effective dielectric constant, D, was taken as 2.5 for 70% dioxane.

The transition state of the 5-isomer was thus found to be stabilized by a coulombic energy of 1.32 kcal./mole and that of the 8-isomer by an energy of 1.13 kcal./mole. If these stabilization energies were subtracted from an accurate value of the energy of activation for ethyl 2-naphthoate, the resulting values should represent the energy of activation for the respective ethyl nitro-2-naphthoates.

The actual experimental energies of activation are too sensitive to errors in the rates to be used for this purpose. Consequently the mean value of log PZ (8.13) and the rates of hydrolysis at 25° were used to calculate comparable activation energies for ethyl 2-naphthoate, ethyl 5-nitro-2-naphthoate and ethyl 8-nitro-2-naphthoate. These values are given below under the title, "Experimental" E_a. When the above stabilization energies were subtracted from the energy of activation for ethyl 2-naphthoate obtained in this manner, the resulting values (calculated E_a) compared favorably with the "Experimental" E_a for ethyl 5-nitro-2-naphthoate and ethyl 8-nitro-2-naphthoate.

	"Experimental"[a] E_a (kcal./mole)	Stabilization energy	Calcd. E_a[b]
Ethyl 2-naphthoate	14.45	..	(14.45)
Ethyl 5-nitronaphthoate	13.15	1.32	13.13
Ethyl 8-nitronaphthoate	13.40	1.13	13.32

[a] $E_a = 2.3\ RT(8.13 - \log k_{25})$. [b] 14.45 minus column 3.

The σ-Values.—The σ^1-values listed in Table II may be looked upon as those of a substituted, unsaturated side chain attached to ethyl benzoate in the meta and para positions. It would be expected then, that the electrical effects of the substituents on this side chain, although weaker, would be qualitatively the same as those of the analogous substituents on the benzene ring. A comparison of such σ-values shows this to be so only in cases where the special properties of the naphthalene nucleus do not enter.

TABLE IV

COMPARISON OF σ-VALUES FOR ANALOGOUS SUBSTITUENTS IN NAPHTHALENE AND BENZENE

6-Methoxy–*p*-methoxy	−0.155	−0.268
7-Methoxy-*m*-methoxy	− .035	.115
8-Amino–*p*-amino	− .196	− .653
5-Amino–*m*-amino	− .059	− .112
8-N,N-Dimethylamino–*p*-N,N-dimethylamino	− .062	− .671[a]
8-Nitro–*p*-nitro	.332	.803
5-Nitro–*m*-nitro	.416	.696

[a] D. C. Lincoln (THIS JOURNAL, **73**, 5838 (1951)) has found that $\sigma = -0.360$ for ethyl 3-methyl-4-dimethylaminobenzoate. Since $\sigma = -0.110$ for the *m*-methyl group, σ for the hindered *p*-dimethylamino group must be approximately −0.250.

Acknowledgment.—We would like to express our appreciation for the aid given to us by Brother Columba Curran, C.S.C., in connection with the measurements of the electric moment of the ethyl nitro-2-naphthoates.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XVII. Addition of Organic Acids to *p*-Quinonedibenzimide and Related Compounds

BY ROGER ADAMS AND D. S. ACKER[1]

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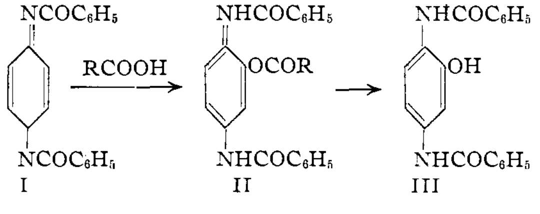
p-Quinonedibenzimide adds various organic acids to yield 2-acyloxy-*p*-phenylenedibenzamides. These are readily hydrolyzed to the 2-hydroxy-*p*-phenylenedibenzamide. Acetic acid has also been added in a similar way to *p*-quinonedicarbethoxyimide, *p*-quinonedicarbobenzoxyimide, 2-methyl- and 2-chloro-*p*-quinonedibenzimides. 2-Acetoxy-*p*-phenylenedibenzamide is oxidized to the corresponding diimide, which is difficult to isolate but readily converted with hydrogen chloride to *x*-chloro-2-acetoxy-*p*-phenylenedibenzamide. *p*-Quinonedibenzenesulfonimide does not react with acetic acid unless a catalyst such as boron fluoride is present; it then forms 2-acetoxy-*p*-phenylenedibenzenesulfonamide.

p-Quinonedibenzenesulfonimides were frequently prepared and crystallized from glacial acetic acid. They were unreactive to this solvent. On the other hand, in the investigation of the *p*-quinonedibenzimide, it was observed that the product reacted with glacial acetic acid to form a stable substance. There are no examples recorded in the literature showing the addition of organic acids to benzoquinones.

Various organic acids were added to *p*-quinonedibenzimide (I) merely by allowing a solution of this substance in the acid to stand at room temperature. Solid acids may be added by melting the reactants. Some acids will add in a neutral solvent. The reaction is quite general and the results are shown in Table I. The 2-acyloxy-*p*-phenylenedibenzamides (II) are obtained in good yields. Infrared spectra confirm the presence of the ester carbonyl. These addition products are easily hydrolyzed by aqueous alkali to the free phenol, 2-hydroxy-*p*-phenylenedibenzamide (III).



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[1] An abstract of a thesis submitted by D. S. Acker to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

TABLE I: ADDITION PRODUCTS OF VARIOUS ACIDS TO *p*-QUINONE DIIMIDES

	Diimide	Acid	Amount of acid	Procedure	Reaction time, hours	Solvent for recrystallization	Crude yield, %	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1	*p*-Quinonedibenzimide[3]	Formic[a]	1.0 ml.; 0.1 g.	A; C	–; 24	$CHCl_3$	82; 37[b]	195 dec.	69.99	4.48	70.11	4.57
2	*p*-Quinonedibenzimide	Acetic	4.0 ml.; 0.14 g.	A; C	0.5; 24	EtAc	84; 66	228–229	70.57	4.85	70.40	4.92
3	*p*-Quinonedibenzimide	Propionic	10 ml.	A	24	EtAc–petroleum ether[c]	65	205–206	71.12	5.19	71.19	5.18
4	*p*-Quinonedibenzimide	*n*-Valeric	10 ml.	A	24	EtAc–petroleum ether[c]	66	205–206	72.09	5.81	71.88	5.88
5	*p*-Quinonedibenzimide	Trifluoroacetic[a]	0.2 g.	C	20	$CHCl_3$	93[d]					
6	*p*-Quinonedibenzimide	Trichloroacetic[a]	1.0 g.; 0.5 g.	B; C	–; –	$CHCl_3$	74; 71	204–206	55.31	3.16	55.50	3.29
7	*p*-Quinonedibenzimide	Crotonic	1.0 g.; 0.5 g.	B; C	–; 48	EtAc	77; 14[e]	228–229	71.99	5.03	71.92	4.90
8	*p*-Quinonedibenzimide	*trans*-Cinnamic	1.0 g.	B	..	EtAc	82	258.5–259.5	75.31	4.80	75.42	4.96
9	*p*-Quinonedibenzimide	Benzoic	1.0 g.	B	..	$CHCl_3$	84	228–230	74.30	4.62	74.42	4.66
10	2-Chloro-*p*-quinonedibenzimide[3]	Acetic	5 ml.	A	15	C_6H_6	73	181–182	64.64	4.19	64.55	4.30
11	2-Methyl-*p*-quinonedibenzimide	Acetic	2 ml.	A	24	C_6H_6	73	192–193	71.12	5.19	71.14	5.14
12	*p*-Quinonedicarbethoxyimide[3]	Acetic	2 ml.	A	15	$EtOH–H_2O$	81	140	54.19	5.85	54.36	6.00
13	*p*-Quinonedicarbethoxyimide	Propionic	5 ml.	A	48	C_6H_{12}	92	141–142	55.55	6.22	55.52	6.37
14	*p*-Quinonedicarbethoxyimide	*n*-Valeric	5 ml.	A	48	C_6H_{12}	14	110–112	57.94	6.87	57.87	6.99
15	*p*-Quinonedicarbobenzoxyimide[2]	Acetic	5 ml.	A	2	$CH_3C_6H_{11}$	93	160–161	66.35	5.11	66.49	5.20
16	*p*-Quinonedibenzenesulfonimide[4]	Acetic	40 ml.	D	24	HOAc	69	191–192	53.80	4.06	53.95	4.10
17	*p*-Quinonedibenzenesulfonimide	Propionic	20 ml.	D	24	$CH_3C_6H_5$	63	155–156	54.77	4.38	54.90	4.49
18	*p*-Quinonedibenzenesulfonimide	Crotonic	1.0 g.; 0.5 g.	B[f]; C[g]	–; 16	C_6H_6	20; 38	183–184	55.92	4.27	56.06	4.21

[a] The addition products formed in these cases were partially hydrolyzed if recrystallized from other than dry solvents. [b] Also obtained 12% of reduction product, *p*-phenylenedibenzamide. [c] The product was dissolved in hot ethyl acetate and then hot petroleum ether (b.p. 80–110°) was added to give a saturated solution. [d] Although a good yield of the crude addition product was obtained, it hydrolyzed so rapidly that it could not be purified. [e] Also obtained 14% of reduction product, *p*-phenylenedibenzamide. [f] Added one drop of a 40% solution of boron fluoride in ether to the fused reactants. There was much decomposition and 16% of reduction product, *p*-phenylenedibenzenesulfonamide, was also obtained. [g] Added 5 drops of the boron fluoride solution. Also obtained 48% of the reduction product, *p*-phenylenedibenzenesulfonamide.

2-Methyl- and 2-chloro-*p*-quinonedibenzimides and acetic acid gave good yields of essentially single products, but the orientation of the entering acetoxy group was not determined. 2,6-Dichloro-*p*-quinonedibenzimide did not give any isolable products, which was not unexpected since the addition of hydrogen chloride to this substance has been shown to be anomalous.[2] *p*-Quinonedicarbethoxyimide and *p*-quinonedicarbobenzoxyimide also added acetic acid.

2-Acetoxy-*p*-phenylenedibenzamide was oxidized by lead tetraacetate in refluxing chloroform or benzene to give a reddish solution from which no crystalline diimide could be isolated. Its formation, however, was established by treatment of this solution with hydrogen chloride. The product, obtained in excellent yield, proved to be the same as that formed by the addition of acetic acid to 2-chloro-*p*-quinonedibenzimide.

When *p*-quinonedibenzenesulfonimide was boiled with the organic acid without catalyst, much decomposition and reduction occurred and the only product isolated was *p*-phenylenedibenzenesulfonamide. Formic acid reacted at room temperature to give *p*-phenylenedibenzenesulfonamide and benzenesulfonamide as the only identifiable products. Although *p*-quinonedibenzenesulfonimide does not react with acetic acid when merely dissolved in it, the presence of a catalyst such as boron fluoride, hydrogen fluoride and concentrated sulfuric acid causes reaction to take place. Boron fluoride is the most useful catalyst and the only one which permitted the formation of 2-propionoxy-*p*-phenylenedibenzenesulfonamide in good yields when propionic acid replaced acetic acid. By the addition of 48% hydrofluoric acid to a propionic acid solution of the diimide, benzenesulfonamide was the main product and by use of concentrated sulfuric acid a mixture resulted from which only a low yield (8%) of the adduct could be isolated.

Acknowledgment.—The authors are indebted to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas and Miss Elizabeth Petersen for the infrared spectra.

Experimental

All melting points are corrected.

General Procedures for Addition of Organic Acids to *p*-Quinone Diimides. Procedure A.—A solution of 0.50 g. of the *p*-quinone diimide in 1 to 10 ml. of the liquid organic acid was prepared by shaking in the cold or by gentle warming if necessary. The yellow solutions became quite red as the reactions proceeded. If the product precipitated, it was collected as soon as the reaction appeared to be com-

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(2) R. Adams and D. S. Acker, THIS JOURNAL, **74**, 3029 (1952).

(3) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).

(4) R. Adams and A. S. Nagarkatti, *ibid.*, **72**, 4601 (1950).

plete. In the other cases the solutions were allowed to stand for longer periods of time (15–48 hours) and then the product was precipitated by the addition of petroleum ether (b.p. 80–110°). Two recrystallizations from the solvents indicated in the table gave pure white products. See Table I.

Procedure B.—When using the solid organic acids, a mixture of 0.50 g. of the *p*-quinone diimide and 1.0 g. of the acid was slowly heated from room temperature to above the melting point of both reactants. The reaction usually occurred as soon as the acid melted; the solution became dark colored and the mass solidified as the addition product formed. After cooling to room temperature, the solid was broken up and boiled with 100 ml. of petroleum ether (b.p. 80–110°) to remove the excess acid. The residues were recrystallized one or more times from appropriate solvents to give pure white products (see Table I).

Procedure C.—Some of the acids could be added in an inert solvent. A solution of 0.50 g. of the *p*-quinone diimide in a minimum of chloroform was treated with an excess of the organic acid and the resulting solution allowed to stand for 48 hours unless there was evidence of complete reaction before this time. The products were precipitated by the addition of petroleum ether (b.p. 80–110°) and recrystallized several times from the solvents indicated (see Table I).

Procedure D.—With *p*-quinonedibenzenesulfonimide it was necessary to use a catalyst. To a hot (80–100°) solution of 1.0 g. of *p*-quinonedibenzenesulfonimide in the organic acid was added 5 drops of a 40% solution of boron fluoride in ether. The solution became dark and was allowed to stand at room temperature for 24 hours. The product was precipitated by the addition of petroleum ether (b.p. 80–110°) and recrystallized several times from the solvents indicated (see Table I). Concentrated sulfuric acid or 48% hydrofluoric acid were satisfactory catalysts with acetic acid, but led to decomposition products with propionic acid.

2-Hydroxy-*p*-phenylenedibenzamide.—A suspension of 0.50 g. of 2-acetoxy-*p*-phenylenedibenzamide in 20 ml. of 10% aqueous sodium hydroxide was heated for 15 minutes on a steam-bath to give a clear solution. After cooling to room temperature, addition of hydrochloric acid precipitated a quantitative yield of the phenol. Three recrystallizations from ethyl acetate gave the pure product, m.p. 295–296°.

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.27; H, 4.85. Found: C, 72.51; H, 5.00.

2-Acetoxy-*p*-quinonedibenzimide.—A suspension of 0.80 g. of 2-acetoxy-*p*-phenylenedibenzamide and 0.95 g. of dry lead tetraacetate in 50 ml. of dry, thiophene-free benzene was heated under reflux for one hour. The red solution was filtered to remove the insoluble material and evaporated *in vacuo* to about 5 ml. Petroleum ether (b.p. 30–60°) was added and the solution chilled in a Dry Ice–methanol mixture. A yellow crystalline product separated but became a yellow oil when allowed to warm to room temperature, either after separation from the mother liquor or while still covered by it. Repeated attempts to recrystallize this viscous oil from petroleum ether (b.p. 45–50°) did not improve its characteristics.

Similar oxidations using lead tetraacetate in dry chloroform at room temperature or active lead dioxide[5] in refluxing benzene gave small amounts of yellow crystals having the same characteristics as those prepared previously. Although a crystalline diimide could not be isolated, it apparently is formed in good yield as demonstrated by the subsequent addition of hydrogen chloride described below.

***x*-Chloro-2-acetoxy-*p*-phenylenedibenzamide.**—A suspension of 1.0 g. of 2-acetoxy-*p*-phenylenedibenzamide and 1.2 g. of lead tetraacetate in 50 ml. of chloroform was stirred under reflux for 15 minutes. The orange solution was filtered to remove the insoluble material and 100 ml. of petroleum ether (b.p. 80–110°) added to the mother liquor. Hydrogen chloride was passed into the solution for 5 minutes causing a partial bleaching and the formation of a white precipitate. The solvents were removed *in vacuo* and the residue recrystallized from an ethyl acetate–petroleum ether solvent pair to give 1.0 g. (92%) of white crystals. Recrystallization from benzene gave the pure product, m.p. 181–182°. Infrared spectra proved that this compound is identical with the one formed by the addition of acetic acid to 2-chloro-*p*-quinonedibenzimide (see Table I).

***x*-Chloro-2-hydroxy-*p*-phenylenedibenzamide.**—A suspension of 0.20 g. of *x*-chloro-2-acetoxy-*p*-phenylenedibenzamide in 50 ml. of 5% aqueous sodium hydroxide was allowed to stand at room temperature for one hour. The solid went slowly into solution. After filtering to remove a slight cloudiness, hydrochloric acid was added to precipitate 0.14 g. (78%) of the phenol. Two recrystallizations from an ethyl acetate–petroleum ether solvent pair gave the pure product, m.p. 246–246.5°.

Anal. Calcd. for $C_{20}H_{15}ClN_2O_3$: C, 65.49; H, 4.12; N, 7.64. Found: C, 65.36; H, 4.32; N, 7.95.

2-Methyl-*p*-phenylenedibenzamide.—To a solution of 23.0 g. of 2-methyl-*p*-phenylenediamine sulfate in 300 ml. of pyridine cooled in an ice-bath, was added, with mechanical stirring and over a period of one hour, 23.5 ml. of benzoyl chloride. After stirring one hour longer at room temperature, the reaction mixture was poured into 1500 ml. of ice-water. The precipitated solid was recrystallized several times from dimethyl formamide to give 15.8 g. (48%) of pure product, m.p. 309–310°.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49. Found: C, 76.52; H, 5.68.

2-Methyl-*p*-quinonedibenzimide.—To a suspension of 2.80 g. of 2-methyl-*p*-phenylenedibenzamide in 100 ml. of refluxing chloroform was added 3.8 g. of lead tetraacetate. The solution became yellow immediately and was stirred under reflux for 2 hours. After cooling to room temperature, the insoluble material was removed by filtration and the chloroform distilled *in vacuo*. One recrystallization of the residue from dry ether gave 2.53 g. (93%) of bright yellow crystals, m.p. 108–109°.

Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91. Found: C, 76.69; H, 5.19.

2-Hydroxy-*p*-phenylenedibenzylcarbamate.—A solution of 0.50 g. of 2-acetoxy-*p*-phenylenedibenzylcarbamate in 20 ml. of methanol and 1 ml. of concentrated hydrochloric acid was heated under reflux for 15 minutes. The white precipitate which formed was collected, after cooling to room temperature, to give 0.44 g. (97%) of the free phenol. One recrystallization from methanol gave the pure product, m.p. 218–219°.

Anal. Calcd. for $C_{22}H_{20}N_2O_5$: C, 67.34; H, 5.14. Found: C, 67.57; H, 5.19.

Attempts to prepare this phenol by alkaline hydrolysis of 2-acetoxy-*p*-phenylenedibenzylcarbamate gave only acid-soluble material.

2-Hydroxy-*p*-phenylenedibenzenesulfonamide (A).—Hydrogen fluoride was bubbled slowly into a solution of 1.0 g. of *p*-quinonedibenzenesulfonimide in 40 ml. of glacial acetic acid contained in a platinum dish. After 30 minutes the solution had become quite black. Addition of water caused precipitation of 0.76 g. (72%) of gray solid. Two recrystallizations from glacial acetic acid (Darco) gave pure white crystals, m.p. 235–237° (dec.). The infrared spectrum showed the presence of a phenolic hydroxyl and absence of a carbonyl group.

Anal. Calcd. for $C_{18}H_{16}N_2O_5S_2$: C, 53.45; H, 3.99; N, 6.93. Found: C, 53.41; H, 3.75; N, 6.71.

When hydrogen fluoride was bubbled into the acetic acid solution for 30 seconds and the reaction vessel stoppered and allowed to stand overnight, a mixture of the acetoxy and free hydroxy compounds was obtained.

(B).—A suspension of 0.50 g. of 2-acetoxy-*p*-phenylenedibenzenesulfonamide in 30 ml. of 20% hydrochloric acid and 10 ml. of ethanol was refluxed for 1.5 hours. Addition of 100 ml. of water precipitated 0.46 g. (99%) of white solid. Recrystallization from glacial acetic acid gave the pure product, m.p. 235–237° (dec.). Infrared spectra proved this compound to be identical with the product formed by method (A).

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[5] R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950).