The Thermal and Photolytic Decomposition of 2,3-Diazido-1,4-naphthoquinone and Certain Related Azidoquinones

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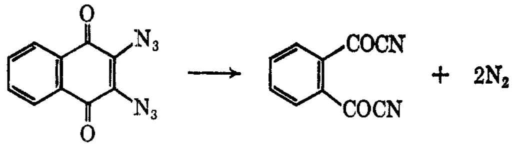
Phthaloyl cyanide was prepared by the decomposition of 2,3-diazido-1,4-naphthoquinone (1) by means of heat or light. The rates of thermal decomposition of 1 and of some related azidoquinones in boiling toluene were determined. The quantum yield for the photolytic decomposition of 1 was 1.04 ± 0.1. Phthaloyl cyanide was photolyzed in ether solution.

The decomposition of solutions of 2,3-diazido-1,4-naphthoquinone (1) by means of heat or light results in a reaction product which is assigned the structure 2.



1 2

The thermal decomposition of 1 was carried out in boiling toluene or xylene. The product (2) was easily hydrolyzed, and if precautions were not taken to exclude moisture during the thermolysis or photolysis, the main product was phthalic anhydride (3) and the secondary product was 2.

Blackstone[1] prepared a compound which he thought was phthaloyl cyanide (2) from phthaloyl chloride and mercuric cyanide. The product was reported to melt at about 300°, its solubility in organic solvents was poor, and it was stable to hot concentrated hydrochloric acid. These data suggest that the material prepared by Blackstone was a polymer rather than 2, and recently it was suggested by Hertler[2] that the material which Blackstone prepared from terephthaloyl chloride and mercuric cyanide was a polymer rather than the *para* isomer of 2. The facts that the nitrile we obtained has properties similar to those of the *para* isomer described by Hertler,[2] that it is readily converted into phthalic anhydride by recrystallization from water, and that physical data, such as the infrared spectrum (carbonyl absorption at 5.83 and 5.91 and cyano absorption at 4.46 μ), nmr spectrum (singlet at δ 8.04), and elemental analysis, are in accord with structure 2 leave little doubt that we have an authentic sample of phthaloyl cyanide (2).

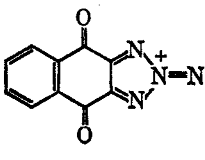
The thermal decomposition of 1 and of the related 2-azido-1,4-naphthoquinone (4) and 2-azido-3-chloro-1,4-naphthoquinone (5) in dry solvents occurs with conveniently measurable rates in the range of 90–120°. This temperature range is much lower than that reported for α-azido ketones,[3] 180–220°, and also considerably lower than the decomposition range for *o*-diazidobenzene,[4] 160–170°. The low thermal stability of the azidoquinone is probably due to the fact that these compounds are vinylogs of acyl azides. Acyl azides have been found[5] to decompose with comparable rates at slightly lower temperatures than those characteristic of the quinone azides.

The rates of thermal decomposition of the azidonaphthoquinones, which were measured by means of a nitrometer connected to a rocking thermostated vessel,[6] were accurately first order in terms of nitrogen evolution over the entire range. Rate data for the thermal decomposition in *m*-xylene of 1, 4, and 5 are shown in Table I. Qualitative thermolysis rates of 2,3-diazido-5,6-dimethylbenzoquinone (6) and 2-azido-3-methoxy-1,4-naphthoquinone (7) in boiling toluene were found to be similar to those for the related compounds shown in Table I. The qualitative rates were determined by the disappearance of the characteristic red color of 6 and 7. The products which were obtained by the thermolysis of 4, 5, 6, and 7 were not characterized.

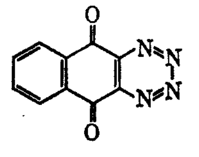
Table I
Rates of Thermolysis

Species	Concn, mol/l. $\times 10^2$	Temp, °C	Rate (±5%), sec^1 $\times 10^4$	E_a, kcal/mol	Log *A*
1	1.2	85.0	0.140	27	12.63
		94.5	0.476		
		100.0	0.772		
		106.5	1.24		
		110.0	2.24		
		120.0	4.49		
4	1.2	90.0	0.221	26	12.11
		94.5	0.399		
		100.0	0.783		
		105.0	1.15		
		110.0	2.58		
		120.0	3.78		
5	1.2	110.0	0.66		

During the thermolysis or photolysis of 1 in inert dry solvents, there was no spectrophotometric evidence of the presence, in significant amounts, of an intermediate, such as A or B, which could result from



A



B

the decomposition of a single azide group. Structures similar to A and B have been postulated as intermediates during the decomposition of *o*-diazidobenzene.[4] The quantum yield for the decomposition of 1 was 1.04 ± 0.1, as determined in dry benzene with

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[1] G. Blackstone, *J. Amer. Chem. Soc.*, **34**, 1080 (1912).

[2] W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *ibid.*, **84**, 3387 (1962).

[3] J. Boyer and D. Straw, *ibid.*, **74**, 4506 (1952); **75**, 1642, 2633 (1953).

[4] J. Hall, *ibid.*, **87**, 1147 (1965).

[5] Y. Yukawa and Y. Tsuno, *ibid.*, **79**, 5530 (1957).

[6] T. Fugley, J. Sutter, and R. Oglukion, *ibid.*, **78**, 5567 (1956).

TABLE II

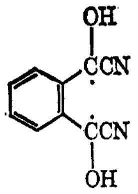
ANALYTICAL AND SPECTRAL DATA

Compd	Empirical formula	Mp, °C	Solvent of crystallization	Calcd over found, % C	H	N	% yield	Electronic spectra, λ (ε × 10^{-3})	Solvent
2	$C_{10}H_4N_2O_2$	103	Ligroin (bp 100–115°)	65.3	2.2	15.2	52	228 (6.3)	
				65.5	2.1	15.0		277 (5.2)	Acetonitrile
4	$C_{10}H_5N_3O_2$	118 dec	Ethanol	60.3	2.5	21.1	85	257 (18.4)	
				60.4	2.8	20.9		296 (14.1)	Methanol
								344 (3.7)	
5	$C_{10}H_4ClN_3O_2$	115	Ethanol	51.4	1.7	18.0	60	404 (2.5)	Chloroform
				51.2	2.0	17.9			
6	$C_8H_6N_6O_2$	75	Ligroin (bp 70–79°)	44.0	2.8	38.5	60	430 (2.4)	Methanol
				43.9	3.1	38.6			
7	$C_{11}H_7N_3O_3$	94	Methanol	57.7	3.0	18.3	71	342 (2.5)	
				57.5	2.9	18.5		430 (2.2)	Acetonitrile

light of 437-mμ wavelength. The measurements were made by following the disappearance of the 455-mμ band of **1** under conditions where the light[7] was totally absorbed by **1**. The amount of light absorbed was determined by ferrioxalate actinometry[8] in parallel experiments.

Several attempts were made to photolyze **1** in aqueous alcohol or dioxane, but the rate of the reaction was much slower than when dry benzene was used as the solvent. The decrease in rate was due to the formation of a red, unidentified product which functions as an internal filter. This species was also photosensitive but disappeared much more slowly than **1**.

The illumination of **2** in ethyl ether resulted in a rapid disappearance of the 270-mμ absorption peak of **2**. The products of this photoreaction have not been identified, but they appear to be largely polymeric. It seems likely on the basis of the recent findings of Raaen,[9] that a photoreduction of **2** proceeds through the radical **8**.



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Experimental Section

The analytical and spectral data for the compounds are collected in Table II.

2,3-Diazido-1,4-naphthoquinone (**1**) was prepared by the method of Fries and Ochwatt[10] and showed absorption (in acetonitrile) at 455 mμ (ε 4200).

Phthaloyl Cyanide (**2**).—A mixture of 100 ml of toluene, 3 g of Linde Type 3A Molecular Sieves, and 5 g of diazidonaphthoquinone (**1**) was refluxed until no more gas was evolved (about 10 min). The reaction mixture was cooled to room temperature and filtered, the filtrate was evaporated to dryness *in vacuo*, and the residue was recrystallized.

The infrared spectrum of **2** showed an absorption at 4.46 μ for the cyano group and strong carbonyl absorption at 5.83 and 5.91 μ. A once crystallized sample contained a small amount of phthalic anhydride as shown by a weak absorption at 5.42 and 5.63 μ. The latter peaks were eliminated when the sample was recrystallized three times from anhydrous petroleum ether (bp 100–115°) in a drybox.

The nmr spectrum of **2** at 60 MHz in deuteriochloroform with tetramethylsilane as an internal standard showed a single peak at δ 8.04 with a width of 3 Hz at half-height. The single peak is due to accidental equivalence of the two pairs of protons.

A solution of 1 g of **2**, 50 ml of toluene, and 0.1 ml of water was refluxed for 15 min and then evaporated to dryness. The residue was a mixture of **2** and phthalic anhydride. When more water was used and the heating period extended to 1 hr, the only material that was isolated was phthalic acid.

2-Azido-1,4-naphthoquinone (**4**).—A solution of 1.2 g of sodium azide in 5 ml of water was added to 2.5 g of 2-chloro-1,4-naphthoquinone and the mixture was stirred at 90–100° for 5 min. The mixture was cooled and the precipitate was collected, washed with water, and crystallized.

Alternatively, 2,3-dichloro-2,3-dihydronaphthoquinone[11] can be substituted for 2-chloro-1,4-naphthoquinone in the procedure to give **4**, in 46% yield.

2-Azido-3-chloro-1,4-naphthoquinone (**5**).—Sodium azide (2.86 g) dissolved in a minimum of water was added all at once, with vigorous stirring, to 10 g of 2,3-dichloro-1,4-naphthoquinone which was dissolved completely in dimethylformamide. After the product had been stirred for 15 min, it was precipitated with water to give 6.2 g of **5**.

2,3-Dichloro-5,6-dimethyl-1,4-benzoquinone.—A solution of 25 g of 2,3-dimethyl-1,4-benzoquinone and 9.5 g of iodine in 250 ml of glacial acetic acid was heated at 90–100° while chlorine gas was passed through for 1 hr. The purple semiquinone precipitated. A solution of 4.5 g of potassium bromate in water was added to the reaction mixture, with vigorous stirring, and the mixture, which became yellow immediately, was cooled and diluted with 500 ml of water. The yellow precipitate was collected and crystallized from ethanol to give 87% yield of product, mp 168°.

Anal. Calcd for $C_8H_6Cl_2O_2$: C, 46.9; H, 29.0. Found: C, 46.9; H, 30.0.

2,3-Diazido-5,6-dimethyl-1,4-benzoquinone (**6**).—A solution of 5 g of sodium azide in the minimum amount of water was added to a solution of 5 g of 2,3-dichloro-5,6-dimethylbenzoquinone in 50 ml of ethanol, and the mixture was diluted with water. The solid was collected and recrystallized.

2-Chloro-3-methoxy-1,4-naphthoquinone.—A solution of 11.3 g of 2,3-dichloro-1,4-naphthoquinone and 9.0 g of sodium acetate in 100 ml of methanol was heated for 4 hr and cooled; the solid which separated was collected by filtration, washed with water, and crystallized from acetic acid to give 7.2 g (65%) of product, mp 153°.

Anal. Calcd for $C_{11}H_7ClO_3$: C, 59.4; H, 3.1. Found: C, 59.6; H, 3.0.

2-Azido-3-methoxy-1,4-naphthoquinone (**7**).—The following procedure is a modification of the method of Mosby and Silva.[12] A solution of 4.4 g of 2-chloro-3-methoxy-1,4-naphthoquinone in 100 ml of methanol was heated with 2.0 g of sodium azide in 20 ml of water. After the reaction mixture had been treated it was filtered hot, and the filtrate was cooled, to give 3.2 g of **7**.

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(7) The light source was the output of a Bausch and Lomb "high-intensity" monochromator with a 200-W mercury source.

(8) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, **235**, 518 (1956).

(9) V. F. Raaen, *J. Org. Chem.*, **31**, 3310 (1966).

(10) K. Fries and P. Ochwatt, *Ber.*, **56**, 1299 (1923).

(11) T. Zincke and M. Schmidt, *ibid.*, **27**, 2753 (1894).

(12) W. L. Mosby and M. L. Silva, *J. Chem. Soc.*, 3990 (1964).

Photolysis of 1.—A solution of 0.026 g of 1 in 100 ml of dry ethyl ether was exposed to blue fluorescent light through a Corning 3-72 filter which removes all light of wavelength below 430 mμ. Under this condition of illumination, the sole product was 2.

Photolysis of 2.—An ether solution of 2, which was continuously flushed with nitrogen was exposed to the light of a high-pressure, water-cooled mercury arc which was filtered through Pyrex glass. An exposure time of 5 min reduced the 277-mμ absorption peak of 2 to less than one-quarter of its original value.

Registry No.—**1**, 6427-95-8; **2**, 15707-28-5; **4**, 15707-29-6; **5**, 15707-35-4; **6**, 15707-30-9; **7**, 15707-33-2; 2,3-dichloro-5,6-dimethyl-1,4-benzoquinone, 15707-31-0; 2-chloro-3-methoxy-1,4-naphthoquinone, 15007-32-1.

The Preparation of Certain Pyrylium Salts by Using Chalcone and Boron Trifluoride Etherate

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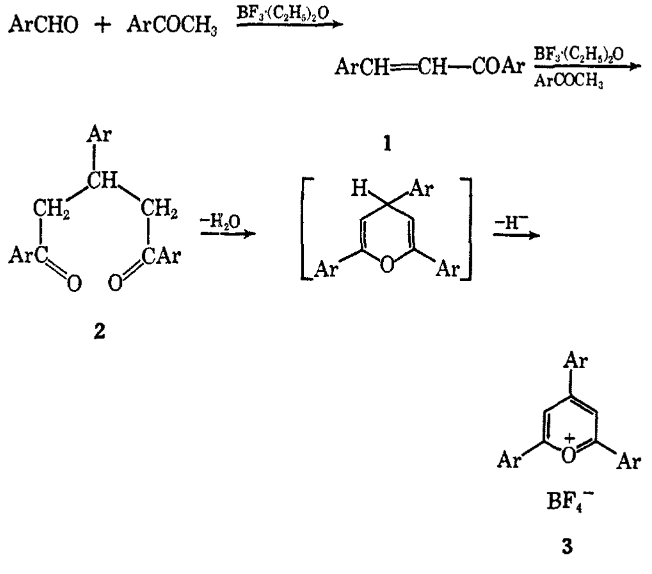
Some pyrylium salts were prepared from 1,5-diketones by using chalcone as a hydride-abstracting agent and boron trifluoride etherate as a cyclization medium. Under these conditions, 2-carbethoxy-1,3,5-triphenylpentane-1,5-dione (**9**) gave the 3-benzyl-2,4,6-triphenylpyrylium salt (**10**) rather than the expected 3-carbethoxy-2,4,6-triphenylpyrylium salt (**11**). An explanation for this result is proposed. Ethyl acetoacetate, chalcone, and boron trifluoride etherate gave 3-carbethoxy-2-methyl-4,6-diphenylpyrylium salt (**14**). Some 3-substituted 2,4,6-triphenylpyrylium salts were prepared from chalcone, α-substituted acetophenone derivatives, and boron trifluoride etherate.

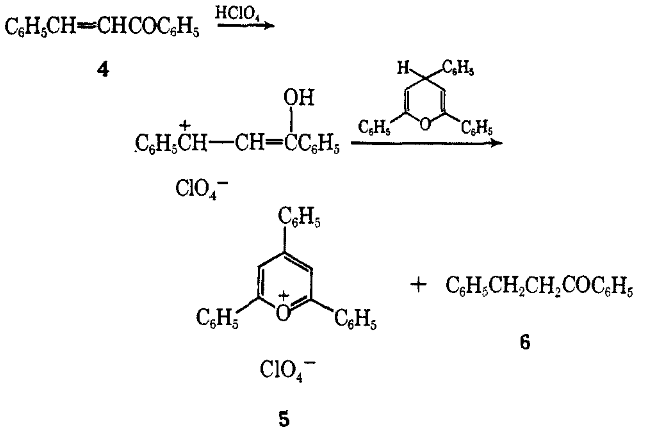
The most common preparative method for synthesizing 2,4,6-triarylpyrylium salts involves the condensation of 1 equiv of an aryl aldehyde and 2 equiv of an arylalkyl ketone in the presence of Lewis acids, strong mineral acids, or dehydrating agents such as polyphosphoric acid. We have found boron trifluoride etherate to be the most generally useful condensing agent for this synthesis. The reaction path is illustrated in Scheme I below. The 1,5-diketone **2** is an intermediate during the formation of **3**, since 1,5-diketones of this type readily yield **3** when treated with boron trifluoride etherate or perchloric acid. Inspection of the sequence shows that a dehydrogenation step is required to form **3**, and, since oxidizing agents are not usually present in the reaction medium, the nature of this dehydrogenation has long been a matter of conjecture.

Scheme I



Recently it was reported[1] that the conjugate acid of the intermediate chalcone serves as a hydride abstractor in the manner shown in Scheme II. Balaban proposed this reaction scheme on the basis of the improved yields of **5** that were obtained by the addition of chalcone (**4**) to 1,3,5-triphenylpentane-1,5-dione (**7**) in perchloric acid, and isolation of **6** from the reaction mixture.

Scheme II



We thought it of interest to investigate boron trifluoride etherate as a condensing agent and chalcone as a hydride abstractor in a synthetic procedure for pyrylium salts. The results obtained when **7** was allowed to react under a variety of conditions are summarized in Table I.

Procedure C (see Table I) was extended to include other 1,5-diketones, and in many cases excellent yields of pyrylium fluoroborates were obtained. For example, **8a** was obtained in 88% yield, **8b** in 93% yield and **8c** in 72% yield.

In some cases, however, this procedure led to un-

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[1] A. T. Balaban, *Comp. Rend.*, **256**, 4239 (1963).