centrated hydrochloric acid were added. The layers were separated and the organic layer was washed with 100 cc. of water. Distillation yielded 124.5 g. (52% recovery) of ethyl malonate, b. p. $87-89^{\circ}$ (13 mm.), n^{25} D 1.4125; 11.0 g. of intermediate, b. p. 89° (13 mm.)- 102° (0.35 mm.), n^{25} D 1.4210; 49 g. (44\% recovery) of methyl *p*-chloromethylbenzoate, b. p. 102-118° (0.35-0.60 mm.), n^{25} D 1.5330-1.5298; 6.5 g. of intermediate, b. p. 118-174° (0.60-0.70 mm.); and 68.0 g. (37% conversion and 68.0 yield based on methyl *p*-chloromethylbenzoate) of ethyl *p*carbomethoxybenzylmalonate, b. p. 174-184° (0.70-0.80 mm.), n^{25} D 1.4960. There was a 17.0 g. residue. In another experiment in which the ratio of ethyl malo-

In another experiment in which the ratio of ethyl malonate to methyl p-chloromethylbenzoate was 1.1/1.0 instead of 2.5/1.0 crystals were observed in the distillation residue. They were separated by filtration, washed with hexane and dried. Crystallization from methanol and then from hexane yielded pure ethyl bis-(p-carboethoxybenzyl)-malonate, m. p. 82-83°.

Anal. Calcd, for $C_{27}H_{\pi_2}O_8$: C, 67.0; H, 6.61. Found: C, 66.9; H, 6.54.

 β -(p-Carboxyphenyl)-propionic Acid.—A mixture of 31 g. of ethyl p-carbomethoxybenzylmalonate, 28 g. of potassium hydroxide and 50 cc. of water was boiled under reflux for three and one-half hours. Upon cooling, the solution was acidified with concentrated hydrochloric acid. The slurry was chilled in an ice-bath, filtered and the precipitate of crude β -(p-carboxyphenyl)-propionic acid was washed with water. It was crystallized twice from water. Two crops were obtained: I, 13.5 g., m. p. 270–280°, neut. equiv., 85.2, 85.0 and II, 5.0 g., m. p. 276–280°, neut. equiv., 82.7, 82.6. The neutral equivalent of pcarboxybenzylmalonic acid is 79 and that of p-carboxyphenylpropionic acid is 87.

A suspension of 43 g, of crude β -(*p*-carboxyphenyl)-propionic acid in 250 cc. of phenyl ether was stirred under reflux for seven hours. After cooling, the mixture was filtered. The precipitate was slurried with hexane, separated by filtration and dried. Recrystallization from glacial acetic acid yielded 29.5 g. of β -(*p*-carboxyphenyl)-propionic acid, m. p. 286–291° (294°).³ Methyl β -(*p*-Carbomethoxyphenyl)-propionate.—A mixture of β control of β contr

Methyl β -(*p*-Carbomethoxyphenyl)-propionate.—A mixture of 28 g. of β -(*p*-carboxyphenyl)-propionic acid, 1 l. of methanol and 10 cc. of concentrated sulfuric acid was stirred under reflux for twenty-three hours. After 900 cc. of methanol had been removed by distillation, the mixture was cooled and some product separated by filtration. The filtrate was diluted with 100 cc. of water and extracted four times with a mixture of benzene and hexane. The original precipitate was dissolved in the combined extracts and then the solution was washed once with aqueous sodium bicarbonate and twice with water. After the solution had been dried over calcium chloride, the solvents were distilled and the residue crystallized by chilling in ice. After two recrystallizations from hexane there was obtained 21.5 g. (46% yield based on ethyl *p*-carbomethoxybenzylmalonate) of methyl $\beta - (p$ -carbomethoxyphenyl)propionate, m. p. 29–31° (33°).³ 2-Ethylhexyl $\beta - (p$ -Carbo-2-ethylhexoxyphenyl)-propion-

2-Ethylheryl β -(p-Carbo-2-ethylhexoxyphenyl)-propionate.—A solution of 21.5 g. of methyl β -(p-carbomethoxyphenyl)-propionate in 65 g. of 2-ethylhexanol containing 1.0 g. of p-toluenesulfonic acid was boiled for four hours (until the pot temperature reached 145-150°) under a 24" Vigreux column while the evolved methanol distilled as formed. The residue was diluted with 35 cc. of benzene, washed once with aqueous sodium bicarbonate, twice with water, and then dried over calcium chloride. After the addition of 1 g. of Norit to the solution, the benzene and 2-ethylhexanol were distilled and the residue was heated for one hour at 150° and 0.5 mm. pressure. Filtration through a sintered glass filter removed the Norit and yielded 33.5 g. (80%) of 2-ethylhexyl β -(p-carbo-2-ethylhexoxyphenyl)-propionate, n^{26} D 1.4829, d^{85} ₂₅ 0.983.

Anal. Calcd. for $C_{26}H_{42}O_4$: C, 74.6; H, 10.04. Found: C, 74.1; H, 9.78.

Summary

p-Chloromethylbenzoyl chloride has been found to be a useful intermediate for the preparation of esters involving both the alcohol and acid functions of the molecule.

Methyl p-chloromethylbenzoate reacted readily with sodium thiocyanate and with malonic ester and could be coupled to give a diphenylethane derivative.

DAYTON 7, OHIO

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

Quinone Imides. II. p-Quinone Diacyl and Diaroylimides

BY ROGER ADAMS AND JOHN L. ANDERSON^{1,2}

During the initial investigation of the oxidation of sulfonamides of p-phenylenediamine³ in glacial acetic acid by means of lead tetraacetate, a few experiments to prepare the diimides from the diacetyl and dibenzoyl derivatives of p-phenylenediamine were attempted, but no identifiable products were isolated. The present investigation was undertaken in an attempt to find conditions under which these latter compounds could be oxidized to quinone diimides. Studies have shown that temperature and, particularly, solvent and concentration are important factors in the

(1) An abstract of a thesis submitted by John L. Anderson to the Graduate College of the University of Illinois, 1950, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(2) University of Illinois Fellow, 1948-1949. Allied Chemical and Dye Corporation Fellow, 1949-1950.

oxidations. By controlling these conditions, the diacyl, diaroyl, and related derivatives of p-phenylenediamine can be converted to the p-quinone diimides by means of lead tetraacetate in very satisfactory yields. This preliminary paper is confined to a description of the derivatives represented by I and II.



where (a) $X = Y = COC_6H_{6}$, (b) $X = Y = COCH_3$, (c) $X = Y = CO_2C_2H_5$, (d) $X = V = CO_2C_2H_5$, (d) X = V = CO

⁽³⁾ Adams and Nagarkatti, THIS JOURNAL, 72, 4601 (1950).

 $COCO_2C_2H_{\delta}$, and (e) $X = COC_6H_{\delta}$ and $Y = SO_2C_6H_{\delta}$.

The compounds Ia, Id and Ie were best oxidized by equivalent portions of lead tetraacetate in dry, thiophene-free benzene at reflux temperature with the formation of IIa, IId and IIe, respectively. Compound Ib was oxidized to IIb by lead tetraacetate in dry, ethanol-free chloroform suspension at reflux temperature, while Ic was best oxidized to IIc in anhydrous ether at room temperature using the same oxidizing agent. The time of reaction varied from four hours for the oxidation of Ib to fifteen hours for the oxidation of Ia. The products were isolated after filtration from the insoluble lead diacetate by direct crystallization from the mother liquor, by addition of petroleum ether and subsequent crystallization, or by evaporation of the solvent in vacuo and crystallization from ether and/or petroleum ether.

Only Id was ever oxidized successfully in glacial acetic acid, and its oxidation product, IId, was isolated only in very small yield. Apparently the acid conditions which are so advantageous in the oxidation of the disulfonamides³ cause undesirable side-reactions in the carboxylic amide series for the starting material is never recovered.

The diacyl and diaroyl diimides have properties not far different from those of the disulfonyl derivatives. All are yellow or yellow-orange in color, but IIc is much more faintly colored than any of the others. Four of these diimides have been characterized by the addition of hydrogen chloride either by means of concentrated hydrochloric acid in glacial acetic acid or by passing dry hydrogen chloride into a chloroform solution. Presumably the addition of hydrogen chloride is 1,4 followed by a tautomeric shift of hydrogen to give the aromatic structure. The corresponding 2-chloro derivatives of the original substituted p-phenylenediamines result. Only in the case of IId was no addition product isolated. The chloro substituted p-phenylenedibenzamide is readily oxidized to the corresponding diimide in benzene solution.



These p-quinone diimides resemble p-benzoquinone in their reactions. They are reduced readily by sodium hydrosulfite to the benzene derivatives from which they are derived, and both add one molecule of hydrogen chloride to give the corresponding monochloro benzenoid structure. The p-quinone dibenzimide may also be reduced with aqueous sodium hydroxide in a similar manner to that described for p-quinone dibenzenesulfonimide. The solubilities of the *p*-quinone diimides are remarkably different from those of the parent diamides. While *p*-phenylenedibenzamide and diacetamide are virtually insoluble in the common organic solvents, that is, ethanol, benzene, ether, etc., all the *p*-quinone diimides are very soluble in these reagents. The diimides may even be recrystallized from such solvents as petroleum ether and cyclohexane.

The p-quinone dibenzimide (Ia) and p-quinone benzimide monobenzenesulfonimide (Ie) are apparently completely stable at room temperature, even if impure. The diacetimide, dicarbethoxyimide and diethoxalylimide decompose gradually at room temperature in air with change in color. In presence of moisture at elevated temperatures the decomposition is more rapid. The stability of these substances is appreciably less than that of the p-quinone disulfondiimides.

The near ultraviolet absorption maxima of various parent p-phenylenediamides and p-quinone diimides which are under investigation in this laboratory are listed in Table I. The similarity of the absorption maxima and intensity of absorption of the p-quinone diacetimide, dicarbethoxyimide, and diethoxalylimide is marked and is undoubtedly due to the same conjugated system in each. Because of the modification of the p-quinone diamide conjugated system by the substituents on the nitrogen atoms, the characteristic absorption for the basic nucleus could not be determined.

The authors are indebted to Miss Emily Davis, Miss Rachel Kopel and Mr. Maurice Dare for the microanalyses and to Mr. John Gardner for the ultraviolet absorption spectra.

Experimental

All melting points below 300° were taken on a Fisher melting point block and are corrected.

p-Phenylene Monobenzamide Monobenzenesulfonamide.—To a solution of 4.96 g. of *p*-phenylene monoamine monobenzenesulfonamide⁴ in 50 ml. of pyridine cooled to 5°, 2.82 g. of benzoyl chloride was added all at once. The solution was shaken vigorously, the temperature rose to 80°, and then the solution was allowed to cool slowly. On pouring the reaction mixture into water, a white powder separated. This was dissolved in 95% ethanol, decolorized with Darco, and cooled. There was obtained 3.25 g. of white plates. A second crop, slightly reddish, weighing 1.52 g. was obtained by the addition of water to the ethanolic mother liquor and was recrystallized from ethanol (Darco) before addition to the main portion. The total yield of pure product was 4.21 g. (60%). Recrystallization from ethanol did not raise the m. p. which was 222-223°.

Anal. Calcd. for $C_{19}H_{16}O_{8}N_{2}S$: C, 64.75; H, 4.58; N, 7.95. Found: C, 64.69; H, 4.72; N, 7.88.

p-Quinone Monobenzimide Monobenzenesulfonimide. —A suspension of 1.06 g. of p-phenylene monobenzamide monobenzenesulfonamide and 1.33 g. of lead tetraacetate (free of odor of acetic acid) in 90 ml. of dry, thiophene-free benzene was heated under reflux for eight and one-half hours. The reddish-yellow solution was filtered from the insoluble lead diacetate. The solvent was removed in vacuo and the quinone diimide was taken up in petroleum

⁽⁴⁾ Morgan and Micklethwait, J. Chem. Soc., 87, 80 (1905).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF *p*-QUINONE DI-IMIDES AND *p*-PHENYLENEDIAMIDES

All determinations were made on solutions containing 20 mg./liter of 95% EtOH. Compounds 6 and 6a were prepared by Dr. R. C. Walter; 7, 7a, 9 and 9a, were prepared by Dr. J. H. Looker; 8 and 8a were prepared by Dr. K. R. Eilar. Compounds 10 and 10a are included for comparison.

λ

	Compound	mµ	\times 10 ⁻³
1	CH ₃ CON=C ₆ H ₄ =NCOCH ₃	280	28.0
2	$C_2H_5O_2CN = C_6H_4 = NCO_2C_2H_5$	282	28.0
3	$C_2H_5O_2CCON = C_6H_4 = NCOCO_2C_2H_5$	277	19.5
4	C ₆ H ₅ CON=C ₆ H ₄ =NCOC ₆ H ₅	239	22.6
		288	35.2
5	$C_6H_5SO_2N=C_6H_4=NCOC_6H_4$	219	12.4
		240	14.5
		301	32.4
6	$CH_3SO_2N=C_6H_4=NSO_2CH_3$	242	5.4
		305	19.4
7	$CH_3SO_2N=C_6H_4=O$	276	17.5
8	$C_6H_5SO_2N=C_6H_4=NSO_2C_6H_6$	217	20.8
		252	10.2
		265	11.4
		271	12.7
		306	15.1
9	$C_{a}H_{5}SO_{2}N=C_{a}H_{4}=O$	218	11.5
		245	9.8
		252	10.4
		262	12.1
		277	13.3
10	$O = C_{f}H_{4} = O$	242	16.6
	•	281	0.6
1a	CH ₃ CONHC ₆ H ₄ NHCOCH ₃	265	22.2
2a	C ₂ H ₅ O ₂ CNHC ₆ H ₄ NHCO ₂ C ₂ H ₅	254	22.3
		285	1.3
3a	$C_2H_4O_2CCONHC_6H_4NHCOCO_2C_2H_4$	216	8.5
		306	16.2
4a	C ₆ H ₅ CONHC ₆ H ₄ NHCOC ₆ H ₅	222	20.2
		298	21.3
5a	$C_6H_5SO_2NHC_6H_4NHCOC_6H_5$	215	21.6
		275	17.2
6a	CH ₃ SO ₂ NHC ₆ H ₄ NHSO ₂ CH ₃	249	17.8
		281	0.9
7a	CH ₃ SO ₂ NHC ₆ H ₄ OH	231	11.1
		283	1.9
8a	$C_6H_5SO_2NHC_6H_4NHSO_2C_6H_5$	213	19.8
		241	13.2
9a	C₀H₅SO₂NHC₀H₄OH	258	9.1
		265	7.9
		272	6.6
		218	13.5
		226	12.5
		258	3.5
		266	3.6
10		273	3.4
10a	HUC6H4OH (nydroquinone)	225	ə.1 97
		293	2.7

ether (b. p. 80-110°). Upon cooling in a Dry Ice-methanol mixture, the product separated. After filtration and drying at room temperature, the product weighed 0.80 g. (75%). The m. p. after one recrystallization from petroleum ether (b. p. 80-110°) was 102-103°, unchanged by further recrystallization. The quinone diimide dissolves in coned. sulfuric acid with some carbonization to a dark orange solution.

Anal. Caled. for $C_{19}H_{14}O_3N_2S$: C, 65.13; H, 4.03; N, 8.00. Found: C, 65.07; H, 4.03; N, 8.19.

x-Chloro-p-phenylene Monobenzamide Monobenzenesulfonamide.—To a solution of 0.40 g. of p-quinone monobenzimide monobenzenesulfonimide in 15 ml. of glacial acetic acid was added one ml. of concd. hydrochloric acid with stirring at room temperature. The yellow color disappeared immediately. The solution was poured into cold water and a quantitative yield of x-chloro-p-phenylene monobenzamide monobenzenesulfonamide separated. Solution in ethanol (Darco) and addition of an equal volume of water gave 0.35 g. of product upon cooling, m. p. 177-178°.

Anal. Caled. for $C_{19}H_{18}O_3N_2SC1$: C, 58.99; H, 3.91; N, 7.24. Found: C, 59.24; H, 3.93; N, 7.03.

p-Phenylenediurethan.—*p*-Phenylenediurethan was prepared by the reaction of the calculated amount of ethyl chlorocarbonate with *p*-phenylenediamine in pyridine. The crude product was obtained in 76% yield with a 75% recovery after one recrystallization. The diurethan melted at 194–195° (lit. m. p. 196–196.5°).⁶

The crude product was obtained in $10\%_0$ yield with a $15\%_0$ recovery after one recrystallization. The diurethan melted at 194–195° (lit. m. p. 196–196.5°).⁵ *p*-Quinone Dicarbethoxyimide.—A suspension of 2.52 g. of *p*-phenylenediurethan and 4.44 g. of lead tetraacetate in 300 ml. of dry ether was stirred vigorously at room temperature (25°) for ten hours. After filtration, the reddish solution was cooled in a Dry Ice-methanol mixture; the product that separated weighed 1.79 g. (72%). Recrystallization once from dry ether gave yellow crystals of the quinone diimide, m. p. 76.5–77°. *p*-Quinone dicarbethoxyimide dissolves in concd. sulfuric acid with a very dark orange color.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.71; H, 5.77; N, 10.99.

Impure product turns red on standing in air and recrystallization of such a product leads to a low yield of pure material.

2-Chloro-*p*-phenylenediurethan.—Dry hydrogen chloride was passed into a solution of 1.0 g. of *p*-quinone dicarbethoxyimide in 10 ml. of dry chloroform; the yellow color disappeared almost instantaneously. After evaporation of the chloroform *in vacuo*, the residue was crystallized from petroleum ether (b. p. $80-110^{\circ}$) to give 1.0 g. (87%). One recrystallization from the same solvent (Darco) gave a pure product, m. p. $119.5-120^{\circ}$.

Anal. Calcd. for $C_{12}H_{15}O_4N_2Cl$: C, 50.26; H, 5.27; N, 9.77. Found: C, 50.59; H, 5.44; N, 9.88.

p-Phenylenedibenzamide.—To a solution of 10.8 g. of *p*-phenylenediamine in 100 ml. of pyridine, cooled in an ice-bath, was added 28.1 g. of benzoyl chloride over a period of two minutes with vigorous shaking. A solid separated immediately. The suspension was poured into ice water. After filtration, the precipitate was washed with dilute hydrochloric acid, water, hot ethanol and finally with ether. The yield of crude product was quantitative and melted at 335-340° (lit. m. p. >300°).⁶ The product was recrystallized from dimethyl formamide.

p-Quinone Dibenzimide.—A suspension of 1.35 g. of *p*-phenylenedibenzamide and 1.87 g. of lead tetraacetate in 90 ml. of dry, thiophene-free benzene was heated under reflux for fifteen hours. The reddish solution was filtered to remove the insoluble lead diacetate and reduced in volume to about 25 ml. Petroleum ether (b. p. 80–110°) was added and the solution chilled in a Dry Ice-methanol mixture. The yield of quinone dimide was 1.05 g. (78%). Two recrystallizations from petroleum ether (b. p. 80–110°) gave yellow crystals, m. p. 140–141.5°. This quinone dimide dissolves in concd. sulfuric acid with an orange color which changes on long standing to olive green.

Anal. Calcd. for $C_{20}H_{14}O_2N_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.67; H, 4.67; N, 9.06.

⁽⁵⁾ Schiff and Ostrogovich, Ann., 293, 375 (1896).

⁽⁶⁾ Hinsberg and von Udranszky, Ann., 254, 254 (1889),

It is quantitatively reduced to the diamide by heating with an ethanolic-aqueous solution of sodium hydrosulfite and is reduced in 60% yield merely by heating with 5% aqueous sodium hydroxide for two or three minutes.

2-Chloro-*p*-phenylenedibenzamide.—Upon adding *p*quinone dibenzimide to a mixture of glacial acetic acid and concentrated hydrochloric acid, the yellow color disappeared almost immediately, and, on pouring the acid solution into water, the white product separated in 95% yield. Two recrystallizations from benzene gave white crystals, m. p. 226-228°, which is that recorded in the literature.⁷

2-Chloro-*p*-quinone Dibenzimide.—A suspension of 0.70 g. of 2-chloro-*p*-phenylenedibenzamide and 0.89 g. of lead tetraacetate in 60 ml. of dry benzene was heated under gentle reflux for three hours. After filtration from the insoluble lead diacetate, and reduction in volume to 15 ml. the solution was diluted to 100 ml. with petroleum ether (b. p. 80–110°) and cooled in a Dry Ice-methanol bath. Three recrystallizations from petroleum ether (b. p. 80–110°) gave the pure product, m. p. 127–128.5°.

Anal. Calcd. for C₂₀H₁₃O₂N₂Cl: C, 68.87; H, 3.76; N, 8.03. Found: C, 68.92; H, 3.96; N, 8.20.

p-Phenylenediacetamide.—A solution of 10.8 g. of *p*-phenylenediamine in 300 ml. of water and 16.6 ml. of concd. hydrochloric acid was treated with Darco in the cold. After filtration, 23.3 ml. of acetic anhydride was added at room temperature. Then, with vigorous stirring, a solution of 30 g. of sodium acetate trihydrate in 100 ml. of water was added all at once. A white precipitate separated immediately which was thoroughly washed with water, dilute hydrochloric acid, water, ethanol and ether; after drying it weighed 16.7 g. (87%). One recrystallization from dimethyl formamide gave a pure product, m. p. $317-319^{\circ}$ (lit., m. p. 307°).⁸

Anal. Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.57; H, 6.41; N, 14.50.

p-Quinone Diacetimide.—A suspension of 1.92 g. of p-phenylenediacetamide and 4.44 g. of dry lead tetraacetate in 150 ml. of dry, ethanol-free chloroform was heated under reflux with stirring for three and one-half hours. The brownish suspension at the start of the reaction became a bright yellow after fifteen or twenty minutes and remained a bright yellow throughout the reaction. After filtering the chloroform solution from the insoluble lead diacetate, 100 ml. of petroleum ether (b. p. 80–100°) was added and the volume reduced *in vacuo* to 100 ml. On cooling the solution in a Dry Ice-methanol-bath, 1.18 g. of yellow crystals was isolated. Recrystallization from petroleum ether (b. p. 80–110°) gave 0.83 g. (44%) of crude quinone diimide. Three recrystallizations from dry

(8) Biedermann and Ledoux, Ber., 7, 1531 (1874); Träger and Westerkamp, Arch. Pharm., 247, 663 (1909).

ether gave pure quinone diimide, m. p. 125-126°. The product dissolves in concd. sulfuric acid with a dark orange color but carbonizes in part almost immediately. The pquinone diimide is unstable in the presence of heat and moisture; recrystallizations must be made from dry solvents with as little heat as possible. Even pure product gradually decomposes on standing as evidenced by change from yellow to a rust color.

Anal. Calcd. for $C_{10}H_{10}O_{2}N_{2}$: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.40; H, 5.48; N, 14.89.

2-Chloro-*p*-phenylenediacetamide.—The addition of hydrogen chloride was carried out on the crude dimide in glacial acetic acid with concd. hydrochloric acid. The yellow color disappeared immediately and the adduct was obtained by dilution with water. One recrystallization from ethanol gave the product, m. p. 195-197°. The reported m. p. of this product is 196° .^{7,9}

p-Quinone Diethoxalylimide.—A suspension of 3.08 g. of p-phenylenediethoxalylimide¹⁶ and 4.44 g. of lead tetraacetate in 150 ml. of dry, thiophene-free benzene was heated under reflux with stirring for six hours. After filtration of the red solution and dilution with petroleum ether (b. p. 80–110°), the solution was cooled; 1.40 g. (46%) of yellow orange product was obtained. This product was recrystallized three times from dry ether and gave yellow crystals, m. p. 124.5–126°. The quinone diimide dissolves in concd. sulfuric acid with the formation of an orange solution. Its stability resembles that of the dicarbethoxyimide.

Anal. Calcd. for $C_{14}H_{14}O_6N_2$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.78; H, 4.61; N, 9.04.

The diimide is quantitatively reduced in ethanolicaqueous sodium hydrosulfite to the diamide. The diimide does not, however, give a normal hydrogen chloride adduct by the methods used with the other diimides.

Summary

Diacyl and diaroyl derivatives of p-phenylenediamine have been oxidized to the corresponding p-quinone diimides by means of lead tetraacetate in benzene, chloroform, or ether solution or suspension. The diurethan and diethoxalyl derivatives behaved similarly. The products are less stable than the disulfonimides.

These quinone diimides are readily reduced to the original diamides from which they were formed and add hydrogen chloride to yield monochloro-p-phenylenediamine derivatives.

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⁽⁷⁾ Cohn, Chem. Zentr., 73, I, 752 (1902).

⁽⁹⁾ Kehrmann and Grab, Ann., 803, 11 (1898).

⁽¹⁰⁾ Meyer and Seeliger, Ber., 29, 2643 (1896).