficult, we have found it convenient to convert everything to the ketone 3 as outlined above, work up the ketone, and then convert the ketone back to the *gem*-dihalide 2 if it is desired. This can be done quickly and quantitatively merely by warming the ketone with thionyl chloride.

For example, treatment of bis-*p*-fluorophenylcyclopropenone with SOCl₂ followed by recrystallization from cyclohexane containing a small amount of SOCl₂

(2) B. Bak, J. N. Shoolery, and G. A. Williams, III, *J. Mol. Spectry.*, **2**, 525 (1958).

(3) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(4) R. Breslow, *ibid.*, **79**, 5318 (1957).

(5) R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

(6) See also R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(1) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).