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Quinone Imides. XXXV. *o*-Quinonedibenzimides

BY ROGER ADAMS AND JOHN W. WAY[1]

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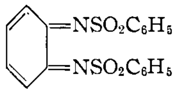
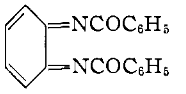
o-Quinonedibenzimide and the 4-chloro and 4-nitro derivatives have been synthesized by oxidation with lead tetraacetate of the corresponding *o*-phenylenedibenzamides. The unsubstituted diimide adds hydrogen chloride to give a mixture of the two monochloro dibenzamides; it adds acetic acid, methanol, hydrazoic acid, piperidine, malonic ester and acetylacetone to yield 4-substituted diamides, the structures of which were determined in the first three cases: it oxidizes thiophenol. 4-Chloro-*o*-quinonedibenzimide adds the same reagents as well as thiophenol and benzenesulfinic acid. The groups enter the 6-position as determined by proof of the structure of the hydrogen chloride adduct and of the benzoxazole formed in a secondary reaction from the acetic acid adduct. 4-Nitro-*o*-quinonedibenzimide adds hydrogen chloride and the chlorine enters the 3-position.

The syntheses of substituted *o*-quinonedibenzenesulfonimides and their reactions with hydrogen chloride have been reported in a previous paper.[2] *o*-Quinonedibenzenesulfonamide (I) could not be isolated from the oxidation of *o*-phenylenedibenzenesulfonamide in acetic acid; instead an amorphous product was obtained which it was not possible to characterize. It was postulated that a diimide was first formed which then polymerized by an intermolecular Diels–Alder type of reaction. However, several substituted *o*-quinonedibenzenesulfonimides were obtained in monomeric form.



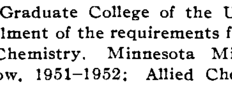
I



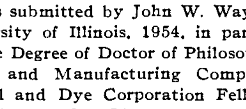
II

p-Quinonedibenzimide was resistant to the addition of conjugated dienes[3] whereas the *p*-quinonedibenzenesulfonimides added dienes with great ease. As a consequence, it was deduced that *o*-quinonedibenzimide (II) might be more stable in monomeric form than the *o*-quinonedibenzenesulfonimide (I). An investigation has confirmed this postulation. *o*-Quinonedibenzimide and some of its substitution products have been prepared and subjected to a variety of addition reactions.

o-Phenylenedibenzamide, 4-chloro- and 4-nitro-*o*-phenylenedibenzamide were oxidized by lead tetraacetate to the corresponding diimides, II, III and IV. To avoid contamination of the *o*-quinonedibenzimides with their acetic acid adducts which are formed far more readily than in the *para* series,[4] the oxidations were carried out in relatively dilute solutions of benzene or chloroform and, before isolation was attempted, the solutions of the diimides were washed with aqueous sodium bicarbonate. Removal of the solvent then gave satisfactory yields of essentially pure diimides. On the other hand, only diimides contaminated with their acetic acid adducts could be obtained when the 4-methyl- and 4-methoxy-*o*-phenylenedibenzamides were treated in a similar manner. If however, acetic acid was added to the benzene solution after oxidation, pure acetic acid adducts of the diimides were isolated. The use of lead dioxide[5] in place of lead tetraacetate in order to avoid the presence of any acetic acid failed to give oxidation products.



III

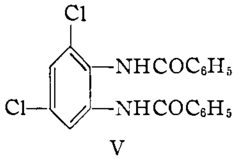


IV

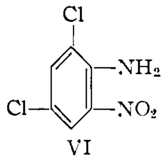
Both II and III were obtained as stable yellow crystalline solids; IV, however, was stable only in the benzene solution, since removal of the solvent resulted in a yellow amorphous solid which quickly decomposed to a dark red tar at room temperature. Both II and III were sensitive to heat, either in the solid state or in concentrated solutions.

The addition reactions of the *o*-quinonedibenzimides were similar to those of the *p*-quinonedibenzimides. When hydrogen chloride was added to *o*-quinonedibenzimide (II), a mixture of the two monochloro *o*-phenylenedibenzamides resulted, which was not further investigated.

Treatment of the monochloro derivative III with hydrogen chloride led to the formation exclusively of 4,6-dichloro-*o*-phenylenedibenzamide (V). This illustrates in the series of *o*-quinone diimides the difference in orientation induced by benzoyl groups and benzenesulfonyl groups on the nitrogens. The product of addition of hydrogen chloride to 4-chloro-*o*-quinonedibenzenesulfonimide is principally 4,5-dichloro-*o*-phenylenedibenzenesulfonamide.[2] The structure of V was proved through an unequivocal synthesis by the following series of intermediates: *o*-nitroaniline; 2,4-dichloro-6-nitroaniline[6] (VI); 4,6-dichloro-*o*-phenylenediamine; 4,6-dichloro-*o*-phenylenedibenzamide. The products made by the two methods had identical melting points and infrared spectra.



V



VI

4,5-Dichloro-*o*-phenylenedibenzamide (VII) was also prepared for comparison. The steps used were the following: 1,2-dichlorobenzene; 4,5-dinitro-

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[1] An abstract of part of a thesis submitted by John W. Way to the Graduate College of the University of Illinois, 1954, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry. Minnesota Mining and Manufacturing Company Fellow, 1951–1952; Allied Chemical and Dye Corporation Fellow, 1952–1953; University of Illinois Fellow, 1953–1954.

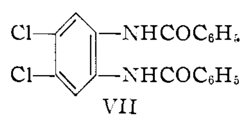
[2] R. Adams and C. N. Winnick, THIS JOURNAL, **73**, 5687 (1951).

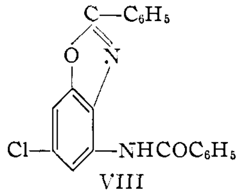
[3] R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952).

[4] R. Adams and D. S. Acker, *ibid.*, **74**, 3657 (1952).

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

[6] R. L. Datta and H. K. Mitter, THIS JOURNAL, **41**, 2036 (1919).

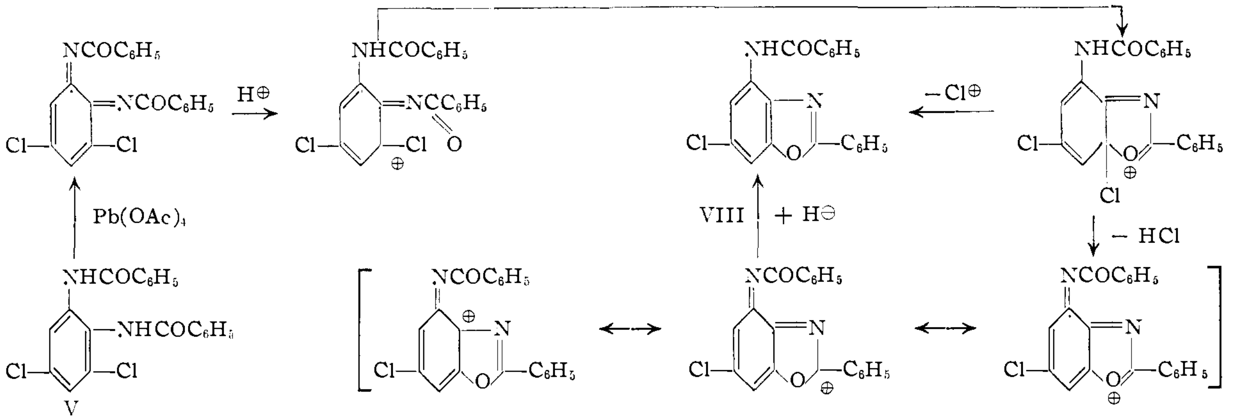

VII


VIII

1,2-dichlorobenzene[7]; 4,5-dichloro-*o*-phenylenediamine; 4,5-dichloro-*o*-phenylenedibenzamide. The product differed from that obtained from II and hydrogen chloride.

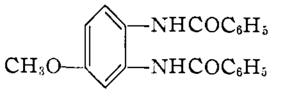
An adduct formed rapidly when acetic acid and II were mixed. The product was 4-acetoxy-*o*-phenylenedibenzamide as determined by hydrolysis to the known 4-hydroxy-*o*-phenylenedibenzamide. Upon addition of acetic acid to the 4-methyl- and 4-methoxy-*o*-quinonedibenzimides, acetoxy derivatives formed with the acetoxy group probably in the 6-position as judged by analogy to the position of this group in the 4-chloro diimide and acetic acid adduct. Acetic acid added with equal ease to the 4-chloro diimide (III) but in this case a secondary reaction occurred with the formation of 4-benzamido-6-chloro-2-phenylbenzoxazole (VIII). The position of the groups in this compound was established by its unexpected identity with the product obtained by the oxidation of the known 3,5-dichloro-*o*-phenylenedibenzamide (V). The acetoxy and chlorine groups from the acetic acid and hydrogen chloride are thus oriented similarly in the addition reactions to 4-chloro-*o*-quinonedibenzimide (III).

The formation of VIII by lead tetraacetate oxidation of V may be explained by the accompanying reaction scheme



Protonation of the diimide by a hydrogen ion from the acetic acid produced in the oxidation, followed by cyclization would give an intermediate which could decompose in two ways. Loss of a positive chlorine ion would produce VIII directly. Loss of a hydrogen ion and a chloride ion would lead to a structure with the indicated possible resonance structures. In either case it must be assumed that the positive ion produced is reduced by unreacted diamide V.

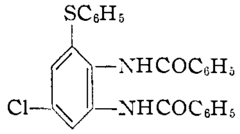
Boron trifluoride catalyzed the addition of methanol to II and III to give, respectively, 4-methoxy-*o*-phenylenedibenzamide (IX) and 4-chloro-6(?)-methoxy-*o*-phenylenedibenzamide. The structure of IX was demonstrated by its preparation as follows: 2-nitro-4-methoxyaniline; 4-methoxy-*o*-phenylenediamine; 4-methoxy-*o*-phenylenedibenzamide. The position of the methoxyl group as 6 in the 4-chloro derivative was assumed on the basis of analogy to the positions established for the acetoxy and chlorine.

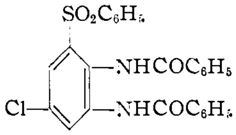

IX

Piperidine added to II and III to form monoadducts, presumably the 4-piperidino and 4-chloro-6-piperidino diamides, respectively.

Treatment of II and III with hydrazoic acid produced 4-azido-*o*-phenylenedibenzamide and probably the 6(?)-azido-4-chloro-*o*-phenylenedibenzamide, respectively. The structure of the former was established by catalytic reduction to 4-amino-*o*-phenylenedibenzamide, identical with a sample prepared by reduction of 4-nitro-*o*-phenylenedibenzamide.

Although thiophenol or benzenesulfinic acid caused reduction of *o*-phenylenedibenzimide (II), they added to the chloro derivative III (the thiophenol with triethylamine as catalyst) to form, respectively, 4-chloro-6(?)-phenylmercapto-*o*-phenylenedibenzamide (X) and 4-chloro-6(?)-benzenesulfonyl-*o*-phenylenedibenzamide (XI).


X


XI

The latter XI was also formed by hydrogen peroxide oxidation of X. The orientation of groups was not proved but it is likely that the entering group is in the 6-position on the basis of previous results.

Representative active methylene compounds added to the *o*-quinonedibenzimides. Diethyl malonate and acetylacetone reacted with II in the presence of catalytic amounts of sodium methoxide to give the corresponding substituted diamides. Under the same conditions acetylacetone added to III to give an easily purified product but diethyl malonate and III formed an oil which could not be crystallized.

Aniline and dimethylaniline reacted with II, but

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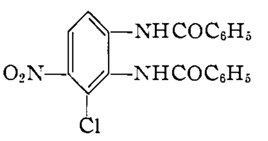
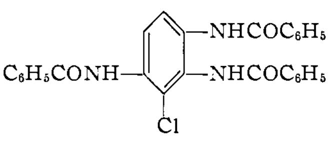
(7) J. J. Blanksma, *Rec. trav. chim.*, **21**, 419 (1902).

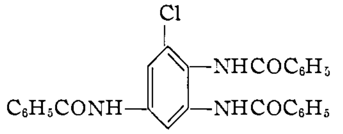
the resulting products could not be characterized. The reaction of phenol with II or III in the presence of triethylamine led to unidentified mixtures.

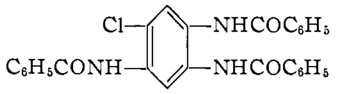
When a strongly electron-attracting group was present in *p*-quinonedibenzenesulfonimide the orientation of the groups in adducts differed from that when the diimide had electron-donating substituents.[8] It is not surprising therefore that the same difference would be found in the *o*-quinone diimides. When hydrogen chloride was added to 4-nitro-*o*-quinonedibenzimide (IV) in benzene solution a single product resulted, 3-chloro-4-nitro-*o*-phenylenedibenzamide (XII). The orientation was determined by conversion to 3-chloro-1,2,4-tribenzamidobenzene (XIII) which was not identical with the other two isomeric monochloro 1,2,4-tribenzamidobenzenes.


XII

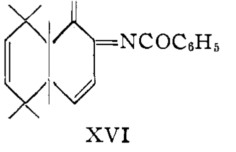

XIII

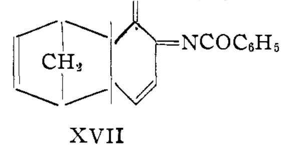
The series of intermediates for preparation of 6-chloro-1,2,4-tribenzamidobenzene (XIV) follows: 2,4-dinitroaniline; 6-chloro-2,4-dinitroaniline[9]; 6-chloro-2,4-dinitrobenzanilide; 6-chloro-2,4-diaminobenzanilide; 6-chloro-1,2,4-tribenzamidobenzene (XIV). To synthesize 5-chloro-1,2,4-tribenzamidobenzene (XV) the following intermediates were used: 1,3-dichlorobenzene; 4,6-dinitro-1,3-dichlorobenzene[10]; 4,6-dinitro-3-chloroaniline[10]; 4,6-dinitro-3-chlorobenzanilide; 4,6-diamino-3-chlorobenzanilide; 5-chloro-1,2,4-tribenzamidobenzene (XV). The melting points and infrared spectra of XIII, XIV and XV were all different, thus establishing XIII as the 3-chloro-1,2,4-tribenzamidobenzene.

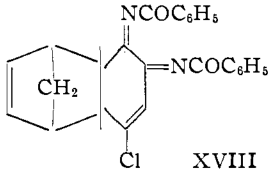

XIV


XV

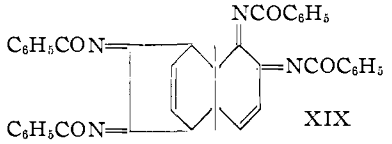
An unrearranged monoadduct XVI was obtained from the reaction of butadiene with II. The infrared spectrum of XVI is consistent with the indicated structure; there are no –NH– bands present but a band corresponding to absorption of carbon–nitrogen double bonds conjugated with carbon–carbon double bonds at 1510 cm.$^{-1}$. Attempts to rearrange XVI to the aromatic structure failed. Cyclopentadiene and II combined to form an analogous product XVII. 2,3-Dimethylbutadiene did not react with II. Cyclopentadiene reacted with III to form a compound probably with structure XVIII. This was deduced from the infrared spectrum which exhibits absorption at 1500 cm.$^{-1}$ corresponding to a conjugated carbon–nitrogen double bond. This shift in frequency would not be observed if the chlorine was located on a bridgehead carbon. Butadiene and III formed a product which could not be characterized.


XVI


XVII


XVIII

To test the possibility that *o*-quinonedibenzimide might also react as a diene, II was treated with maleic anhydride and with *p*-quinone. The expected adduct were not obtained but instead the same product XIX was isolated from both reactions. It proved to be a dimer of II as shown by elemental analyses and molecular weight.


XIX

The infrared spectrum is consistent with the structure to be expected from a Diels–Alder type of self-condensation. There are three carbonyl bands: a strong band at 1670 cm.$^{-1}$, a stronger band at 1645 cm.$^{-1}$, and a medium strong band at 1635 cm.$^{-1}$. Other pertinent bands are those corresponding to a carbon–carbon double bond at 1597 cm.$^{-1}$ and another at 1585 cm.$^{-1}$ corresponding to a carbon–carbon double bond conjugated with a carbon–nitrogen double bond. The formation of XIX under these conditions lends support to the explanation advanced previously for the fact that monomeric *o*-quinonedibenzenesulfonimide (I) could not be isolated. It is also interesting from the viewpoint that II is a stronger dienophile than maleic anhydride or *p*-quinone but these latter substances apparently have a catalytic action.

Acknowledgment.—The authors are indebted to Mrs. Esther Fett, Mrs. Lucy Chang and Mr. J. Nemeth for microanalyses and to Miss Helen Miklas and Mr. James Brader for the determination and interpretation of the infrared spectra.

Experimental[11]

***o*-Quinonedibenzimide (II).**—A suspension of 5.0 g. of *o*-phenylenedibenzamide and 7.0 g. of lead tetraacetate in 400 ml. of chloroform was refluxed with stirring for $^{1}/_{2}$ hour. The orange-red suspension was then filtered hot and the lead diacetate precipitate washed with 50 ml. of chloroform. The filtrate and washings were placed in a separatory funnel and washed with 200 ml. of 5% aqueous sodium bicarbonate and then with 200 ml. of water. The organic layer, dried

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[8] R. Adams, T. E. Young and R. W. P. Short, This Journal, **76**, 1114 (1954).

[9] P. G. Van de Vliet, *Rec. trav. chim.*, **43**, 606 (1924).

[10] H. H. Hodgson, *J. Soc. Dyers Col.*, **42**, 367 (1926).

[11] All melting points are corrected.

over anhydrous magnesium sulfate, was concentrated *in vacuo* to 15 ml. volume using a water-bath at 40–50° and then 170 ml. of cyclohexane added. Slight scratching induced the formation of a yellow precipitate. After cooling in the refrigerator 3.33 g. (66%) of a bright yellow solid was obtained. Recrystallization was accomplished by dissolving in the minimum quantity of benzene at room temperature and adding 100 ml. of cyclohexane for every 5 ml. of benzene used. After cooling in the refrigerator yellow needles resulted, m.p. 136–137° dec.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.69; H, 4.51; N, 8.62.

The operations described must be carried out without delay up to the point where the product is in crystalline form, otherwise a lower yield of less pure product is obtained.

The infrared spectrum of the product showed C=N absorption at 1587 cm.$^{-1}$ and no –NH– bands.

Addition of Hydrogen Chloride to *o*-Quinonedibenzenesulfonimide.—A solution of 1.39 g. of *o*-quinonedibenzenesulfonimide in 30 ml. of chloroform was saturated with hydrogen chloride. The red color rapidly faded to a light brown. The solution was evaporated to about 3 ml. and the residue dissolved in boiling ethyl acetate. On cooling 1.03 g. (66%) of white needles separated, m.p. 186–215°. This material was recrystallized twice from glacial acetic acid and then three times from ethyl acetate; white needles, m.p. 220–227°. It is obviously a mixture of monochloro derivatives.

Anal. Calcd. for $C_{20}H_{15}ClN_2O_2$: C, 68.47; H, 4.31; N, 7.99. Found: C, 68.79; H, 4.26; N, 8.07.

4-Chloro-*o*-phenylenedibenzamide.—To a solution of 50.0 g. of 4-chloro-*o*-phenylenediamine in 200 ml. of pyridine was slowly added 100 g. of benzoyl chloride with stirring. The temperature was maintained at from 40 to 60° by use of a cold water-bath. After standing 10 hours, the dark red solution was poured into 500 ml. of 6 *N* hydrochloric acid. The suspension was filtered and the brown precipitate washed with water. After two recrystallizations from dioxane, 87.6 g. (71%) of white needles, m.p. 227–228° (lit.[12] m.p. 230°), was obtained.

4-Chloro-*o*-quinonedibenzimide (III).—A suspension of 10.00 g. of 4-chloro-*o*-phenylenedibenzamide and 12.6 g. of lead tetraacetate (dried over phosphoric anhydride) in 800 ml. of dry, thiophene-free benzene was refluxed with stirring for 10 min. The red solution was filtered hot from lead diacetate and the precipitate washed with benzene. The filtrate was washed in a separatory funnel with 400 ml. of 5% aqueous sodium bicarbonate and then with 200 ml. of water. After drying over anhydrous magnesium sulfate the benzene was removed by vacuum distillation. The oily red residue on treatment with 100 ml. of petroleum ether (b.p. 35–40°) gave 8.32 g. (83%) of a yellow solid. Recrystallization from a carbon tetrachloride–petroleum ether (b.p. 35–40°) solvent pair gave yellow crystals, m.p. 98.5–99.5°.

Anal. Calcd. for $C_{20}H_{13}ClN_2O_2$: C, 68.87; H, 3.76; N, 8.03. Found: C, 69.07; H, 3.97; N, 8.07.

The infrared spectrum shows C=N absorption at 1639 cm.$^{-1}$ and 1588 cm.$^{-1}$ and no –NH– bands.

4,6-Dichloro-*o*-phenylenedibenzamide (V). Method A.—To a boiling solution of 7.27 g. of 2,4-dichloro-6-nitroaniline[6] in 50 ml. of ethanol was added slowly 26 g. of sodium hydrosulfite dissolved in 100 ml. of water. The solution was filtered and concentrated to the cloud point. After cooling in the refrigerator, 2.53 g. (41%) of a buff colored solid was obtained, m.p. 59–61° (lit.[13] m.p. 60.5°). The material was benzoylated immediately without purification.

A solution of 2.06 g. of 4,6-dichloro-*o*-phenylenediamine and 3.4 ml. of benzoyl chloride in 10 ml. of pyridine was heated on the steam-bath for 2 hours. Isolation in the usual manner gave 3.36 g. (75%) of tan needles. Recrystallization from glacial acetic acid (Darco) and then from ethyl acetate gave white needles, m.p. 222–224°.

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66; N, 7.27. Found: C, 62.63; H, 3.66; N, 7.17.

Method B.—A solution of 1.00 g. of 4-chloro-*o*-quinonedibenzimide (III) in 10 ml. of chloroform was saturated with dry hydrogen chloride. The red color lightened to a pale yellow. Evaporation of the chloroform by an air stream gave 1.02 g. (93%) of a yellow-white solid. Recrystallization from ethyl acetate gave the pure compound; white prisms, m.p. 223.5–224.5°, identical with the product formed by method A.

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66; N, 7.27. Found: C, 62.63; H, 3.68; N, 7.10.

The infrared spectra of the two products were identical.

Method C.—A convenient method of preparation without isolation of the intermediate diimide follows. The same procedure and quantities were used as given under the preparation of 4-chloro-*o*-quinonedibenzimide, except that the solvent was not removed. The resulting solution was saturated with hydrogen chloride. Evaporating the solution to 75 ml. and then cooling gave 7.53 g. of white needles, m.p. 221–223°. Concentration of the mother liquor to 10 ml. gave a further 1.33 g. of product. The total yield was 81%.

4,5-Dichloro-*o*-phenylenedibenzamide (VII).—To a boiling solution of 2.36 g. of 4,5-dinitro-1,2-dichlorobenzene[7] in 100 ml. of 50% aqueous ethanol was added portionwise 11.7 g. of sodium hydrosulfite. The solution first turned red, then at the end became light tan. A further 180 ml. of water was added and the solution boiled for 1/2 hour. On cooling in the refrigerator 0.30 g. of brown plates separated. The filtrate was made basic with 15% aqueous sodium hydroxide and then extracted with 50 ml. of ether. Removal of the ether gave a further 0.15 g. Thus a 25% yield of product was realized; m.p. 161–162° (lit.[2] m.p. 162–163°).

A solution of 0.45 g. of 4,5-dichloro-1,2-phenylenediamine and 0.7 ml. of benzoyl chloride in 20 ml. of pyridine was heated on the steam-bath for 2.5 hours. The brown solution was poured into 200 ml. of 6 *N* hydrochloric acid which caused the precipitation of 0.77 g. (79%) of a brown solid. Several recrystallizations from glacial acetic acid (Darco) gave a pure compound; white needles, m.p. 261.5–262.5°.

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66; N, 7.27. Found: C, 62.53; H, 3.71; N, 7.30.

4-Acetoxy-*o*-phenylenedibenzamide.—A suspension of 2.00 g. of *o*-quinonedibenzimide in 10 ml. of glacial acetic acid was treated with 4 drops of boron trifluoride etherate. The mixture became warm with the color changing from red to brown. After standing 24 hours, 1.25 g. of a tan solid separated and was removed by filtration. Treatment of the mother liquors with 50 ml. of water yielded a further 0.57 g. of a brown solid. Thus a total yield of 77% was realized. Several recrystallizations from ethanol (Darco) gave a pure product; white needles, m.p. 217–218°.

Anal. Calcd. for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.84; N, 7.48. Found: C, 70.42; H, 5.08; N, 7.49.

4-Hydroxy-*o*-phenylenedibenzamide.—A suspension of 1.76 g. of 4-acetoxy-*o*-phenylenedibenzamide in 25 ml. of 5% aqueous sodium hydroxide was heated on the steam-bath for 1/2 hr. After filtration to remove a small amount of insoluble material, the brown solution was acidified with 6 *N* hydrochloric acid. A dark red-brown solid weighing 1.21 g. (78%) was obtained. Six recrystallizations from ethyl acetate were necessary to obtain a pure product; white prisms, m.p. 206.5–207.5° (lit.[14] m.p. 203–205°).

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.27; H, 4.85; N, 8.43. Found: C, 72.37; H, 4.99; N, 8.23.

4-Benzamido-6-chloro-2-phenylbenzoxazole (VIII). A.—When 10 ml. of acetic acid was added to 1.00 g. of 4-chloro-*o*-quinonedibenzimide the red solution immediately began to deposit a white solid. After standing 1 hour, 0.98 g. (98%) of product was collected. Recrystallization from dioxane, then glacial acetic acid and finally benzene gave a pure product; silky white needles, m.p. 201.5–202.0°.

Anal. Calcd. for $C_{20}H_{13}ClN_2O_2$: C, 68.87; H, 3.76; N, 8.03. Found: C, 68.77; H, 3.71; N, 7.94.

The infrared spectrum shows the presence of an –NH– band at 3295 cm.$^{-1}$ and C=N bands at 1622, 1606 and 1587 cm.$^{-1}$.

When 2.00 g. of this material was heated with 50 ml. of 5% aqueous sodium hydroxide on the steam-bath for 4 hours, no solution occurred and the starting material was recovered.

B.—A stirred suspension of 3.00 g. of 4,6-dichloro-*o*-phenylenedibenzamide (V) and 3.44 g. of lead tetraacetate

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(12) O. Fischer and F. Limmer, *J. prakt. Chem.*, [2] **74**, 62 (1906).

(13) O. Witt, *Ber.*, **7**, 1601 (1874).

(14) P. Jacobson and F. Hönigsberger, *ibid.*, **36**, 4125 (1903).

in 300 ml. of benzene was refluxed for 17 minutes. The hot suspension was filtered and the lead diacetate precipitate washed with benzene. The combined filtrates were washed with 200 ml. of 5% aqueous sodium bicarbonate followed by 100 ml. of water. After drying over anhydrous magnesium sulfate, the solution was concentrated by vacuum distillation to a volume of 10 ml. On cooling, 1.34 g. (44.3%) of white crystals separated. Upon recrystallization from benzene white needles, m.p. 201–202°, were obtained. The melting point of a mixture with the product from A was 200.5–201.5°. The infrared spectra of the two products were identical.

4-Methoxy-*o*-phenylenedibenzamide (IX). Method A.—4-Amino-3-nitroanisole was reduced with sodium hydrosulfite as previously described. After cooling the reaction mixture in the refrigerator, greenish plates separated in 85% yield, m.p. 130–131.5°. The product was benzoylated immediately without further purification.

A solution of 17.4 g. of the above product in 150 ml. of pyridine was treated slowly with 31 ml. of benzoyl chloride, stirring constantly and cooling in an ice-bath. After standing 1 hour the tan suspension was poured into 200 ml. of 6 *N* hydrochloric acid. The pink solid which precipitated was removed, washed with water and dried. The product weighed 37.4 g. (86%). Recrystallization from dioxane or glacial acetic acid gave the pure product; white needles, m.p. 252–253° (lit.[15] m.p. 251–252°).

Method B.—To a suspension of 2.0 g. of *o*-quinonedibenzimide in 20 ml. of redistilled methanol was added 4 drops of boron trifluoride etherate. The solution decolorized rapidly, forming a thick suspension. After standing 4 hours, 1.81 g. (82%) of a tan solid was removed by filtration. Recrystallization from ethyl acetate gave the pure product, m.p. 252–253°.

The melting point of a mixture of this product and that from method A was undepressed.

4-Chloro-6(?)-methoxy-*o*-phenylenedibenzamide.—From 4-chloro-*o*-quinonedibenzimide (III) and methanol in presence of boron trifluoride etherate after 24 hours a solid separated, more of which was obtained by addition of water. The yield was 76%. Recrystallization from ethyl acetate gave a pure compound; white needles, m.p. 234.5–235.0°.

Anal. Calcd. for $C_{21}H_{17}ClN_2O_3$: C, 66.23; H, 4.50; N, 7.36. Found: C, 66.26; H, 4.57; N, 7.39.

6(?)-Acetoxy-4-methyl-*o*-phenylenedibenzamide.—A suspension of 5.00 g. of 4-methyl-*o*-phenylenedibenzamide and 6.71 g. of lead tetraacetate in 400 ml. of thiophene-free benzene was stirred at reflux temperature for 20 minutes. The red suspension was filtered and the filtrate treated with 10 ml. of glacial acetic acid. The solvent was removed by an air stream to yield 4.69 g. (80%) of a dark brown solid. Several recrystallizations from benzene and then ethyl acetate gave small white needles, m.p. 217–218°.

Anal. Calcd. for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19. Found: C, 71.12; H, 5.05.

6(?)-Acetoxy-4-methoxy-*o*-phenylenedibenzamide.—From 5.00 g. of 4-methoxy-*o*-phenylenedibenzamide and 6.40 g. of lead tetraacetate in 400 ml. of thiophene-free benzene following the same procedure used for the 4-methyl derivative, 4.49 g. (77%) of a red-brown solid resulted. Recrystallization from benzene and then ethyl acetate gave white needles, m.p. 188.5–189.5°.

Anal. Calcd. for $C_{23}H_{20}N_2O_5$: C, 68.31; H, 4.99. Found: C, 68.30; H, 4.98.

4(?)-Piperidino-*o*-phenylenedibenzamide.—To a solution of 0.75 g. of *o*-quinonedibenzimide in 10 ml. of dry redistilled chloroform was added 0.21 g. of redistilled piperidine. The solution warmed and turned purple. After standing 12 hours the solution was filtered to remove 0.04 g. of *o*-phenylenedibenzamide. The chloroform was evaporated from the filtrate by an air stream to give 0.89 g. (94%) of a dark purple solid. The pure product was obtained after several recrystallizations from ethyl acetate; white needles, m.p. 241–242°.

Anal. Calcd. for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52. Found: C, 75.33; H, 6.31; N, 10.72.

Gummy, amorphous solids were obtained from the reaction of II with either aniline or dimethylaniline in chloroform solution.

4-Chloro-6(?)-piperidino-*o*-phenylenedibenzamide.—From 4-chloro-*o*-quinonedibenzimide and piperidine a 43% yield of product resulted. Recrystallization from ethyl acetate gave a pure compound; white prisms, m.p. 245.0–246.5°.

Anal. Calcd. for $C_{25}H_{24}ClN_3O_2$: C, 69.19; H, 5.57; N, 9.68. Found: C, 69.18; H, 5.81; N, 9.87.

4-Azido-*o*-phenylenedibenzamide.—A benzene solution of hydrazoic acid was prepared by adding 0.40 g. of concentrated sulfuric acid to a solution of 0.50 g. of sodium azide in 25 ml. of water covered by 25 ml. of benzene. After shaking in a separatory funnel, the benzene layer was dried over anhydrous sodium sulfate.

A solution of 1.00 g. of *o*-quinonedibenzimide in 200 ml. of benzene was treated with 15 ml. of the hydrazoic acid solution prepared above. The red solution became quite warm and decolorized. After 15 hours, 0.35 g. (32%) of a pink solid had separated. Recrystallization of this solid from ethanol gave a pure product; creamy white needles. m.p. 205.5° dec. with gas evolution.

Anal. Calcd. for $C_{20}H_{15}N_5O_2$: C, 67.22; H, 4.23; N, 19.60. Found: C, 67.48; H, 4.03; N, 19.32.

The yield might have been improved if instead of the equimolar ratio of diimide and hydrazoic acid a half mole excess of hydrazoic acid had been used as in the addition of hydrazoic acid to the 4-chloro diimide described later.

Evaporation of the reaction mother liquors gave a red gum from which no pure compound could be isolated by recrystallization. By boiling an aqueous ethanol solution of the gum with an excess of sodium hydrosulfite and cooling, 0.17 g. of 4-amino-*o*-phenylenedibenzamide separated, m.p. 270–273° dec., indicating the presence of 0.18 g. of the azide in the gum.

4-Amino-*o*-phenylenedibenzamide. Method A.—A boiling suspension of 2.5 g. of 4-nitro-*o*-phenylenedibenzamide in 70 ml. of dioxane and 50 ml. of water was treated with 4.05 g. of sodium hydrosulfite. After boiling 1/2 hour, 100 ml. of water was added and the solution cooled. A white solid weighing 0.81 g. formed. The filtrate was made basic and cooled again to yield a further 0.93 g. or a total yield of 1.74 g. (76%). Several recrystallizations from ethanol gave a pure compound; yellow needles, m.p. 281–282° dec.

Anal. Calcd. for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.26; H, 5.30; N, 12.60.

Method B.—A suspension of 0.45 g. of 4-azido-*o*-phenylenedibenzamide and 50 mg. of platinum oxide in 50 ml. of redistilled ethanol was hydrogenated at 2 atm. pressure for 5 hours. There was no drop in pressure. The white suspension was heated to boiling, filtered to remove the catalyst, and then concentrated to 10 ml. Yellow needles separated which weighed 0.37 g. (91%). Recrystallization from ethanol gave the pure product, m.p. 278–280° dec.

The infrared spectra of the two products were identical.

4-Chloro-6(?)-azido-*o*-phenylenedibenzamide.—From 4-chloro-*o*-quinonedibenzimide and one and one-half moles of hydrazoic acid by a similar procedure, an adduct was readily formed. The reaction mixture was allowed to stand 5 days in the dark. A yield of 86% of a brown gummy solid resulted. Recrystallization from methanol and then from ethyl acetate gave a pure compound; creamy white needles, m.p. 179° dec. with gas evolution.

Anal. Calcd. for $C_{20}H_{14}ClN_5O_2$: C, 61.31; H, 3.60; N, 17.88. Found: C, 61.02; H, 3.72; N, 18.25.

Catalytic hydrogenation of this compound over platinum oxide ethanol gave a crystalline solid which could not be recrystallized to a constant melting point. Probably hydrogenolysis of the chlorine occurred to give a mixture of amines.

4-Chloro-6(?)-phenylmercapto-*o*-phenylenedibenzamide (X).—A solution of 2.00 g. of 4-chloro-*o*-quinonedibenzimide and 0.70 g. of freshly distilled thiophenol in 10 ml. of chloroform was treated with two drops of triethylamine. The color lightened immediately and the solution became quite warm. The chloroform was removed by an air stream to give 0.56 g. (21%) of a red gum. It was dissolved in ethyl acetate and after standing 1 week it crystallized. Recrystallization from an ethanol–water solvent pair gave a pure compound; white prisms, m.p. 201.5–202.5°.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_2S$: C, 68.04; H, 4.17; N, 6.11. Found: C, 67.93; H, 4.24; N, 5.93.

4-Chloro-6(?)-benzenesulfonyl-*o*-phenylenedibenzamide (XI). Method A.—A solution of benzenesulfinic acid was

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[15] R. Medola and J. Eyre, *J. Chem. Soc.*, **81**, 991 (1902).

prepared by grinding together 0.5 g. of sodium benzenesulfinate, 3 ml. of chloroform and 0.15 g. of sulfuric acid. The suspension was warmed and filtered, and the precipitate washed with 10 ml. of boiling chloroform. The filtrate was then added to a solution of 0.75 g. of 4-chloro-*o*-quinonedibenzimide in 10 ml. of chloroform. The red solution warmed spontaneously and the color faded to a light yellow. The solution was evaporated to a volume of 5 ml., after which the remainder of the solvent was removed by an air stream. The brown, oily residue on treatment with methanol gave 0.56 g. (53%) of a white solid. Several recrystallizations from ethyl acetate gave a pure compound; colorless flat needles, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{26}H_{19}ClN_2O_4S$: C, 63.60; H, 3.90; N, 5.71. Found: C, 63.68; H, 4.16; N, 5.50.

Method B.—A solution of 0.21 g. of 4-chloro-6(?)-phenylmercapto-*o*-phenylenedibenzamide in 15 ml. of glacial acetic acid and 1.0 ml. of 30% hydrogen peroxide was refluxed for 1.5 hours, then poured into 75 ml. of water. A white precipitate, weighing 0.20 g. (91%), formed. Recrystallization from ethanol gave a pure compound; white needles, m.p. 213.5–214.5°. *It was shown to be identical with the product formed by method A by melting point and infrared spectrum.*

4-Nitro-*o*-phenylenedibenzamide.—Using the same procedure as in the benzoylation of 4,6-dichloro-*o*-phenylenediamine, 4-nitro-*o*-phenylenediamine was benzoylated. A yellow-brown solid resulted. Recrystallization from glacial acetic acid (Darco) gave 64% of fine white silky needles m.p. 243.5–244.5° (lit.[16] 235–236°).

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.47; H, 4.18; N, 11.63. Found: C, 66.62; H, 4.42; N, 11.86.

3-Chloro-4-nitro-*o*-phenylenedibenzamide (XII).—A suspension of 5.0 g. of 4-nitro-*o*-phenylenedibenzamide in 400 ml. of dry, thiophene-free benzene and 6.10 g. of lead tetraacetate was refluxed with stirring for 1/2 hour. The hot mixture was filtered to remove inorganic salts and the filtrate washed with 200 ml. of 5% aqueous sodium bicarbonate followed by 200 ml. of water. After drying over anhydrous magnesium sulfate the volume of the solution was made up to 325 ml. The benzene was removed *in vacuo* from a 160-ml. portion. A red oil was obtained which was dissolved in 7 ml. of benzene. Addition of 100 ml. of cyclohexane caused precipitation of 0.45 g. of a yellow amorphous solid, m.p. 83–97°. This material was highly charged with static electricity and in a short time decomposed to a dark red tar.

The remaining 165 ml. of diimide solution was saturated with dry hydrogen chloride. The color changed to a light brown. After boiling the solution to 30 ml. and cooling, 1.19 g. (44%) of tan needles was deposited. Two recrystallizations from methanol gave the pure product; white silky needles, m.p. 236–237°.

Anal. Calcd. for $C_{20}H_{14}ClN_3O_4$: C, 60.69; H, 3.57; N, 10.62. Found: C, 60.75; H, 3.61; N, 10.66.

4-Amino-3-chloro-*o*-phenylenedibenzamide.—To a boiling solution of 0.50 g. of 3-chloro-4-nitro-*o*-phenylenedibenzamide in 125 ml. of ethanol and 75 ml. of water was added 0.89 g. of sodium hydrosulfite in small portions. After the addition of 50 ml. of water, the colorless solution was boiled for 1 hour. Addition of a further 150 ml. of water and cooling gave 0.16 g. of white solid. Evaporation of the mother liquors to 50 ml. yielded an additional 0.15 g. The combined precipitates, 0.31 g. (66%), were recrystallized from ethanol; colorless prisms, m.p. 254–255°.

Anal. Calcd. for $C_{20}H_{16}ClN_3O_2$: C, 65.66; H, 4.41; N, 11.49. Found: C, 65.91; H, 4.41; N, 11.36.

3-Chloro-1,2,4-tribenzamidobenzene (XIII).—4-Amino-3-chloro-*o*-phenylenedibenzamide was benzoylated as previously described for the other amines. A yield of 93% resulted. Recrystallization from ethanol gave a pure product, m.p. 271–272°.

Anal. Calcd. for $C_{27}H_{20}ClN_3O_3$: C, 69.01; H, 4.29; N, 8.94. Found: C, 68.88; H, 4.32; N, 8.82.

6-Chloro-2,4-dinitrobenzanilide.—A solution of 21.8 g. of 6-chloro-2,4-dinitroaniline[8] in 200 ml. of pyridine and 13 ml. of benzoyl chloride was heated on the steam-bath for 22 hours. Upon pouring the light yellow solution into 400 ml. of 6 *N* hydrochloric acid a yellow solid precipitated. Recrystallization from ethanol gave 8.79 g. (27%) of light tan needles. Four recrystallizations from glacial acetic acid gave the pure amide, m.p. 202.5–204.5°.

Anal. Calcd. for $C_{13}H_8ClN_3O_5$: C, 48.54; H, 2.51; N, 13.06. Found: C, 48.58; H, 2.46; N, 12.83.

By concentration of the ethanol mother liquors 12.1 g. of unreacted amine was recovered.

6-Chloro-1,2,4-tribenzamidobenzene (XIV).—The reduction of 6-chloro-2,4-dinitrobenzanilide was effected by the procedure described for reduction of 2,4-dichloro-6-nitroaniline. After the reduction, the solution was made basic with 15% aqueous sodium hydroxide. Upon cooling in the refrigerator for two days, a brown gelatinous precipitate was obtained which, after drying in a vacuum desiccator, weighed 0.30 g. (12%), m.p. 207° dec. The product was benzoylated immediately.

A mixture of the 0.30 g. of diamine from the reduction was benzoylated as previously described. A pink precipitate weighing 0.33 g. (61%) resulted. Recrystallization from ethanol and then glacial acetic acid gave the pure product; white needles, m.p. 273–274°.

Anal. Calcd. for $C_{27}H_{20}ClN_3O_3$: C, 69.01; H, 4.29; N, 8.94. Found: C, 69.20; H, 4.26; N, 8.78.

The melting point of a mixture of this product with that obtained from the nitro diimide was depressed.

5-Chloro-2,4-dinitroaniline.[10]—This was made by the method of Hodgson[10] except that the reaction mixture was poured into water. A yield of 98% was obtained. Recrystallization from ethanol and then twice from benzene gave fine yellow needles, m.p. 181–182° (lit.[10] m.p. 174°).

Anal. Calcd. for $C_6H_4ClN_3O_4$: C, 33.12; H, 1.85; N, 19.31. Found: C, 33.36; H, 1.97; N, 19.02.

5-Chloro-2,4-dinitrobenzanilide.—A mixture of 2.00 g. of 5-chloro-2,4-dinitroaniline, 1.40 g. of benzoyl chloride, 2 drops of sulfuric acid and 5 ml. of benzene was heated on the steam-bath for 15 minutes. The mixture partially solidified and became lighter yellow in color. Recrystallization of the product from glacial acetic acid gave 2.47 g. (82%) of pale yellow plates, m.p. 194.5–195.5°.

Anal. Calcd. for $C_{13}H_8ClN_3O_5$: C, 48.54; H, 2.51; N, 13.06. Found: C, 48.66; H, 2.22; N, 13.19.

5-Chloro-1,2,4-tribenzamidobenzene (XV).—5-Chloro-4,6-dinitrobenzanilide was reduced in a manner described for the other nitro compounds. A yield of 11% of the diamine resulted; white needles, m.p. 200–201° dec. This material was benzoylated immediately. It was dissolved in 3 ml. of pyridine and heated on the steam-bath for 45 minutes with 0.10 g. of benzoyl chloride. The colorless solution was poured into 50 ml. of 3 *N* hydrochloric acid which caused precipitation of 0.14 g. (87%) of a white solid. Recrystallization from glacial acetic acid gave white needles, m.p. 279–280°.

Anal. Calcd. for $C_{27}H_{20}ClN_3O_3$: C, 69.01; H, 4.29; N, 8.94. Found: C, 68.81; H, 4.21; N, 8.82.

The melting point of a mixture of this compound with that obtained from the nitro diimide was depressed. The infrared spectra were different.

Butadiene Adduct of *o*-Quinonedibenzimide (XVI).—A solution of 1.77 g. of *o*-quinonedibenzimide and 10 ml. of liquid butadiene in 40 ml. of purified chloroform was allowed to react 12 days at room temperature. After filtration of a small amount of sediment the solvent was removed by an air stream. The light brown oily residue was dissolved in 7 ml. of boiling ethyl acetate. On cooling, 2.0 g. (96%) of chunky colorless prisms was obtained. Recrystallization from ethyl acetate gave a pure product, m.p. 145–146°.

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.61. Found: C, 78.53; H, 5.37; N, 7.73.

The infrared spectrum indicates the absence of NH bands and the presence of $-C{=}N-$ functions.

Treatment of the product with hydrobromic acid in dioxane gave a small amount of *o*-phenylenedibenzamide and mostly a black tar.

Cyclopentadiene Adduct of *o*-Quinonedibenzimide (XVII).—A solution of 0.75 g. of *o*-quinonedibenzimide and 0.62 g. of cyclopentadiene (freshly distilled from iron powder) in 20 ml. of purified chloroform was allowed to react 48 hours. The color slowly changed from red to a light yellow. The solution was filtered from 0.04 g. of solid and the solvent evaporated in an air stream. The tan oil obtained was dis-

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[16] E. Bamberger and B. Berle, *Ann.*, **273**, 351 (1893).

solved in 5 ml. of boiling ethyl acetate. On cooling, 0.45 g. (50%) of yellow crystals was obtained. Recrystallization from ethyl acetate gave colorless needles, m.p. 226–227°.

Anal. Calcd. for $C_{25}H_{20}N_2O_2$: C, 78.92; H, 5.30; N, 7.37. Found: C, 79.11; H, 5.30; N, 7.34.

The infrared spectrum shows the presence of C=N bands at 1587 cm.$^{-1}$ and no –NH– bands.

Cyclopentadiene Adduct of 4-Chloro-*o*-quinonedibenzimide (XVIII).—From 4-chloro-*o*-quinonedibenzimide and cyclopentadiene in a similar way and after reaction for 3 days, a 99% yield of yellow-brown solid resulted. Recrystallization from ethyl acetate gave white needles, m.p. 236–237°.

Anal. Calcd. for $C_{25}H_{19}ClN_2O_2$: C, 72.37; H, 4.62; N, 6.75. Found: C, 72.32; H, 4.61; N, 6.60.

The infrared spectrum showed the presence of a C=N band at 1581 cm.$^{-1}$ and no –NH– band.

Dimer of *o*-Quinonedibenzimide (XIX).—A solution of 0.50 g. of *o*-quinonedibenzimide and 0.30 g. of maleic anhydride in 10 ml. of benzene was allowed to react at room temperature. Colorless chunky crystals began to form after 6 days. At the end of 13 days 0.24 g. of solid was removed by filtration. The pure product was obtained by recrystallization from ethyl acetate as white needles. The melting point with each crystallization varied in the range between 175–176° and 180–181°.

Anal. Calcd. for $C_{40}H_{28}N_4O_4$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.47; H, 4.21; N, 9.09.

Evaporation of the reaction mother liquors to dryness gave a red gum which was discarded.

Replacing the maleic anhydride by an equal weight of *p*-benzoquinone led to the precipitation of crystals after 2 days. At the end of 10 days, 0.35 g. of colorless prisms was removed by filtration. Recrystallization from ethyl acetate gave white needles with the same variable melting point mentioned under A.

Anal. Calcd. for $C_{40}H_{28}N_4O_4$: C, 76.42; H, 4.49; N, 8.91; mol. wt., 628. Found: C, 76.68; H, 4.48; N, 8.77; mol. wt. (Rast), 659.

The infrared spectra of the products from methods A and B were identical.

Diethyl 4(?)-(*o*-Phenylenedibenzamide)-malonate.—A solution of 0.75 g. of *o*-quinonedibenzimide in 10 ml. of dry redistilled dioxane and 0.40 g. of redistilled diethyl malonate was treated with about 50 mg. of sodium methoxide. After standing 5 hours the color had faded to a light brown. Addition of 30 ml. of water caused the separation of a brown oil which changed on standing to 1.09 g. (96%) of a tan solid. Recrystallization from benzene–cyclohexane and then methylcyclohexane served to purify the product; tiny white needles, m.p. 117.5–118.5°.

Anal. Calcd. for $C_{27}H_{26}N_2O_6$: C, 68.34; H, 5.52; N, 5.91. Found: C, 68.32; H, 5.28; N, 6.01.

Only a red amorphous solid was isolated from heating this product with 10% aqueous sodium hydroxide on the steam-bath for 3 hours, followed by acidification with 6 *N* hydrochloric acid.

4(?)-(3-Pentane-2,4-dione)-*o*-phenylenedibenzamide.—Addition of pure acetylacetone to *o*-quinonedibenzimide was carried out in the same manner as the diethyl malonate. The yield was 99% of a white solid. Recrystallization from ethyl acetate and then from ethanol gave a pure product; white prisms, m.p. 237.0–237.5°.

Anal. Calcd. for $C_{25}H_{22}N_2O_4$: C, 72.45; H, 5.35; N, 6.76. Found: C, 72.37; H, 5.49; N, 6.81.

4-Chloro-6(?)-(3-pentane-2,4-dione)-*o*-phenylenedibenzamide.—From 4-chloro-*o*-quinonedibenzimide (III) and pure acetylacetone, a 97% yield of product resulted. Recrystallization from glacial acetic acid gave white prisms, m.p. 271.0–271.5°.

Anal. Calcd. for $C_{25}H_{21}ClN_2O_4$: C, 66.89; H, 4.72; N, 6.24. Found: C, 66.69; H, 4.89; N, 6.25.

Treatment of III with diethyl malonate under the above conditions gave an oil which could not be crystallized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE RICE INSTITUTE]

The Enolization of 9-Phenyl-2,3-benzofluorene-1,4-quinone

BY MARTIN G. ETTLINGER

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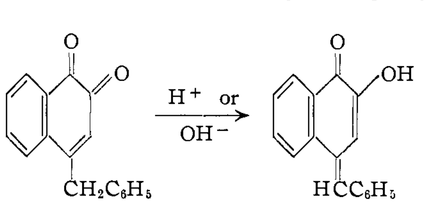
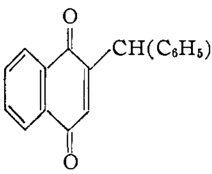
9-Phenyl-2,3-benzofluorene-1.4-quinone (VIII) enolizes in a hydroxylic solvent to form the more stable 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone (V). The enol V is more acidic than acetic acid, whence the dissociation constant of the hydrogen on the 9-carbon atom of VIII, referred to aqueous medium, is probably at least 10^{-3}. The remarkably high acidity of VIII is caused by the five-membered ring. The enol V undergoes sulfonation; in spectra and basicity, it resembles simpler β-naphthofuchsones such as 2-diphenylmethylene-1-naphthone (XIII), a fourfold stronger base than *p*-nitrodiphenylamine.

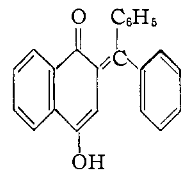
The enolization of 1,2-quinones bearing 4-methinyl substituents, even in the absence of side chain carbonyl groups, has long been firmly established. The preparation of 2-hydroxy-4-fluorenylidene-1-naphthone[1] was succeeded by more thorough studies of 4-benzhydryl-1,2-naphthoquinone[2] and 4-benzyl-1,2-naphthoquinone[3] (I). The enolic equilibrium of 4-benzhydryl-1,2-naphthoquinone seemed to favor the quinone and was highly mobile, so that the two forms were not isolated separately. The transformation of I to the enol II by strong acid or base, in contrast, could not be reversed directly.[4] Enols of methylenedi-*p*-quinone derivatives, which are vinylogs of β-diketones, have also been prepared.[5] However, 2-methinyl-1,4-



I II



III



IV

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(1) F. Sachs and L. Oholm, *Ber.*, **47**, 955 (1914).

(2) L. F. Fieser and J. L. Hartwell, THIS JOURNAL, **57**, 1484 (1935).

(3) L. F. Fieser and M. Fieser, *ibid.*, **61**, 596 (1939).

(4) As Dr. E. S. Lewis has remarked, the inference that II is more stable than I is probable; the instability of the enol of the 4-benzhydryl derivative can be ascribed to steric interference between the 5-hydrogen atom and the *cis*-phenyl group.

(5) L. I. Smith, H. R. Davis, Jr., and A. W. Sogn, THIS JOURNAL, **72**, 3651 (1950); E. F. Pratt and W. E. Boehme, *ibid.*, **73**, 444 (1951).