The picrate was prepared by treating an aqueous solution of the hydrochloride with an excess of a saturated aqueous picric acid solution; clusters of yellow needles, m.p. 181.8–182.6°, *Anal.* Calcd. for $C_{17}H_{17}N_5O_{12}$: N^{a}, 11.60. Found: N^{a}, 11.51.

2-(3-(1-Piperidyl)-propoxy)-4-nitrobenzoic acid hydrochloride, pale yellow cottony needles from absolute alcohol, m.p. 216.8–217.5°. *Anal.* Calcd. for $C_{15}H_{21}ClN_2O_5$: N, 8.16; Cl, 10.28. Found; N, 8.17; Cl, 10.09.

The picrate, canary yellow needles from absolute alcohol, m.p. 143.0–145.0°. *Anal.* Calcd. for $C_{21}H_{23}N_5O_{12}$: N^{a}, 10.43. Found: N^{a}, 10.10.

Alkyl 4-Amino-2-(dialkylaminoalkoxy)-benzoates.—The alkyl 2-(dialkylaminoalkoxy)-4-nitrobenzoate bases or hydrochlorides were reduced by the iron–hydrochloride acid method,[1a] in the appropriate dilute alcohol as solvent, or by catalytic reduction of the hydrochloride (platinum oxide, 25°, alcohol solvent). The crystalline 4-amino bases were recrystallized from benzene or an ethyl acetate–*n*-hexane mixture. The bases did not readily yield crystalline mono- or dihydrochlorides, but the phosphates were easily prepared.[1a,9] The picrates were prepared in the usual manner, using an excess of picric acid. These compounds are listed in Table III.

Alkyl 4-Amino-2-(dialkylaminoalkoxy)-benzoate Quaternary Salts.—The reduction of the alkyl 2-(dialkylaminoalkoxy)-4-nitrobenzoate quaternary salts and bis-quaternary salts was carried out catalytically, using platinum oxide as catalyst, the appropriate alcohol or dilute alcohol as solvent, a temperature of 25° and a pressure of 40 lb. The products were isolated in the usual manner, utilizing a vacuum distillation with ethyl acetate for dehydration prior to crystallization from isopropyl alcohol–ethyl acetate or absolute alcohol. A number of the 4-amino quaternary salts could not be obtained crystalline; in certain cases these were tested as the crude oils. The crystalline 4-amino quaternary salts are listed in Table IV.

4-Amino-2-(dialkylaminoalkoxy)-benzoic Acids.—The 2-(dialkylaminoalkoxy)-4-nitrobenzoic acids or their hydrochlorides were reduced catalytically by the above method.

4-Amino-2-(2-dimethylaminoethoxy)-benzoic acid hydrochloride, white needles from absolute alcohol, m.p. 145.5–147.2° dec. *Anal.* Calcd. for $C_{11}H_{17}ClN_2O_3$: N, 10.75; Cl, 13.60. Found: N, 10.74; Cl, 13.93.

4-Amino-2-(2-diethylaminoethoxy)-benzoic acid, white needles, m.p. 158.0–158.8° dec. *Anal.* Calcd. for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.11. Found: C, 61.88; H, 7.76; N, 11.05.

The picrate, canary yellow needles from alcohol, m.p. 187.5–188.3°. *Anal.* Calcd. for $C_{19}H_{23}N_5O_{10}$: N_{AP}, 5.82. Found: N_{AP}, 5.52.

4-Amino-2-(3-(1-piperidyl)-propoxy)-benzoic acid hydrochloride, tan needles, m.p. 162.1–162.8° dec. *Anal.* Calcd. for $C_{15}H_{23}ClN_2O_3$: N, 8.90; Cl, 11.26. Found: N, 9.20; Cl, 10.96.

4-Alkylamino-2-(dialkylaminoalkoxy)-benzoates.—The reductive alkylation of the 4-amino bases by means of an aldehyde, zinc dust and acetic acid was carried out as previously described.[1a,b]

Ethyl 4-butylamino-2-(2-diethylaminoethoxy)-benzoate hydrochloride, cream-colored needles from absolute alcohol–ethyl acetate, m.p. 160.5–161.8°. *Anal.* Calcd. for $C_{19}H_{33}ClN_2O_3$: N, 7.51; Cl, 9.50. Found: N, 7.36; Cl, 9.45.

The flavianate, yellow-orange plates from alcohol, m.p. 164.6–165.6°. *Anal.* Calcd. for $C_{29}H_{38}N_4O_{11}S$: S, 4.92. Found: S, 4.96.

Ethyl 4-(5-hydroxyamylamino)-2-(2-diethylaminoethoxy)-benzoate hydrochloride, white cottony needles from absolute alcohol–*n*-hexane, m.p. 132.2–133.4°. *Anal.* Calcd. for $C_{20}H_{35}ClN_2O_4$: N, 6.95; Cl, 8.79. Found: N, 7.07; Cl, 9.05.

The flavianate, cottony orange needles, m.p. 126.0–126.4°. *Anal.* Calcd. for $C_{30}H_{40}N_4O_{12}S$: S, 4.71. Found: S, 4.47.

Ethyl 4-(2,2-dimethyl-3-hydroxypropylamino)-2-(2-(2,6-dimethyl-1-piperidyl)-ethoxy)-benzoate, white needles from benzene, m.p. 90.0–91.0°. *Anal.* Calcd. for $C_{23}H_{38}N_2O_4$: C, 67.94; H, 9.42; N, 6.89. Found: C, 68.06; H, 9.31; N, 6.81.

RENSSELAER, N. Y.

[CONTRIBUTION NO. 228 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO., INC.]

Preparation of N,N'-Disubstituted *p*-Quinonediimine-N,N'-dioxides

BY C. J. PEDERSEN

RECEIVED DECEMBER 3, 1956

Several members of a new class of compounds (I, where R and R' are alkyl or aryl groups which may or may not be identical) have been prepared by treating either VI or VII with an excess of perbenzoic acid. They are highly colored compounds whose solutions in organic solvents are very sensitive to light. Many of them are good inhibitors of free radical polymerization as well as efficient inhibitors of autoxidation.

During a study of the action of perbenzoic acid on N,N'-disubstituted derivatives of *p*-phenylenediamine, products were obtained which were found to belong to a new class of compounds having structure I.[1] The closest references in the literature are to N-phenyl-*p*-quinoneimine-N-oxide (II),[2] 5,6-bis-(phenylimino)-2-cyclohexene-1,4-dione-N,N'-dioxide (III)[3] and phenazine-N,N'-dioxide (IV).[4]

The two methods of preparing these compounds are shown in Fig. 2. Method I consists in treating one mole of N,N'-disubstituted *p*-quinonediimine (VI) with slightly more than two moles of perbenzoic acid, and method II of treating one mole of N,N'-disubstituted *p*-phenylenediamine (VII) with a little more than three moles of perbenzoic acid.

N-Substituted *p*-nitroanilines (VIII) are obtained as by-products in method II when R or R', or both, are unsubstituted alkyl groups. The group which comes off the nitrogen atom is always the unsubstituted alkyl group. When both R and R' are substituted *t*-alkyl or aromatic groups, no derivative of *p*-nitroaniline is formed to any extent.

The establishment of the structure of these compounds is based mainly on work with N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide. The molecular weight and the elementary analyses of this compound are consistent with the composition of I (R and R' = phenyl), and its structure is indicated by its hydrogenation to N,N'-diphenyl-*p*-phenylenediamine (VII R and R' = phenyl).

It is an orange, crystalline compound whose solutions are very sensitive to light.[5] Its visible spectrum, shown in Fig. 3 has a peak at 417 mμ, ε 47,000. Structure X (R and R' = phenyl) is

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[1] C. J. Pedersen, United States Patent 2,681,918, June 22, 1954; *C. A.*, **49**, 7595 (1955).

[2] H. Wieland and K. Roth, *Ber.*, **53B**, 210 (1920).

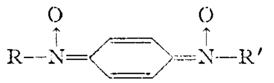
[3] W. Gündel and R. Pummer, *Ann.*, **529**, 11 (1937).

[4] G. R. Clemo and H. McIlwain, *J. Chem. Soc.*, 479 (1938).

[5] The photochemical reactions of N,N'-disubstituted *p*-quinonediimine-N,N'-dioxides will be discussed in another paper.

TABLE I

PREPARATION AND PROPERTIES OF



$R{-}\overset{O\uparrow}{N}{=}C_6H_4{=}\overset{O\uparrow}{N}{-}R'$

R	R′	Method	Solvent	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	M.p., °C.[a]
Methyl	Methyl	II	Chloroform	17	16.9	17.0	148
s-Butyl	*s*-Butyl	II	Benzene	11	11.2	11.1	174
α-Cyanoisopropyl	α-Cyanoisopropyl	II	Acetone	52	20.6	20.8	153
α-Carbamoylisopropyl	α-Carbamoylisopropyl	II	Dimethylformamide	57	18.2	18.4	240
α-Carbethoxyisopropyl	α-Carbethoxyisopropyl	II	Dimethylformamide	69	7.7	8.0	129
Cyclohexyl	Cyclohexyl	II	Benzene	77	9.3	9.4	213
1-Cyanocyclohexyl	1-Cyanocyclohexyl	II	Acetone	79	15.9	16.0	196
Cyclohexyl	Phenyl	II	Benzene	30	9.5	9.5	117
Phenyl	Phenyl	I	Chloroform	83	9.7	9.5	205
p-Dodecylphenyl	*p*-Dodecylphenyl	I	Benzene	36	4.5	4.6	116
Phenyl	β-Naphthyl	I	Chloroform	*ca.* 60–80	8.2	8.0	177
β-Naphthyl	β-Naphthyl	I	Benzene	62	7.1	7.4	215
o-Methyl-*m*-chlorophenyl	*o*-Methyl-*m*-chlorophenyl	I	Chloroform	*ca.* 60–80	7.2	7.0	222
p-Anisyl	*p*-Anisyl	I	Chloroform	*ca.* 60–80	8.0	7.8	219
Phenyl[b]	2,4-Dinitrophenyl	II	Benzene	59	14.7	14.7	215

[a] These points were determined on a bronze block and are uncorrected. In general the compounds decomposed on melting and the melting point is not considered a good index of identity for these compounds. [b] A 40% solution of peracetic acid in glacial acetic acid was used instead of perbenzoic acid.

excluded because the spectrum of the "di-isonitrone"[6] should resemble that of *p*-quinone (peaks in ethanol: 244 mμ, ε 19,000; *ca.* 300 mμ, ε 400; 436 mμ, ε 19) and not have such a strong absorption band in the visible region. Its infrared spectrum, shown in Fig. 5, has bands at 8.03 and 13.06 μ which are characteristic for the N,N′-dioxides.

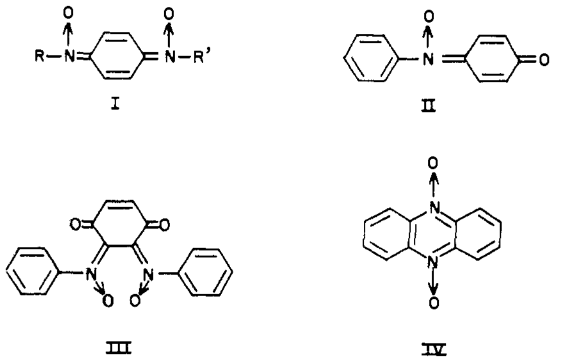


Fig. 1.

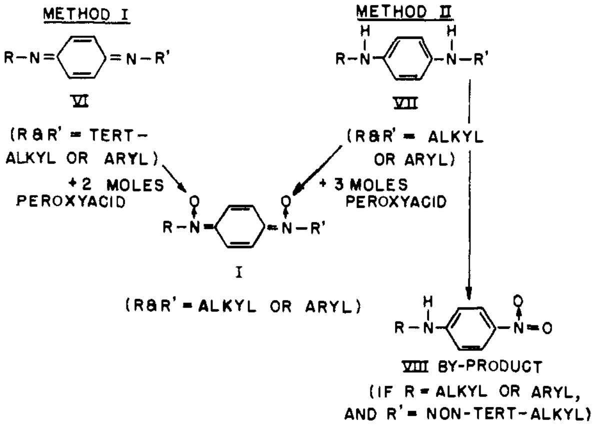


Fig. 2.

The band at 6.3 μ which is characteristic for the *p*-quinonediimines (VI), is either absent or very weak in the spectra of N,N′-dioxides (I).

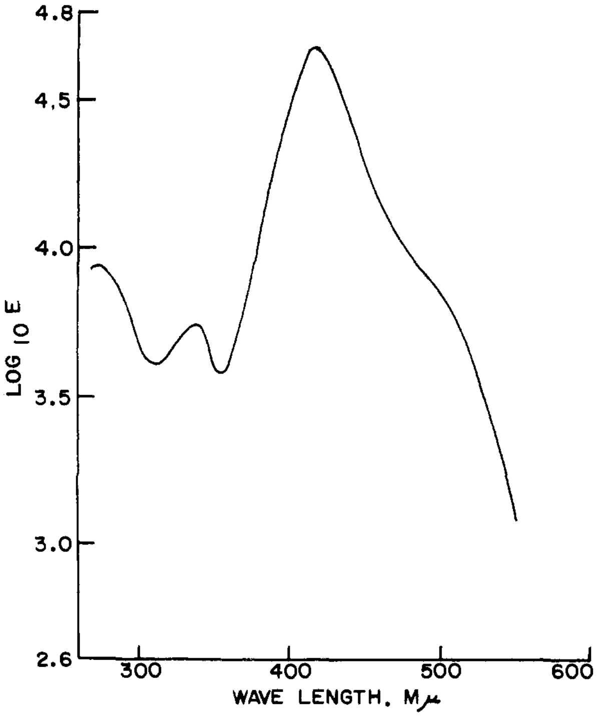


Fig. 3.—Spectrum of N,N′-diphenyl-*p*-quinonediimine-N,N′-dioxide.

Since I (R and R′ = phenyl) is an excellent inhibitor of free radical polymerization and autoxidation,[1] structure XII (R and R′ = phenyl), N,N′-(*p*-phenylene)-bis-(phenylnitroxide), was also considered, but paramagnetic resonance measurements failed to detect the presence of any unpaired electron either in the crystals or in solution.

It is concluded, therefore, that I (R and R′ = phenyl) is the correct structure of N,N′-diphenyl-

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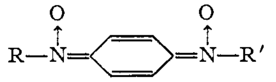
(6) British Patent 743,940, January 25, 1956.

TABLE II

VISIBLE ABSORPTION MAXIMA OF

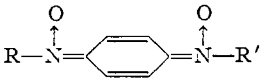


R	R'	Solvent	Max., mμ[a]	Extinction coeff.
Methyl	Methyl	Methanol	385	17,000
s-Butyl (XIII)	*s*-Butyl	Ethanol	403	66,000
α-Cyanoisopropyl	α-Cyanoisopropyl	Ethanol	406	85,000
α-Carbamoylisopropyl	α-Carbamoylisopropyl	Methanol	410	45,000
α-Carbethoxyisopropyl	α-Carbethoxyisopropyl	Methanol	406	78,000
Cyclohexyl	Cyclohexyl	Methanol	404	65,000
1-Cyanocyclohexyl	1-Cyanocyclohexyl	Chloroform	415	63,000
Cyclohexyl	Phenyl	Chloroform	415	44,000
Phenyl (IX)	Phenyl	Methanol	417	47,000
		Chloroform	423	43,000
Phenyl	β-Naphthyl	Chloroform	432	45,000
β-Naphthyl	β-Naphthyl	Chloroform	435	35,000
o-Methyl-*m*-chlorophenyl	*o*-Methyl-*m*-chlorophenyl	Chloroform	414	62,000
p-Anisyl	*p*-Anisyl	Chloroform	431	40,000
Phenyl	2,4-Dinitrophenyl	Chloroform	408	34,000

[a] Determined with a Cary model 11 recording spectrophotometer. Note that the absorption peaks occur within a relatively narrow range of wave lengths and they are influenced by the substituents on the nitrogen atoms and by the solvent.

TABLE III

CHARACTERISTIC INFRARED ABSORPTION BANDS OF

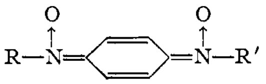


R = R' =	Bands, μ[a]	
s-Butyl	8.17s	12.92w
α-Carbethoxyisopropyl	8.04s	13.06s
Cyclohexyl	8.16s	12.99s
Phenyl	8.03s	13.06s

[a] Determined with a Perkin-Elmer model 12-C spectrophotometer using a NaCl prism and Nujol mulls.

TABLE IV

IDENTIFIED BY-PRODUCTS[a] OBTAINED IN PREPARING



R	R'	By-product	Identified by
Methyl	Methyl	N-Methyl-*p*-nitroaniline	Mixed m.p. 150–151°, spectrum in MeOH 381 mμ, ε 18,000
s-Butyl	*s*-Butyl	N-(*s*-Butyl)-*p*-nitroaniline	Spectrum similar to first compound
Cyclohexyl	Cyclohexyl	N-Cyclohexyl-*p*-nitroaniline	Spectrum similar to first compound
Cyclohexyl	Phenyl	*p*-Nitrodiphenylamine	Mixed m.p. 135°; N, 12.9; spectrum in MeOH 389 mμ, ε 21,000

[a] If any derivative of *p*-nitroaniline had been formed in the other preparations, the quantity was too small for ready identification.

p-quinonediimine-N,N'-dioxide. The compound is a dinitrone and may also be considered the N,N'-diphenyl ether of *p*-quinonedioxime.

The structure of the other compounds of this class is considered also proved because they are prepared in the same way, possess similar properties and their elementary analyses are in accord. They are strongly colored compounds, usually yellow or orange, with molecular extinction coefficients in the visible region, ranging from 17,000 to 85,000. Although their solubility is influenced by the substituents on the nitrogen atoms, they are, in general, moderately soluble at room temperature in organic solvents such as benzene, chloroform, acetone and dimethylformamide, and insoluble in water. Their solutions are rapidly decomposed on exposure to sunlight.[5] Data on these compounds are summarized in Tables I, II and III.

It should be mentioned that no attempt was made to secure maximum yields in these preparations, and it is likely that improved yields could be obtained readily by further work.

Observe that all these spectra contain bands near 8 and 13 μ which are considered to be characteristic for compounds belonging to this class.

It was mentioned previously that derivatives of *p*-nitroaniline are obtained as by-products in certain cases. Those which were identified are listed in Table IV.

N,N'-Dioxides, especially those having aryl substituents on the nitrogen atoms, are inhibitors of free radical polymerization and autoxidation, and examples of their uses for these purposes have been published.[1] The data in Table V show the effects of several N,N'-dioxides on the induction period of terpinolene autoxidizing in an atmosphere of oxygen. A number of other compounds are included for the purpose of comparison.

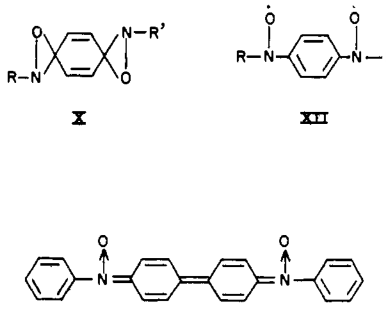


Fig. 4.

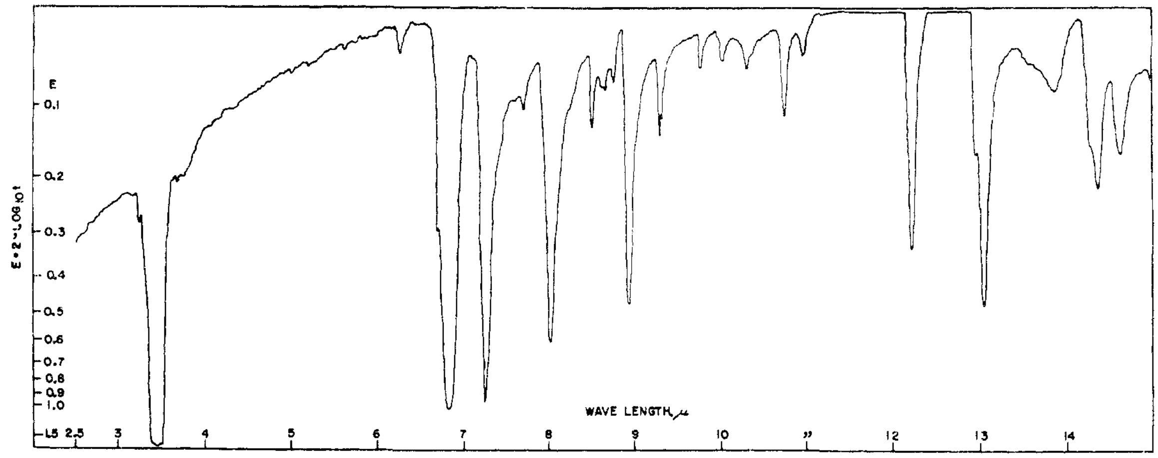


Fig. 5.—Infrared spectrum of N,N'-diphenyl-*p*-quinonediimine-N,N'-dioxide.

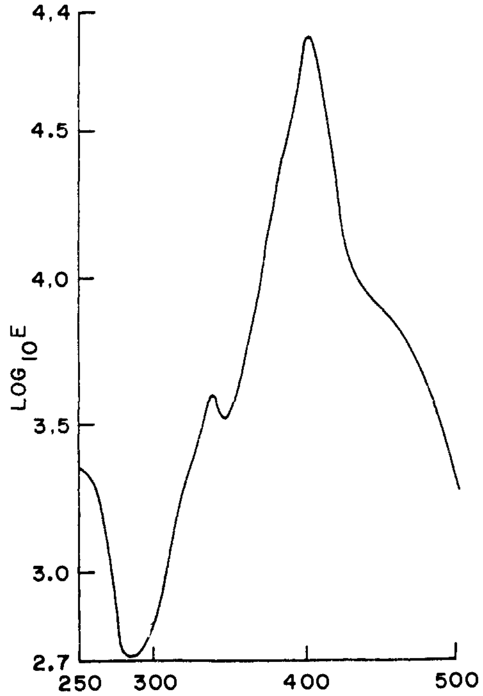


Fig. 6.—Spectrum of N,N'-di-(*sec*-butyl)-*p*-quinonediimine-N,N'-dioxide.

Note that the aryl substituted N,N'-dioxides, as a group, are more effective than the others, but there also appears to be some relationship between efficiency and the ease of removal of the oxygen atom from the nitrogen. It was found that N,N'-diphenyl-*p*-quinonediimine is obtained when N,N'-diphenyl - *p* - quinonediimine - N,N' - dioxide and N,N'-azo-bis-(α-isobutyronitrile) are refluxed in benzene under nitrogen. This brings up the possibility that N,N'-dioxides may function as inhibitors by reacting, not with peroxy chain-carriers but with carbon free radicals.[7]

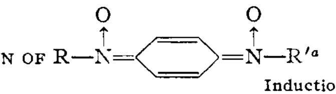
Acknowledgment.—The author wishes to thank T. D. Boice and John Willister for preparing many of the compounds; H. S. Jarrett and R. C. Ferguson for the paramagnetic resonance measurements; H. A. Kubitz for interpreting the infrared spectra; and H. E. Schroeder for his advice.

Experimental

Perbenzoic acid was prepared in chloroform or benzene by Braun's method[8] and used directly. All other materials were either laboratory samples or commercially available products.

TABLE V

ANTIOXIDANT ACTION OF



$R{-}\overset{\overset{O}{\uparrow}}{N}{=}C_6H_4{=}\overset{\overset{O}{\uparrow}}{N}{-}R'^{a}$

R	R'	Induction period of terpinolene, hours[b]
No additive		1 to 2
Cyclohexyl	Cyclohexyl	3
α-Carbamoylisopropyl	α-Carbamoylisopropyl	3
s-Butyl	*s*-Butyl	10
α-Carbethoxyisopropyl	α-Carbethoxyisoproyl	19
α-Cyanoisopropyl	α-Cyanoisopropyl	28
Cyclohexyl	Phenyl	31
1-Cyanocyclohexyl	1-Cyanocyclohexyl	33
β-Naphthyl	β-Naphthyl	38
o-Methyl-*m*-chlorophenyl	*o*-Methyl-*m*-chlorophenyl	41
p-Anisyl	*p*-Anisyl	58
p-Dodecylphenyl	*p*-Dodecylphenyl	75
Phenyl	β-Naphthyl	87
Phenyl	Phenyl	93
Phenazine-N,N'-dioxide (IV)		1 to 2
N,N'-Bis-(α-carbethoxyisopropyl)-*p*-quinonediimine		2
p-Quinone		3
5,6-Bis-(phenylimino)-2-cyclohexene-1,4-dione-N,N'-dioxide (III)		4
Hydroquinone		5
N,N'-Diphenyl-*p*-quinonediimine		26
N,N'-Diphenyldiphenoquinonediimine-N,N'-dioxide (XIV)		109
N-Phenyl-*p*-quinoneimine-N-oxide (II)		113

[a] All the compounds were tested at 1.6 × 10^{-5} mole per liter. [b] Terpinolene in an atmosphere of oxygen at 26–28° in the dark.

Method II is applicable to the preparation of all N,N'-dioxides, but method I can be used only if the correspond-

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(7) C. J. Pedersen, *Ind. Eng. Chem.*, **48**, 1881 (1956).

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

ing *p*-quinonediimine is stable. The preparation of a number of *p*-quinonediimines with aliphatic groups on the nitrogen atoms has been described previously.[9] The *p*-quinonediimines with aromatic groups on the nitrogen atoms can be prepared in nearly quantitative yields by treating a mole of the corresponding *p*-phenylenediamine with a mole of benzoyl peroxide in benzene or chloroform. These solutions can be used for the preparation of the N,N′-dioxides without further ado.

Since the N,N′-dioxides, especially in solution, are extremely sensitive to light, their preparation must be protected from light. This property tends to make it difficult to obtain reproducible analytical and spectral data on these compounds.

N,N′-Diphenyl-*p*-quinonediimine-N,N′-dioxide (Method I).—N,N′-Diphenyl-*p*-quinonediimine (12.9 g., 0.05 mole) in 425 ml. of chloroform was mixed with 250 ml. of benzene containing 15.2 g. of perbenzoic acid (0.11 mole), and allowed to stand for 30 minutes at room temperature. The solution was washed with 500 ml. of water containing 4.8 g. of sodium hydroxide (0.12 mole), twice with water and then dried with anhydrous sodium sulfate. The solution was concentrated to 350 ml. under reduced pressure and added to 600 ml. of petroleum ether (30–60°). The orange crystals which separated overnight were filtered, washed with petroleum ether and dried at room temperature to give 12 g. of product (yield 83%).

Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.5; H, 4.8; N, 9.7; mol. wt., 290. Found: C, 74.8; H, 5.1; N, 9.5; mol. wt., 288 (elevation of the boiling point of benzene).

An 84% yield of the product was obtained by using a 40% solution of peracetic acid in glacial acetic acid instead of perbenzoic acid in the above method.

N,N′-Diphenyl-*p*-phenylenediamine was obtained by hydrogenating the N,N′-dioxide in methanol with a platinum catalyst. It was identified by mixed melting point (147°), and spectrum (absorption peak in ethanol, 304 mμ, ϵ 27,000).

N,N′-Diphenyl-*p*-phenylenediamine is also obtained by treating the N,N′-dioxide with ascorbic acid in methanol at room temperature. The N,N′-dioxide is reduced much more slowly than the corresponding quinonediimine by ascorbic acid.

N,N′-Diphenyl-*p*-quinonediimine was obtained (yield over 82%) by refluxing one mole of the N,N′-dioxide with two moles of N,N′-azo-bis-(α-isobutyronitrile) in benzene under nitrogen for three hours. No diimine was formed in the absence of the azo-catalyst. The diimine was identified by mixed melting point (185–186°), and spectrum (absorption peaks in ethanol, 304 mμ, ϵ 27,000; 442 mμ, ϵ 7,000).

The visible spectrum of the N,N′-dioxide is shown in Fig. 3. Its spectrum in concentrated sulfuric acid, when fresh, is yellow and has an absorption peak at 468 mμ, ϵ 1,700, but the solution becomes bright blue within 24 hours at room temperature and has a peak at 670 mμ, ϵ 44,000. The blue solid product which was recovered from the blue sulfuric acid solution has not yet been identified.

Instead of getting a mole of mono-N-oxide by treating one mole of N,N′-diphenyl-*p*-quinonediimine with one mole of perbenzoic acid, half a mole of the N,N′-dioxide was obtained.

The thermal stability of the N,N′-dioxide was investigated by dissolving 3×10^{-5} mole in one liter of a mixture of trichlorobenzenes, and spectrophotometrically determining the amount of the compound left after exposure to different times and temperatures. The results are shown in Table VI.

N,N′-Dioxides in which both substituents on the nitrogen atoms are aromatic are most conveniently synthesized by first making the *p*-quinonediimine with benzoyl peroxide and using this solution in method I. Method I and method II have been varied by changing the solvent as indicated in Table I. The choice of solvent is dictated by the solubility of the starting compound and the resistance of the solvent to the action of perbenzoic acid.

TABLE VI

THERMAL STABILITY OF N,N′-DIPHENYL-*p*-QUINONEDIIMINE-N,N′-DIOXIDE IN TRICHLOROBENZENE[a]

Temp., °C.	Minutes at temp.	Decomposed,[b] %
50	10	Nil
94	20	2
152	20	6
176	20	42
202	20	Over 82
202	140	100

[a] Concentration, 3×10^{-5} mole per liter. [b] Determined spectrophotometrically.

N,N′-Bis-(1-cyanocyclohexyl)-*p*-quinonediimine-N,N′-dioxide (Method II).—1,1′-(*p*-Phenylenediimino)-carbonitrile, 3.2 g. (0.01 mole), dissolved in 200 ml. of acetone was added to 118 ml. of benzene containing 4.35 g. of perbenzoic acid (0.0315 mole). The mixture was shaken and allowed to stand overnight at room temperature. On chilling the solution in ice-water, a precipitate formed which was filtered, washed with acetone and dried at room temperature to give 2.8 g. of orange crystals (yield 79%). The properties of this compound are given in the tables.

N,N′-Dicyclohexyl-*p*-quinonediimine-N,N′-dioxide (Method II).—N,N′-Dicyclohexyl-*p*-phenylenediamine (12.2 g., 0.045 mole), dissolved in 100 ml. of benzene was added dropwise with agitation to 468 ml. of benzene containing 19.8 g. of perbenzoic acid (0.143 mole), and kept at 5° with external cooling. The mixture was stirred for 1 hour more and washed three times with 10% aqueous sodium bicarbonate to remove the benzoic acid. The solution was dried with anhydrous sodium sulfate, concentrated under reduced pressure and cooled to yield 10.5 g. of yellow crystals (yield 77%). Other properties of this compound are given in the tables.

Anal. Calcd. for $C_{18}H_{26}N_2O_2$: C, 71.6; H, 8.61; N, 9.3. Found: C, 71.8; H, 8.62; N, 9.4.

N,N′-Diphenyldiphenoquinonediimine-N,N′-dioxide (XIV) (Method II).—N,N′-Diphenylbenzidine (0.5 g., 0.00149 mole) dissolved in 7.5 ml. of dimethylformamide was added with stirring at room temperature to 16.4 ml. of benzene containing 0.678 g. of perbenzoic acid (0.0049 mole). After 22 hours the reaction product which had precipitated was filtered, washed with benzene and petroleum ether, and dried to give 0.45 g. of purplish brown crystals (yield 83%) which melted with decomposition at 280°; maximum absorption in chloroform, 485 mμ, ϵ 33,000.

Anal. Calcd. for $C_{24}H_{18}N_2O_2$: N, 7.65. Found: N, 7.5.

N-Phenyl-N′-(2,4-dinitrophenyl)-*p*-quinonediimine-N,N′-dioxide (Method II).—N-Phenyl-N′-(2,4-dinitrophenyl)-*p*-phenylenediamine (7 g., 0.02 mole) partially dissolved in 200 ml. of benzene was mixed with 34 g. of 40% solution of peracetic acid in glacial acetic acid (0.179 mole of peracid) and allowed to stand in the dark at room temperature for 12 days. The deposits were filtered, washed with benzene and dried to yield 4.5 g. of maroon crystals (yield 59%). The properties of this compound are given in the tables.

Neither *p*-quinone dibenzenesulfonimide[10] nor N,N′-bis-(2,4-dinitrophenyl)-*p*-phenylenediamine could be converted to the corresponding N,N′-dioxides with perbenzoic acid.

WILMINGTON 99, DEL.

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(9) C. J. Pedersen, United States Patent 2,741,625, April 10, 1956.

(10) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).