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Quinone Imides. XXIII. Addition Reactions of *p*-Quinonedibenzimide and Related Compounds

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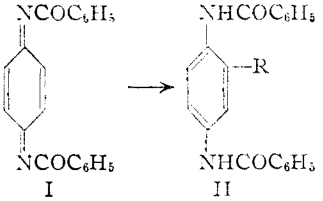
p-Quinonedibenzimide and related diimides add mercaptans to yield the 2-thioethers of the corresponding diamides; in a similar manner, they add aromatic amines and secondary aliphatic amines. *p*-Quinonedibenzimide does not add butadiene but adds cyclopentadiene under forced conditions to give a monoadduct; it adds methanol and ethanol in presence of boron trifluoride; diethyl malonate and acetylacetone in the presence of sodium ethoxide; phenol to give a 2-hydroxyphenyl diamide, but not benzene; it reacts with sulfuric acid in benzene to give as the main product, 2-phenyl-6-benzamidobenzoxazole. The reactivity of *p*-quinonedibenzimide and *p*-quinonedibenzenesulfonimide with various reagents is compared.

The similarities and differences between the reactivity of *p*-quinonedibenzimide and *p*-quinonedibenzenesulfonamide were discussed in previous papers.[2,3] The reactions of hydrogen chloride and organic acids with *p*-quinonedibenzimide (I), were described. This study has now been extended.

Mercaptans were easily added to *p*-quinonedibenzimide (I) to give *p*-phenylenedibenzamides with thioether groups in the 2-position. The additions were accompanied by less reduction of the diimide and formation of disulfide than was observed with *p*-quinonedibenzenesulfonimide.[4] Although sulfuric acid in dioxane was used as a convenient catalyst and medium for the thiophenol addition to get the best results, good yields could be obtained without a catalyst although some reduction occurred. *p*-Quinonedicarbethoxyimide and *p*-quinonedicarbobenzoxyimide also reacted smoothly with thiophenol in a similar manner. Benzylmercaptan added to *p*-quinonedibenzimide without the necessity of a basic catalyst which was found so advantageous with the benzenesulfonimides. 2-Phenylmercapto-*p*-phenylenedibenzamide (IIa) was readily oxidized with lead tetraacetate to the corresponding diimide which was difficult to isolate but readily added a molecule of thiophenol to yield a dimercapto dibenzamide.



I II

a, R = C_6H_5S–
b, R = CH_3O–
c, R = $O(CH_2CH_2)_2N$–; $CH_2(CH_2CH_2)_2N$–; C_6H_5NH–
d, R = $(C_2H_5O_2C)_2CH$–; $(CH_3CO)_2CH$–

The greater ease with which *p*-quinonedibenzimide reacted with organic acids[3] as compared to *p*-quinonedibenzenesulfonimide made it of interest to attempt the addition of alcohols. Boron fluoride was used as catalyst to increase the acid strength of the alcohol.[5] Both methanol and ethanol added under these conditions to give 2-methoxy- and 2-ethoxy-*p*-phenylenedibenzamide. The structure of the methoxy derivative (IIb) was demonstrated by an unequivocal synthesis through reduction of 5-nitro-2-aminoanisole and benzoylation. Use of zinc chloride as the catalyst for addition of ethanol as used by Knoevenagel[6] in adding ethanol to benzoquinone resulted in a mixture from which only *p*-phenylenedibenzamide could be isolated.

The reaction of morpholine, piperidine and aniline with *p*-quinonedibenzimide proved to be much less complex than with *p*-quinonedibenzenesulfonimide.[7] In chloroform solution of the dibenzimide, the monoadducts (IIc) were formed in good yield although some reduction product was found in the reaction mixture. The reaction of *n*-butylamine with *p*-quinonedibenzimide gave a high yield of benzamide with the formation of a great deal of tar. This reaction is undoubtedly analogous to that with *p*-quinonedibenzenesulfonimide where benzenesulfonamide was formed with other products resulting from the polymerization of the N,N′-dibutyldiimine.[7] Morpholine added also to *p*-quinonedicarbethoxyimide and *p*-quinonedicarbobenzoxyimide to give good yields of 2-morpholino-*p*-phenylenediethylcarbamate and 2-morpholino-*p*-phenylenedibenzylcarbamate, respectively.

p-Quinonedibenzimide reacted smoothly with the active methylene compounds, diethyl malonate and acetylacetone, in dioxane solution in the presence of sodium methoxide as catalyst to give the 2-substituted diamides (IId). The use of triethylamine in chloroform solution, which was found to be effective with 1,4-naphthoquinonedibenzenesulfonimide,[8] failed to give the desired product with diethyl malonate; with acetylacetone, under these conditions, only a low yield of the adduct was formed.

Although the *p*-quinonedibenzenesulfonimides have proved to be versatile dienophiles for Diels–Alder type reactions,[9] *p*-quinonedibenzimide is quite resistant to the addition of conjugated dienes. Butadiene did not add to I. However, cyclopentadiene, one of the most reactive dienes, did add to form only the monoadduct (III). The re-

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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; Standard Oil of Indiana Fellow, 1950–1951; Allied Chemical and Dye Fellow, 1951–1952.

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

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

[4] R. Adams, E. F. Elslager and T. E. Young, *ibid.*, in press.

[5] H. Meerwein, *Ann.*, **455**, 227 (1927).

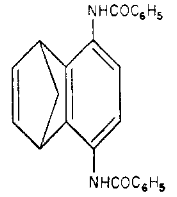
[6] E. Knoevenagel and C. Bückel, *Ber.*, **34**, 3993 (1901).

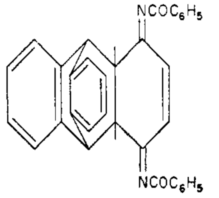
[7] R. Adams and K. A. Schowalter, THIS JOURNAL, **74**, 2597 (1952).

[8] R. Adams and W. Moje, *ibid.*, **74**, 5557 (1952).

[9] (a) R. Adams and C. R. Walter, Jr., *ibid.*, **73**, 1152 (1951); (b) R. Adams and W. Moje, *ibid.*, **74**, 2593 (1952); (c) R. Adams and J. D. Edwards, Jr., *ibid.*, **74**, 2603 (1952).

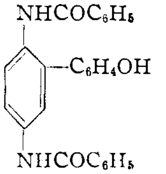
action was very slow at room temperature and gave good yields only when the reactants were heated in boiling benzene or chloroform solution. The product isolated was aromatic and proved to be the diamide formed by a shift of two hydrogens in the intermediate adduct. In contrast, cyclopentadiene reacted so readily with *p*-quinonedibenzenesulfonimide that it was impossible to obtain a monoadduct even when the reactants were mixed in a 1:1 ratio at room temperature.[9a]

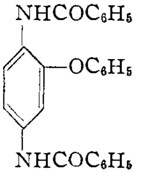

III

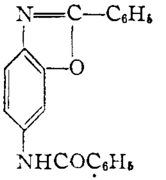

IV

Attempts to cause *p*-quinonedibenzimide to react with anthracene led to a high melting compound which was not soluble in any available solvent. An analysis of the crude material indicated it to be a compound formed from one molecule of I and one molecule of anthracene. The infrared spectrum revealed the absence of any NH grouping and, therefore, the product is probably the Diels–Alder type of adduct (IV) which had not rearranged. Triptycene-2,5-dibenzamide was synthesized from the diamine for purposes of comparison but an attempt to rearrange the addition product to the triptycene by heating a suspension of the material in glacial acetic acid containing a few drops of 48% hydrobromic acid led only to decomposition products.

In chloroform solution, with boron fluoride as a catalyst, phenol added to I in good yield, although some tar was formed. The same product was obtained in lower yields if the catalyst was not present. Since the reaction product was very insoluble in dilute aqueous alkali and did not give a phenol test with phosphomolybdic acid and ammonia[10] it was considered that a 2-phenoxy derivative might have formed. 2-Phenoxy-*p*-phenylenedibenzamide (VI) was synthesized for comparison by an unequivocal route; the known 5-nitro-2-aminodiphenyl ether was reduced to the diamine and benzoylated. The product was very different in solubility and melting point from the reaction product of phenol and I. Attempts to acetylate the phenol adduct (V) failed but a phenylurethan was prepared to demonstrate the presence of the hydroxyl group.


V


VI


VII

The addition of other aromatic compounds such as benzene or anisole was unsuccessful using either anhydrous aluminum chloride or boron fluoride as catalyst. Such reactions are not favored by the *p*-quinonedibenzimide, although they take place readily with the *p*-quinonedibenzenesulfonimides.[11]

When a solution of *p*-quinonedibenzimide in dry thiophene-free benzene was treated with concentrated sulfuric acid, the quinone diimide color bleached. The main product from the reaction mixture was identified as 2-phenyl-6-benzamidobenzoxazole (VII). This compound was probably formed by addition of a proton from the sulfuric acid and then ring closure by reaction with the polarized form of the imide carbonyl as previously suggested for the formation of an oxazole when 2,6-dichloro-*p*-phenylenedipivalimide reacted with hydrogen chloride.[12]

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Experimental

All melting points are corrected.

2-Phenylmercapto-*p*-phenylenedibenzamide.—A solution of 0.50 g. of *p*-quinonedibenzimide[13] in 5 ml. of dioxane was added to a solution of 0.21 g. of thiophenol in 5 ml. of dioxane containing 2 drops of concentrated sulfuric acid. There was no evidence of immediate reaction but the yellow color gradually bleached upon standing at room temperature. After 18 hours, the product was precipitated by the addition of 100 ml. of water and then was recrystallized from dilute ethanol to give 0.61 g. (90%) of white crystals. One recrystallization from ethanol gave the pure product, m.p. 197–197.5°.

Anal. Calcd. for $C_{26}H_{20}N_2O_2S$: C, 73.56; H, 4.75. Found: C, 73.68; H, 4.75.

When the sulfuric acid catalyst was not used, 0.05 g. (10%) of *p*-phenylenedibenzamide was formed along with 0.51 g. (75%) of the addition product. When chloroform was used as the reaction solvent, the yellow color bleached immediately with the formation of 0.11 g. of *p*-phenylenedibenzamide and 0.52 g. (77%) of impure adduct. Several recrystallizations from dilute ethanol were necessary to give the pure adduct, m.p. 197–197.5°. When one drop of sulfuric acid was added as catalyst, 0.09 g. (18%) of *p*-phenylenedibenzamide and 0.50 g. (74%) of the crude adduct were obtained. When one drop of morpholine was added to the thiophenol solution, there was 68% reduction and only 25% of the impure adduct could be isolated.

Oxidation of 2-Phenylmercapto-*p*-phenylenedibenzamide.—A solution of 0.50 g. of 2-phenylmercapto-*p*-phenylenedibenzamide in 100 ml. of chloroform was treated with 0.52 g. of dry lead tetraacetate. The solution became orange at once and was stirred at room temperature for one hour. The insoluble lead salts were removed by filtration and the chloroform was removed by distillation *in vacuo*. The red residue was dissolved in petroleum ether (b.p. 90–95°) but no crystals separated upon chilling in the freezer. By cooling in a Dry Ice–methanol mixture, orange crystals formed which started to decompose when collected and exposed to the air. They were immediately dissolved in dry ether for use in the next preparation.

2,x-Diphenylmercapto-*p*-phenylenedibenzamide.—The ether and petroleum ether solutions from the oxidation of 2-phenylmercapto-*p*-phenylenedibenzamide were combined and then treated with excess of thiophenol dissolved in 5 ml. of dioxane containing 2 drops of concentrated sulfuric acid. The mixture decolorized at once. The solvents were removed *in vacuo* and the residue recrystallized from ethanol to give 0.30 g. (48%) of white crystals. Two recrystallizations from ethyl acetate gave the pure product, m.p. 223–224°.

Anal. Calcd. for $C_{32}H_{24}N_2O_2S_2$: C, 72.15; H, 4.54. Found: C, 72.23; H, 4.74.

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[10] K. Brauer, *Chem. Ztg.*, **50**, 553 (1926).

[11] R. Adams and K. R. Eilar, THIS JOURNAL, **73**, 1149 (1951).

[12] R. Adams and J. M. Stewart, *ibid.*, **74**, 3660 (1952).

[13] R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).

2-Benzylmercapto-*p*-phenylenedibenzamide.—A solution of 0.50 g. of *p*-quinonedibenzimide in 5 ml. of chloroform was added to a solution of 0.2 g. of benzylmercaptan in 5 ml. of chloroform containing a drop of morpholine. The color gradually bleached and after 16 hours the reduced product, *p*-phenylenedibenzamide, which had precipitated (0.05 g., 10%) was collected by filtration. Evaporation of the mother liquor gave 0.625 g. (89%) of the adduct. One recrystallization from ethyl acetate–petroleum ether gave the pure product, m.p. 173–174°.

Anal. Calcd. for $C_{27}H_{22}N_2O_2S$: C, 73.94; H, 5.06. Found: C, 74.23; H, 5.29.

When the addition was attempted without the morpholine catalyst, there was formed 22.5% of the reduction product and 77.5% of the adduct.

2-Phenylmercapto-*p*-phenylenediethylcarbamate.—A solution of 1.25 g. of *p*-quinonedicarbethoxyimide[13] in 10 ml. of chloroform was treated with 0.65 g. of thiophenol. After standing at room temperature for 10 minutes, the yellow color had bleached and a fine white precipitate (0.20 g., 16%) of *p*-phenylenediethylcarbamate was collected. Evaporation of the mother liquor gave 1.4 g. (78%) of the addition product. Two recrystallizations from cyclohexane gave the pure product, m.p. 131°.

Anal. Calcd. for $C_{18}H_{20}N_2O_4S$: C, 59.98; H, 5.59. Found: C, 59.82; H, 5.75.

2-Phenylmercapto-*p*-phenylenedibenzylcarbamate.—Solutions of 0.50 g. of *p*-quinonedicarbobenzoxyimide[2] and 0.15 g. of thiophenol in 5 ml. of chloroform were mixed After standing at room temperature for 2 hours, the yellow color had bleached and a fine white precipitate (0.08 g., 16%) of *p*-phenylenedibenzylcarbamate was collected. Evaporation of the mother liquor gave 0.53 g. (82%) of the addition product. Two recrystallizations from cyclohexane gave pure product, m.p. 110–112°.

Anal. Calcd. for $C_{28}H_{24}N_2O_4S$: C, 69.40; H, 4.99. Found: C, 69.42; H, 5.17.

2-Methoxy-*p*-phenylenedibenzamide. (A).—A suspension of 0.50 g. of *p*-quinonedibenzimide in 10 ml. of methanol was treated with 2 drops of a 40% solution of boron fluoride in ether. The imide dissolved slowly to give an amber colored solution. After one hour, crystals began to separate. Addition of water caused the precipitation of 0.48 g. (87%) of product. Three recrystallizations from chloroform–petroleum ether gave the pure product, m.p. 214–215°.

Anal. Calcd. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.62; H, 5.25; N, 8.04.

When a larger amount of the boron fluoride catalyst was used, the same product was obtained in lower yield. Use of 1 ml. of catalyst led to 64% of the adduct; 2 ml. of catalyst, 67% of the adduct. The use of 2 drops of sulfuric acid as catalyst gave an 84% yield of the crude adduct.

(B).—This same compound was synthesized by another route for proof of structure. A solution of 5.0 g. of 5-nitro-2-aminoanisole in 150 ml. of thiophene-free benzene was hydrogenated in a low pressure apparatus over platinum oxide catalyst. The theoretical amount of hydrogen was absorbed in 40 minutes. Pyridine was added to bring the amine into solution and the catalyst was removed by filtration. A solution of 8.4 g. of benzoyl chloride in 50 ml. of benzene was added to the cooled solution of the amine and white crystals began to separate immediately. After standing at room temperature for 2 hours, the solid was collected and recrystallized from ethanol to give 8.62 g. (84%) of product. Recrystallization from chloroform–petroleum ether gave the pure product, m.p. 214–215°.

The crystals of this authentic 2-methoxy-*p*-phenylenedibenzamide did not depress the melting point of the amide formed by the addition of methanol to *p*-quinonedibenzimide. The infrared spectra of the two compounds were identical.

2-Ethoxy-*p*-phenylenedibenzamide.—A suspension of 0.50 g. of *p*-quinonedibenzimide in 5 ml. of ethanol was treated with 2 drops of a 40% solution of boron fluoride in ether. After 10 minutes, the imide had all dissolved to give a red solution from which the product started to precipitate in another 10 minutes. Evaporation of the solvent and recrystallization of the residue from methanol (Darco) gave 0.39 g. (68%) of the adduct. Recrystallization from methanol gave the pure product, m.p. 211–211.5°.

Anal. Calcd. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.34; H, 5.83; N, 7.61.

An attempt to cause ethanol to react with *p*-quinonedibenzimide using the procedure of Knoevenagel[6] failed. The only crystalline product isolated from the reaction was a small amount of *p*-phenylenedibenzamide.

2-Morpholino-*p*-phenylenedibenzamide.—A solution of 3.1 g. of *p*-quinonedibenzimide in 13 ml. of chloroform was treated with 0.9 g. of redistilled morpholine. A red color developed and the solution warmed slightly. After 2 hours, a white precipitate began to form. After standing at room temperature for 24 hours, the products were precipitated by the addition of 100 ml. of petroleum ether (b.p. 30–60°). Recrystallization from dilute ethanol gave 2.3 g. (58%) of the morpholine adduct and 0.15 g. (5%) of the reduction product, *p*-phenylenedibenzamide. Two recrystallizations from ethyl acetate gave pure 2-morpholino-*p*-phenylenedibenzamide, m.p. 213–214°.

Anal. Calcd. for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77. Found: C, 71.96; H, 5.76.

Attempts to oxidize this product in dry benzene or chloroform solution with lead tetraacetate were unsuccessful. No quinone diimide could be isolated from the red solutions which were rapidly formed.

2-Piperidino-*p*-phenylenedibenzamide.—A solution of 1.00 g. of *p*-quinonedibenzimide in 10 ml. of chloroform was mixed with a solution of 0.28 g. of redistilled piperidine in 10 ml. of chloroform. After 20 hours, a precipitate of 0.06 g. (6%) of *p*-phenylenedibenzamide was removed by filtration. The mother liquor was heated to boiling and hot petroleum ether (b.p. 80–110°) was added to form a solvent pair. Upon cooling, 1.14 g. (89%) of the addition product was obtained. Recrystallization from methylcyclohexane gave the pure product, m.p. 177.5–178.5°.

Anal. Calcd. for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52. Found: C, 75.31; H, 6.55; N, 10.28.

2-Anilino-*p*-phenylenedibenzamide.—A solution of 2.00 g. of *p*-quinonedibenzimide in 20 ml. of chloroform was mixed with a solution of 0.60 g. of redistilled aniline in 20 ml. of chloroform. There was no immediate evidence of reaction, but after 1.5 hours the orange solution had turned red-brown. After standing at room temperature for 15 hours, a precipitate of 0.08 g. (4%) of *p*-phenylenedibenzamide was removed by filtration and the product was precipitated by the addition of petroleum ether (b.p. 80–110°). Recrystallization from an ethyl acetate–petroleum ether solvent pair (Darco) gave 1.46 g. (56%) of brown crystals. Two recrystallizations from toluene gave the pure product, m.p. 222–223.5°.

Anal. Calcd. for $C_{26}H_{20}N_3O_2$: C, 76.64; H, 5.20; N, 10.31. Found: C, 76.51; H, 5.47; N, 10.25.

The reaction of *n*-butylamine and *p*-quinonedibenzimide in either chloroform or carbon tetrachloride solution did not lead to the expected adduct but gave a high yield (80%) of benzamide as the only isolable product.

2-Morpholino-*p*-phenylenediethylcarbamate.—A solution of 1.25 g. of *p*-quinonedicarbethoxyimide in 10 ml. of chloroform was treated with 0.45 g. of redistilled morpholine. After standing at room temperature for 20 hours, the red solution was heated to boiling and petroleum ether (b.p. 40–55°) was added to turbidity. Upon cooling, 1.2 g. (71%) of white crystals was deposited. Two recrystallizations from cyclohexane gave the pure product, m.p. 163.5–165°.

Anal. Calcd. for $C_{16}H_{23}N_3O_5$: C, 56.96; H, 6.87. Found: C, 57.19; H, 6.95.

2-Morpholino-*p*-phenylenedibenzylcarbamate.—A solution of 1.00 g. of *p*-quinonedicarbobenzoxyimide in 10 ml. of chloroform was treated with 0.25 g. of redistilled morpholine. After standing at room temperature for 20 hours, a red color had developed and a precipitate of 0.15 g. (15%) of *p*-phenylenedibenzylcarbamate was collected by filtration. Evaporation of the chloroform gave 0.93 g. (75%) of the adduct. Recrystallization from methanol gave the pure product, m.p. 155–156°.

Anal. Calcd. for $C_{26}H_{27}N_3O_5$: C. 67.66; H, 5.90. Found: C, 67.74; H, 6.13.

Addition of Acetylacetone to *p*-Quinonedibenzimide. (A).—A solution of 0.50 g. of *p*-quinonedibenzimide in 5 ml. of dry dioxane and 0.20 g. of redistilled acetylacetone was treated with a small amount of sodium methoxide. After standing at room temperature for 24 hours, the product was precipitated by the addition of petroleum ether (b.p. 30-

60°). Recrystallization from ethyl acetate gave 0.50 g. (76%) of the addition product. Two recrystallizations from methanol gave the pure product, m.p. 228.5–229.5°.

Anal. Calcd. for $C_{25}H_{22}N_2O_4$: C, 72.45; H, 5.35; N, 6.76. Found: C, 72.65; H, 5.39; N, 6.57.

(B).—A solution of 1.00 g. of *p*-quinonedibenzimide in 10 ml. of chloroform and 0.40 g. of acetylacetone was treated with 2 drops of triethylamine and allowed to stand at room temperature for 8 days. A precipitate of 0.25 g. of *p*-phenylenedibenzamide was removed by filtration and the mother liquor evaporated to dryness. Recrystallization of the residue from chloroform–carbon tetrachloride gave 0.28 g. (21%) of adduct. Several recrystallizations from methanol gave the pure product, m.p. 228.5–229.5°.

Addition of Diethyl Malonate to *p*-Quinonedibenzimide.—A solution of 0.50 g. of *p*-quinonedibenzimide in 5 ml. of dry dioxane and 0.28 g. of redistilled diethyl malonate was treated with a small amount of sodium methoxide. After standing at room temperature for 30 hours, petroleum ether (b.p. 80–110°) was added and the product collected by filtration. Recrystallization from benzene–petroleum ether gave 0.57 g. (75%) of the adduct. Two recrystallizations from chloroform–petroleum ether gave the pure product, m.p. 170–171°.

Anal. Calcd. for $C_{27}H_{26}N_2O_6$: C, 68.34; H, 5.52; N, 5.91. Found: C, 68.21; H, 5.35; N, 6.05.

When the addition was attempted in chloroform solution using triethylamine as catalyst, 60% of the diimide was recovered unchanged after 8 days. *p*-Phenylenedibenzamide (11%) was the only other product isolated.

Addition of Cyclopentadiene to *p*-Quinonedibenzimide.—A solution of 2.00 g. of *p*-quinonedibenzimide in 10 ml. of dry benzene and 0.84 g. of freshly distilled cyclopentadiene was allowed to stand at room temperature. After 25 hours there was no evidence of reaction but after 70 hours there was a small amount of white precipitate which was collected. The orange solution was then heated to boiling. The color bleached rapidly with the precipitation of a large amount of white product. Recrystallization from ethyl acetate gave 2.17 g. of material identical with the first small precipitate formed. Several recrystallizations from ethanol gave the pure product, m.p. 229–231°. The infrared spectrum revealed the presence of NH groupings and the analysis showed that only one molecule of cyclopentadiene had added. The yield was 90%.

Anal. Calcd. for $C_{25}H_{20}N_2O_2$: C, 78.92; H, 5.30; N, 7.37. Found: C, 78.73; H, 5.44; N, 7.32.

When the same amounts of reactants were dissolved in 15 ml. of dry chloroform and allowed to stand at room temperature for 70 hours there was no evidence of reaction. Upon heating the orange solution to boiling, the color bleached rapidly with the precipitation of 1.86 g. (77%) of the monoadduct. Several recrystallizations from ethanol gave the pure product, m.p. 229–231°.

All attempts to obtain a stable addition product with butadiene and *p*-quinonedibenzimide were unsuccessful. The reaction was tried in benzene and chloroform solutions by allowing to stand at room temperature for extended periods of time; in benzene solution at 50° for two weeks; and in benzene solution at 100° for 48 hours. The only materials isolated from any of the reactions were *p*-phenylenedibenzamide and recovered *p*-quinonedibenzimide.

Reaction of Anthracene with *p*-Quinonedibenzimide.—A solution of 1.00 g. of *p*-quinonedibenzimide and 0.57 g. of anthracene in 50 ml. of dry benzene was heated under reflux for 2 weeks. At the end of this time the white precipitate which had formed was collected to give 0.99 g. of material, m.p. 321–333°. The mother liquor yielded 0.16 g. of unchanged diimide. The high melting material was insoluble in all solvents tried including acetone, ethanol, dimethyl formamide, pyridine, glacial acetic acid, toluene, nitrobenzene, ethyl cellosolve and chloroform. Prolonged heating with the higher boiling solvents gave evidence of decomposition. After boiling 0.50 g. of the material with 400 ml. of absolute ethanol, 100 ml. of acetone and finally with 100 ml. of chloroform, the sample, m.p. 317–324°, was dried and submitted for analysis. The analysis indicates that it is a compound formed from one molecule of anthracene and one molecule of the diimide. The infrared absorption spectrum revealed the absence of the NH grouping, indicating a Diels–Alder type product which had not rearranged.

Anal. Calcd. for $C_{34}H_{24}N_2O_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 81.90; H, 5.13; N, 5.66.

When the same amounts of reactants were dissolved in 30 ml. of dry benzene and allowed to stand at room temperature for 5 months, 0.41 g. of a product, m.p. 326–338°, was formed. This material had the same characteristics and appearance as the product formed in the refluxing solution. There was also 0.50 g. of the diimide recovered.

An attempt to rearrange these products to triptycene-2,5-dibenzamide by heating a suspension of the material in glacial acetic acid containing a few drops of 48% hydrobromic acid failed. The only product isolated was *p*-phenylenedibenzamide.

Triptycene-2,5-dibenzamide.—A solution of 0.47 g. of triptycene-2,5-diamine dihydrochloride (prepared by Dr. C. R. Walter, Jr.[9a]) in 225 ml. of pyridine was treated with 1.0 g. of benzoyl chloride and the mixture allowed to stand at room temperature for 40 hours. The solution was concentrated *in vacuo* to 25 ml. and the product precipitated by the addition of ice-water. Recrystallization from absolute ethanol gave 0.34 g. (54%) of white product, m.p. 321–323°. Further recrystallization from the same solvent did not change this melting point. The infrared spectrum of this compound is quite different from that obtained from the reaction product of *p*-quinonedibenzimide and anthracene.

Anal. Calcd. for $C_{34}H_{24}N_2O_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 82.79; H, 5.02; N, 5.68.

2-(*p*-Hydroxyphenyl)-*p*-phenylenedibenzamide.—A solution of 0.6 g. of phenol in 10 ml. of chloroform was treated with 2 drops of a 40% solution of boron fluoride in ether and then was mixed with a solution of 2.00 g. of *p*-quinonedibenzimide in 10 ml. of chloroform. A dark brown color developed immediately and after a few minutes a solid began to precipitate. After 3 hours, boiling acetone was added to dissolve the solid and the resulting solution was treated with Darco. Hot water was added dropwise to form a solvent pair and the product allowed to crystallize to give 2.03 g. (78%) of white material. Several recrystallizations from acetone, dioxane, chloroform or ethyl acetate brought the product to a constant melting point of 285–286°. The material was still not absolutely pure as indicated by the analysis.

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 75.82; H, 5.01; N, 6.71.

The same product was formed in 60% yield merely by melting the reactants together in the absence of a catalyst. There was also formed 24% of the reduction product, *p*-phenylenedibenzamide, in this reaction. When the diimide and phenol were allowed to stand in chloroform solution without any catalyst, there was 60% reduction and 32% of the adduct was isolated.

This compound is very insoluble in dilute aqueous sodium hydroxide and does not give a phenol test with phosphomolybdic acid and ammonia.[10] The compound reacted with acetic anhydride in pyridine solution to give a derivative which was recrystallized from toluene to a constant melting point of 193.5–194°. It was not absolutely pure and further attempts at recrystallization led to a solid melting over the range 130–145° which was not characterized.

Anal. Calcd. for $C_{28}H_{22}N_2O_4$: C, 74.65; H, 4.92. Found: C, 75.28; H, 5.22.

The compound reacted with phenyl isocyanate by warming the reactants in dry pyridine solution for one hour. The derivative formed was recrystallized from ethanol to give the pure product, m.p. 219–220°.

Anal. Calcd. for $C_{33}H_{25}N_3O_4$: C, 75.13; H, 4.77; N, 7.97. Found: C, 75.30; H, 4.92; N, 7.85.

2-Phenoxy-*p*-phenylenedibenzamide.—A solution of 1.0 g. of 5-nitro-2-aminodiphenyl ether[14] in 50 ml. of dry thiophene-free benzene was hydrogenated in a low pressure apparatus over platinum oxide catalyst. After 1 hour, the water-white solution was filtered from the catalyst and diluted with 25 ml. of pyridine. A solution of 1.22 g. of benzoyl chloride in 15 ml. of benzene was added all at once and the resulting mixture was allowed to stand at room temperature for 1 hour and then was warmed on the steam-bath for 1 hour. The product was obtained by pouring into water and then heating to remove the benzene. Recrystallization

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[14] H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, 529 (1931).

from ethanol gave 1.70 g. (96%) of the pure product, m.p. 212–213°.

Anal. Calcd. for $C_{26}H_{20}N_2O_3$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.60; H, 4.96; N, 6.89.

Other Attempted Friedel–Crafts Reactions.—When the dibenzimide was added to a suspension of anhydrous aluminum chloride in carbon disulfide, the yellow diimide color bleached immediately with the formation of 2-chloro-*p*-phenylenedibenzamide in good yield. A similar reaction using dry thiophene-free benzene bleached very slowly (19 hours) and gave a mixture of products which could not be separated by repeated recrystallization from ethanol or ethyl acetate. The mixture gave a very good Beilstein test and sodium fusion confirmed the presence of halogen. Attempts to treat benzene or anisole with the diimide in the presence of small amounts of boron fluoride led only to the formation of a brown amorphous material which could not be crystallized.

Reaction of *p*-Quinonedibenzimide and Sulfuric Acid in Benzene Solution.—An attempt to use concentrated sulfuric acid as a Friedel–Crafts type catalyst led to an unexpected result. A solution of 0.50 g. of *p*-quinonedibenzimide in 20 ml. of dry thiophene-free benzene was added to a suspension of 0.5 ml. of concentrated sulfuric acid in 10 ml. of benzene and the mixture shaken for 5 minutes. The yellow color disappeared and a black tar formed in the acid layer. After standing at room temperature for 40 hours there was no apparent change. Addition of 100 ml. of water caused the precipitation of a product which was recrystallized from ethanol and then from toluene to give 0.21 g. of white crystals. An analytical sample was prepared by recrystallization from chloroform–petroleum ether, m.p. 199–200°.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.58; H, 4.27; N, 9.00.

The analysis checks for 2-phenyl-6-benzamidobenzoxazole. The melting point of a pure sample of that compound was not depressed when mixed with the above product. The infrared spectrum revealed that the product was a mixture, consisting mainly of the benzoxazole. Continued recrystallization from chloroform–petroleum ether and then from methylcyclohexane gave a solid, m.p. 200–201°. This material did not depress the melting point of 2-phenyl-6-benzamidobenzoxazole but the infrared spectra revealed that the mixture was being resolved and the compound being retained was not the benzoxazole. The impurity was not identified, but the infrared spectra ruled out the possibility of its being 2-hydroxy-*p*-phenylenedibenzamide which could be formed by hydrolysis of the benzoxazole.

2-Phenyl-6-benzamidobenzoxazole.—2-Hydroxy-*p*-phenylenedibenzamide[3] was dehydrated by heating the melted substance at 300° in an evacuated tube (30 mm. press.). The vigorous boiling at the start of the heating subsided after 5 minutes. The cooled melt from 0.30 g. of the phenol was dissolved in hot chloroform and then petroleum ether (b.p. 80–110°) added to form a solvent pair. Upon cooling, 0.28 g. (99%) of white product precipitated, m.p. 199–200°.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.51; H, 4.35; N, 9.21.

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

Quinone Imides. XXIV. *o*-Quinonemonoimides

BY ROGER ADAMS AND JOHN MORROW STEWART[1]

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Acetyl, benzoyl and benzenesulfonyl derivatives of certain *o*-aminophenols have been subjected to oxidation with lead tetraacetate. The *o*-quinone monoimides in most cases are unstable and cannot be isolated before decomposition or polymerization occurs. Substituents in the benzene ring in the position para to the amide function tend to induce stabilization in the products and isolation is then possible. The following monoimides were isolated: 4-methyl-*o*-quinone-1-benzimide, 4,6-dimethyl-*o*-quinone-1-benzimide (an oil), 5-chloro-4,6-dimethyl-*o*-quinone-1-benzimide, 1,2-naphthoquinone-1-benzimide. The monoimides add hydrogen chloride to give the corresponding monochloro amides. The monobenzimides are more stable than the acetyl or benzenesulfonyl analogs.

Previous papers have described researches involving the synthesis and reactions of *p*-quinone diimides,[2] *o*-quinone diimides[3] and *p*-quinone monoimides.[4] The preparation of *o*-quinone monoimides has now been undertaken.

Oxidation of *o*-aminophenol results in the formation not of *o*-quinonemonoimine, but of a dimer, aminophenoxazone.[5a] On the other hand, with substituents present in the ring, the *o*-quinone monoimines are sometimes stable. Henrich and his co-workers were successful in preparing 4-methoxy-6-methyl-*o*-quinone-1-imine[5b] and 3-methyl-6-methoxy-*o*-quinone-1-imine.[5c] *o*-Quinone monochloroimines, where the hydrogen on the nitrogen is substituted by a chlorine, are slightly more stable, and several *o*-benzoquinone monochloroimines[5d,e] and 1,2-naphthoquinone monochloroimines[5f,g] have been described. The oxidation of N-(2-nitro-4-chlorophenylsulfenyl)-*o*-aminophenol yields a yellow, amorphous substance for which the authors have proposed an *o*-quinone monoimine structure.[5h]

More complex quinone monoimines, some of which are relatively stable, have been synthesized by condensation reactions, rather than by oxidation of *o*-aminophenols. *m*-Fluorophenol, when treated with nitrous acid or nitrosylsulfuric acid, gives compounds of the indophenol type with an ortho configuration.[5i] The condensation of substituted 1-naphthols with aryl amines leads to substituted 1,2-naphthoquinone-2-amines.[5j] 9,10-Phenanthraquinone reacts with ammonia to form 9,10-phenan-

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[1] An abstract of a thesis submitted by John Morrow Stewart to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Eastman Kodak Fellow, 1951–1952.

[2] R. Adams, *et al.*, THIS JOURNAL, **72**, 4601, 5154 (1950); **73**, 131, 1149, 1152, 2219 (1951); **74**, 2593, 2597, 2603, 2608 (1952).

[3] R. Adams and C. N. Winnick, *ibid.*, **73**, 5687 (1951).

[4] R. Adams, *et al.*, *ibid.*, **73**, 1145 (1951); **74**, 2605 (1952).

[5] (a) O. Fischer and O. Jonas, *Ber.*, **27**, 2784 (1894); (b) F. Henrich and W. Herold, *ibid.*, **61**, 2343 (1928); (c) F. Henrich and O. Fleischmann, *ibid.*, **63**, 1335 (1930); (d) Z. Blaszkowska, *Roczniki Chem.*, **15**, 350 (1935); (e) E. Noelting and G. Thesmar, *Ber.*, **35**, 628 (1902); (f) P. Friedländer and O. Reinhardt, *ibid.*, **27**, 240 (1894); (g) W. Swietoslawski, *et al.*, *Roczniki Chem.*, **11**, 40 (1931); (h) E. Gebauer-Fulnegg and E. Riesz, *Monatsh.*, **49**, 31 (1928); (i) H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 1405 (1939); 205 (1940); (j) V. Tulagin, U. S. Patent 2,445,252 (1948); (k) J. Schmidt and J. Söll, *Ber.*, **41**, 3679 (1908); (l) T. Zincke and P. Jörg, *ibid.*, **44**, 614 (1911).