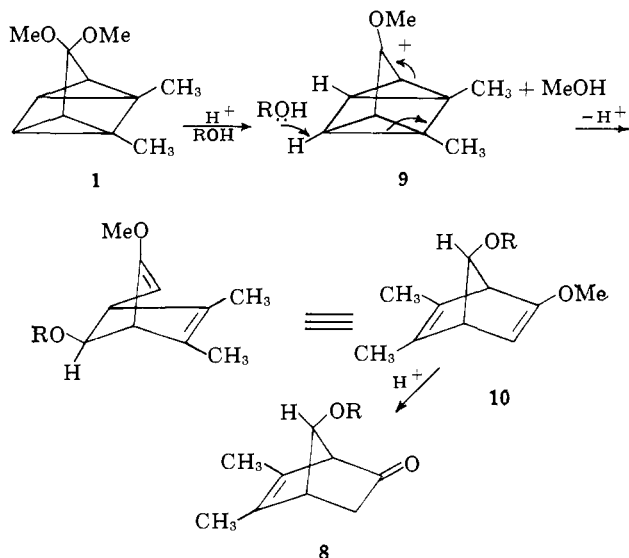


τ 6.67 (singlet), two protons at τ 8.82 (doublet), and two protons as a doublet at τ 8.51. The doublet at τ 8.51 was assigned to the hydrogens α to the ketal function and the doublet at τ 8.82 was attributed to the remaining two cyclopropyl hydrogens. The near-infrared spectrum, $\lambda_{\text{max}}^{\text{CCl}_4}$ 1.667 μ (ϵ 1.587), and the ultraviolet spectrum, end absorption 210 $m\mu$ (ϵ 380), were also consistent with the postulated structure.

Attempts to hydrolyze **1** to 2,3-dimethylquadracyclonone (**7**) led to an unexpected and intriguing result. Under the conditions of acid catalysis **1** was converted to the keto ether **8**. This conversion most likely occurs through a complex rearrangement of the initially formed carbonium ion **9**, as shown below. The manner in which **9** rearranges sheds considerable light on the fate



of a carbonium ion in the 7-position on the quadracyclane skeleton. The theoretical implications of this rearrangement in relation to nonclassical carbonium ion theory will be discussed in a future publication.

The structure of **8** was established on the basis of combined spectral and chemical evidence. The appearance of a carbonyl band at 5.72 μ coupled with the facile formation of a 2,4-dinitrophenylhydrazone confirmed the presence of a ketone function. The position of this ketone function relative to the rest of the molecule was obvious after measurement of the rearrangement product's ultraviolet spectrum (see Table I). The anomalous $n \rightarrow \pi^*$ absorption at 299 $m\mu$ (ϵ 487)

Structure	$\lambda_{\text{max}}^{\text{isoctane}}$		$\lambda_{\text{max}}^{\text{c-hexane}}$	
	μ	ϵ	μ	ϵ
11	296.5	242	294	436
8	307.5	277	304	413
	319.5	177	316	242

could only be reconciled with the dehydronorcamphor skeleton,¹⁴ **11**. Since the absence of norbornenyl vinyl hydrogens was evident from both nuclear magnetic resonance and near-infrared spectroscopy, the vinylic positions must have been substituted. The presence of the methyl hydrogens at τ 8.33 and 8.41 in the nuclear magnetic resonance spectrum confirmed the placement of the methyl groups in the vinylic positions. The pres-

(14) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

ence of the methoxy group was obvious from the sharp singlet at τ 6.80 and from the infrared spectrum. Although the n.m.r. spectrum of **8** was extremely complex it was consistent with the methoxy in the 7-position being *anti* to the double bond. This was obvious from the complex nature (six broad peaks spread over 8 c.p.s.) of the single hydrogen at C-7 which appeared at τ 6.22. As was recently shown¹⁵ this requires that the C-7 proton be *syn* to the olefinic linkage with coupling to the bridgehead hydrogens and to the *endo*-hydrogen at C-6. Since there are no olefinic hydrogens, any C-7 proton *anti* to the double bond would only be split by the bridgehead hydrogens and hence would possess a simplified splitting pattern.

Acknowledgment.—The authors are indebted to the Petroleum Research Fund administered by the American Chemical Society for partial support of this work.

(15) P. Laszlo and P. von Ragué Schleyer, *ibid.*, **86**, 1171 (1964); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(16) (a) The Ohio State University Undergraduate Research Scholar, 1962–1963; (b) The Ohio State University Undergraduate Research Scholar, 1963–1964; National Science Foundation Undergraduate Research Participant, Summer, 1963.

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RECEIVED JULY 27, 1964

The Photochemistry of 4,5-Diphenyl-2-pyrone. A Mechanistic Study

Sir:

In a recent publication¹ we reported that the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (I) gave, depending on the conditions of the irradiation, a number of products. Brief irradiation of I afforded in almost quantitative yield a compound which had been identified as 4,5-diphenyl-2-pyrone (II).¹ We now wish to present evidence which assigns structures to the remaining products and to report on the unusual photochemistry of 4,5-diphenyl-2-pyrone.

Photolysis of I in anhydrous ether at 25° with ultraviolet light of wave length above 260 $m\mu$ ² afforded a mixture of products. Consideration of the product distribution obtained in a number of photolyses *vs.* time showed an initial buildup of 4,5-diphenyl-2-pyrone (II) followed by a decrease in the amount present. Evidence that 4,5-diphenyl-2-pyrone (II) is an intermediate in the formation of the remaining products was confirmed by the finding that the photolysis of II itself in anhydrous ether afforded III, IV, and V in about the same distribution as found in runs beginning with 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (Table I).

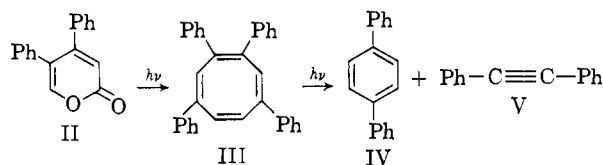
TABLE I
PHOTOLYSIS OF 4,5-DIPHENYL-2-PYRONE (II)

Run	Time, hr.	Products, % yield			
		II	III	IV	V
1	0.16	96	0	0	0
2	1	52	24	0	0
3	2	38	19	10	6
4	4	10	14	25	17

(1) A. Padwa, *Tetrahedron Letters*, No. **15**, 813 (1964).

(2) The initial photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a corex filter to eliminate wave lengths below 260 $m\mu$.

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.

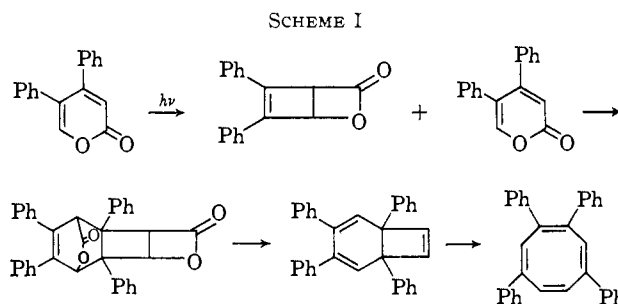
The light-induced rearrangement of 4,5-diphenyl-2-pyrone to 1,2,4,7-tetraphenylcyclooctatetraene represents the most complex step in the sequence outlined above. A recent report describing an internal photoaddition reaction of α -pyrone suggests a likely mechanism, however. Corey⁵ found that the low-temperature 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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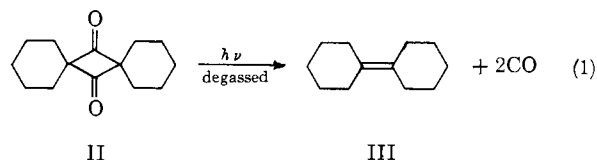
ALBERT PADWA
RICHARD HARTMAN⁷

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 cyclohexylidenecyclohexane (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.