

The Photochemistry of Pyracycloquinone

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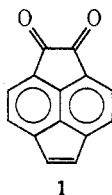
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Irradiation of pyracycloquinone in methanol gave dimethyl 5,6-acenaphthenedicarboxylate in 30% yield. Photolysis of pyracycloquinone in ethanol and in 2-propanol gave the corresponding diesters, while photolysis in benzene containing *p*-anisidine yielded the diamide. These observations represented indirect evidence for the formation and reaction of a diketene intermediate, formed in a photoinitiated benzenoid-quinoid valence isomerism. A detailed study of the luminescence spectra of pyracycloquinone in protic media as well as kinetic studies of the reaction between pyracycloquinone and protic solvents leads to the conclusion that the initially formed excited state is a singlet species represented as a diketene. The dark reactions which led to the formation of diesters (when the photolysis took place in aliphatic alcohol solution) were postulated to occur by attack of alcohol on the diketene to give labile intermediates. Although no photochemical reaction between pyracycloquinone and cyclohexane was observed, irradiation (3500 Å) of a solution of the quinone in cyclohexene resulted in the formation of a mixture of bicyclohexenyl derivatives and 1,2-dihydroxypyrracene. The major product isolated from this mixture was identified as 1,1'-dehydro-2,2'-bicyclohexenyl. The quantum efficiency for the disappearance of pyracycloquinone during photolysis in cyclohexene was found to be only 0.02, but the high yield of bicyclohexenyl derivatives was 20 times greater than for a 1:1 mole reaction. This indicated that a radical chain mechanism which involved abstraction of hydrogen from the solvent by the triplet state of pyracycloquinone was operative. Luminescence studies of the quinone in nonprotic media were consistent with this mechanism and indicated highly efficient intersystem crossing.

The objective of this work was the preparation and photochemical investigation of aromatic compounds expected to undergo light-induced benzenoid-quinoid valence isomerizations. Although valence isomerism involving benzenoid-nonbenzenoid systems has been well documented in the literature,²⁻⁷ few examples of benzenoid-quinoid transformations have been reported.

Pyracycloquinone (**1**) was considered an excellent



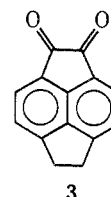
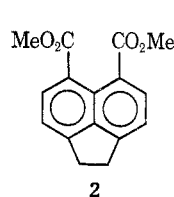
candidate for study, since it bears a formal resemblance to conjugated unsaturated ketones, a series of compounds the photochemistry of which has been extensively investigated over the past several years.⁸⁻¹² In addition, the compound could be prepared (albeit in low yield) from readily available acenaphthene by a three-step synthesis.^{13,14} The discovery¹⁵ that this

compound reacted photochemically with protic substances prompted a detailed investigation of the photochemistry of pyracycloquinone in both protic and nonprotic solvents. The detailed mechanism by which these products are formed is the subject of the present paper. The results indicate that pyracycloquinone is an example of a compound which reacts from either a singlet or a triplet excited state depending upon the nature of the coreactant.

Photoreactions of Pyracycloquinone in Protic Solvents.

—Irradiation of **1** in various solvents was initially carried out for periods in excess of 24 hr. When the isolation of intermediates was desired, however, shorter periods of irradiation were employed.

A. Prolonged Irradiation.—Irradiation of a methanolic solution of **1** under argon led to the formation of a yellow-orange photoproduct, which was conveniently isolated by chromatography as a colorless solid in 30% yield. Elemental and spectroscopic analysis identified the material as dimethyl 5,6-acenaphthenedicarboxylate (**2**). In addition, the physical and spectral properties of this material were identical with those of an authentic sample prepared from 1,2-diketopyrracene (**3**) by peracid oxidation followed by Fischer



esterification. In contrast to the behavior of **1**, no photoreaction of **3** was found.

That this reaction occurs with other protic substances was indicated by the photolysis of **1** in the presence of ethanol, 2-propanol, and *p*-anisidine, which resulted in the formation of diethyl 5,6-acenaphthenedicarboxylate (11% yield), diisopropyl 5,6-acenaphthenedicarboxylate (13% yield), and acenaphthene-5,6-di-

(1) (a) Taken from the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements of the degree of Doctor of Philosophy (Chemistry), June 1969. (b) To whom inquiries should be addressed.

(2) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962).

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(5) H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molymoux, and V. Boekelheide, *J. Amer. Chem. Soc.*, **87**, 130 (1965).

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(7) V. Boekelheide and E. Sturm, *ibid.*, **91**, 902 (1969).

(8) P. J. Kropp, "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 55-67.

(9) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960).

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(12) J. D. Roberts and F. B. Mallory, *ibid.*, **83**, 898 (1961).

(13) B. M. Trost, *ibid.*, **88**, 853 (1966).

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TABLE I
 PRODUCTS DERIVED FROM PYRACYLOQUINONE PHOTOLYSIS IN POLAR SOLVENTS AT 25°

Solvent ^a	Other constituents	Time of irradiation, hr	Products		Yield, %	Major <i>m/e</i> peaks in mass spectrum
			R	X		
Methanol		48	CH ₃ O	H	30	270, 239, 196, 180, 152
Methanol	H ₂ SO ₄ ^e	65	CH ₃ O	H	33	270, 239, 196, 180, 152
Methanol- <i>O-d</i>		48	CH ₃ O	D	30	272, 241, 198, 182, 154
Ethanol		40	C ₂ H ₅ O	H	11	224, 180, 152
2-Propanol ^b		40	<i>i</i> -C ₃ H ₇ O	H	13	224, 180, 152
Benzene ^c	<i>p</i> -Anisidine ^d	25	<i>p</i> -CH ₃ OC ₆ H ₄ NH	H	51 (crude)	329, 180, 123, 152, 108
Methanol	NaOMe ^f	42	4		90	268, 237, 194, 178, 150

^a Concentration of 1 was 2.5×10^{-4} M. ^b Concentration of 1 was 1.25×10^{-4} M. ^c Concentration of 1 was 2.5×10^{-3} M. ^d Concentration of *p*-anisidine was 0.10 M. ^e pH of solution was 1.5. ^f pH of solution was 10.5.

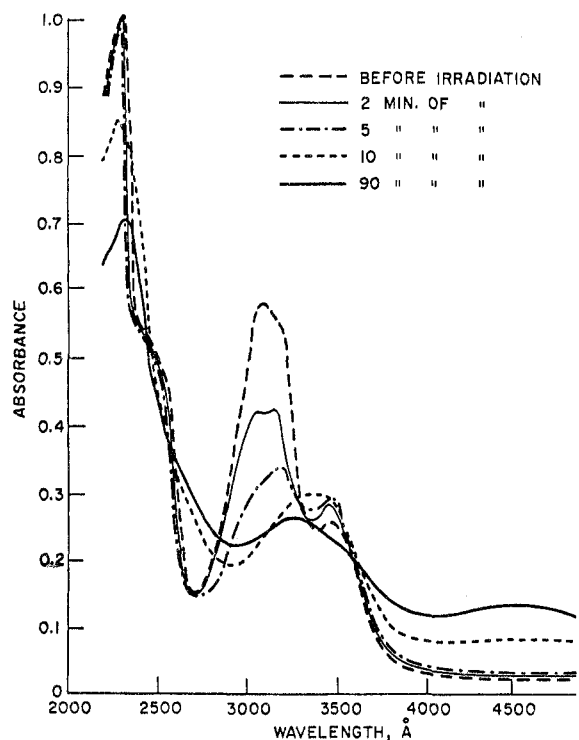


Figure 1.—Changes in the ultraviolet absorption spectrum of pyracloquinone during photolysis in methanol.

carboxylic acid di-*p*-methoxyanilide (51% yield), respectively.

In an effort to determine the nature of proton transfer during the reaction of photoexcited 1 with protic substances, irradiation of 1 in methanol-*O-d* was carried out. The product, which was isolated in 30% yield, was characterized by infrared and mass spectral analysis as dimethyl 1,2-dideuterio-5,6-acenaphthenedicarboxylate. That only two deuterium atoms had been incorporated was indicated by the mass fragmentation pattern, which was identical with that of 2 with the exception that the mass/charge ratio of each fragment ion was increased by two units.

The effect of acid and base on the course of this photochemical reaction was also studied. Irradiation of a methanolic solution of 1 containing 4 mequiv of sulfuric acid (pH 1.5) gave a 33% yield of 2. Thus,

no dramatic change in the overall course of the reaction was observed in the presence of acid. In contrast, when photolysis of a methanol solution containing 4 mequiv of sodium methoxide (pH 10.5) was carried out for an extended period, separation and purification of the product in the usual manner led to the isolation of an ortho ester (4) in 90% yield. That this compound was not formed as a result of methoxide ion attack on 2 was established by a control experiment. A summary of the photoproduct study is presented in Table I.

B. Brief Irradiation.—In an effort to obtain a better understanding of the overall mechanism of the photo-reactions of 1 in protic solvents, the spectral changes associated with the irradiation of 1 in methanol solution were monitored by both visible and ultraviolet spectrophotometry. In a typical run, a stirred solution of 1 in methanol was flushed with argon for 2 hr followed by short periods of irradiation. The ultraviolet absorption spectrum of 1 during photolysis (Figure 1) showed a rapid decrease in the absorption band at 3080 Å after only 5 min. Concomitant with this decrease in the concentration of 1 was an increasing coloration¹⁶ (red) of the solution. The increase in the red color as a function of irradiation time was illustrated by the visible absorption spectrum changes associated with the photolysis. The rate of formation of the species with a long wavelength (~ 5000 Å) absorption band approximately corresponded to the rate of disappearance of 1. As irradiation was continued, however, this species reacted slowly over a period of hours, during which time the diester 2 was formed. The formation of the latter was determined by isolation of 2 from the reaction mixture at various time intervals.

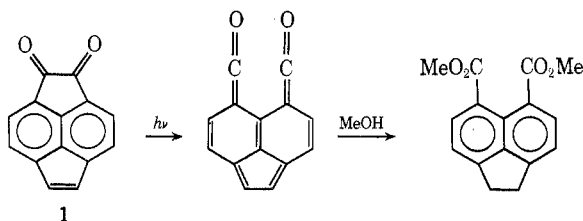
That the formation of the diester from the red species was not the result of a thermal reaction was established by the following experiments. A solution of 1 in methanol was irradiated for 30 min (at this time, essentially all of 1 is converted to the red intermediate) and subsequently refluxed for 24 hr. No changes in the absorption spectrum of the red solution were observed during this period. After evaporation of the solvent, the residue was chromatographed and a 15% yield

(16) This appeared green initially but changed to a deep red on standing.

of **2** (based on **1**) was obtained with chloroform as the eluent. This was the expected yield for this period of irradiation. Further elution of the column with methanol led to the isolation of a red solid (80% of weight of **1**). This material was redissolved in spectroquality methanol and the solution (10^{-4} M) was irradiated for 26 hr. Treatment of the reaction mixture in the usual way led to the isolation of an additional 17% yield of diester **2** (based on starting **1**). These observations indicated that two photochemical reactions occurred during the photolysis of **1** and that an isolable intermediate was produced. In a related experiment, the red intermediate was converted to the ortho ester **4** on treatment with a methanolic solution of sodium methoxide in the dark.

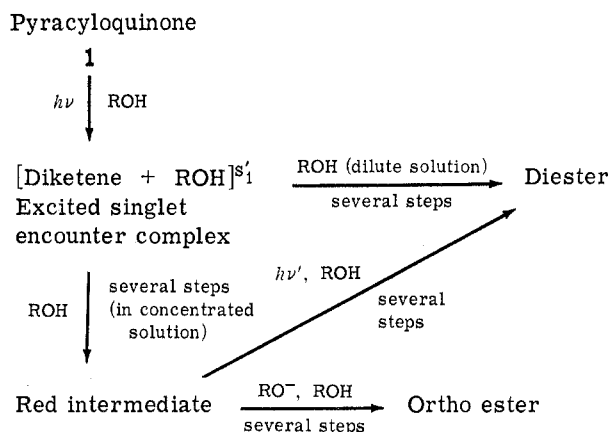
The possibility of diketene formation in the initial stage of the photoreaction in protic solvents has already been mentioned. However, an attempt to observe this intermediate directly by infrared spectroscopy at -78° was unsuccessful. The concentration of diketene present (if it indeed forms) is apparently too low for detection by this technique.

Mechanism of Photoreactions in Protic Solvents.—The intermediate formation of diketenes in photochemical reactions of unsaturated diketones has previously been invoked and is supported by indirect evidence. Specific examples are the photolysis of 3-phenylcyclobutene-1,2-dione¹⁷ and benzocyclobutenedione¹⁸ in which simple mechanisms are postulated to account for the various products formed. A simplified mechanism was also presented in our preliminary report¹⁵ on the photolysis of pyracycloquinone (**1**) in



methanol. In that paper,¹⁵ however, we suggested that the mechanism of the overall reaction was more complicated than that depicted above. This suggestion was based largely on the observation of a transient (thermally stable) species absorbing at long wavelength. A subsequent paper by Trost¹⁴ on the photolysis of **1** in moist 1,2-dimethoxyethane also presented results which suggested the intermediate formation of the diketene from **1**; 5,6-acenaphthenedicarboxylic anhydride was postulated to form by attack of water on the diketene. This diketene was also postulated to be responsible for a transient red color.

The present results confirm our earlier suggestion¹⁵ that the mechanism of the photochemical reaction of pyracycloquinone with protic substances is complex. A schematic representation of the postulated overall mechanism of the photochemical reaction of **1** with aliphatic alcohols is illustrated below; a discussion of the individual steps in this mechanism follows.



A. Nature of the Excited State.—A determination of the nature of the initially formed excited species responsible for the processes involved was accomplished, in part, by a study of the luminescence spectra of **1** and 1,2-diketopyracene (**3**) in protic and aprotic solvents. All the studies were conducted with 1:4 mixtures of isopentane-methylcyclohexane (aprotic medium) and 1:4 mixtures of methanol-ethanol (protic medium); these gave clear, rigid glasses at the temperature of liquid nitrogen (77°K).¹⁹ Since the absorption bands for both **1** and **3** occur in the region 3100–3700 Å, the excitation wavelength was varied within this range.

The O–O band for fluorescence of **3** occurs at 3679 Å and corresponds to an energy of 77.6 kcal/mol for the first excited singlet state of the $n-\pi^*$ transition. The absorption spectrum shows more fine structure than the fluorescence spectrum, with the O–O band for absorption appearing at 3645 Å. The luminescence spectrum of **3** in the hydrocarbon glass at 77°K shows a strong, broad peak at 4200 Å due to fluorescence and weak phosphorescence peaks at 5400 (shoulder) and 5600 Å. The 5400 Å peak was taken as the O–O band of the phosphorescence, and an energy of 53 kcal/mol for the lowest triplet state was thus obtained. The lifetime of the triplet state ($\tau = 1.3 \times 10^{-2}$ sec) was determined by measurements of the exponential decay of the 5600-Å emission (greenish-yellow) as a function of time. The low intensity of phosphorescence, relative to fluorescence, indicates that intersystem crossing from the first excited singlet state of **3** to the first excited triplet state is less efficient than in most other aromatic carbonyl compounds. The large energy difference between the states is presumably responsible for this situation.²⁰

In contrast to the behavior of **3**, pyracycloquinone exhibits a higher singlet \rightarrow triplet efficiency in aprotic solvents. The fluorescence spectrum exhibited emission from the first excited singlet state at 3660 Å (78 kcal/mol), which coincides with the corresponding O–O band for absorption. The phosphorescence spectrum showed strong peaks at 4600, 4700, and 4754 Å. The energy of emission from the first excited triplet state was, therefore, calculated to be 62 kcal/mol. The blue phosphorescence had a half-life τ of 5.9 sec.

The fluorescence spectrum of **3** in methanol-ethanol at 77°K showed weak but discrete fluorescence peaks

(17) J. D. Roberts and F. B. Mallory, *J. Amer. Chem. Soc.*, **83**, 898 (1961).

(18) R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966).

(19) D. R. Scott and J. B. Allison, *J. Phys. Chem.*, **66**, 561 (1962).

(20) D. M. Hercules, Ed., "Fluorescence and Phosphorescence Analysis," Interscience, New York, N. Y., 1966.

TABLE II
 ENERGIES AND LIFETIMES OF EXCITED STATES OF PYRACYLOQUINONE AND 1,2-DIKETOPYRACENE

Compd	Solvent system	E_{S_1} , kcal/mol	τ , sec	E_{S_1} , kcal/mol	τ , sec	Intersystem crossing efficiency
1,2-Diketopyracene	Aprotic ^a	77.6	$<10^{-5}$	53	1.3×10^{-2}	Low
	Protic ^b	75	$<10^{-5}$	57	2×10^{-2}	High
Pyracyloquinone	Aprotic ^a	78	$<10^{-5}$	62	5.9	High
	Protic ^b	48.5 ^c	$<10^{-5}$			

^a 1:4 mixture (by volume) of isopentane-methylcyclohexane. ^b 1:4 mixture (by volume) of methanol-ethanol. ^c Estimated energy of $S_1 \rightarrow S_0$ transition of complex.

at 3818, 4031, and 4256 Å. An energy of 75 kcal/mol was obtained for the $S_1 \rightarrow S_0$ transition assuming 3818 Å for the O-O band. In addition, there was a very strong phosphorescence with peaks at 5000 (57 kcal/mol), 5140, and 5420 Å and a half-life of 2×10^{-2} sec. Therefore, the differences in the energy levels of **3** in protic and aprotic solvents are not very large (Table II).

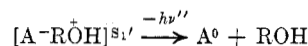
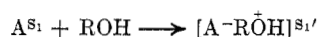
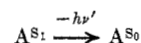
The behavior of pyracylquinone in protic and aprotic solvents was found to be quite different. Since **1** reacted rapidly with protic substances, it was not possible to measure its luminescence spectrum in the polar solvent mixture at room temperature. However, at liquid nitrogen temperatures (77°K), no changes in the absorption spectrum of this solution were noted, even after prolonged irradiation with the full mercury vapor lamp. The luminescence spectrum at 77°K showed a weak, broad emission which peaked at 5885 Å (48.5 kcal/mol). The half-life τ of the orange luminescence was less than 5×10^{-5} sec, which was the limit of experimental observation. Since this decay was observed visually, the lifetime of the excited state was estimated to be $\sim 10^{-6}$ sec.

The results of these luminescence studies (summarized in Table II) indicate that the excited species which forms in solutions of **1** in alcoholic solvents is quite different from that which forms in aprotic solvents. The absence of emission from the 3500-4500-Å region indicated that the first excited singlet state of **1** was quenched by the solvent and that a new species, which emitted at 5885 Å, was formed. The short lifetime of this long-wavelength emission indicates that a singlet species is probably involved.

The formation of a new species with a characteristic emission has previously²⁰ been postulated to occur via a transient dimer ("excimer") or encounter complex. Since the concentration of **1** in the solutions used in the luminescence studies was 10^{-5} M, it is highly unlikely that "normal" excimer formation occurs. The formation of "mixed excimer,"²¹ however, is possible. Thus, a second substance, S, can quench the fluorescence of $^1A^*$ by forming a mixed excimer (AS^*), even if no energy-transfer process (in the usual sense) takes place. This effect has been studied with mixtures of pyrene (A) and substituted pyrenes (S) (where the singlet energies of each component are not far apart).

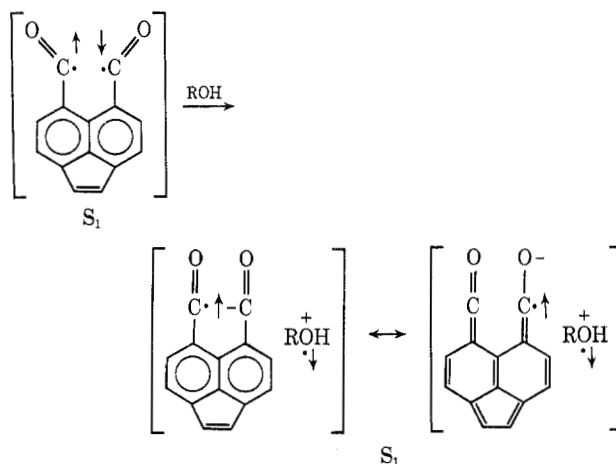
A mechanism for solvent quenching of fluorescence which specifically involves chemical interaction between the solvent and excited solute has been postulated^{22,23} to lead to formation of an encounter complex. This complex may form through transfer of one electron

from the solvent to an excited molecule of **1** (A) as illustrated below.



The molecular form of **1** absorbs radiation to form its lowest excited singlet state, S_1 , which can either emit its molecular fluorescence, $h\nu'$, or react with ROH to produce an excited-state ion pair, S_1' . If the latter reaction occurs in a time which is short compared to the lifetime of the excited singlet state, the excited ion pair S_1' can emit its own characteristic fluorescence $h\nu''$ as observed. The net outcome of this process is emission of fluorescence characteristic of an ionic species in a solution which does not contain ions in the ground state. A mechanism very similar to this was used to explain the luminescence spectrum of phenol.²⁰

The structure of the excited singlet state, S_1' , may



be represented as a diketene. The lifetime of this state ($\sim 10^{-6}$ sec) is sufficiently long to allow the two carbonyl groups to move apart (after the bond has been broken as in S_1) and to form the diketene-alcohol complex (vibrational processes occur in $\sim 10^{-8}$ sec). At liquid nitrogen temperatures, collisions between the excited complex (S_1') and other ground-state alcohol molecules are minimized. Thus, the excited diketene complex emits its excess energy as fluorescence and returns to the ground state. The resulting ground-state diketene, which is most likely higher in energy than the diketone, may be spontaneously converted (radiationless process) to ground-state diketone. An

(21) J. B. Birks and L. G. Christophorou, *Nature (London)*, **196**, 33 (1962).

(22) E. J. Bowen and R. J. Cook, *J. Chem. Soc.*, 3059 (1953).

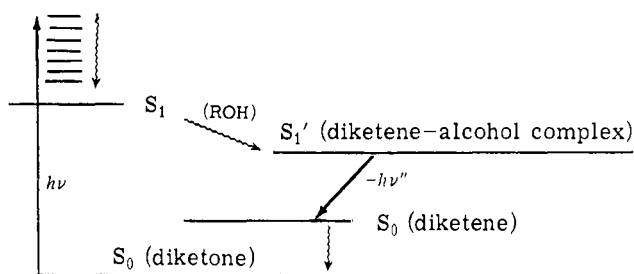
(23) E. J. Bowen and K. West, *ibid.*, 4394 (1955).

TABLE III
QUANTUM EFFICIENCIES FOR DISAPPEARANCE OF PYRACYCLOQUINONE IN PROTIC SOLVENTS AT 25°

Solvent ^a	Other constituents	Concentration of other constituents	Φ	Mean deviation
Methanol	None		0.30	± 0.01
Methanol	Air	Saturated ($10^{-2} M$) ^b	0.30	± 0.01
Methanol	H ₂ SO ₄	$3 \times 10^{-3} N$	0.16	± 0.01
Methanol	NaOCH ₃	$3 \times 10^{-3} M$	0.59	± 0.02
Methanol	<i>trans</i> -1,3-Pentadiene (piperylene)	0.2 M	0.30	± 0.01
Methanol	1,3-Cyclohexadiene	0.2 M	0.30	± 0.01
Methanol- <i>O-d</i>			0.29	± 0.01
Ethanol			0.27	± 0.03
2-Propanol			0.23	± 0.01
2-Butanol			0.20	± 0.01

^a Concentration of pyracycloquinone was $1.00 \times 10^{-5} M$ for all solvents. ^b Solubility of oxygen in methanol at 20°: "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 262. The actual value given is 175 cm³ of O₂/1 of methanol, or $7.8 \times 10^{-3} M$.

energy level diagram illustrating this situation is depicted below.

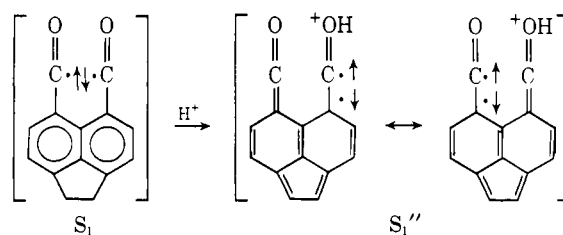


At room temperature, attack of alcohol on the excited complex S₁' (or ground-state diketene) leads to the formation of ground-state intermediates which undergo additional thermal and/or photochemical reactions.

Ferrioxalate actinometry²⁴ was used to determine the quantum efficiency for disappearance of 1 in protic solvents and the results of this study are summarized in Table III. The small decrease in quantum efficiency for disappearance of pyracycloquinone (or S₁') with increasing molecular weight of the attacking alcohol is related to two factors. An increase in basicity of the alcohol would be expected to increase the efficiency of electron transfer from the alcohol to S₁. Complexes (S₁') with methanol, ethanol, 2-propanol, and 2-methylpropanol would be required to have decreasing energies and hence increasing efficiencies of decay to the ground state. The picture is further complicated, however, by a second factor, the rates of diffusion of the various alcohols. Since the differences in the basicities of the alcohols are smaller than the differences in rates of diffusion, it would appear that the latter factor is more important in determining the efficiency of disappearance of S₁'. Since the lifetime of the excited singlet, S₁', is long ($\tau \cong 10^{-6}$ sec) compared with diffusion-controlled processes ($\sim 10^{-9}$ sec),²⁰ this concept appears valid. Thus, it is postulated that diffusion of solvent molecules into the "cage" containing the excited species, S₁', is the primary factor which controls the rate of disappearance of S₁'. That proton transfer does not take place (in neutral solution) during attack of ROH

on S₁' was indicated by the absence of a deuterium isotope effect (see Table III).

Although profound changes in the quantum efficiency for disappearance of the quinone 1 in methanol were observed with large changes in pH, negligible changes in the absorption spectrum were noted. This phenomenon suggested a decrease in the acidity of 1 upon electronic excitation. Such changes have been observed for a variety of organic compounds.²⁰ In particular, aromatic ketones such as acridone²⁵ and acetophenone²⁶ exhibit a decrease in acidity in the first excited singlet state relative to the ground state. Thus, a change in the mechanism of the reaction may occur in the presence of strong acid. Transfer of a proton to the carbonyl oxygen (in the presence of acid) of the S₁ state of 1 might lead to a new excited singlet state S₁''. The efficiency of conversion of this less acidic



state to ground-state products by attack of ROH would therefore be considerably reduced. Conversely, at high pH the efficiency of conversion of S₁ and S₁' would be increased and would account for the higher quantum efficiency. The result at high pH, however, is further complicated by the fact that methoxide ion leads to a product different from that obtained in neutral or acidic media.

The results summarized above lead to the conclusion that the excited species responsible for the photochemical reaction between 1 and protic substances (specifically aliphatic alcohols) is a singlet encounter complex (or "mixed excimer") in a solvent "cage." The multiplicity (singlet) of the state was established by (1) the short lifetime of emission from the complex; (2) the lack of a change in the quantum efficiency for disappearance of 1 in the presence of triplet-state quenchers such as O₂, piperylene, and 1,3-cyclohexadiene²⁴ (see Table III); (3) absence of photoproducts arising from

(24) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 783, presents an excellent description of the experimental details involved in this system.

(25) H. Kokubun, *Z. Electrochem.*, **62**, 599 (1958).

(26) A. Weller and W. Urban, *Angew. Chem.*, **66**, 336 (1954).

hydrogen abstraction processes, which are known²⁷ to occur through excited triplet states. In addition, no triplets could be detected by electron spin resonance measurements (77°K) when a 10^{-4} M solution of **1** in 1:4 methanol-ethanol was irradiated with the full emission from a mercury vapor lamp. On the other hand, irradiation of 1,2-diketopyracene (**3**) under identical conditions produced a strong esr spectrum characteristic of methyl radicals. This type of spectrum has been observed²⁸ upon irradiation of a number of other aromatic carbonyl compounds (triplet-state sensitizers) in alcohol glasses.

B. Nature of the Intermediates.—In an effort to further elucidate the mechanism of this reaction with regard to the steps following the formation of the excited singlet species, a detailed study was made of the photolysis of the quinone **1** in neutral methanol. These experiments resulted in the isolation of a red intermediate, **5**.

The photolysis of **5** under conditions identical with those used in the photolysis of the quinone led to the formation of the diester, dimethyl 5,6-acenaphthenedicarboxylate (**2**). That the photolysis of this intermediate was a less efficient process than that of the quinone **1** was indicated by a determination of the quantum efficiency for the disappearance of **5** in methanol. A value of 0.10 ± 0.01 was obtained by monitoring the disappearance of the absorption (shoulder) at 4820 Å during the photolysis. This compares with a value of 0.30 for disappearance of **1** in methanol (Table III).

The solutions used for the *product* study were sufficiently concentrated (10^{-3} – 10^{-4} M) to allow dimerization of the initially formed ground-state intermediates to occur. Since the red intermediate had a molecular weight (determined by vapor osmometry in methylene chloride solution) in excess of 500 (537 ± 18), dimerization is indicated.

An attempt to elucidate the structure of this dimeric intermediate by a combination of chemical and spectroscopic techniques has not been successful to date. Further work will be required to establish the structure of this material.

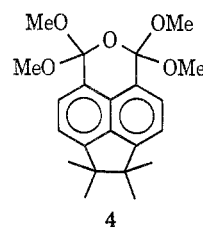
Photolysis of the quinone **1** in a methanol solution containing methoxide ion resulted in formation of a new compound, **4**. This compound also formed when the red intermediate was treated with a solution of sodium methoxide in methanol. It was not found, however, on treatment of diester **2** with a similar solution.

The infrared spectrum of this compound did not exhibit hydroxyl or carbonyl absorptions but instead exhibited a strong ether absorption at ν 1250 cm^{-1} . The only peak observed in the nmr spectrum of **4** was a large singlet at τ 6.28 due to equivalent methoxyl protons. The ultraviolet spectrum exhibited bands with $\lambda_{\text{max}}^{\text{MeOH}}$ at 225 and 310 $\text{m}\mu$. Acenaphthylene derivatives generally have absorptions in the 320–350- $\text{m}\mu$ region (*i.e.*, acenaphthylene, 322 $\text{m}\mu$; dimethyl 5,6-acenaphthylenedicarboxylate, 335 $\text{m}\mu$), while acenaphthene compounds exhibit these absorptions at shorter wavelengths (*i.e.*, dimethyl 5,6-acenaphthene-

dicarboxylate, 315 $\text{m}\mu$). Thus, it appears that the compound does not have unsaturation at the 1,2 position. Since the nmr spectrum could only be obtained in CD_3OD solution, where the undeuterated solvent has peaks in the τ 6.5 region, it was impossible to observe absorption due to the benzylic protons. The solubility of **4** in methylene chloride was insufficient to give an accurate molecular weight determination by vapor osmometry.

The mass fragmentation pattern of **4** exhibited strong peaks at m/e 268, 237 (base peak), 194, 178, 151, and 150. This spectrum was very similar to that of dimethyl 5,6-acenaphthylenedicarboxylate.³⁰ Since the other spectroscopic evidence indicates that **4** is not an unsaturated ester, we conclude that the molecular ion derived from **4** is very unstable and fragments with loss of oxygen and methanol to give the m/e 268 species. Fragmentation of this species then occurs by processes similar to those described for other pyracene derivatives.²⁹

On the basis of the spectroscopic evidence, **4** is



postulated to be an ortho ester. Its formation may occur by attack of methoxide ion on the red intermediate followed by dissociation and solvolysis.

It is highly unlikely that a dimeric species was formed in the solutions used for the *kinetic* studies, since the concentration of quinone was only 10^{-5} M. Thus, our scheme (*vide supra*) indicates that at this concentration the diester was formed solely from the diketene.

Photoreactions in Aprotic Solvents.—The possibility of photocycloaddition of olefins to **1** prompted an investigation of the photochemistry of **1** in cyclohexene. This type of reaction has been reported to occur with 9,10-phenanthraquinone and various olefins.³⁰

Irradiation of a cyclohexane solution of **1** was carried out for 24 hr with 3500-Å light. No changes in the absorption spectrum or the appearance of the solution were noted during this time. However, the photolysis of **1** in cyclohexene solution under identical conditions resulted in disappearance of the absorption at 3080 Å in the spectrum of **1**. In addition, the solution gradually became intensely fluorescent (blue). Column chromatography of the yellow oil formed in this reaction led to the isolation of a mobile liquid and a small amount of pale yellow solid.

Preparative gas-liquid chromatography of the liquid was carried out and two products were isolated. The minor product, a nonfluorescent liquid, was found to be a mixture of compounds with very similar retention times. The mass spectrum of this mixture showed a peak at m/e 162 (1.5%) and strong peaks at m/e 81 (54%) and 68 (100%) in addition to a number of other moderately strong peaks between m/e 98 and 27. The

(27) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 139.

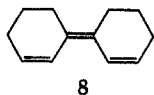
(28) A. Terenin, V. Rylkov, and V. Kholmogorov, *Photochem. Photobiol.*, **5**, 543 (1966), and references cited therein.

(29) J. A. Castellano, F. M. Beringer, and R. E. K. Winter, unpublished work.

(30) M. B. Rubin and R. A. Reith, *Chem. Commun.*, 431 (1966).

major peaks in the nmr spectrum consisted of a complex multiplet between τ 7.5 and 8.5 due to the saturated ring protons, a singlet at τ 6.3 (presumably due to protons on tertiary carbon atoms), and a multiplet at τ 4.25 due to olefinic protons. These results indicate that the mixture consists of bi-2-cyclohexen-1-yl (6) and 2-cyclohexenylcyclohexane (7). The strong peak at m/e 68 suggests the presence of 7. The formation of this fragment has been reported³⁹ to occur through loss of a methyl radical from various cycloalkyl derivatives.

The major product (8), a blue fluorescent liquid,



was initially believed to be 1,1'-bicyclohexenyl. However, the infrared, nmr, and mass spectrum and gas chromatographic retention time of an authentic sample of 1,1'-bicyclohexenyl did not coincide with those of 8.³¹ The nmr spectrum of 8 exhibited two broad complex multiplets (12 H) in the τ 7.8–8.5 region due to saturated ring protons and a sharp multiplet (4 H) centered at τ 4.45 due to olefinic protons. The mass spectrum (70 eV) showed the molecular ion peak at m/e 160 (2%) and strong peaks at m/e 79 (33%), 80 (69%), and 81 (base peak).³² Symmetrical cleavage of the molecular ion to give cyclohexenyl radical cation (m/e 80) suggested 1,1'-dehydro-2,2'-bicyclohexenyl as the structure for 8. The nmr spectrum confirms this assignment.

The pale yellow solid was chromatographed and two fractions were obtained. This first fraction had a mass spectrum which exhibited major peaks at m/e 212, 194, 152, 166, and 165. Since these peaks were also found in the spectrum of 1,2-dihydroxypyrene, it appeared that this compound formed from 1. The second fraction exhibited a mass spectrum with weak peaks at m/e 109, 97, 81, 79, and 67, which are characteristic of bicyclohexenyl derivatives. This material appeared to be polymeric.

Mechanism of Photoreactions in Aprotic Solvents.

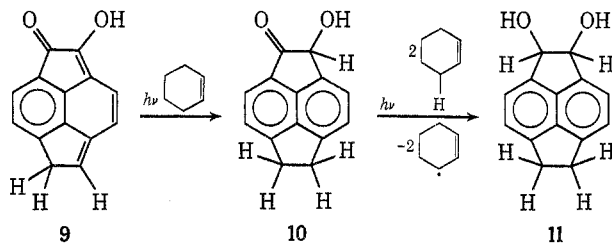
The luminescence spectrum of pyracycloquinone (1) in aprotic solvents at 77°K shows a high intersystem crossing efficiency for transition from the first excited singlet state to the first excited triplet state. In addition, the triplet state was found to have a long lifetime. These facts present strong evidence that the species responsible for formation of the photoproducts in aprotic solvents was the first excited triplet state of 1. Since the excitation of 1 was achieved with 3500-Å light, it was presumed that $n \rightarrow \pi^*$ excitation was involved. The isolation of products which could only have been formed through hydrogen abstraction processes is consistent with this hypothesis.

The low quantum efficiency for disappearance of 1 concomitant with the relatively high yield of C₁₂ hydrocarbons indicated that a radical chain process was involved. Thus, the initiation process is postu-

(31) The nmr spectrum of 1,1'-bicyclohexenyl (CCl₄) exhibited similar intense multiplets (16 H) for the saturated ring protons at τ 7.85 and 8.38 but the resonance at τ 4.30 due to olefin protons (2 H) was half the intensity of the corresponding peak in the spectrum of 8. The mass spectrum exhibited base peaks at m/e 162 (molecular ion) and 79 with moderately strong peaks at m/e 81 and 80.

(32) In the low voltage (14 eV) mass spectrum, however, the base peak was found at m/e 80.

lated to proceed through abstraction of allylic hydrogen atoms from cyclohexene by the $n \rightarrow \pi^*$ triplet state of pyracycloquinone. The triplet states of ketones 9 and 10 would, by appropriate hydrogen abstraction processes, give additional cyclohexenyl radicals and result in complete reduction of 1 to 1,2-dihydroxypyrene (11). Hydrocarbons are produced by chain



propagation steps through attack of the cyclohexenyl radical on cyclohexene. This would result in the formation of C₁₂ hydrocarbons as well as oligomeric polycyclohexenes.

A process which competes with these reactions is dimerization of cyclohexenyl radicals to produce 6. As the concentration of C₁₂ hydrocarbons (such as 6, cyclohexenylcyclohexane, cyclohexylcyclohexane) increases, they compete with cyclohexene in the initial allylic hydrogen abstraction reaction. Abstraction of the allylic hydrogens at the bridgehead carbon atoms of 6 should be more facile than those of cyclohexene (due to the intermediate formation of a tertiary radical) and would account for the formation of 8.

The by-product formation of 6 has been reported to occur in the photolysis of cyclohexene solutions of ethyl chloroformate,^{33a} maleic anhydride,^{33b} diethyl maleate,^{33c} benzoyl diazomethane,^{33d} biacetyl,^{33e} and ethyl pyruvate.^{33e} All of these reactions have been postulated to occur through allylic hydrogen abstraction by free radicals. In the last two cases, the $n \rightarrow \pi^*$ triplet of the carbonyl compound was postulated to be the initiating species. It is interesting to note, however, that 8 was not isolated as a product of any of these reactions.

Conclusions

The photolysis of pyracycloquinone in protic solvents proceeds through a singlet encounter complex which is attacked by the solvent to yield ground-state intermediates. These intermediates condense to form thermally stable quinoid species which are converted to diesters photochemically. Thus, overall benzenoid-quinoid valence isomerism occurs upon photoexcitation of pyracycloquinone in protic solvents.

The photolysis of pyracycloquinone in cyclohexene, however, yields bicyclohexenyl derivatives which are postulated to form through abstraction of hydrogen from the solvent by the first excited triplet state of pyracycloquinone, which is reduced in the process.

These results present an example of a compound which reacts from either a singlet or a triplet state depending upon the protic nature of the solvent medium.

(33) (a) C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **36**, 234 (1963); (b) J. A. Barltrop and R. Robson, *Tetrahedron Lett.*, 597 (1963); (c) P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964); (d) G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); (e) P. W. Jolly and P. de Mayo, *Can. J. Chem.*, **42**, 170 (1964).

Experimental Section³⁴

Materials.—The starting materials used for the preparation of the pyracene derivatives were either reagent grade compounds or were purified directly before use. Deuterated solvents were purchased from Merck Sharp and Dohme Co., Ltd., Montreal, Canada. *p*-Anisidine (Eastman Kodak) was recrystallized three times from water and three times from benzene to give colorless crystals, mp 57–58° (lit.³⁵ mp 57.2°). 1,1'-Bicyclohexenyl was purchased from Frinton Laboratories.

Elemental analyses were performed by B. L. Goydish and A. Murray of RCA Laboratories, Princeton, N. J.

Spectra.—Nmr spectra were recorded with a Varian Model A-60 spectrometer at 25°. The solvents used were deuteriochloroform, deuterioacetone, deuteriomethanol (CD₃OD), and carbon tetrachloride, with tetramethylsilane as internal standard. The mass spectra were recorded by Morgan-Schaffer Corp. with a Hitachi Perkin-Elmer RMU-6D spectrometer equipped with a heated direct inlet. Ionization was generally achieved with 70-eV electrons, but a lower voltage (12–14 eV) was used in an attempt to identify parent ions. Infrared spectra were recorded with a Perkin-Elmer Model 221 spectrophotometer (KBr disks) while the ultraviolet-visible spectra were recorded with a Cary 14R spectrophotometer.

Photochemical Equipment.—The preparative photochemical experiments with pyracycloquinone were carried out in Pyrex flasks and were conducted in a Rayonet reactor equipped with 16 8-W bulbs emitting at 3500 Å. The solutions were degassed by purging with argon for several hours directly prior to irradiation. The solvents used for all the photolysis studies were spectro-quality reagents purchased from Matheson Coleman and Bell.

Pyracycloquinone.^{13,14,36}—A solution of 17.60 g (0.114 mol) of acenaphthene in 1500 ml of carbon disulfide was prepared under nitrogen. After cooling in an ice-salt bath at –5°, 25.0 g (0.116 mol) of oxalyl bromide was added. The mixture was stirred vigorously and 62.50 g (0.234 mol) of fresh aluminum bromide was added over a period of 10–15 min. A black gum slowly formed and, after about 30–40 min, stirring became impossible and was discontinued. The mixture was allowed to warm to room temperature overnight. After the mixture was warmed to 35° for 30 min, the carbon disulfide was decanted. The black gum was treated with 1000 ml of cold 10% aqueous HCl and the mixture was stirred for 30 min. The dark brown solid was filtered and thoroughly washed with water before it was mixed with 7.5 g of Norit and 7.5 g of Celite filter aid. This mixture was suspended in 500 ml of 4% aqueous sodium bisulfite solution and the solution was heated for 30 min at 80°. The hot suspension was filtered and the filtrate was acidified to pH 1 with concentrated HCl. This solution was heated at 80° until a fluffy yellow solid formed. The mixture was allowed to stand for about 30 min, and the yellow solid was collected by filtration. The material was washed with water and anhydrous methanol and vacuum dried. The extraction process was repeated six times on the dark brown, Norit-Celite mixture to yield a total of 3.5 g (14.5% yield) of 1,2-diketopyracene, mp 288–290° dec. The material was recrystallized from dimethylformamide to give 2.0 g of yellow crystals, mp 303–305° dec (lit.³⁷ mp 309–311°).

A solution of 2.1 g (10 mmol) of 1,2-diketopyracene, 4.0 g (23 mmol) of *N*-bromosuccinimide, 150 ml of carbon tetrachloride, and a trace of benzoyl peroxide was refluxed for 8 hr. The solution was filtered hot to give 1.8 g (18 mmol, 91%) of succinimide. The filtrate was cooled, and the crystals which separated were collected to yield 2.0 g (5.5 mmol, 55%) of 5,6-dibromo-1,2-diketopyracene, mp 170–174° dec. This material was recrystallized from ethanol to give 1.0 g of pure product, mp 187–189° (lit.¹³ mp 191°).

A solution of 1.0 g (2.8 mmol) of 5,6-dibromo-1,2-diketopyracene, 2.0 g (15 mmol) of potassium iodide, and 100 ml of acetone was refluxed for 24 hr. The solvent was removed *in vacuo*, and the residue was treated with a saturated aqueous solution of sodium thiosulfate. The orange solid was collected, washed with water, and vacuum dried. The solid was recrystallized from benzene to give 0.40 g (1.9 mmol, 71%) of pyracyclo-

quinone (1), mp >350° (lit.¹³ mp >350°). The ultraviolet, infrared (ν_{\max}^{CO} 1680, 1730 cm⁻¹), nmr (CD₃COCD₃) [τ 1.60 (4 H), quartet ($J_{AB} = 8$ Hz), 2.38 (2 H) singlet] and mass spectrum were identical with those reported in the literature.^{13,14}

Photolysis of Pyracycloquinone in Methanol. Prolonged Irradiation. A. Neutral Solution.—A degassed solution of 50 mg (0.25 mmol) of pyracycloquinone in 1000 ml of methanol was irradiated for 48 hr. After solvent removal, the residue was taken up in chloroform and chromatographed over 100 g of Florisil. Elution of the product with a large volume of chloroform was followed by its strong blue fluorescence. Evaporation of the solvent furnished 20 mg (0.074 mmol, 30%) of dimethyl 5,6-acenaphthenedicarboxylate (2), mp 170–175°. The nmr spectrum consisted of an AB quartet (aromatic protons) centered at τ 2.25 (4 H, $J_{AB} \cong 7$ Hz), a singlet at τ 6.12 (6 H) due to methyl protons, and a singlet due to bridge protons at τ 6.51 (4 H). The infrared, ultraviolet, and mass spectrum were identical with those of an authentic sample. In addition, a mixture of the photoproduct and the authentic sample melted at 170–175°.

B. Acid Solution.—A degassed solution of 25 mg (0.13 mmol) of pyracycloquinone, 4 mequiv of sodium methoxide, and 500 ml of methanol was irradiated for 65 hr. The solution was neutralized with 10 ml of a methanol solution containing 0.4 mequiv of sodium methoxide per 1 ml. The solvent was removed *in vacuo* and the residue was chromatographed as above to yield 11 mg (0.041 mmol, 33%) of dimethyl 5,6-acenaphthenedicarboxylate (2), mp 169–174°. The infrared and mass spectra were identical with those of the authentic sample.

C. Basic Solution.—A degassed solution of 25 mg (0.13 mmol) of pyracycloquinone, 4 mequiv of sodium methoxide, and 500 ml of methanol was irradiated for 42 hr. The solution was neutralized with 10 ml of a methanol solution containing 0.4 mequiv of sulfuric acid per 1 ml. After solvent removal, the residue was chromatographed as above. The fluorescence of the material eluted with chloroform, however, was very weak. Evaporation of the solvent produced 36 mg of white crystals, mp 205–206° dec. Characterization of this compound (4) by spectroscopic analysis is discussed in the text.

In order to establish that this compound was not formed as a result of methoxide ion attack on the product diester, a solution of 8 mg of dimethyl 5,6-acenaphthenedicarboxylate in 2 ml of methanol was treated with several drops of methanolic sodium methoxide solution (0.4 mequiv/ml). The solution immediately became deeply colored (red). Neutralization of the solution with several drops of methanolic sulfuric acid solution (0.4 mequiv/ml) produced decolorization. The solvent was evaporated and the residue was taken up in a minimum amount of chloroform-methanol and filtered. The solvent was removed *in vacuo* to yield 6 mg (75%) of off-white solid. The infrared spectrum of this material was identical with that of the starting diester.

Photolysis of Pyracycloquinone in Methanol. Brief Irradiation.—A stirred, degassed solution of 50 mg (0.25 mmol) of pyracycloquinone in 1000 ml of methanol was irradiated for short periods of time. After each period of irradiation, an aliquot of the solution was transferred to a 0.100-cm quartz cell and the ultraviolet spectrum was recorded. The results of this analysis are shown in Figure 1. In a related experiment, a stirred, degassed solution of 80 mg (0.40 mmol) of pyracycloquinone in 1000 ml of methanol was also irradiated for short periods of time. An aliquot of the solution was removed after each period of irradiation and transferred to a 5.000-cm quartz cell. The visible spectral changes were recorded and it was established that pyracycloquinone was entirely converted to the red intermediate in about 30 min.

A series of experiments were conducted in order to establish the approximate rate of formation of dimethyl 5,6-acenaphthenedicarboxylate. This involved irradiation of degassed solutions of 50 mg of pyracycloquinone in 1000 ml of methanol for various time intervals and isolation of the diester by the procedure described above for long irradiation time. The results of this study are as follows [minutes of irradiation (% yield)]: 5 (3–5), 20 (8), 30 (16), 60 (21), 120 (26), 1440 (30).

The intermediacy of a red species was established by the following set of experiments. A stirred, degassed solution of 50 mg of pyracycloquinone in 1000 ml of methanol was irradiated for 30 min. The resulting deep green solution became deep red almost immediately after removal from the Rayonet reactor. This solution was refluxed for 24 hr under argon. The solution remained intensely colored during this period and no changes in the absorption spectrum were noted. At the end of this time, the solvent was removed *in vacuo* and the red residue was chro-

(34) All melting points are corrected.

(35) N. A. Lange, "Handbook of Chemistry," 10th ed. Handbook Publishers, Sandusky, Ohio, 1961.

(36) The assistance of Professor B. M. Trost, Department of Chemistry, University of Wisconsin, in providing this procedure is gratefully acknowledged.

(37) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 366 (1959).

matographed over 100 g of Florisil. Elution with a large volume of chloroform led to the isolation of 10 mg (15% yield) of dimethyl 5,6-acenaphthenedicarboxylate, mp 170–175°. Further elution with 500 ml of methanol gave 40 mg of a deep red, crystalline solid, mp >350° (turned black above 150°). This material was redissolved in 1000 ml of methanol and the resulting solution was degassed and irradiated for 26 hr. Work-up of the reaction mixture in the usual way led to the isolation of 13 mg (17% yield) of dimethyl 5,6-acenaphthenedicarboxylate.

In order to establish the course of the reaction in the presence of base, a stirred, degassed solution of 26.5 mg of pyracloquinone in 500 ml of methanol was irradiated for 30 min, and the resulting red solution was treated with 10 ml of methanolic sodium methoxide (0.4 mequiv/ml). The very deep red solution was neutralized with 10 ml of methanolic sulfuric acid (0.4 mequiv/ml) and evaporated to dryness. The residue was chromatographed as above and 37 mg of a white, crystalline solid, mp 205–206° dec, was obtained. The infrared and mass spectra of this material were identical with those of the material obtained in the photolysis of pyracloquinone in basic methanol. In addition, a 1:1 mixture of the two solids had a melting point of 205–206° dec.

A sample of the red intermediate was obtained by the following procedure. The photolysis of 50 mg of pyracloquinone in 1000 ml of methanol was carried out in the usual way for 30 min. The solvent was removed *in vacuo* and the residue was chromatographed over Florisil. The diester was removed by elution with chloroform and the red band was eluted with methanol. The methanol was evaporated and the residue was chromatographed over Florisil with ethyl acetate as the eluent. Finally, the red solid was chromatographed over silica gel (Fischer), with ethyl acetate as the eluent. After a number of runs, about 30 mg of the red intermediate was obtained. Attempts at characterization of this compound by spectroscopic analysis were unsuccessful.

An attempt to monitor the reaction by infrared spectroscopy was made. A saturated solution of pyracloquinone in methanol was prepared by stirring 10 mg of the diketene with 5 ml of methanol for several hours. The solution was filtered and the filtrate was introduced into a 1.00-mm infrared cell (sodium chloride windows). The cell was placed into a variable-temperature jacket (Beckman J-3), and cold (–78°) acetone was circulated through the unit. The cell was irradiated with an 8-W mercury vapor lamp (3500 Å) while the spectrum was scanned. Weak, broad absorptions in the 2000–2500-cm⁻¹ range (due to a small amount of carbon dioxide) were observed but no sharp absorption indicative of ketene groups at 2100 cm⁻¹. Similar results were obtained when a more viscous medium, polypropylene polyol (Union Carbide), was used as the solvent.

Photolysis of Pyracloquinone in Methanol-*O-d*.—A degassed solution of 50 mg (0.25 mmol) of pyracloquinone in 1000 ml of methanol-*O-d* was irradiated for 48 hr. The reaction mixture was worked up in exactly the same way as described above for the neutral methanol photolysis to yield 23 mg (0.075 mol, 30%) of dimethyl 1,2-dideuterio-5,6-acenaphthenedicarboxylate, mp 163–166°. This was recrystallized from methanol to give 9 mg of colorless solid: mp 167–170°; $\nu_{\text{max}}^{\text{CO}}$ 1725 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 272 (40), 241 (100), 198 (10), 182 (30), 154 (30).

Photolysis of Pyracloquinone in Ethanol.—A degassed solution of 25 mg (0.13 mmol) of pyracloquinone in 1000 ml of ethanol was irradiated for 42 hr. The reaction mixture was worked up in exactly the same way as described above for the neutral methanol photolysis to yield 4.5 mg (0.015 mmol, 11%) of diethyl 5,6-acenaphthenedicarboxylate, mp 180–185°, $\nu_{\text{max}}^{\text{CO}}$ 1720 cm⁻¹. The mass spectrum showed the moderately intense peaks at *m/e* 152 and 180 which are observed in the spectrum of the dimethyl ester. However, the molecular ion of the diethyl ester is much less stable than that of 2 and fragmentation by a number of alternate pathways gives other peaks at *m/e* 268, 238, and 154.

Photolysis of Pyracloquinone in 2-Propanol.—A degassed solution of 25 mg (0.13 mmol) of pyracloquinone in 1000 ml of 2-propanol was irradiated for 40 hr. The reaction mixture was worked up in exactly the same way as described above for the neutral methanol photolysis to yield 5.3 mg (0.016 mmol, 13%) of diisopropyl 5,6-acenaphthenedicarboxylate, mp 143–146°, $\nu_{\text{max}}^{\text{CO}}$ 1710 cm⁻¹. The mass spectrum showed moderately intense peaks at *m/e* (rel intensity) 224 (15), 180 (23), and 152 (16) and a very low intensity peak for the molecular ion at *m/e* 326.

Fragmentation processes characteristic of higher esters³⁸ were also observed in the spectrum (*m/e* 282, 240, and 238).

Photolysis of Pyracloquinone in Benzene with *p*-Anisidine.—A degassed solution of 50 mg (0.25 mmol) of pyracloquinone, 600 mg (4.9 mmol) of *p*-anisidine, and 50 ml of benzene was irradiated for 25 hr. The solvent was removed *in vacuo* and the residue was taken up in chloroform and filtered. The filtrate was evaporated to dryness to yield 57 mg (0.13 mmol, 51%) of crude 5,6-acenaphthenedicarboxylic acid di-*p*-methoxyanilide, mp 255–260° dec, $\nu_{\text{max}}^{\text{CO}}$ 1650 cm⁻¹. The mass spectrum did not exhibit a molecular ion peak (*m/e* 452) but a number of very weak peaks between *m/e* 451 and 330 were observed. The major fragments appeared at *m/e* (rel intensity) 329 (100), 180 (5), 152 (20), 123 (75), and 108 (92). The presence of species at *m/e* 180 (5) and 152 (20), which are characteristic of 5,6-disubstituted acenaphthene derivatives,³⁰ was again observed.

Photolysis of Pyracloquinone in Cyclohexene.—A solution of 25 mg (0.13 mmol) of pyracloquinone in 1000 ml of cyclohexene was degassed in the usual manner and irradiated for 24 hr. As the photolysis proceeded, the solution became intensely fluorescent (blue). The cyclohexene was removed *in vacuo* to yield 2.0 g of yellow, viscous oil. Chromatography of this material over Florisil with chloroform as the eluent led to the isolation of 1.93 g of a mobile, pale yellow liquid (A). Further elution of the column with methanol produced 60 mg of a pale yellow solid (B). Further separation of the liquid A into two fractions was accomplished by gas-liquid chromatography.³⁹ Under identical conditions, 1,1'-bicyclohexenyl had a retention time of 18.8 min. The major fraction, which had a retention time of 11.8 min, was characterized as 1,1'-dehydro-2,2'-bicyclohexenyl (8): ir 1690 cm⁻¹ (C=C); nmr (CCl₄) τ 7.8–8.5 (12 H), 4.45 (4 H); mass spectrum (70 eV) *m/e* (rel intensity) 160 (2), 79 (33), 80 (69), 81 (100).

Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.48; H, 10.51.

The minor fraction, which had a retention time of 2.4 min, was a nonfluorescent liquid. Gas chromatography of this liquid at a lower temperature showed it to be a mixture of products with very similar retention times. The mass spectrum of this mixture showed a molecular ion peak at *m/e* 162 and strong peaks at *m/e* 81 and 68 in addition to a number of other moderately strong peaks between *m/e* 98 and 27. The major peaks in the nmr spectrum (CCl₄) consisted of a complex multiplet between τ 7.5 and 8.5 due to the saturated ring protons, a singlet at τ 6.3 (presumably due to protons on tertiary carbon atoms), and a multiplet at τ 4.25 due to olefinic protons.

The solid B was chromatographed over Florisil and two fractions were obtained. The first fraction, which was isolated by elution with ether-methanol, had a mass spectrum which exhibited major peaks at *m/e* 212, 194, 152, 166, and 165. These peaks were also found in the spectrum of 1,2-dihydroxypyrene.¹⁹ However, other peaks at low *m/e* values not present in this spectrum indicated that this material was impure.

The second fraction isolated from the chromatography of B had a very weak spectrum with peaks at *m/e* 109, 97, 81, 79, and 67.

Determination of Quantum Yields.²⁴—All of the determinations were carried out with 10⁻⁵ M solutions of pyracloquinone in the appropriate spectroquality solvents. The optical density of these solutions was high enough to absorb all incident light. A 14.00-ml aliquot of the solution was transferred to a 5.000-cm quartz cell. The cell was placed on an optical bench equipped with a Hanovia 150-W high-pressure mercury vapor lamp, 3650 Å filter (Oriol #6-572-3650), lens system, and mechanical shutter. The solution was degassed by a conventional²⁴ freeze-thaw technique under high vacuum. After each period of irradiation, the solution was agitated for several minutes, and the absorption spectrum was measured with the Cary 14R spectrometer. Measurements were made between 2 and 40% conversion of 1. Immediately before and after each run, a 6 × 10⁻³ M solution of potassium ferrioxalate was irradiated in the same cell for 60 sec. A 10.00-ml aliquot of this irradiated solution was withdrawn and transferred to a 25.00-ml volumetric flask. After the addition of 5.0 ml of a buffer solution and 2 ml of 1,10-phenanthroline solu-

(38) C. Djerassi, H. Budzikiewicz, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(39) Gas-liquid chromatography of A was carried out with an Aerograph Autoprep Model 700 equipped with a 6-ft column containing 10% silicone oil (SF96) on 60/80 firebrick. A column temperature of 110° and a flow rate of 100 ml of He per minute was used.

tion, the solution was made to volume and the absorbance at 5100 Å was measured. The number of ferrous ions produced per unit time was then determined from a standard calibration graph prepared by the reported procedure.²⁴

Luminescence Studies.—The luminescence spectra were prepared with apparatus similar to that which was previously described.²⁴ The degassed solutions [conventional freeze (−78°C)–thaw (25°C) technique] were contained in 1.00-cm quartz cells which were sealed under vacuum.

Registry No.—1, 5253-87-2; 2, 4599-96-6; 3, 5254-01-3; 4, 35191-44-7; 8, 35140-90-0; dimethyl 1,2-dideuterio-5,6-acenaphthenedicarboxylate, 35140-91-1; diisopropyl 5,6-acenaphthenedicarboxylate, 35140-92-2; 5,6-acenaphthenedicarboxylic acid di-*p*-methoxyanilide,

35140-93-3; diethyl 5,6-acenaphthenedicarboxylate, 35140-94-4.

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The Photochemistry of Aryl Alkyl Carbonates. II. The Methoxyphenyl Ethyl Carbonates

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The photochemical reaction of the three methoxyphenol ethyl carbonates has been examined. Each of the compounds undergoes a photo-Fries type of reaction to produce methoxyhydroxybenzoates. A free-radical mechanism is proposed based on the substitution patterns observed in the products and on the quantum yields of the reactions. A minor reaction observed was the apparent free-radical displacement of the methoxy group by the carboethoxy radical to produce the corresponding hydroxybenzoate.

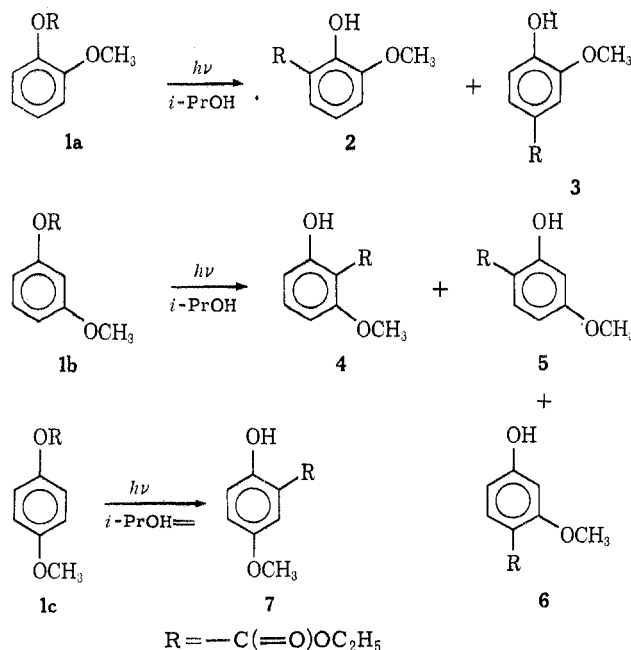
As part of our continuing study of the photochemistry of the aryl alkyl carbonates,² we would like to report our observations on the photolysis of the methoxyphenyl ethyl carbonates. Several investigators have shown that phenyl ethyl carbonate undergoes a photo-Fries type of reaction to give ethyl salicylate and ethyl *p*-hydroxybenzoate.^{2,3} In contrast with this, we have shown that the chlorophenyl ethyl carbonates do not undergo the photo-Fries type of reaction, but instead undergo photodechlorination.² However, the methoxyphenyl ethyl carbonates do undergo a photo-Fries type of reaction and, in addition, an apparent free-radical displacement of the methoxy group also occurs.

Results

o-, *m*-, and *p*-methoxyphenyl ethyl carbonate (1a–c) have been photolyzed in isopropyl alcohol, and the major reaction products are indicated as follows. In addition to the photo-Fries products obtained in this reaction, there is also obtained in each case a product that results from the substitution of the carboethoxy group (−COOC₂H₅) for the methoxyl group.

***o*-Methoxyphenyl Ethyl Carbonate (1a).**—Two photo-Fries-type products were isolated from the reaction mixture ethyl 2-hydroxy-3-methoxybenzoate (2), constituting about 10% of the reaction mixture, and ethyl 4-hydroxy-3-methoxybenzoate (3), constituting about 13% of the reaction mixture (see Table I). The remainder of the reaction mixture was mostly unreacted starting material.

Compound 2 was obtained by preparative gas-liquid partition chromatography (glpc) and its structure was ascertained through the use of nmr, ir, and mass spectroscopy (ms). The second photo-Fries-type product isolated was ethyl vanillate (3), a well-



characterized compound. A sample isolated from the reaction mixture by preparative glpc was identical in all respects to an authentic sample of ethyl vanillate. The presence of ethyl salicylate in the reaction mixture was shown by the identity of its mass spectrum with that of an authentic sample of ethyl salicylate.

(1) Abstracted from the Ph.D. Thesis of Ira Rosenberg, The George Washington University, 1969.

(2) Part I: E. Caress and I. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971).

(3) C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 1392 (1964); C. Pac, S. Tsutsumi, and H. Sakurai, *Kogyo Kagaku Zasshi*, **72** (1), 224 (1969).