The Effect of Substituents on the Rate of Formation of Substituted Anthraquinones[1,2]

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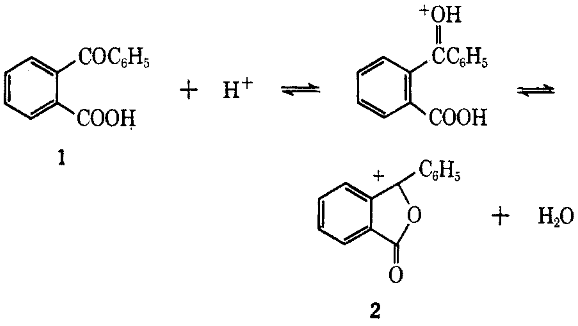
The effect of both electron-withdrawing and electron-donating substituents at various positions in 2-benzoylbenzoic acid on the rate of formation of substituted anthraquinones has been studied. Reactivity patterns which emerge from these data are considered.

The conversion of *o*-benzoylbenzoic acid to anthraquinone has been investigated extensively under preparative conditions because of its industrial importance. However, there has been little study of the detailed kinetics of the reaction. Dougherty and Gleason[5] found that the yield of substituted anthraquinones under standard reaction times was sensitive to substituents in the benzoyl moiety, particularly in the 3′ position. Other studies[6-9] were concerned with the effect of sulfuric acid concentration on the rate of reaction and possible correlations with the acidity function. Oda and Tamura[10] reported rate data for five compounds at various temperatures and noted that 2-(4-methylbenzoyl)benzoic acid reacts more slowly in concentrated sulfuric acid than *o*-benzoylbenzoic acid. Recently, Vinnik, Ryabova, and Chirkov[11] reported a particularly careful study of the variation of rate with both temperature and sulfuric acid concentration, pointing out that the reaction rate should be correlated not with H_0, but with J_0 (or C_0).

In polyphosphoric acid, Downing and Pearson[12] have measured the rate of formation of anthraquinone. They note that the rate reaches a maximum in polyphosphoric acid (near 80% P_2O_5 content) and that under these conditions *o*-benzoylbenzoic acid reacts about five times more rapidly than 2-(4-methylbenzoyl)benzoic acid and about 70 times more rapidly than 2-(4-chlorobenzoyl)benzoic acid. It is to be noted that the rate constants reported by Downing and Pearson are, within a factor of 3, the same as those observed in 98% sulfuric acid in spite of the other very striking differences in the two acidic media. This agreement strongly supports the conclusion that the cyclization is an intramolecular reaction of the lactol carbonium ion.

We have previously reported[1,13] our studies of the effect of substituents on the complex ionization of **1**, which support Newman's[14] suggestion that the behavior of 2-benzoylbenzoic acid (**1**) in concentrated sulfuric acid is best represented by eq 1, involving protonation

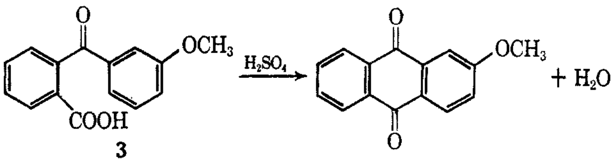


(1)

on the ketone (in about 80% sulfuric acid) followed by a second stage involving loss of water (occurring in more concentrated sulfuric acid) to give the lactol carbonium (**2**).

Results

2-(3-Methoxybenzoyl)benzoic acid (**3**) reacts rapidly in concentrated sulfuric acid at room temperature to form 2-methoxyanthraquinone (**4**) (eq 2); no 1-methoxyanthraquinone could be detected. Data for the rate of formation of **4** are given in Table I. The data are best examined in three portions. First to be noted is that in sulfuric acid more concentrated than 97% the reaction rate does not increase appreciably even though the acidity changes sharply. This corresponds to the region in which the predominant species in solution is the lactol carbonium ion (C^+). In the region of 85–95% sulfuric acid, the reaction rate increases in parallel to the changing activity of water in the medium; this corresponds to the region of acidity in which the predominant species in solution is the salt of 2-(3-methoxybenzoyl)benzoic acid (BH^+). Below 80% the reaction rate changes very sharply; this corresponds to the region in which the predominant species in solution is the unprotonated keto acid.



(2)

Assuming that the reaction sequence is properly represented by eq 3–6, it is possible to derive eq 7, which rep-

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[1] Previous paper, D. S. Noyce and P. A. Kittle, *J. Org. Chem.*, **30**, 1899 (1965).

[2] Supported in part by Grants NSF-G 13125 and G.P. 1572 from the National Science Foundation.

[3] National Science Foundation Cooperative Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1962–1963.

[4] Taken from the dissertation of P. A.K. submitted in partial satisfaction of the requirements for the Ph.D., 1963.

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[10] R. Oda and K. Tamura, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **32**, 263 (1937); *cf. Chem. Abstr.*, **31**, 8330 (1937); R. Oda and K. Tamura, *Bull. Inst. Phys. Chem. Research* (Tokyo), **16**, 984 (1937); *cf. Chem. Abstr.*, **32**, 5631 (1938).

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[13] D. S. Noyce and P. A. Kittle, *J. Org. Chem.*, **30**, 1896 (1965).

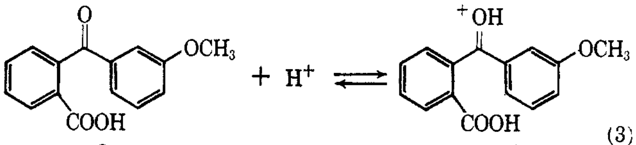
[14] M. S. Newman, *J. Am. Chem. Soc.*, **64**, 2324 (1942).

TABLE I

RATE OF FORMATION OF 2-METHOXYANTHRAQUINONE FROM 2-(3-METHOXYBENZOYL)BENZOIC ACID

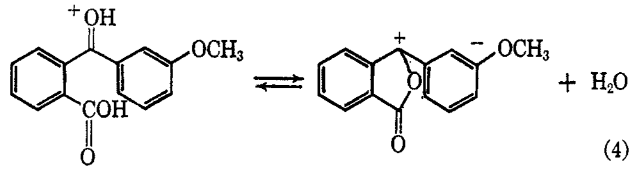
H_2SO_4, %	H_0	$H_{0\,50}$[a]	k_{obsd}, sec^{-1}	Log a_{H_2O}	Method[b]	Log k	Log [C$^+$]	R[c] (S)[d]
			Temperature, 25.00°					
86.98	−8.44		$1.60 \pm 0.05 \times 10^{-5}$	−3.19	A	−4.796	−2.10	−2.27
89.49	−8.84		$4.30 \pm 0.15 \times 10^{-5}$	−3.56	A	−4.367	−1.72	−2.31
92.70	−9.43		$1.98 \pm 0.05 \times 10^{-4}$	−4.05	A	−3.704	−1.24	−2.22
94.21	−9.71		$3.34 \pm 0.15 \times 10^{-4}$	−4.31	A	−3.476	−0.99	−2.29
95.48	−9.94		$7.51 \pm 0.21 \times 10^{-4}$	−4.57	B	−3.124	−0.76	−2.21
96.91	−10.19		$2.22 \pm 0.07 \times 10^{-3}$	−4.92	B	−2.674	−0.50	−2.08
97.91	−10.39		$3.32 \pm 0.10 \times 10^{-3}$	−5.25	B	−2.479	−0.30	−2.12
98.82	−10.62		$4.08 \pm 0.04 \times 10^{-3}$	−5.74	B	−2.390	−0.12	−2.24
98.82	−10.62		$3.48 \pm 0.02 \times 10^{-3}$	−5.74	B	−2.458	−0.11	−2.31
98.82	−10.62		$4.20 \pm 0.1 \times 10^{-3}$	−5.74	B	−2.377	−0.12	−2.23
99.76	−11.70		$6.77 \pm 0.09 \times 10^{-3}$	−6.93	B	−2.169	−0.01	−2.15
100.1	−12.3		$7.54 \pm 0.11 \times 10^{-3}$	−9.02	B	−2.123	−0.0	−2.12
			Temperature, 50.00°					
65.12	−5.10	−4.99	$8.17 \pm 0.4 \times 10^{-8}$	−0.96	C	−7.092	−6.39	(−0.70)
70.15	−5.82	−5.70	$2.20 \pm 0.09 \times 10^{-7}$	−1.25	C	−6.658	−5.41	(−1.25)
76.39	−6.77	−6.64	$5.06 \pm 0.32 \times 10^{-6}$	−1.73	A	−5.296	−4.10	(−1.20)
82.07	−7.67	−7.51	$5.51 \pm 0.15 \times 10^{-5}$	−2.33	A	−4.259	−3.06	(−1.21)
84.03	−7.98	−7.80	$1.57 \pm 0.07 \times 10^{-4}$	−2.56	B	−3.801	−2.71	(−1.09)
86.98	−8.44	−8.26	$4.06 \pm 0.12 \times 10^{-4}$	−2.94	A	−3.392	−2.33	(−1.06)
89.49	−8.84	−8.65	$1.33 \pm 0.12 \times 10^{-3}$	−3.28	A	−2.876	−2.00	(−0.88)
94.21	−9.71	−9.50	7.00×10^{-3}	−3.98	B	−2.155	−0.73	(−1.42)

[a] Temperature corrections of A. I. Gelbstein, G. G. Schleglova, and M. I. Temkin [*Zh. Neorgan. Khim.*, **1**, 282 (1956)] applied to H_0 scale of M. J. Jorgenson and D. R. Hartter [*J. Am. Chem. Soc.*, **85**, 878 (1963)]. [b] The following methods were used in rate measurements. A. A 2.54×10^{-5} *M* solution of **3** in sulfuric acid was used. The change in absorbance at λ 2950 A was followed. B. For fast reactions a small amount of solid **3** was rapidly dissolved in sulfuric acid of the appropriate concentrations and the change in absorbance at 2950 A followed. C. A 2.54×10^{-5} *M* solution of **3** in sulfuric acid was used. The change in absorbance at 2750 A was followed. [c] $R = \log k - 1.2 \log [C^+]$; $R = -2.21 \pm 0.06$. [d] $S = \log k - \log [C^+]$; $S = -1.10 \pm 0.2$.



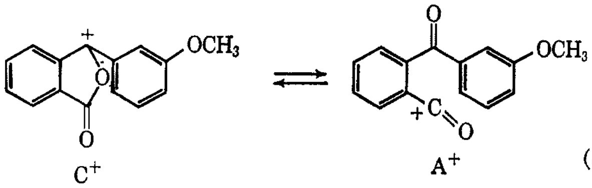
3 SH$^+$ (3)

where $K_{SH^+} = \dfrac{[3]a_{H^+}}{[SH^+]}$



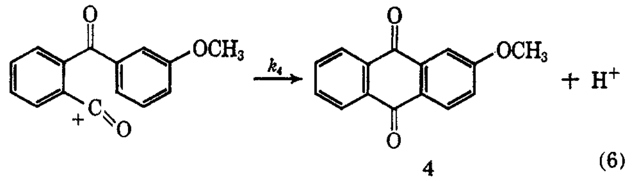
SH$^+$ C$^+$ (4)

where $K_{C^+} = \dfrac{[SH^+]}{[C^+]a_{H_2O}}$



C$^+$ A$^+$ (5)

where $K_{A^+} = \dfrac{[A^+]}{[C^+]}$



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$$[C^+] = h_0/(K_{SH^+}K_{C^+}a_{H_2O} + h_0 + K_{C^+}a_{H_2O}h_0) \qquad (7)$$

resents the concentration of the lactol carbonium.[15] From eq 6, then, the expected rate is given by eq 8.

$$k_4[A^+] = k_4K_{A^+}[C^+] \qquad (8)$$

Thus the manner in which the fraction of **3** present as the lactol carbonium ion responds to changing sulfuric acid concentrations is characterized by three different situations. When the acidity is high enough and water activity is sufficiently low, all **3** is present as C$^+$. This situation prevails above 97% sulfuric acid. In an intermediate region (85–95% sulfuric acid) the fraction of C$^+$ present is controlled largely by the activity of water and at lower acidities the fraction of C$^+$ is controlled both by acidity and activity of water (corresponding to J_0).

In column 6 of Table I we have calculated the fraction of **3** present as the lactol carbonium ion using values for $\log K_{C^+} = -5.25$ and $\log K_{BH^+} = -7.09$. From a plot of the logarithm of the observed rate of formation of **4** at 25° against this logarithm of the fraction of lactol carbonium ion present (log [C$^+$]), a sensibly straight line is obtained over the region of 86–99% sulfuric acid with a slope of 1.2. Thus, these data are represented by eq 9. The fact that the best

$$\log k_{obsd} - 1.2 \log [C^+] = -2.21 \qquad (9)$$

correlation as represented by eq 7 is not given with unit slope, but with a slope of 1.2, reflects the problem with activity coefficients. Similar treatment of the data at 50° results in eq 10, which now encompasses

$$\log k - \log [C^+] = -1.10 \pm 0.2 \qquad (10)$$

nearly a millionfold change in the fraction of lactol carbonium ion present.

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[15] For the sake of clarity, the melange of activity coefficients in eq 7 has been omitted. This corresponds to the practice of discarding them in making correlations with the acidity function H_0.

Vinnik, Ryabova, and Chirkov[11] have treated the rate data for the parent compound (1) in similar manner with success. Vinnik and his co-workers[16] have also examined data for two other compounds, 2-(3′,4′-dimethylbenzoyl)benzoic acid[16a] and 2-(4′-methylbenzoyl)benzoic acid.[16b] Somewhat analogous situations have been discussed by Shechter[17] in dealing with the acidity dependence of the Schmidt reaction and Shechter derives a very similar relationship which successfully predicts the rate behavior of a variety of hindered aromatic acids.

Other Compounds.—In Table II we present data for the rate of formation of anthraquinone from **1**. These data correspond very closely to the data reported by Vinnik, *et al.*[11] Also included in Table II are more limited data on several substituted benzoylbenzoic acids. The rates reported in Table II, taken in conjunction with our previously reported values for the basicity constants[13] and equilibrium constants for the formation of the appropriate lactol carbonium ion,[1] make possible a fairly complete prediction of the rates of formation of substituted anthraquinones under a variety of conditions. In the following sections we discuss the more cogent conclusions to be drawn from these data.

TABLE II

RATE OF FORMATION OF SUBSTITUTED ANTHRAQUINONES FROM BENZOYLBENZOIC ACIDS UNDER VARIOUS CONDITIONS

Compound	H_2SO_4, %	Temp, °C	k_{obsd}, sec^{-1}
2-benzoylbenzoic	86.98	80.00	1.98×10^{-5}
acid **1**	86.98	100.00	2.58×10^{-4}
	89.49	80.00	5.32×10^{-5}
	91.93	80.00	1.02×10^{-4}
	94.21	80.00	1.72×10^{-4}
	96.19	80.00	3.09×10^{-4}
	97.04	80.00	3.41×10^{-4}
	99.80	80.00	3.98×10^{-4}
	99.80	50.00	1.54×10^{-5}
5-Nitro-2-benzoyl-	96.19	50.00	9.76×10^{-7}
benzoic acid	100.1	50.00	7.87×10^{-5}
	95.48	60.00	4.57×10^{-6}
	100.1	60.00	1.67×10^{-4}
4-Nitro-2-benzoyl-	96.19	50.00	3.28×10^{-6}
benzoic acid	100.1	50.00	9.84×10^{-5}
	95.48	60.00	1.06×10^{-5}
	100.1	60.00	1.92×10^{-4}
5-Methoxy-2-benzoyl-	96.19	60.00	3.77×10^{-6}
benzoic acid	98.36	100.00	3.83×10^{-4}
2-(4-Methylbenzoyl)-	99.80	50.00	3.70×10^{-6}
benzoic acid	98.36	80.00	9.83×10^{-5}
2-(3-Methylbenzoyl)-	99.76	25.00	1.01×10^{-4}
benzoic acid	95.48	50.00	9.55×10^{-4}

Effect of Substituents in the Benzoyl Ring.—The rate of formation of substituted anthraquinones from benzoylbenzoic acids substituted in the benzoyl ring is summarized in Table III. All rates have been extrapolated to 25.0° and are calculated for reaction in 99–100% sulfuric acid. In this medium, the benzoylbenzoic acid has been converted to the lactol carbonium ion.

TABLE III

RATE OF CYCLIZATION OF 2-(X-BENZOYL)BENZOIC ACIDS AT 25° IN SULFURIC ACID

X	k_{obsd}, sec^{-1}	Relative rate
H	6.20×10^{-7} [a]	1.00
	6.1×10^{-7} [b]	
3′-Methoxy	6.7×10^{-3}	10,800
4′-Methoxy	$<10^{-9}$ [c]	<0.0016
3′-Methyl	1.01×10^{-4}	164
4′-Methyl	1.59×10^{-7} [d]	0.25
	1.52×10^{-7} [b]	
3′,4′-Dimethyl	1.37×10^{-5} [e]	22
4′-Chloro	$\sim 2 \times 10^{-9}$ [d]	<0.003

[a] Value[11] extrapolated from data at higher temperatures. [b] Extrapolated from the data in Table II. [c] Extrapolated from fragmentary studies in these laboratories at 80° by assuming a reasonable E_a. [d] Reference 16b. [e] Reference 16a.

The results show the expected strong dependence upon the electron-donating ability of substituents in the 3′ position. Using σ^+ substituent constants, ρ can be evaluated from the data for the three compounds 3′-methoxy, 3′-methyl, and H and ρ is about -5. More striking is the observation that introduction of a 4′-methyl group causes a decrease in the observed rate of anthraquinone formation. This phenomenon is observed in both cases recorded in Table III.

If one recognized that the observed rate constant is properly given by eq 11, the reasons for this observation become much clearer.

$$k_{\mathrm{obsd}} = K_{\mathrm{A}}k_4 \qquad (11)$$

The equilibrium constant K_A is for the equilibrium of the lactol carbonium ion with the open-chain acylium ion. This equilibrium favors the lactol carbonium ion. Introduction of carbonium ion stabilizing groups in the 4′ position has the effect of stabilizing the lactol carbonium ion *vis-à-vis* the open-chain acylium ion. Hence, the net result is a substantial decrease in the value of K_A and little change in the value of k_4. Downing and Pearson[12] reach similar conclusions regarding the cyclization reactions in polyphosphoric acid. The situation described here is in some respects similar to that discussed by White and his co-workers[18] and by Goering and Jacobson[19] for the Claisen rearrangement. Jaffé[20] has also discussed the possibilities of the nature of the Hammett correlation when two positions of the aromatic ring are involved in the reaction under discussion.

Effect of Substituents in the Acid Ring.—Turning now to the effects of substituents in the phthaloyl ring, the influence of these substituents is much more modest. 2-Benzoyl-5-methoxybenzoic acid reacts more slowly than the parent compound, while 2-benzoyl-5-nitrobenzoic acid reacts more rapidly. Data for the rate of cyclization of these three substances are collected in Table IV and extrapolated to common conditions and conditions where the lactol carbonium ion is the nearly exclusive species in solution. Again these data show that the influence of the substituent upon the stability

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(16) (a) M. I. Vinnik, R. S. Ryabova, and G. B. Belova, *Russ. J. Phys. Chem.*, **36**, 495 (1962); *Zh. Fiz. Khim.*, **36**, 942 (1962). (b) R. S. Ryabova and M. I. Vinnik, *Russ. J. Phys. Chem.*, **37**, 1364 (1963); *Zh. Fiz. Khim.*, **37**, 2529 (1963). (c) M. I. Vinnik, R. S. Ryabova, Zh. E. Grabovskaya, Kh. Koslov, and I. Kyubar, *Russ. J. Phys. Chem.*, **37**, 44 (1963); *Zh. Fiz. Khim.*, **37**, 94 (1963).

(17) H. Shechter, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 4P.

(18) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958); W. N. White and C. D. Slater, *J. Org. Chem.*, **27**, 2908 (1962).

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(20) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

TABLE IV

RATE OF FORMATION OF SUBSTITUTED ANTHRAQUINONE FROM 2-BENZOYL-5-X-BENZOIC ACIDS AT 60°

X	H_2SO_4, %	k_{obsd}, sec^{-1}
H	99.80	4.0×10^{-5} [a]
H	99.10	4.2×10^{-5} [b]
OCH_3	96.19	3.77×10^{-6}
NO_2	100.1	1.67×10^{-4}

[a] Interpolated from Table II. [b] Reference 11.

of the lactol carbonium ion is an important feature which must be considered in evaluating the reaction sequence. The lactol carbonium ion formed from 2-benzoyl-5-nitrobenzoic acid is less stable than that formed from 2-benzoylbenzoic acid; it requires substantially higher concentrations of sulfuric acid to cause its formation, as may be seen from the data of Table I in ref 1. Once formed it is more reactive; hence the rate of formation of 2-nitroanthraquinone from 2-benzoyl-5-nitrobenzoic acid is larger. This implies that the formal positive charge is moving away ("retreating") from the ring bearing the nitro group at the activated complex. This is, of course, completely consistent with the results and interpretation in the previous section.

Finally, the rate data for 2-benzoyl-4-nitrobenzoic acid help to delineate the situations under which the Hayashi rearrangement need be considered. The fact that the rate for the 4-nitro isomer is distinctive from the 5-nitro isomer shows that the Hayashi rearrangement does not intrude in this case.[21] It would appear from a consideration of the examples in the literature that the Hayashi rearrangement is largely restricted to 3- or 6-substituted 2-benzoylbenzoic acids or to situations in which the point of attachment of the phthaloyl moiety to the other aromatic system is a strongly activated aromatic site.

Experimental Section

The preparation of all materials used in this study has been previously described.[13]

Kinetic Procedures.—Reaction rates were followed by ultraviolet absorption spectroscopy. For runs at temperatures above 50°, the usual sealed-tube technique was used. At temperatures of 50 and 25°, the reactions were followed directly with a Beckman DU spectrophotometer using 1.0-cm cells and a thermostated cell block. The wavelength chosen was selected to give the largest change in absorbance. The spectrum of the reaction mixture on completion matched that of the appropriate anthraquinone.

Registry No.—**1**, 85-52-9; **3**, 2159-36-6; **4**, 3274-20-2; 5-nitro-2-benzoylbenzoic acid, 2159-46-8; 4-nitro-2-benzoylbenzoic acid, 2158-91-0; 5-methoxy-2-benzoylbenzoic acid, 2159-48-0; 2-(4-methylbenzoyl)benzoic acid, 85-55-2; 2-(3-methylbenzoyl)benzoic acid, 2159-37-7; 2-(4′-methoxybenzoyl)benzoic acid, 1151-15-1.

(21) An excellent discussion of the factors involved in the Hayashi rearrangement is given by M. S. Newman and K. G. Ihrman, *J. Am. Chem. Soc.*, **80**, 365 (1958).

Photochemical Reactions of Mesityl Oxide in 2-Propanol

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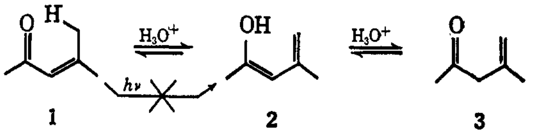
Irradiation of mesityl oxide in boiling 2-propanol with a low-pressure mercury–argon source yielded 4-methyl-2-pentanone, a furanol (**9**), and a dihydrofuran (**10**) among other products. The reaction was apparently initiated by the photodecomposition of 2-propanol by 1849-A emission of the light source. Irradiation of mesityl oxide in methanol yielded similar results.

α,β-Unsaturated aliphatic ketones undergo *cis–trans* isomerization under the influence of ultraviolet light, but are otherwise considerably less reactive than their saturated analogs.[2-4] Phorone[5] and some α,β-unsaturated ketones with secondary and tertiary γ hydrogens undergo photodeconjugation and β-*t*-butyl α,β-unsaturated ketones undergo photocyclization to give acetonylcyclopropanes.[6]

Mesityl oxide (**1**) possessing two groups of active allylic γ hydrogens may be expected to undergo a photodeconjugation by a mechanism analogous to the type II process. The product would be an enol (**2**) which may ketonize to its β,γ isomer, isomesityl oxide (**3**) (eq 1). The acid-catalyzed isomerization of mesityl oxide to isomesityl oxide occurs readily[7] and pure mesityl oxide, after extended storing at room temperature, is isomerized to an equilibrium mixture of the two isomers. However, mesityl oxide does not undergo a photochemical isomerization, no isomesityl oxide was found, and no loss of starting material was detected under a variety of conditions.[3] Only when a low-pressure mercury–argon quartz lamp was used as the light source did the photolysis of mesityl oxide prove to be successful. This lamp effects extensive photolysis of simple alcohols, indicating that a substantial amount of the 1849-A emission of mercury was transmitted.[8] Under comparable conditions, no photolysis was detected with a similar lamp constructed with Vycor



1 2 3 (1)

[1] The authors wish to acknowledge the U. S. Atomic Energy Commission for the support of this work, Contract No. AT(11-1)-1043. The authors also wish to thank the National Science Foundation and the Louis P. Block Fund of the University of Chicago for grants to purchase the mass spectrometer and the nmr spectrometer used in this work.

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