

scribed in the section on the pyrolysis. The chromatography column was wrapped in aluminum foil to keep out light.

The course of the reaction usually was followed by the production of benzil, and the concentration of monothiobenzil can be determined spectrophotometrically. Benzil was recovered by the flash evaporation of the chloroform at room temperature followed by extraction with hot 95% ethanol and filtration.

The benzil yield was determined either by weight or by ultraviolet spectroscopy. Data on yields are given in Table I and Table II and results with various quenchers and sensitizers are summarized in Table I.

Registry No.—2,3-Dibenzoyl-2,3-diphenylthiirane 1-oxide, 988-04-5.

Photolysis of Bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] Terephthalate

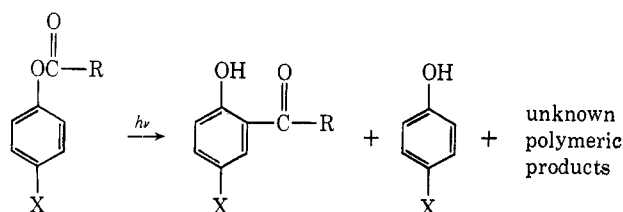
G. R. LAPPIN* AND J. S. ZANNUCCI

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662

Received April 30, 1970

The photolysis of bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] terephthalate in various solvents resulted in two consecutive photo-Fries rearrangements, whose quantum efficiencies were much lower than for simple aryl esters. Changes in solvent polarity and moderate changes in viscosity had little effect on the photolysis, but the efficiency in a rigid matrix was lowered considerably. In aqueous dioxane, the chief reaction was a photohydrolysis to give *p*-(1,1,3,3-tetramethylbutyl)phenol and terephthalic acid.

The photolysis of aryl esters has recently been reviewed.¹ The course of the reaction is well established, but whether the photo-Fries rearrangement involves a separated free-radical intermediate² or a 1,3-sigmatropic shift³ is not known. The quantum efficiency for ketone formation,^{3,4} ϕ_k , is usually 0.15–0.20,



and the quantum efficiency, ϕ_p , for phenol production, is about 0.05–0.15 in nonviscous, inert solvents.³ The effect of solvents on this photolysis is poorly understood. An increase in solvent polarity was reported to be without effect on either ϕ_k or ϕ_p in the photolysis of *p*-tolyl acetate³ but was reported to increase both ϕ_k and ϕ_p in the photolysis of 3,5-di-*tert*-butylphenyl benzoate.⁵ Increased solvent viscosity reduced ϕ_p .³ In fluid solvents the yield of ketone is only 10–50%, and much of the ester is converted to unknown products; however, photolysis of aryl benzoates in a polymeric matrix has been reported to proceed without side reactions.^{6,7} Many aryl esters of aromatic monocarboxylic acids have been studied; however, the photo-Fries rearrangement of nonpolymeric esters of aromatic dicarboxylic acids has not been reported. Photolysis of polymeric esters such as poly(isopropylidenedi-*p*-phenylene isophthalate) resulted in the formation of 2-hydroxybenzophenone moieties in the polymer.⁶

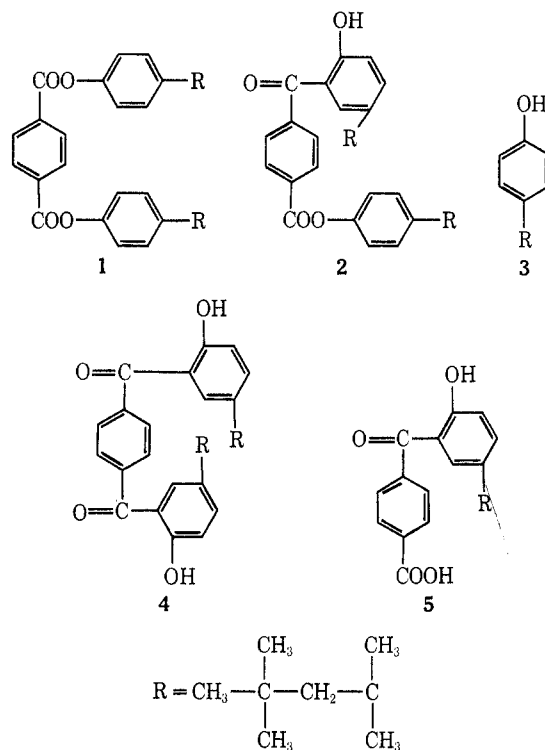
We report here the results of the photolysis of a nonpolymeric diester, bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] terephthalate (**1**), in a number of fluid solvents and in a rigid, polymeric matrix.

* To whom correspondence should be addressed

- (1) D. Belluš and P. Hrdlovič, *Chem. Rev.*, **67**, 599 (1967).
- (2) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).
- (3) M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).
- (4) D. Belluš, P. Hrdlovič, and P. Sláma, *Collect. Czech. Chem. Commun.*, **33**, 2646 (1968).
- (5) R. A. Finnegan and D. Knutson, *Tetrahedron Lett.*, 3429 (1968).
- (6) S. B. Maerov, *J. Polym. Sci.*, **3**, 487 (1965).
- (7) G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

Results and Discussion

Photolysis of **1** in anhydrous solvents gave four products which could be separated by glc: **2**, **3**, **4**, and **5**.



Each of these was also isolated and characterized by other means. In the presence of water, terephthalic acid was also a major product. Table I gives the product distribution, as determined by glc, for photolysis of **1** in various solvents.

Approximate quantum efficiencies for some of the reactions are given in Table II. These values were determined by using polychromatic light; loss of **1** was 10% or less. Because of the complexity of the mixture, the values are not corrected for absorption of light by the products.⁴

For further information on the effect of solvent polarity and viscosity, photolyses were carried out in mixtures of dioxane and acetonitrile. The results are shown in Table III.

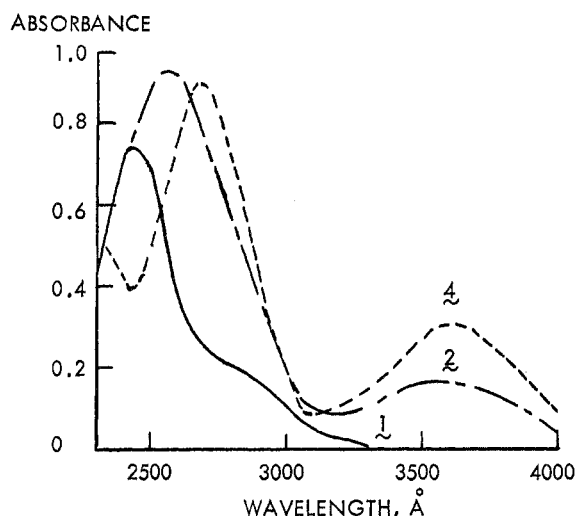


Figure 1.—Absorption spectra in methylene chloride of 1 (0.07 g/l.), 2 (0.10 g/l.), and 4 (0.07 g/l.). Cell length, 0.25 cm.

TABLE I
DISTRIBUTION OF PRODUCTS FROM PHOTOLYSIS OF 1
IN VARIOUS SOLVENTS

Solvent	Time, hr	Compd, 10 ⁻⁶ mol				
		1 ^a	2	3	4	5
Benzene	4	6.7	2.6	2.6	0.4	0.2
	12	b	4.9	3.3	2.3	1.1
	75	b	0.6	4.5	6.2	1.9
Dioxane ^c	4	6.0	3.5	2.5	0.7	b
	12	b	1.7	4.8	4.6	0.4
	75	b	b	8.2	6.5	0.4
Dioxane-water, ^d 50:1	4	7.3	3.9	4.7	1.3	b
	12	0.1	1.0	23.6	3.6	0.5
	75	b	b	23.8	3.8	0.9
Dioxane-1-octanol, 1:1	12	1.0	3.1	15.2	3.7	b
Polystyrene ^e	48	6.6	2.6	b	1.0	b
Benzene ^e	20	8.0				

^a Initial charge of 1 was 19.4 × 10⁻⁶ mol. ^b Not detected by glc. ^c Contained 50–75 ppm of water. ^d Terephthalic acid found in significant quantity. ^e Irradiation in Rayonet reactor.

TABLE II
APPROXIMATE QUANTUM EFFICIENCIES FOR PHOTOLYSIS OF 1

Solvent	Quantum efficiency ^a		
	φ ₂	φ ₃	φ ₄
Benzene	0.02	0.004	0.01
Dioxane	0.02	0.010	b
Dioxane-water, 50:1	0.01	0.034	b

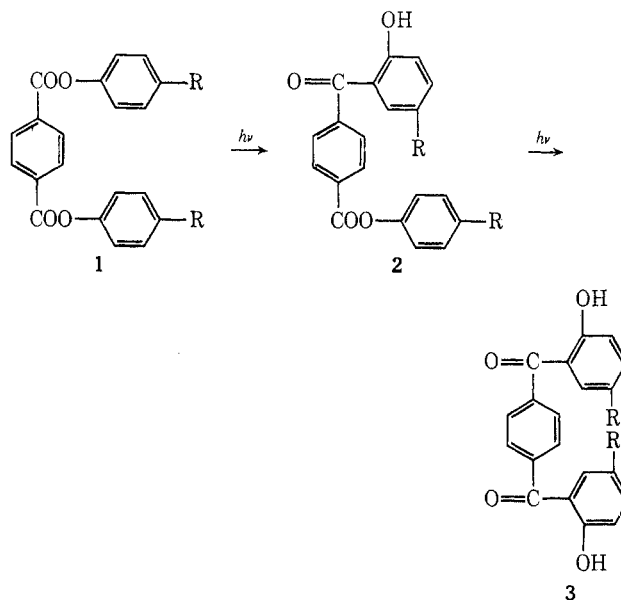
^a φ₂ is for appearance of 2; φ₃ is for appearance of 3; φ₄ is for 2 → 3 in the absence of 1. ^b Not determined.

TABLE III
PRODUCTS FROM PHOTOLYSIS^a OF 1 IN
DIOXANE-ACETONITRILE SOLUTION

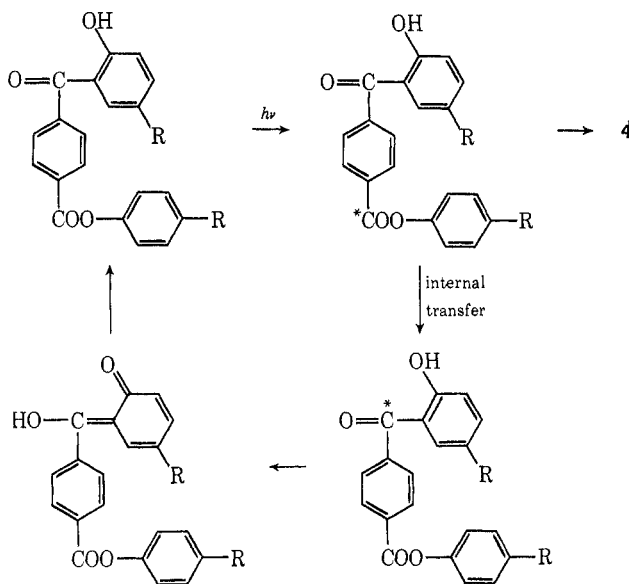
Aceto- nitrile, vol %	Viscosity, cp (30°)	Compd, 10 ⁻⁶ mol				
		1 ^b	2	3	4	5
0	1.087	2.7	5.0	7.6	3.3	0.9
1		3.0	5.3	8.2	3.5	1.0
5		2.8	5.0	8.2	3.5	1.0
10		2.2	4.7	8.0	3.5	1.1
20	0.793	2.2	4.7	9.5	3.3	1.2

^a Time was 9.4 hr. ^b Initial charge of 1 was 22 × 10⁻⁶ mol.

Aryl terephthalates can undergo two consecutive photo-Fries rearrangements. Because there appears to be no appreciable substituent effect in the photo-Fries rearrangement, the first reaction (1 → 2) should



proceed as efficiently as the rearrangement of an aryl benzoate. However, 2 has a possible means of self-stabilization by energy transfer between the two chromophores. If excitation energy were transferred from the ester moiety to the 2-hydroxybenzophenone moiety, 2 should be resistant to further photochemistry.⁸



When 2 was irradiated at 360 nm (Rayonet reactor, 360-nm lamps), where only the 2-hydroxybenzophenone carbonyl absorbs, as seen in Figure 1, it was recovered unchanged; hence, only light absorbed by the ester group leads to rearrangement. The absorption of polychromatic ultraviolet light by 2 will be divided between the two chromophores and, in the absence of efficient energy transfer from the ester carbonyl to the ketone carbonyl, the quantum efficiency for rearrangement of 2 would be somewhat lower than that for 1.

(8) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 150.

However, if energy is efficiently transferred in this direction, the quantum efficiency for rearrangement of 2 would be greatly decreased. The observed value is about half that for the rearrangement of 1 and supports the hypothesis that energy transfer from the ester carbonyl to the ketone carbonyl is not an efficient process.

Both ϕ_s and ϕ_k are about an order of magnitude lower than ϕ_k and ϕ_p for aryl benzoates. We believe that the inefficiency of the photoreactions of 1 results from the extended conjugation of the terephthalate system, which may offer facile routes for internal conversion.⁹

In accord with the findings of Sandner, Hedaya, and Trecker,³ solvent polarity was without effect on either the photo-Fries reactions of 1 or its cleavage to the phenol. Photolysis in dioxane-acetonitrile mixtures of varying polarity gave identical product ratios. Solvent viscosity, over a moderate range in fluid solvents, was also without effect on the photolysis of 1. However, in a rigid medium, polystyrene, the production of the phenol 3 was completely suppressed, as would be expected in a highly viscous medium.³ Unexpectedly, the rate of the photo-Fries rearrangement was reduced twofold in this rigid matrix. Earlier workers³ reported that ϕ_k for the photolysis of *p*-tolyl acetate was the same in Carbowax 600 poly(ethylene glycol) as in ethanol, which differ in viscosity by a factor of 100. The bulky alkyl groups in 1 may hinder the mobility required for rearrangement in a rigid medium.

In anhydrous solutions, the conversion of 1 to the isolated products was low; less than half of the *p*-alkylphenyl content was accounted for. The nature of the major product of the photolysis of 1, and of most other aryl esters reported, remains unknown. The data in Table I show that the production of 3 continues at a significant rate after its isolable precursors, 1 and 2, have nearly disappeared; hence, the unknown product must retain the ester group.

The photolysis of 1 in polystyrene gave the same low conversion to the 2-hydroxybenzophenones as was obtained in fluid solvents. The major product of this reaction was an insoluble, fibrous, apparently polymeric, yellow substance. This finding is in contrast to previous reports^{6,7} that no side reactions accompanied the photo-Fries rearrangement in a polymeric matrix. In these earlier investigations, the hydroxybenzophenone product was determined by ultraviolet absorption analysis. Because an ultraviolet-absorbing major product of unknown structure was formed, ultraviolet analysis is unreliable in this application.

The most dramatic and unexpected solvent effect was that of water in dioxane. It was reported³ that benzene and aqueous dioxane solutions gave the same results in the photolysis of *p*-tolyl acetate. However 1 showed a large increase in ϕ_s for aqueous dioxane as compared to benzene. Furthermore, after 12 hr of irradiation, more than 60% of the *p*-(1,1,3,3-tetramethylbutyl)phenyl content was recovered as *p*-(1,1,3,3-tetramethylbutyl)phenol (3). Significantly, only 4.7×10^{-5} mol of 3 was formed in the first 4 hr of irradiation but about four times this amount, 18.9×10^{-5} mol, was produced in the next 8 hr, even though the precursors of 3 were decreasing *via* the photo-Fries rearrangement. A considerable amount of terephthalic acid was also pro-

duced in aqueous dioxane, but none was formed in anhydrous solvents. No hydrolysis occurred when solutions of 1 and its various photoproducts in aqueous dioxane were kept in the dark for several days. These results show that some photoexcited species is involved in the hydrolysis but direct reaction of an excited state of 1 with water does not occur. The first excited singlet of a phenol is a relatively strong acid;¹⁰ hence, we believe the hydrolysis is catalyzed by the excited singlet of 3. The effect of water is so pronounced that we believe the increased yield of 3 in "dry" dioxane (50–75 ppm water) is due to hydrolysis rather than to any effect of dioxane. Photolysis of 1 in dioxane-1-octanol solution also gave a considerably greater yield of 3 than expected. A similar result, attributed to a photochemical solvolysis, was observed³ when *p*-tolyl acetate was photolyzed in ethanol. A catalyzed solvolysis, similar to the hydrolysis reported here, might also be involved when esters are photolyzed in alcohol solutions. Further work is under way to elucidate the mechanism of the apparent photochemical hydrolysis and solvolysis of 1.

Experimental Section

Preparation of Bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] Terephthalate (1).—To a cooled solution of 20.6 g (0.1 mol) of *p*-(1,1,3,3-tetramethylbutyl)phenol and 4.0 g of sodium metal in 250 ml of ethanol was added slowly 10.2 g (0.05 mol) of terephthaloyl chloride dissolved in 150 ml of ether. The mixture was then chilled and filtered. The product was dissolved in isooctane, and the solution was filtered. The filtrate was cooled at 5°, and the precipitate was collected by filtration. The product was then dried to obtain 25 g (95%) of white crystals, mp 174–175°, ir (KBr) 1742 cm⁻¹ (C=O).

Anal. Calcd for C₃₆H₄₆O₄: C, 79.68; H, 8.54; O, 11.80. Found: C, 79.56; H, 8.54; O, 11.90.

General Irradiation Procedure.—Solutions of 1 (1.0 wt %) in the appropriate solvent, contained in Vycor glass test tubes, were irradiated in a "merry-go-round" apparatus with a 550-W Hanovia medium-pressure arc light. Aliquots, 0.1 ml, were removed from time to time and treated with 0.9 ml of Tri-Sil trimethylchlorosilane. The mixture was allowed to stand 5 min, and then 40 μ l of the resulting solution was injected onto a 1/4 in. \times 5 ft 15% SE-30 column. The column temperature was programmed from 85 to 340° at a rate of 10°/min and held at the upper limit until the last fraction was eluted. Actinometry for the photolysis was done with the uranyl oxalate actinometer solution of Masson, Boekelheide, and Noyes.¹¹

The quantum efficiency for the photolysis of 2 was similarly determined by using a 1.0% solution of 2 in dioxane.

Attempted Photolysis of 2 with 3600-Å Light.—A 1.0% solution of 2 in dioxane was irradiated for 24 hr with a 3660-Å lamp (1.35×10^{-1} einstein/min). Only 2 was detected by glc.

Isolation of 2,2'-(*p*-Phenylenedicarbonyl)bis[*p*-(1,1,3,3-tetramethylbutyl)phenol] (4) and *p*-(1,1,3,3-Tetramethylbutyl)phenol (3).—A solution of 2.0 g of 1 in 150 ml of anhydrous dioxane was irradiated for 144 hr with a 2.5-W 2537-Å immersion lamp. The solution was evaporated to a paste. The residue was taken up in a small amount of acetone and cooled in dry ice. The yellow precipitate was collected and recrystallized twice from acetone-water to give a yellow crystalline product, mp 143–145°, identified as 4: ir (KBr) 1627 cm⁻¹ (C=O); nmr (CDCl₃) singlet at 11.7 ppm (2 H, OH).

Anal. Calcd for C₃₆H₄₆O₄: C, 79.68; H, 8.54; O, 11.80. Found: C, 79.00; H, 8.55; O, 12.45.

The acetone filtrate from the above precipitation was evaporated to a paste and sublimed at atmospheric pressure. Two recrystallizations of the sublimate from isooctane produced a white crystalline material, mp 73–75°, identified as 3 by mixture

(9) We found that bis(2,4,6-trimethylphenyl) terephthalate, which cannot undergo a photo-Fries rearrangement, is very resistant to photolysis.

(10) G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961).

(11) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," 2nd ed., Vol. II, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, pp 294–298.

melting point and comparison of its ir spectrum with that of an authentic sample.

Isolation of *p*-(1,1,3,3-Tetramethylbutyl)phenyl *p*-[2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)benzoyl]benzoate (2).—A solution of 2.0 g of 1 in 150 ml of anhydrous dioxane was placed in a Pyrex glass test tube and irradiated with a 550-W Hanovia mercury arc for 37 hr. The yellow solution was evaporated to a paste, and the residue was taken up in acetone. The insoluble material, 1.0 g, was filtered out and the filtrate was concentrated, cooled in dry ice, and filtered. Five recrystallizations of the yellow precipitate from acetone-water produced a material, mp 156–157°, identified as 2: ir (KBr) 1631 (C=O), 1743 cm⁻¹ (C=O); nmr (CDCl₃) singlet at 11.7 ppm (1 H, OH).

Anal. Calcd for C₂₈H₄₀O₄: C, 79.68; H, 8.54; O, 11.80. Found: C, 79.68; H, 8.54; O, 11.48.

Isolation of *p*-[2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)benzoyl]benzoic Acid (5).—A solution of 12.0 g of 1 in 600 ml of dioxane (0.5% water) was irradiated for 26 hr with a 2.5-W 2537-Å immersion lamp. The yellow solution was evaporated to a paste and the residue was taken up in ether. The ether solution was filtered and then shaken with a 10% sodium hydroxide solution. The yellow precipitate formed was dissolved in warm water, and the resulting solution was acidified with hydrochloric acid. The precipitate was collected and sublimed at 0.5 mm pressure and 206° bath temperature. The initial fraction was discarded and the yellow, crystalline material, mp 196–197°, was identified as 5: ir (KBr) 1628 (C=O), 1692 cm⁻¹ (C=O); nmr singlet at 11.8 ppm (2 H, OH and CO₂H).

Anal. Calcd for C₂₂H₂₆O₄: C, 74.70; H, 7.41; O, 17.89. Found: C, 74.92; H, 7.54; O, 17.54.

Isolation of Terephthalic Acid.—A solution of 1.0 g of 1 in 100 ml of 10:1 dioxane-water solution was irradiated for 48 hr

in several Pyrex glass tubes with a 550-W Hanovia mercury arc. The solutions were combined and evaporated to dryness on a steam bath. The residue was extracted with warm sodium bicarbonate solution. The sodium bicarbonate solution was acidified with 6 *N* hydrochloric acid and filtered. The precipitate was washed with water and ether. The precipitate had a melting point greater than 300° and its ir spectrum was identical with that of a known sample of terephthalic acid.

Photolysis of 1 in Polystyrene.—A hot solution of 4.0 g of polystyrene and 0.08 g of 1 in 100 ml of methylene chloride was poured into a petri dish and allowed to stand until a hard film was obtained. The dish was then left overnight on a hot plate set at 50°. Half of the resulting film was irradiated in a Rayonet reactor (3100-Å lamps) for 48 hr. Samples (approximately 0.50 g) of the above films were dissolved in 50 ml of methylene chloride containing 4.0 ml of a 0.30% solution of *o*-hydroxybenzophenone (glc internal standard). The resulting solutions were cooled, diluted with 200 ml of acetone, filtered, and evaporated to dryness in a rotary evaporator. The residue was taken up in 2 ml of dioxane. A 0.2-ml portion of this solution was treated with 1.0 ml of Tri-Sil and chromatographed as previously described. As a control, a solution of 1 in benzene at the same concentration was photolyzed under the same conditions.

Registry No.—1, 3637-39-6; 2, 26157-65-3; 4, 26157-66-4; 5, 26157-67-5.

Acknowledgment.—The authors gratefully acknowledge the help of Professor David Whitten, of the University of North Carolina, with whom many fruitful discussions of this work were held.

Photolysis of 2,2,5,5-Tetramethyldihydro-3-furanone^{1,2}

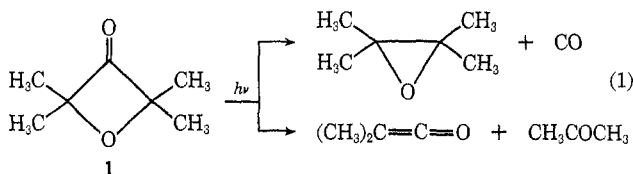
GRAHAM HAGENS, JOHN P. WASACZ, MADELEINE JOULLIÉ, AND PETER YATES*

Departments of Chemistry of the University of Pennsylvania, Philadelphia, Pennsylvania 19104, and the University of Toronto, Toronto 5, Ontario, Canada

Received May 4, 1970

The photolysis of 2,2,5,5-tetramethyldihydro-3-furanone in methanol gives methyl 3-isopropoxy-3-methylbutanoate, methyl 3-methyl-2-butenate, isopropyl 3-methyl-2-butenate, methyl 3-methyl-3-butenate, and isopropyl alcohol. These products are all considered to arise *via* the ketene formed by Norrish type I cleavage of the dihydrofuranone followed by intramolecular hydrogen abstraction. Corroboration for this view is provided by the observation that photolysis of 2,2,5,5-tetramethyldihydro-3-furanone-4-*d*₂ in methanol gives methyl 3-(isopropoxy-1-*d*)-3-methylbutanoate-2-*d* and methyl 3-methyl-2-butenate-2-*d*.

Although the photolysis of cyclic ketones has been studied extensively, the only previous investigation of the photolysis of an oxacycloalkanone appears to be that of Hammond and coworkers,³ who found that 2,2,4,4-tetramethyl-3-oxetanone (1) undergoes both decarbonylation and cleavage to a ketene and ketone (eq 1). These reactions are closely analogous to



* Author to whom correspondence should be addressed.

(1) Taken from dissertations presented by J. P. Wasacz and G. R. Hagens in partial fulfillment of the requirements of the Ph.D. degree at the University of Pennsylvania, 1969, and the University of Toronto, 1970, respectively.

(2) Part of this work was discussed at the Second IUPAC Symposium on Photochemistry, Enschede, Holland, 1967; P. Yates, *Pure Appl. Chem.*, **18**, 93 (1968).

(3) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1242 (1966).

reactions observed in the case of cyclobutanones,⁴ and were interpreted as involving initial Norrish type I cleavage of the oxetanone.

We report now a study of the photolysis of the related 2,2,5,5-tetramethyldihydro-3-furanone (2) in methanol. This investigation was undertaken (1) to extend our knowledge of the photochemistry of oxacycloalkanones, and (2) as part of the search for new cases of the photochemical conversion of cyclic ketones to cyclic acetals.² With respect to the latter quest, it was considered that the absence of hydrogen atoms at the ring atoms bearing a β relationship to the carbonyl group might inhibit alkenal formation⁵ and that the circumstance that the ring is five membered might inhibit ketene formation.⁶ It was hoped that if these two pathways were thus made more difficult, an oxacarbene² might be formed, leading to the formation of a cyclic acetal. In the event, however, this goal was not achieved.

(4) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

(5) R. Srinivasan, *ibid.*, **81**, 1546 (1959).

(6) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).