

m.p. 247–248° (dec.). The infrared spectrum showed the presence of the –NH– and methylene linkages.

Anal. Calcd. for $C_{45}H_{36}N_4O_8S_2$: C, 60.79; H, 4.08; N, 6.30. Found: C, 60.79; H, 4.08; N, 5.93.

Bis-(1,4-naphthoquinonedibenzesulfonimido-2)-methane (XV).—A solution of 0.33 g. of XIV and 1 g. of lead tetraacetate in 10 ml. of acetic acid was heated to the boiling point and then allowed to cool. To this solution was added 0.8 ml. of ethylene glycol. After standing overnight

the orange prisms that had separated were collected, washed with acetic acid and dried. The yield was 0.30 g. (91%). Recrystallization from nitromethane gave orange prisms, m.p. 199–200° (dec.). The infrared spectrum showed the presence of the carbon–nitrogen double bond and the methylene linkage.

Anal. Calcd. for $C_{45}H_{32}N_4O_8S_2$: C, 61.07; H, 3.64; N, 6.33. Found: C, 60.89; H, 3.63; N, 6.40.

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

Quinone Imides. XX. Additions to 1,4-Naphthoquinonedibenzesulfonimide

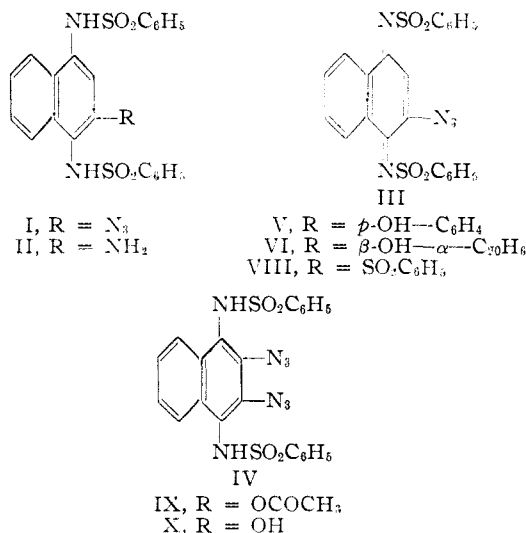
BY ROGER ADAMS AND WILLIAM MOJE

RECEIVED JULY 3, 1952

Hydrazoic acid, diazomethane, benzenesulfonic acid, acetic acid, phenol and β -naphthol add to 1,4-naphthoquinonedibenzesulfonimide to give the corresponding 2-substituted 1,4-naphthalenedibenzesulfonamides.

The addition of hydrazoic acid to quinones was first studied by Oliveri-Mandalá,¹ who reported that *p*-benzoquinone with hydrazoic acid gives azido-hydroquinone.¹ From α -naphthoquinone or β -naphthoquinone, however, the products are, respectively, 2-amino-1,4-naphthoquinone and 4-amino-1,2-naphthoquinone² which arise presumably by intramolecular oxidation–reduction of the initially formed azidonaphthoquinones.

When 1,4-naphthoquinonedibenzesulfonimide in acetic acid was treated with an aqueous solution of sodium azide, 2-azido-1,4-naphthalenedibenzesulfonamide (I) was formed in 94% yield. This was reduced with aqueous sodium hydrosulfite to 2-amino-1,4-naphthalenedibenzesulfonamide (II).

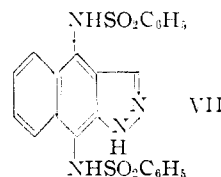


The 2-azido-1,4-naphthalenedibenzesulfonamide was readily oxidized in acetic acid to the orange 2-azido-1,4-naphthoquinonedibenzesulfonamide (III). This added a molecule of hydrazoic acid to give 2,3-diazido-1,4-naphthalenedibenzesulfonamide (IV). All of the azides prepared showed

infrared absorption spectra characteristic of the azido grouping.³

Aromatic compounds add to *p*-quinonedibenzesulfonimide to give monoaryl *p*-phenylenedibenzesulfonamide derivatives.⁴ This reaction has now been extended to 1,4-naphthoquinonedibenzesulfonimide. In the presence of a small amount of boron trifluoride etherate as a catalyst, phenol and β -naphthol added to 1,4-naphthoquinonedibenzesulfonimide. The products, 2-(*p*-hydroxyphenyl)-1,4-naphthalenedibenzesulfonamide (V) and 2-(β -hydroxy- α -naphthyl)-1,4-naphthalenedibenzesulfonamide (VI) were obtained in very good yields. Attempts to arylate 1,4-naphthoquinonedibenzesulfonimide with aryldiazonium salts⁵ and *N*-nitrosoarylamides,⁶ which have been used for the arylations of *p*-quinones, were unsuccessful.

Diazomethane and its derivatives⁷ have been added to various *p*-quinones to give substituted pyrazoles.⁷ The addition of ethereal diazomethane to a chloroform solution of 1,4-naphthoquinonedibenzesulfonimide gave the corresponding pyrazole (VII). Attempts to add phenylazide to 1,4-



naphthoquinonedibenzesulfonimide, which gave substituted triazoles with *p*-quinones,⁸ were unsuccessful.

Benzenesulfonic acid and some of its derivatives have been added to *p*-quinone to give the corre-

(3) J. H. Boyer, *THIS JOURNAL*, **73**, 5248 (1951).

(4) R. Adams and K. R. Eilar, *ibid.*, **73**, 1149 (1951).

(5) D. E. Kvalnes, *ibid.*, **56**, 2478 (1934); G. B. Marini-Bettolo and C. Rossi, *Gazz. chim. ital.*, **72**, 208 (1942).

(6) M. Akagi and K. Hirose, *J. Pharm. Soc. Japan*, **62**, 191 (1942); *C. A.*, **45**, 6169 (1951).

(7) H. von Pechmann, *Ber.*, **28**, 855 (1895); **32**, 2292 (1899); L. F. Fieser and M. A. Peters, *THIS JOURNAL*, **53**, 4080 (1931); E. Bergmann and F. Bergmann, *J. Org. Chem.*, **3**, 125 (1938).

(8) L. Wolff, *Ann.*, **394**, 68 (1912); **399**, 274, 287 (1913); F. D. Chattaway and G. D. Parks, *J. Chem. Soc.*, **127**, 1309 (1925).

(1) E. Oliveri-Mandalá and E. Calderao, *Gazz. chim. ital.*, **45**, 1, 307 (1915); E. Oliveri-Mandalá, *ibid.*, **45**, II, 120 (1915).

(2) L. F. Fieser and J. L. Hartwell, *THIS JOURNAL*, **57**, 1482 (1935); see also A. Korezynski, *Bull. soc. chim.*, [4] **35**, 1186 (1924).

sponding dihydroxydiaryl sulfones.⁹ When a warm acetic acid solution of 1,4-naphthoquinonedibenzenesulfonamide was treated with aqueous sodium benzenesulfinate, 2-benzenesulfonyl-1,4-naphthalenedibenzenesulfonamide (VIII) separated in nearly quantitative yield.

Acetyl chloride alone does not react with quinones; however, with an acid catalyst such as acetic acid¹⁰ or aluminum chloride¹¹ chlorodiacetylhydroquinones are formed. When a chloroform solution of 1,4-naphthoquinonedibenzenesulfonamide and acetyl chloride was refluxed, no reaction took place; however, addition of a few drops of boron trifluoride etherate at room temperature resulted in the formation of 2-chloro-1,4-naphthalenedibenzenesulfonamide.¹²

The addition of various organic acids to *p*-quinone diimides to give the corresponding 2-acyloxy-*p*-phenylenediamides has previously been studied.¹³ With *p*-quinonedibenzimide, addition of organic acids takes place readily without catalysts. With *p*-quinonedibenzenesulfonamide, however, addition occurs only under the influence of acid catalysts. Under these latter conditions, acetic acid did not add to 1,4-naphthoquinonedibenzenesulfonamide but the primary reaction was hydrolysis to α -naphthoquinone and benzenesulfonamide. Under the influence of a basic catalyst, addition took place readily. When 1,4-naphthoquinonedibenzenesulfonamide in acetic acid was treated with triethylamine or with sodium acetate, 2-acetoxy-1,4-naphthalenedibenzenesulfonamide (IX) was formed in yields of 68 and 77%, respectively. The product was hydrolyzed with hydrochloric acid in methyl cellosolve to 2-hydroxy-1,4-naphthalenedibenzenesulfonamide (X).

Acknowledgment.—The authors are indebted to Miss Emily Davis, Mrs. Ester Fett, Mrs. Katherine Pih and Mr. J. Nemeth for the microanalyses and to Miss Helen Miklas for the infrared spectra determinations.

Experimental

All melting points are corrected.

2-Azido-1,4-naphthalenedibenzenesulfonamide (I).—To a solution of 2 g. of 1,4-naphthoquinonedibenzenesulfonamide in 50 ml. of hot glacial acetic acid was added a solution of 1 g. of sodium azide in 4 ml. of water. The yellow solution decolorized immediately and white crystals separated. After cooling, the product was collected, washed with water and dried. The yield was 2.06 g. (94%). Recrystallization from nitromethane gave colorless needles, m.p. 185–186° (dec.) with darkening at 142°. The compound gradually turned orange when allowed to stand in the light. The infrared spectrum indicated the presence of the azido grouping and the –NH– linkage.

Anal. Calcd. for C₂₂H₁₇N₃O₅S₂: C, 55.10; H, 3.57; N, 14.61. Found: C, 55.24; H, 3.74; N, 14.84.

2-Amino-1,4-naphthalenedibenzenesulfonamide (II).—A solution of 0.45 g. of 2-azido-1,4-naphthalenedibenzenesulfonamide in 15 ml. of 5% aqueous sodium hydroxide was treated with 2 g. of sodium hydrosulfite in 10 ml. of water. The pale yellow solution was boiled for 10 minutes, cooled, diluted with water and acidified. The cream colored pre-

cipitate that formed was filtered, washed with water and dried. The yield was 0.34 g. (80%). Recrystallization from aqueous methanol gave white needles, m.p. 236.5–237° (dec.), in a bath preheated to 233°. The infrared spectrum indicated the presence of the amino grouping and the –NH– linkage.

Anal. Calcd. for C₂₂H₁₉N₃O₄S₂: C, 58.26; H, 4.22; N, 9.27. Found: C, 58.29; H, 4.23; N, 9.24.

2-Azido-1,4-naphthoquinonedibenzenesulfonamide (III).—To a suspension of 1.5 g. of 2-azido-1,4-naphthalenedibenzenesulfonamide in 25 ml. of glacial acetic acid was added 2 g. of lead tetraacetate. The mixture was heated at 90° for 1 minute during which time the amide went into solution. After the orange solution had cooled, 1 ml. of ethylene glycol was added. After cooling in an ice-bath, the product was filtered, washed with acetic acid and dried. The yield was 1.22 g. (82%). Recrystallization from chloroform-cyclohexane gave pale orange plates, m.p. 146–147° (dec.). The infrared spectrum indicated the presence of the carbon–nitrogen double bond and the azido grouping.

Anal. Calcd. for C₂₂H₁₆N₃O₅S₂: C, 55.33; H, 3.17; N, 14.67. Found: C, 55.37; H, 3.33; N, 14.77.

2,3-Diazido-1,4-naphthalenedibenzenesulfonamide (IV).—To a solution of 0.5 g. of 2-azido-1,4-naphthoquinonedibenzenesulfonamide in 20 ml. of warm glacial acetic acid was added a solution of 0.3 g. of sodium azide in 5 ml. of water. The pale orange solution decolorized immediately and white crystals separated. After cooling, the filtered product weighed 0.54 g. (99%). Recrystallization from ethylene dichloride or chloroform gave small white needles, m.p. 155° (dec.). The infrared spectrum indicated the presence of the –NH– linkage and the azido grouping.

Anal. Calcd. for C₂₂H₁₆N₅O₅S₂: C, 50.76; H, 3.10; N, 21.53. Found: C, 50.81; H, 3.25; N, 21.66.

No reaction took place when a chloroform solution of 1,4-naphthoquinonedibenzenesulfonamide and phenylazide was refluxed for 2 days or heated in a pressure bottle at 100° for 10 hours.

2-(*p*-Hydroxyphenyl)-1,4-naphthalenedibenzenesulfonamide (V).—To a solution of 1 g. of 1,4-naphthoquinonedibenzenesulfonamide in 20 ml. of chloroform was added 0.5 g. of phenol and 10 drops of boron trifluoride etherate. The orange-red solution was heated to the boiling point and allowed to cool. After standing for 30 minutes, the heavy white crystalline product was filtered, washed with chloroform and dried. The yield was 1 g. (83%). Recrystallization from glacial acetic acid gave small white needles, m.p. 213–214° (dec.). The infrared spectrum indicated the presence of the hydroxyl and –NH– linkages.

Anal. Calcd. for C₂₃H₂₂N₂O₆S₂: C, 63.38; H, 4.18; N, 5.28. Found: C, 63.36; H, 4.20; N, 5.52.

2-(β -Hydroxy- α -naphthyl)-1,4-naphthalenedibenzenesulfonamide (VI).—To a solution of 2.18 g. of 1,4-naphthoquinonedibenzenesulfonamide and 1 g. of β -naphthol in 25 ml. of chloroform was added 5 drops of boron trifluoride etherate. The red solution was heated to the boiling point and allowed to stand at room temperature for 3 hours. The crystalline product that had separated was filtered, washed with chloroform and dried. The yield was 2.30 g. (79%). Recrystallization from ethanol gave small white needles, m.p. 247–248° (dec.), with previous softening at 196–197°. The infrared spectrum indicated the presence of the hydroxyl and –NH– linkages.

Anal. Calcd. for C₂₈H₂₄N₂O₆S₂: C, 66.19; H, 4.17; N, 4.83. Found: C, 66.03; H, 4.29; N, 4.72.

Addition of Diazomethane to 1,4-Naphthoquinonedibenzenesulfonamide (VII).—To a solution of 4 g. of 1,4-naphthoquinonedibenzenesulfonamide in 100 ml. of chloroform at 0° was added 40 ml. of ethereal diazomethane prepared from 4 g. of nitrosomethylurea. After standing for 5 hours at 0°, the pale yellow crystalline product was collected, washed with chloroform and dried. The yield was 1.65 g. (38%). Recrystallization from aqueous ethanol gave pale yellow needles, m.p. 214–215° (dec.). The infrared spectrum indicated the presence of the –NH– linkage.

Anal. Calcd. for C₂₃H₁₈N₄O₄S₂: C, 57.72; H, 3.79; N, 11.71. Found: C, 57.95; H, 4.02; N, 11.79.

2-Benzenesulfonyl-1,4-naphthalenedibenzenesulfonamide (VIII).—To a solution of 1 g. of 1,4-naphthoquinone-

(9) O. Hinsberg, *Ber.*, **50**, 953 (1917), and earlier papers; W. B. Price and S. Smiles, *J. Chem. Soc.*, 3154 (1928).

(10) J. Cason, R. E. Harman, S. Goodwin and C. A. Allen, *J. Org. Chem.*, **15**, 860 (1950).

(11) A. Oliverio, *Gazz. chim. ital.*, **78**, 105 (1948).

(12) R. Adams and R. A. Wankel, *THIS JOURNAL*, **73**, 131 (1951).

(13) R. Adams and D. S. Acker, *ibid.*, **74**, 3657 (1952).

dibenzenesulfonimide in 25 ml. of hot glacial acetic acid was added 0.8 g. of hydrated sodium benzenesulfinate. The yellow solution decolorized immediately. The hot solution was diluted with 15 ml. of water and cooled. The small colorless needles that separated were collected, washed with water and dried. The yield was 1.32 g. (99%). Recrystallization from ethyl acetate-cyclohexane gave white prisms, m.p. 195-196° (dec.). The infrared spectrum indicated the presence of the -NH- linkage.

Anal. Calcd. for $C_{23}H_{22}N_2O_6S_2$: C, 58.11; H, 3.83; N, 4.84. Found: C, 58.06; H, 3.66; N, 4.69.

Action of Acetyl Chloride on 1,4-Naphthoquinonedibenzenesulfonimide.—To a solution of 2 g. of 1,4-naphthoquinonedibenzenesulfonimide in 50 ml. of chloroform was added 10 ml. of freshly distilled acetyl chloride. The solution was refluxed for 44 hours and then allowed to stand at room temperature for 2 days. The clear yellow solution was evaporated to dryness and the yellowish-green residue washed with cyclohexane. It weighed 2 g. Recrystallization from acetic acid gave yellow needles, m.p. 218-219° (dec.). There was no depression when a melting point was taken of this compound with 1,4-naphthoquinonedibenzenesulfonimide.

To a solution of 1 g. of 1,4-naphthoquinonedibenzenesulfonimide in 20 ml. of chloroform was added 5 ml. of freshly distilled acetyl chloride and 10 drops of boron trifluoride etherate. The solution was allowed to stand at room temperature for 2 days. The product that had separated was filtered and washed with benzene. The yield was 0.53 g. (49%). Recrystallization from ethylene dichloride gave long feathery white needles, m.p. 228.5-229.5° (dec.). There was no depression when a melting point was taken of this compound with an authentic sample of 2-chloro-1,4-naphthalenedibenzenesulfonamide.¹² Their infrared spectra were also identical.

2-Acetoxy-1,4-naphthalenedibenzenesulfonamide (IX).—A mixture of 2 g. of 1,4-naphthoquinonedibenzenesulfonimide, 25 ml. of glacial acetic acid and 1 ml. of triethylamine was heated on the steam-bath for 2.5 hours. After standing overnight at room temperature the solid that had separated from the deep red solution was filtered and washed with acetic acid. Recrystallization from acetic acid gave 1.55 g. (68%) of small white prisms, m.p. 216-217° (dec.). The infrared spectrum indicated the presence of the carbon-oxygen double bond and the -NH- linkage.

Anal. Calcd. for $C_{24}H_{20}N_2O_6S_2$: C, 58.05; H, 4.06; N, 5.64. Found: C, 58.25; H, 4.16; N, 5.79.

A mixture of 5 g. of 1,4-naphthoquinonedibenzenesulfonimide and 20 g. of anhydrous sodium acetate in 200 ml. of acetic acid was heated with stirring at 60-70° for 3 hours. The red solution was diluted with 200 ml. of water and allowed to stand overnight. The solid that had separated was filtered and washed with acetic acid. Recrystallization from acetic acid gave 4.35 g. (77%) of small white prisms, m.p. 216-217° (dec.). There was no depression when a melting point was taken of this compound with that described above.

2-Hydroxy-1,4-naphthalenedibenzenesulfonamide (X).—A solution of 0.5 g. of 2-acetoxy-1,4-naphthalenedibenzenesulfonamide and 3 ml. of concentrated hydrochloric acid in 15 ml. of methyl cellosolve was heated on the steam-bath for 2 hours. The pale yellow solution was diluted with water and cooled. The pink solid that separated was filtered and washed with water. Recrystallization from acetic acid gave 0.41 g. (90%) of small white feathery needles, m.p. 228-229° (dec.). The infrared spectrum indicated the presence of the hydroxyl and -NH- linkages.

Anal. Calcd. for $C_{22}H_{18}N_2O_6S_2$: C, 58.13; H, 3.99; N, 6.16. Found: C, 58.03; H, 4.05; N, 6.04.

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

Quinone Imides. XXI. Addition of Hydrogen Cyanide to 1,4-Naphthoquinonedibenzenesulfonamide

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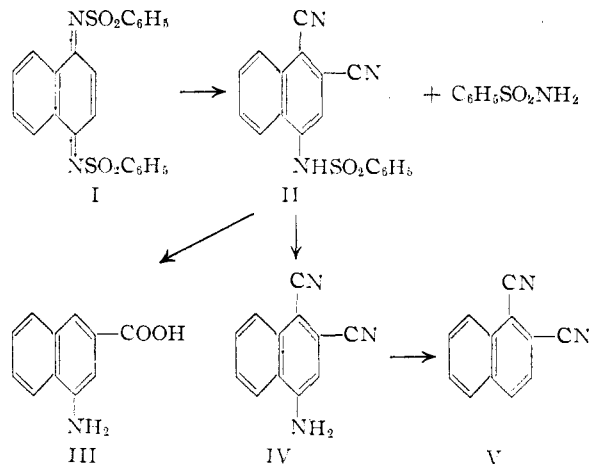
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1,4-Naphthoquinonedibenzenesulfonimide and hydrogen cyanide react to give 3,4-dicyano-1-naphthalenebenzenesulfonamide and benzenesulfonamide. Various degradation reactions of the product are described.

Addition of hydrogen cyanide to *p*-benzoquinone gives 2,3-dicyanohydroquinone.¹ It was anticipated from a knowledge of the previously studied reactions of 1,4-naphthoquinonedibenzenesulfonimide that the addition of hydrogen cyanide to this product would give 2-cyano-1,4-naphthalenedibenzenesulfonamide. Instead the substance that was formed in good yield was 3,4-dicyano-1-naphthalenebenzenesulfonamide (II).

When a benzene solution of 1,4-naphthoquinonedibenzenesulfonimide (I) and liquid hydrogen cyanide was treated with a small amount of triethylamine, two products were obtained, 3,4-dicyano-1-naphthalenebenzenesulfonamide (II) and benzenesulfonamide. No reaction took place without the addition of triethylamine as a catalyst. Hydrolysis of II with hydrochloric acid in acetic acid gave 4-amino-2-naphthoic acid (III). This was identified by comparison with an authentic sample kindly furnished by Cason.² Formation of this compound instead of the expected 4-amino-1,2-

naphthoic acid is not too surprising since 4-amino-phthalic acid decarboxylates on treatment with hydrochloric acid to give 3-aminobenzoic acid.³ On the other hand, treatment of II with warm con-



(1) J. Thiele and J. Meisenheimer, *Ber.*, **33**, 675 (1900); C. F. H. Allen and C. V. Wilson, *This Journal*, **63**, 1756 (1941).

(2) J. Cason, *ibid.*, **63**, 828 (1941).

(3) M. T. Bogert and R. R. Renshaw, *ibid.*, **30**, 1135 (1908).