due was extracted with ether and acidified. An oil separated which crystallized on standing; wt. 45.4 g. (100%) of crude material. Several recrystallizations from dilute aqueous methanol furnished colorless needles soluble in hot water; m.p. 173° with gas evolution. Analysis indicated that it was a hydrate.

Anal. Calcd. for $C_{19}H_{18}O_6 \cdot H_2O$: C, 63.33; H, 5.59. Found: C, 63.77; H, 5.36.

2-*o*-Carboxybenzyl-4-phenylbutyric Acid.—The crude malonic acid, wt. 44.5 g., was heated at 190° until the evolution of carbon dioxide had stopped. The material crystallized on standing. It was taken up in 200 ml. of hot ethanol, treated with charcoal, filtered, concentrated to about 150 ml., diluted with water, reheated and allowed to cool. There was obtained 32.5 g. (84%) of cream-colored crystals, including material recovered from the mother liquors. Further recrystallizations from aqueous ethanol furnished colorless needles, m.p. 149–149.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.25; H, 6.02.

2-(*o*-Carboxybenzyl)-1-tetralone (IV).—A solution of 15 g. of the preceding acid in 120 ml. of concd. sulfuric acid was kept at room temperature for two hours (if during the mixing and subsequently the temperature was allowed to rise, the desired product was contaminated by considerable amounts of the spirodiketone) and then poured over cracked ice. The precipitate was filtered (wt. 13 g., 92%) and recrystallized several times from benzene–petroleum ether. The shiny white needles melted at 115–116°, lit. 113–115°.[5] The infrared spectrum exhibited typical acid–OH absorption and an asymmetrical carbonyl band centered at 1685 cm.$^{-1}$ (conjugated ketone) with indications of bands near 1705 (dimeric carboxyl) and 1735 cm.$^{-1}$ (monomeric carboxyl). The substance was somewhat sternutatory, as observed previously.[5]

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.73. Found: C, 77.21; H, 5.89.

Several attempts to prepare a semicarbazone resulted in recovery of starting material. The dinitrophenylhydrazone, orange-red crystals from ethyl acetate, melted at 240° (dec).

Anal. Calcd. for $C_{24}H_{20}N_4O_6$: C, 62.60; H, 4.38; N, 12.1. Found: C, 62.91; H, 4.57; N, 11.9.

The methyl ester was prepared by saturating a solution of 1 g. of IV in 25 ml. of methanol with dry hydrogen chloride in the cold and allowing to stand for several days. The solvent was removed at reduced pressure and the residue was recrystallized several times from methanol. The product, m.p. 86.5–88°, exhibited two strong bands in the carbonyl region of the infrared spectrum, 1719 (conjugated ester) and 1680 cm.$^{-1}$ (tetralone).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.48; H, 6.47.

Hydrolysis of the methyl ester with acid or base resulted in regeneration of IV. When IV was refluxed with a mixture of acetic acid and hydrochloric acid only starting material was recovered. Refluxing with 70% sulfuric acid converted IV to the spirodiketone III.

Attempts were made to prepare the amide of ketoacid IV by partial hydrolysis of the ketonitrile II with hydrogen peroxide (recovery of impure starting material) and sulfuric acid (formation of the spirodiketone), ammonolysis of the methyl ester of IV (recovery of starting material) and ammonolysis of the acid chloride of IV (formation of an amorphous neutral solid which could not be converted to material melting sharply but whose infrared spectrum indicated the presence of at least some amide).

2-(*o*-Carboxybenzyl)-1,2,3,4-tetrahydronaphthalene.—Reduction of 1 g. of ketoacid IV by the Huang-Minlon modification of the Wolff–Kishner reaction resulted, after several recrystallizations, in 0.5 g. of colorless crystals, m.p. 160.5–162°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.37; H, 6.90.

Condensation of 1-Tetralone and Phthalaldehydic Acid.—To a solution of 1 g. of 1-tetralone and 1 g. of phthalaldehydic acid in 10 ml. of ethanol was added 0.2 ml. of 40% potassium hydroxide solution. After standing overnight, the purple solution was diluted with water and acidified. A yellow oil separated and solidified on standing, wt. 1.3 g. Two recrystallizations from benzene–ligroin (b.p. 65–110°) resulted in needles which melted unsharply in the range 121–126°. A third recrystallization produced a sudden rise to 136.5–138°; further purification did not alter the m.p. The infrared spectrum had bands at 1760 (lactone) and 1680 (2-tetralone); this together with the analysis indicated structure VI. Although the substance was neutral it dissolved in dilute alkali. Neutralization of the alkaline solution reprecipitated the lactone.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.39; H, 5.08.

The red dinitrophenylhydrazone was recrystallized from ethyl acetate, m.p. 262–263°.

Anal. Calcd. for $C_{24}H_{18}N_4O_6$: C, 62.88; H, 3.96. Found: C, 62.99; H, 4.07.

TALLAHASSEE, FLORIDA

[CONTRIBUTION NO. 229 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO., INC.]

Products of the Photochemical Decomposition of N,N'-Disubstituted *p*-Quinonediimine-N,N'-dioxides

BY C. J. PEDERSEN[1]

RECEIVED MARCH 19, 1957

A new class of photochemical reaction has been discovered. N,N'-Disubstituted *p*-quinonediimine-N,N'-dioxides (I) when exposed to light of 300–450 mμ wave lengths, decompose very rapidly and quantitatively into N-substituted *p*-quinoneimine-N-oxides (IV) and azo compounds, and the resulting N-oxides decompose into *p*-quinone and azo compounds. The two reactions can be separated because the wave length required for the second is approximately 20 mμ shorter than for the first. The composition of the azo compounds depends upon the substituents on the nitrogen atoms: nitrogen atoms attached to similar groups react at about the same rate, but the nitrogen atom carrying an aromatic group reacts more readily than the nitrogen atom attached to an aliphatic group. Mixtures of azo compounds, including unsymmetrical ones, are obtained from unsymmetrically substituted N,N'-dioxides II or from mixtures of symmetrically substituted N,N'-dioxides I and III.

During the preparation of N,N'-disubstituted *p*-quinonediimine-N,N'-dioxides (I),[2] it was observed that solutions of these compounds are very sensitive to light. For example, a 1-cm. layer of a 10^{-5} molar solution of N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide in benzene, which is light yellow in color, is decolorized within one second by direct sunlight. A stronger solution which had been exposed to sunlight for several days was found to contain azobenzene. It thus appeared that the compound had decomposed intramolecularly into azobenzene and *p*-quinone, and the

---

[1] Elastomer Chem. Dept., E. I. du Pont de Nemours and Co., Inc.

[2] C. J. Pedersen, THIS JOURNAL, **79**, 2295 (1957).

TABLE I

PHOTOCHEMICALLY DECOMPOSED N,N'-DIOXIDES AND IDENTIFIED PRODUCTS

No.	Type	Compound decomposed R or R'	Compound decomposed R or R'	Quantity, mole	Solvent	Volume, ml.[a]	Exposure[b]	Identified products	Quantity, mole
1	I	Phenyl	Phenyl	1.38×10^{-2}	Benzene	800	4 hours	IV, R = phenyl	1.21×10^{-2c}
								V, R = phenyl	5.3×10^{-3c}
2	I	Phenyl	Phenyl	1.72×10^{-3}	Benzene	100	1 hour	IV, R = phenyl	8.6×10^{-4a}
								V, R = phenyl	8.4×10^{-4d}
								p-Quinone	3.4×10^{-4c}
3	I	2-Methyl-3-chlorophenyl		3.45×10^{-4}	Benzene	60	6 days	V, R = 2-methyl-3-chlorophenyl	2.16×10^{-4c}
4	III	*p*-Methoxyphenyl		3.45×10^{-4}	Benzene	60	6 days	V, R = *p*-methoxyphenyl	3.05×10^{-4c}
5	II	Phenyl	2-Naphthyl	1.47×10^{-3}	Benzene	150	6 days	V, R = phenyl	3.19×10^{-4c}
								VI, R = phenyl, R' = 2-naphthyl	5.69×10^{-4c}
								VII, R' = 2-naphthyl	3.05×10^{-4c}
6	I	Phenyl	Phenyl	7.35×10^{-4}	Benzene	300	3 days	V, R = phenyl	3.35×10^{-4c}
	III	*p*-Methoxyphenyl		7.35×10^{-4}				VI, R = phenyl, R' = *p*-methoxyphenyl	5.10×10^{-4d}
								VII, R' = *p*-methoxyphenyl	2.55×10^{-4c}
7	II	Phenyl	Cyclohexyl	1.5×10^{-5}	Methanol	500	2 minutes	IV, R = cyclohexyl	1.35×10^{-5d}
								V, R = phenyl	6.5×10^{-6d}
8	II	Phenyl	Cyclohexyl	1.5×10^{-6}	Methanol	500	2 hours	IV, R = cyclohexyl	3.7×10^{-6d}
								V, R = phenyl	6.6×10^{-6d}
								Hydroquinone[e]	.........[d]
9	I	Cyclohexyl	Cyclohexyl	1.5×10^{-5}	Methanol	500	30 minutes	IV, R = cyclohexyl	7.8×10^{-6d}
10	I	Cyclohexyl	Cyclohexyl	1.5×10^{-6}	Methanol	500	2 hours	Hydroquinone[e]	.........[d]
11	IV	Phenyl	....	1.0×10^{-3}	Benzene	50	19 days	V, R = phenyl	3.6×10^{-4c}
								p-Quinone	.........[d]

[a] In stoppered erlenmeyer flasks of appropriate size. [b] No. 1 was exposed to a mercury vapor lamp with a filter which cut off wave lengths shorter than 390 mμ. All the other numbers were exposed to direct sunlight. [c] Isolated and identified chemically. [d] Not isolated but determined in solution with a Cary model 11 recording spectrophotometer. [e] Formed by photochemical reduction of *p*-quinone by methanol.

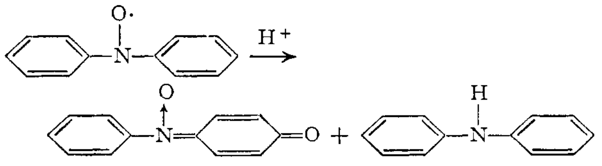
latter compound was actually found in the solution. The photochemical decomposition of N-phenyl -N'- (2-naphthyl) -*p*- quinonediimine-N,N'-dioxide, however, gave a mixture of three azo compounds: azobenzene, 2-naphthaleneazobenzene and 2,2'-azonaphthalene. These compounds could not have resulted from an intramolecular reaction, for in this case 2-naphthalene azobenzene would have been the sole azo product. Further study showed that N,N'-dioxides decompose photochemically into azo compounds and *p*-quinone and that N-substituted *p*-quinoneimine-N-oxides (IV) are formed as intermediates.

The identified products obtained by photochemically decomposing several different N,N'-dioxides are shown in Table I. Note that numbers 5, 7 and 8 are unsymmetrically substituted compounds and that number 6 is a mixture of two symmetrically substituted N,N'-dioxides.

These results indicate that under the influence of light the N,N'-dioxides are converted by some, yet undetermined, reactions into the decomposition products. If the substituents on the nitrogen atoms of a molecule are different but similar in nature, the nitrogens are activated with equal probability and three different azo compounds are formed with structures and in proportions according to random statistics. If the substituents on the nitrogen atoms are sufficiently different, for example, aliphatic on one and aromatic on the other, the aryl-nitrogen is activated more easily than the alkyl-nitrogen and the azo compound formed initially is the symmetrical aromatic compound.

Because of similarity in properties and behavior, it is assumed that aliphatically substituted N,N'-dioxides yield aliphatic azo compounds. Proof of their formation has not yet been obtained. Their relatively feeble absorption bands (*ca.* 340–350 mμ, ε *ca.* 10–20) would be lost among the much stronger bands of the other reaction products, and they were not isolated from the reaction mixtures.

N-Phenyl-*p*-quinoneimine-N-oxide (IV, R = phenyl) has been reported previously in the literature.[3] It was prepared by shaking an ether solution of diphenyl nitroxide with 2 *N* hydrochloric acid for 90 minutes when the following reaction occurred quantitatively



The yield of N-phenyl-*p*-quinoneimine-N-oxide from N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide is quantitative, but the yield of *p*-quinone from the N-oxide is not due to side reactions. The data which give the approximate rate of photochemical conversion of N,N'-diphenyl-*p*-quinonediimine-N,-N'-dioxide into N-phenyl-*p*-quinoneimine-N-oxide

---

(3) H. Wieland and K. Roth, *Ber.*, **53B**, 210 (1920).

(5×10^{-5} molar in benzene) are shown in Table II.

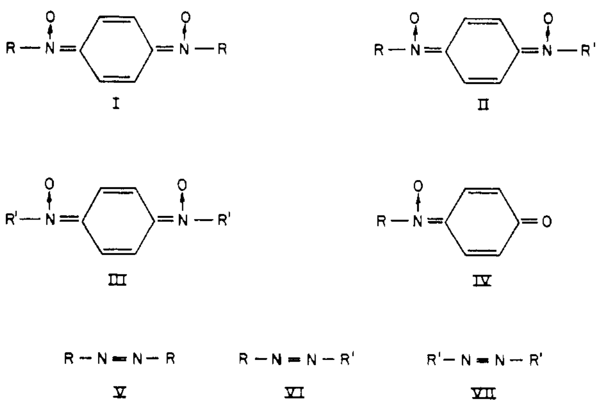


Fig. 1.

TABLE II

RATE OF PHOTOCHEMICAL CONVERSION OF N,N'-DIPHENYL-*p*-QUINONEDIIMINE-N,N'-DIOXIDE

No.	Exposure,[a] sec.	Converted,[b] %
1	0	Nil
2	7	9
3	22	25
4	37	36
5	103	47
6	274	62
7	445	99^+

[a] To a given source of light having little power to decompose N-phenyl-*p*-quinoneimine-N-oxide. [b] Determined spectrophotometrically.

Some of the absorption curves from which the data in Table II were derived are shown in Fig. 2.

The conversion of the N,N'-dioxide to the N-oxide is seen to be quantitative since all the curves for the different stages of the conversion (including curves not shown in Fig. 2) pass through the isosbestic point, and the optical density at 375 mμ for curve 3 (when all the N,N'-dioxide is decomposed) corresponds closely to that of a 5×10^{-5} molar solution of the pure N-oxide in benzene. Curve 3, however, is not that for the pure N-oxide since azobenzene is formed simultaneously and causes the shoulder at about 320 mμ. The absorption curve for pure N-phenyl-*p*-quinoneimine-N-oxide would slope down smoothly to an optical density of 0.18 at 320 mμ.

The yield of *p*-quinone and azobenzene after complete photochemical decomposition of the N,N'-dioxide and the N-oxide is not quantitative. This is indicated by the fact that curve 4 does not pass through the dots (curve 5) which outline the curve for 100% yield.

N-Phenyl-*p*-quinoneimine-N-oxide was the only intermediate which was isolated and chemically identified. The similarity of the spectra of the different N,N'-dioxides at various stages of photochemical decomposition indicated, however, that the intermediate N-oxides always are formed. The spectral data on these compounds are presented in Table III. The extinction coefficients must be considered approximate because the spectra were not necessarily determined at that stage when the intermediates were at the highest concentration.

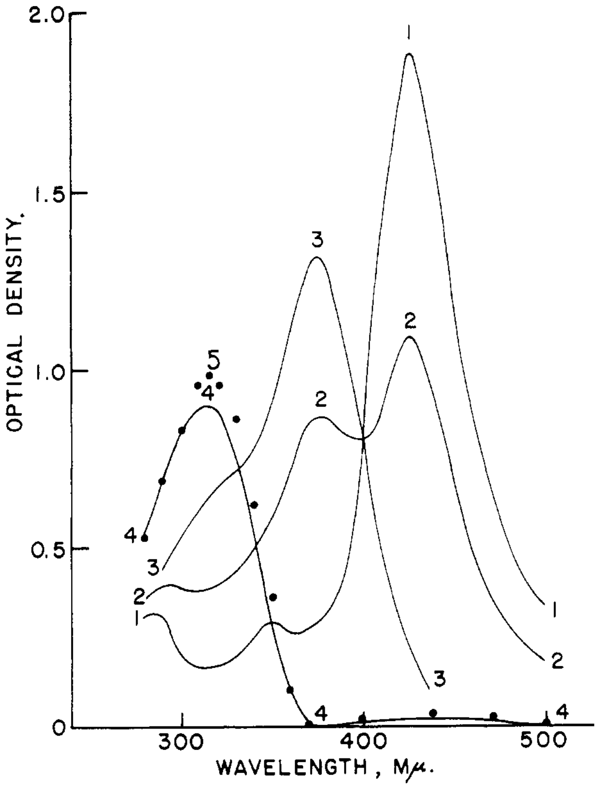
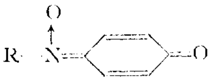
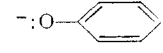


Fig. 2.—Rate of photochemical decomposition of N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide: concentration, 5×10^{-5} molar; light path, 1 cm.; instrument, Cary model 11 recording spectrophotometer. Curve-Table II correspondence: curve 1, no. 1 unexposed; curve 2, no. 5 103 sec. exposure; curve 3, no. 7 445 sec. exposure; curve 4 is that of the same solution which had been exposed to direct sunlight for 25 minutes; curve 5 is that of a benzene solution containing *p*-quinone and azobenzene each at 5×10^{-5} mole per liter.

TABLE III

VISIBLE ABSORPTION MAXIMA OF R–



R	Solvent	Max., mμ	Extinction coeff.
α-Carbethoxyisopropyl	Methanol	373	23,000
Cyclohexyl	Methanol	377	26,000
Phenyl	Methanol	371	25,000
	Benzene	375	24,000
	CHCl$_3$	374	28,000
2-Naphthyl	CHCl$_3$	375	27,000
2-Methyl-3-chlorophenyl	CHCl$_3$	366	31,000
p-Methoxyphenyl	CHCl$_3$	375	31,000
p-Hydroxyphenol	Ethanol	382	16,000
p-Phenoxide 	Ethanol	672	35,000

Note that the absorption peaks occur within a relatively narrow range of wave lengths (except the *p*-phenoxide compound), and they are affected by the substituent on the nitrogen atom and to some extent by the solvent.

Acknowledgment.—The author wishes to thank John Willister for preparing some of the compounds, and H. E. Schroeder for his advice.

TABLE IV

NITROGEN CONTENTS AND MELTING POINTS OF RECOVERED PRODUCTS

Compound	Recovered sample[a] M.p., °C.[b]	Recovered sample[a] Nitrogen, % Found	Authentic sample Nitrogen, % Calcd.	Authentic sample Nitrogen, % Found	Authentic sample M.p., °C.[b]	Reference
Azobenzene	68	15.5	15.4	15.6	68	4
2-Naphthaleneazobenzene	81	11.7	12.1	12.0	83	..
2,2'-Dimethyl-3,3'-dichloroazobenzene	152	9.5	10.0	9.7	156	5
2,2'-Azonaphthalene	200	9.6	9.9	10.0	207	6
p,p'-Dimethoxyazobenzene	161–162	..	11.6	11.3	164	7
N-Phenyl-*p*-quinoneimine-N-oxide	141–142	7.0	7.0	7.0	141	3

[a] Except for azobenzene and N-phenyl-*p*-quinoneimine-N-oxide, these samples could not be rigorously purified because of the small quantities recovered. No significant lowering of the mixed melting points with the authentic samples was observed in any case. [b] Determined on a bronze block and are uncorrected.

TABLE V

ABSORPTION MAXIMA OF RECOVERED PRODUCTS

Compound	Decomposition product Mμ[a]	A'[b]	Mμ[a]	A''[b]	A'/A''	Authentic sample Mμ[a]	ϵ'[c]	Mμ[a]	ϵ''[c]	ϵ'/ϵ''
Azobenzene	317	1.64	438	0.04	41.0	318	21,000	441	490	42.8
2-Naphthaleneazobenzene	328	1.15	437	.06	19.2	327	21,000	441	1,100	19.1
2,2'-Dimethyl-3,3'-dichloroazobenzene	330	2.00	450	.07	28.6	329	18,000	445	600	30.0
2,2'-Azonaphthalene	335	1.45	443	.13	11.2	336	25,000	443	2,000	12.5
p-Methoxyazobenzene[d]	235	0.86	344	1.60	0.54	235	12,000	345	20,000	0.60
p,p'-Dimethoxyazobenzene	355	.76	430	0.07	10.9	355	25,000	430	2,200	11.4
Hydroquinone	226	.70	285	0.48	1.46	227	6,800	292	4,100	1.66
p-Quinone	244	1.24	..	....	...	244	19,000	436	19	...
p-Hydroxydiphenylamine	..	.....	..	....	...	282	17,000	..	....	...
N-Phenyl-*p*-quinoneimine	..	.....	..	....	...	262	17,000	449	3,200	...
N-Phenyl-*p*-quinoneimine-N-oxide	257	3700[c]	371	25,000[c]	...	257	3,700	371	25,000	...
α,α'-Azobisisobutyronitrile[e]	..	.....	..	....	...	346	13	..	....	..
1,1'-Azobiscyclohexanecarbonitrile[e]	..	.....	..	....	...	350	17	..	....	...
Phenazine-N,N'-dioxide[e]	..	.....	..	....	...	283	58,000	475	11,000	...
5,6-Bis-(phenylimino)-2-cyclohexene-1,4-dione-N,N'-dioxide	..	......	..	....	...	*Ca.* 300	12,000	383	2,900	...

[a] Absorption peaks in ethanol (unless otherwise noted) with a Cary model 11 recording spectrophotometer. [b] Optical densities. [c] Extinction coefficients. $A'/A'' = \epsilon'/\epsilon''$ for the same compound. [d] Has another peak at 430 mμ (ε 1,300). [e] In methanol instead of ethanol.

Experimental

Many of the compounds are very sensitive to light and adequate precautions must be taken when working with them. A rerun of the same sample of a benzene solution of N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide in the spectrophotometer gave identical absorption curves, hence the intensity of light used in the instrument was not enough to cause appreciable decomposition.

The samples of N,N'-dioxides used were those fully described in a previous publication.[2] The benzene used was anhydrous and thiophene-free; the methanol was the anhydrous synthetic product. The alumina used for chromatography was Eimer and Amend 80–200 mesh adsorption alumina without further treatment. All other materials were either laboratory samples or commercial products which were adequately purified.

The nitrogen contents and the melting points of the recovered products are compared with those of the authentic samples in Table IV. The data on some of the recovered products are not quite what normally would be desired due to the very small quantities involved, but in conjunction with the spectral data they serve to establish the identities of the compounds. Their absorption characteristics are listed in Table V.

Photochemical Production of N-Phenyl-*p*-quinoneimine-N-oxide (IV, R = Phenyl).—Since this compound is sensitive to light of wave lengths shorter than 370 mμ, this experiment was performed in the absence of such light. N,N'-Diphenyl-*p*-quinonediimine-N,N'-dioxide (1 g., 0.00345 mole) dissolved in 200 ml. of benzene in a 300-ml. erlenmeyer flask was exposed for 4 hr. at room temperature to the radiation of a Hanovia high pressure mercury quartz lamp type A (385–580 watts) through a filter (Corning 3060) which cut off wave lengths below 390 mμ. Four such batches were combined and concentrated to 40 ml. at room temperature under reduced pressure. The concentrate was warmed to 50° to effect complete solution and diluted with 2 volumes of petroleum ether (30–60°). The brown crystals (A) were filtered and when dry weighed 2.415 g.; 1.3 g. of dark orange crystals (B) were recovered by evaporating the filtrate to dryness under vacuum.

Spectral analysis showed that B consisted of 82% azobenzene (1.07 g., 0.0059 mole). After recrystallizing from aqueous ethanol, it melted at 68° (mixed melting point with authentic azobenzene, 68°).

Anal. Calcd. for $C_{12}H_{10}N_2$: N, 15.4. Found: N, 15.5.

The spectrum of A indicated it to be nearly pure N-phenyl-*p*-quinoneimine-N-oxide (2.415 g., 0.0121 mole). It was purified by dissolving in benzene and diluting with 3 volumes of petroleum ether. The brown flocculent precipitate which formed immediately was filtered off, and the clear filtrate was allowed to stand at room temperature in the dark for 24 hr. Long reddish-brown crystals were obtained which melted at 141–142° (literature[3] 142°).

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.4; H, 4.5; N, 7.0; mol. wt., 199. Found: C, 72.2; H, 4.0; N, 7.0; mol. wt., 203 (freezing point of benzene).

The spectrum of this product was identical to that of authentic N-phenyl-*p*-quinoneimine-N-oxide.

p-Hydroxydiphenylamine was obtained by hydrogenating this product in neutral methanol with a platinum oxide catalyst at 30 p.s.i. for 40 minutes at room temperature; m.p. 70°; mixed melting point with an authentic sample 70°.

Photochemical Decomposition of N,N'-Diphenyl-*p*-quinonediimine-N,N'-dioxide (I, R = Phenyl).—N,N'-Diphenyl-*p*-quinonediimine-N,N'-dioxide (0.5 g., 1.72 × 10^{-3} mole), dissolved in 100 ml. of benzene in a 250-ml. erlen-

---

(4) P. Pfeiffer and O. Angern, *Z. angew. Chem.*, **39**, 253 (1926).

(5) P. Cohn, *Monatsh. Chem.*, **22**, 473 (1901).

(6) R. Kuhn and P. Goldfinger, *Ann.*, **470**, 183 (1929).

(7) D. Vorlander *Ber.*, **40**, 1415 (1907).

meyer flask was exposed to direct sunlight for 1 hr. The solution was passed through a column of alumina and eluted with benzene (total volume of eluate, 460 ml. containing 8.4×10^{-4} mole of azobenzene). The column was then eluted with absolute ethanol (total volume of eluate, 280 ml. containing 8.6×10^{-4} mole of N-phenyl-*p*-quinoneimine-N-oxide and approximately 3.4×10^{-4} mole of *p*-quinone).

On distilling at room temperature under reduced pressure, the ethanol eluate gave a yellow distillate which had the following properties: absorption peak at 244 mμ (the expected peak at 436 mμ for *p*-quinone was too weak for detection), had the characteristic pungent smell of *p*-quinone, was decolorized at once by ascorbic acid, and oxidized a weakly acid solution of N,N′-di-(*sec*-butyl)-*p*-phenylenediamine to the bright red semiquinone.

The other photochemical decomposition experiments, unless discussed below in detail, were run in the same way, but the concentrations, solvents and duration of irradiation were different as shown in Table I.

Although phenazine-N,N′-dioxide and 5,6-bis-(phenylimino)-2-cyclohexene-1,4-dione-N,N′-dioxide have structures somewhat similar to that of the N,N′-dioxides, they are not particularly photosensitive to sunlight.

Photochemical Decomposition of N-Phenyl-N′-(2-naphthyl)-*p*-quinonediimine-N,N′-dioxide (II, R = Phenyl, R′ = 2-Naphthyl).—N-Phenyl-N′-(2-naphthyl)-*p*-quinonediimine-N,N′-dioxide (0.5 g. 1.47×10^{-3} mole), dissolved in 150 ml. of benzene in a 250-ml. erlenmeyer flask, was exposed to direct sunlight for 6 days. The solution was passed through a column of alumina and eluted with benzene (total volume of eluate 225 ml.). This was evaporated to dryness, the residue was put on a column of alumina and eluted with a mixture (1–9 by volume) of benzene–petroleum ether. Three distinct bands formed and were separated cleanly into three yellow solutions which were evaporated to dryness under reduced pressure.

The solids from the first band consisted of 3.19×10^{-4} mole of azobenzene, from the second band 5.69×10^{-4} mole of 2-naphthaleneazobenzene, and from the third band 3.05×10^{-4} mole of 2,2′-azonaphthalene. The properties of the recovered samples are compared with those of the authentic samples in Tables IV and V.

The total recovery of azo compounds was 81% (1.19×10^{-3} mole), and the proportions of the azo compounds are close to those for random statistics: 1.00:1.78:0.96, instead of 1:2:1.

Photochemical Decomposition of an Equimolar Mixture of N,N′-Diphenyl-*p*-quinonediimine-N,N′-dioxide and N,-N′-Bis-(*p*-methoxyphenyl)-*p*-quinonediimine-N,N′-dioxide (I, R = Phenyl) and (III, R′ = *p*-Methoxyphenyl).—N,N′-Diphenyl-*p*-quinonediimine-N,N′-dioxide (0.213 g., 7.35×10^{-4} mole) and N,N′-bis-(*p*-methoxyphenyl)-*p*-quinonediimine-N,N′-dioxide (0.257 g., 7.35×10^{-4} mole), dissolved in 300 ml. of benzene in a 500-ml. erlenmeyer flask, was exposed to direct sunlight for 6 days. The solution was passed through a column of alumina and eluted with benzene (total volume of eluate 298 ml.). This was evaporated to dryness, the residue was put on a column of alumina and eluted with a mixture (1–9 by volume) of benzene–petroleum ether. Three bands were formed and separated into three yellow solutions which were evaporated to dryness under reduced pressure.

The solids from the first band consisted of 3.35×10^{-4} mole of azobenzene, from the second band 5.10×10^{-4} mole of *p*-methoxyazobenzene, and from the third band 2.55×10^{-4} mole of *p,p*′-dimethoxyazobenzene. The properties of the recovered samples are compared with those of the authentic samples in Tables IV and V.

The total recovery of azo compounds was 75% (1.10×10^{-3} mole), and the proportions of the azo compounds are still not too far from those for random statistics: 1.00: 1.52:0.76; instead of 1:2:1.

Photochemical Decomposition of N-Phenyl-*p*-quinoneimine-N-oxide (IV, R = Phenyl).—N-Phenyl-*p*-quinoneimine-N-oxide (0.2 g., 0.001 mole), dissolved in 50 ml. of benzene in a 100-ml. fused quartz flask, was exposed to direct sunlight for 19 days. The solution was passed through a column of alumina and eluted with benzene. The benzene eluate (188 ml.) contained 3.6×10^{-4} mole of azobenzene. The column was then eluted with acetone, the eluate was carefully evaporated to dryness, the residue was dissolved in methanol and analyzed spectrophotometrically. The presence of *p*-quinone was indicated by an absorption peak at 244 mμ.

Orange crystals were obtained by evaporating the benzene eluate to dryness. On recrystallizing from aqueous ethanol they melted at 68° (mixed melting point with authentic azobenzene, 68°).

The photochemical decomposition of the N-oxides is not quantitative because of side-reactions. Some evidence for the formation of N-phenyl-*p*-quinoneimine by the removal of the oxygen atom from the N-oxide was obtained and also for the production of hydroquinone and *p*-hydroxybiphenyl when the photodecomposition occurred in reducing solvents, such as methanol and ethanol.

The rate of photochemical decomposition of N-phenyl-*p*-quinoneimine-N-oxide is influenced by the solvent: it did not decompose in concentrated sulfuric acid and decomposed about three times faster in benzene than in methanol.

Rate of Photochemical Decomposition of N,N′-Diphenyl-*p*-quinonediimine-N,N′-dioxide.—A solution of this compound in benzene, 0.0145 g. per liter (5×10^{-5} molar), in a 1-cm. cell was exposed to light for different periods of time in a Cenco–Sheard–Sanford photelometer. The light was from a 50 C.P. bulb (6.5 amp. at 6 v.) which had passed through a Cenco Filter No. 87309A (blue in color) and fixed aperture. The solution was removed at intervals and the spectrum was determined on the spectrophotometer. The results are given in Tables VI and II and Fig. 2.

TABLE VI

CHANGES IN SPECTRUM DUE TO IRRADIATION

No.	Exposure, sec.	Optical density at different times at 316 mμ	375 mμ	425 mμ
1	0	..	(0.29)[a]	1.90
2	7	..	(.43)	1.74
3	22	..	(.65)	1.48
4	37	..	.74	1.28
5	103	..	.88	1.10
6	274	..	1.13	0.85
7	445	..	1.33	0.20
8	25 min.[b]	0.91	...	..

[a] The values in parentheses indicate shoulders rather than peaks. [b] Exposure to direct sunlight.

Preparation of N-Phenyl-*p*-quinoneimine-N-oxide (IV, R = Phenyl).—This must be done in subdued light. N-Phenyl-*p*-quinoneimine (27.4 g., 0.15 mole), dissolved in 400 ml. of benzene was added dropwise at room temperature to 370 ml. of benzene containing 21 g. (0.157 mole) of peroxybenzoic acid[8] and stirred for 24 hr. The solution was passed through a column of alumina, the red product was eluted with benzene, the eluate was evaporated to 50 ml. under reduced pressure and cooled. The crystals were filtered, washed with petroleum ether and air-dried on a porous plate; 24 g. of brown crystals (yield 80%) were obtained which melted at 141° (literature[3] 142°).

Anal. Calcd. for $C_{12}H_9NO_2$: N, 7.0. Found: N, 7.0; absorption maxima in methanol or ethanol: 257 mμ, ε 3,700; 371 mμ, ε 25,000.

N-(*p*-Hydroxyphenyl)-*p*-quinoneimine-N-oxide (IV, R = *p*-Hydroxyphenyl).—This preparation must be conducted in subdued light. N-(*p*-hydroxyphenyl)-*p*-quinoneimine (indophenol, 20.9 g., 0.105 mole) dissolved in 3 liters of *o*-dichlorobenzene was added at room temperature over 5 minutes into 310 ml. of benzene containing 14.6 g. (0.106 mole) of peroxybenzoic acid. The charge was stirred for 24 hr. and filtered. The brown crystals were washed with cold benzene and air-dried on a porous plate; 20.5 g. of product (yield 88%) was obtained which charred on heating to about 160° on a bronze block (literature[9]: 6% yield from phenol and concentrated nitric acid; reddish-brown crystals from ligroin-chloroform which charred on heating).

Anal. Calcd. for $C_{12}H_9NO_3$: N, 6.5. Found: N, 6.3. Absorption maximum in ethanol: 382 mμ, ε 16,000. The blue anion of this compound formed with benzyltrimethylammonium hydroxide has the following absorption maxima in ethanol: 420 mμ, ε 7,000, and 672 mμ, ε 35,000.

---

(8) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(9) K. H. Meyer and W. E. Elbers, *Ber.*, **54**, 337 (1921).

Cursory experiments showed that both N-(*p*-hydroxyphenyl)-*p*-quinoneimine-N-oxide and its anion are photosensitive and decompose at about the same rate when exposed to direct sunlight in a 1–1 mixture of benzene and methanol.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE DETROIT LABORATORIES OF THE ETHYL CORPORATION]

Some Reactions of 2,6-Dialkylphenols[1]

BY T. H. COFFIELD, A. H. FILBEY, G. G. ECKE AND A. J. KOLKA

RECEIVED MARCH 21, 1957

Several reactions of 2,6-diisopropylphenol and 2,6-di-*t*-butylphenol are reported. In all cases the diisopropylphenol underwent reaction in a normal manner. The di-*t*-butylphenol behaved in an anomalous manner in certain reactions, probably because of steric hindrance resulting from two *t*-butyl groups *ortho* to the hydroxyl group. Thus, benzoylation and cyanoethylation gave *para* products, and catalytic reduction stopped at the cyclohexanone stage. This paper describes some reactions of 2,6-diisopropyl- and 2,6-di-*t*-butylphenol with both normal and anomalous results being observed.

Catalytic reduction of 2,6-diisopropylphenol (DIP) proceeded as expected to give 2,6-diisopropylcyclohexanol. Phenylurethan derivatives of DIP and the cyclohexanol readily were prepared indicating the hydroxyl groups to be relatively unhindered. However, reduction of 2,6-di-*t*-butylphenol (DTB) ceased after uptake of two moles of hydrogen per mole of phenol to give the corresponding cyclohexanone. This cessation was also noted by Whitaker[2] in his work on 2,6-di-*t*-butyl-4-methylphenol. Distillation of the reduced DTB gave two stereoisomeric cyclohexanones (I and II) in yields of 80 and 20%, respectively. The configurations of I and II were established by lithium aluminum hydride reduction of I to two stereoisomeric cyclohexanols, III and IV. Since only the cyclohexanone in which the *t*-butyl groups are in a *cis* relationship can yield two isomers on reduction, the *cis* configuration has been assigned to I. Similar reduction of II, the *trans*-cyclohexanone, gave only one cyclohexanol (V). It was not possible to prepare hydroxyl or carbonyl derivatives of DTB, the cyclohexanones or the cyclohexanols by the usual methods.

Both DIP and DTB were oxidized readily by alcoholic ferric chloride and formed brilliantly colored 3,3′,5,5′-tetralkyldiphenoquinones which were reduced to the corresponding 4,4′-dihydroxydiphenyl compounds. The tetra-*t*-butyl derivatives have been reported previously by Jones.[3,4]

The phenols underwent a smooth conversion to Mannich products on treatment with formalin and dimethylamine in ethanol. The resulting N,N-dimethyl-3,5-dialkyl-4-hydroxybenzylamines were isolated in high yields.

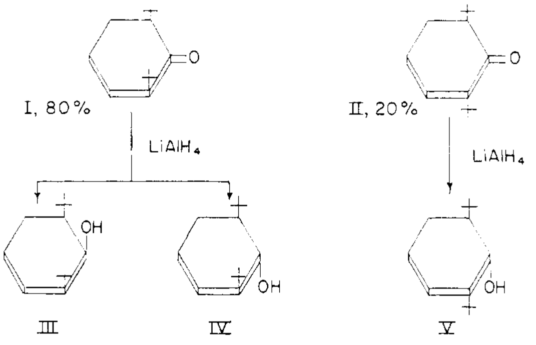


Fig. 1.

The base-catalyzed condensation of DTB with aldehydes was investigated. Treatment of DTB with benzaldehyde in ethanolic sodium hydroxide gave bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-phenylmethane as the only product. However, use of formalin under similar conditions gave 3,5-di-*t*-butyl-4-hydroxybenzyl ethyl ether in addition to the expected 4,4′-methylene-bis-(2,6-di-*t*-butylphenol). The ether formed resulted from solvent participation in the reaction and the amount formed varied with reaction conditions and alcohol used. Use of stoichiometric base and low molecular weight primary alcohols, such as methanol or ethanol, increased the yield of the corresponding ether, whereas catalytic base and secondary alcohols such as isopropyl alcohol, gave exclusively the bis-methylene product in high yield.

The anhydrous sodium salt of DTB was prepared through the reduced pressure evaporation of a methanol solution containing equivalent amounts of sodium methoxide and DTB. The powdery salt was decomposed rapidly by water to regenerate DTB and proved to be a reactive intermediate. Whereas DTB gave no derivative on treatment with phenyl isocyanate, its sodium salt gave a phenylurethan in 32% yield. The DTB was recovered on basic hydrolysis of the urethan.

The anhydrous sodium salt of DIP was prepared by direct reaction with sodium dispersion in toluene. The reaction was slow and hampered by the fact that the sodium salt as formed was insoluble in toluene and thus impaired stirring. The anhydrous salts of DTB and DIP were carboxylated under pressure to give the corresponding 3,5-dialkyl-4-hydroxybenzoic acids.

Cyanoethylation of DIP and DTB was carried out and found to yield different types of products. Treatment of DIP with acrylonitrile in the presence of the sodium salt gave the normal aryloxy product, β-(2,6-diisopropylphenoxy)-propionitrile. However, under similar conditions DTB cyano-

---

[1] Presented before the Division of Organic Chemistry, 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 11-16, 1955.

[2] A. C. Whitaker, THIS JOURNAL, **69**, 2414-2415 (1947).

[3] D. G. Jones, British Patent 686,261, January 21, 1953; *C. A.*, **48**, 4593 (1954).

[4] D. G. Jones, British Patent 687,293, February 11, 1953; *C. A.*, **48**, 3385 (1954).