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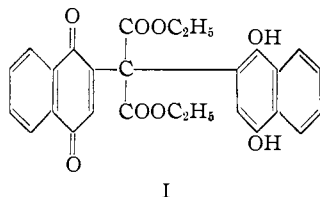
Quinone Imides. XIX. Addition of Active Methylene Compounds to 1,4-Naphthoquinonedibzenzenesulfonimide

BY ROGER ADAMS AND WILLIAM MOJE

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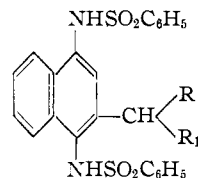
1,4-Naphthoquinonedibzenzenesulfonimide adds one molecule of malonic ester, ethyl benzoylacetate, acetylacetone and nitroethane to give the corresponding 2-substituted 1,4-naphthalenedibzenzenesulfonamides. The product from nitromethane and 1,4-naphthoquinonedibzenzenesulfonimide is a bis-adduct. Various degradation reactions of these products are described. Oxidation of the 2-substituted 1,4-naphthalenedibzenzenesulfonamide derivatives from ethyl benzoylacetate, acetylacetone and nitroethane with lead tetraacetate give the corresponding 1,4-naphthoquinonedibzenzenesulfonimides, whereas that from malonic ester gives an *o*-quinone monoimide derivative.

p-Quinones participate in the Michael reaction with active methylene compounds to give various products depending on the substituents in the quinone molecule, the active methylene compound and the catalyst used in the reaction. The reaction between substituted 1,4-benzoquinones having one or two open positions and metallic enolates has been extensively investigated by Smith and co-workers.¹ 1,4-Benzoquinone itself reacted with ethyl cyanoacetate, malononitrile and cyanoacetamide to give 2,5-substituted hydroquinones²; however, when the active methylene compound was acetylacetone, the products were not adequately characterized.³ 1,4-Naphthoquinone and diethyl malonate react in pyridine solution to give the bis compound I.⁴



The Michael reaction has now been extended to 1,4-naphthoquinonedibzenzenesulfonimide. When a benzene solution of 1,4-naphthoquinonedibzen-

zenesulfonimide and diethyl malonate was treated with a drop of triethylamine and allowed to stand at room temperature for one week, a product separated in 83% yield which had structure II. The reaction of 1,4-naphthoquinonedibzenzenesulfonimide with ethyl benzoylacetate in chloroform under similar conditions gave a 90% yield of III and with



- II, R = R₁ = COOC₂H₅
III, R = COC₆H₅; R₁ = COOC₂H₅
IV, R = R₁ = COCH₃
V, R = H; R₁ = COOH
VI, R = H; R₁ = COCH₃
VII, R = CH₃; R₁ = NO₂
VIII, R = CH₃; R₁ = NH₂

acetylacetone, IV in 84% yield. The products II, III and IV crystallized from the reaction mixtures in colors ranging from tan to white whereas the reactions of *p*-quinones were reported usually to give low yields of highly colored products. Both II and III were hydrolyzed with aqueous alkali to the acetic acid derivative V. Treatment of IV with aqueous alkali gave the ketone (VI); the latter gave no color with ferric chloride whereas the former gave a deep purple color.

Nitroethane and 1,4-naphthoquinonedibzenzenesulfonimide in a mixture of chloroform and ethanol containing a drop of triethylamine gave VII and a very small amount of a yellow compound which

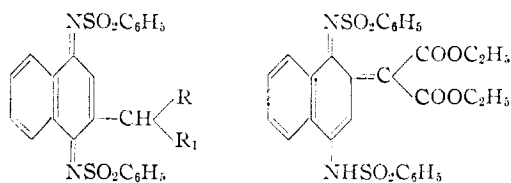
(1) L. I. Smith, *et al.*, THIS JOURNAL, **58**, 629 (1936); *J. Org. Chem.*, **4**, 342 (1939); THIS JOURNAL, **62**, 133 (1940); **65**, 441, 1739 (1943); **68**, 894 (1946); *J. Org. Chem.*, **15**, 832 (1950).

(2) J. H. Wood, C. S. Colburn, L. Cox and H. C. Garland, THIS JOURNAL, **66**, 1540 (1944).

(3) M. V. Ionescu, *Bull. soc. chim.*, **41**, 1094 (1927); E. Bernatek, *Acta Chem. Scand.*, **6**, 160 (1952).

(4) E. F. Pratt and W. E. Boehme, THIS JOURNAL, **73**, 444 (1951).

was not further identified. The reaction was unsuccessful if conducted in chloroform in the absence of ethanol. 2-Nitropropane and 1,4-naphthoquinonedibenzenesulfonimide failed to react under the various conditions tried. Catalytic reduction of VII with hydrogen resulted in the absorption of three moles with formation of the corresponding amine (VIII). The 1,4-naphthalenedibenzenesulfonamides, III, IV and VII, were easily oxidized with lead tetraacetate in acetic acid at room temperature to the corresponding yellow crystalline diimides, IX, X and XI. Oxidation of II, however, gave the *o*-quinone monoimide (XII), which was deep red in color. The infrared spectrum of XII showed the presence of an unsaturated ester carbonyl, an -NH- grouping and a carbon nitrogen double bond.



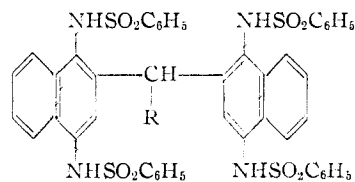
IX, R = COC₆H₅; R₁ = COOC₂H₅

X, R = R₁ = COCH₃

XI, R = CH₃; R₁ = NO₂

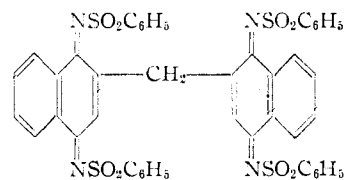
XII

When a chloroform solution of 1,4-naphthoquinonedibenzenesulfonimide and nitromethane was treated with a drop of triethylamine and allowed to stand at room temperature for two days the bis compound (XIII) was formed in 84% yield. A small amount of yellow solid, obtained



XIII, R = NO₂

XIV, R = H



XV

as a by-product, was similar, if not identical, to that formed in the nitroethane reaction as shown by infrared spectra. They both showed bright fluorescence when examined under ultraviolet light. Compound XIII formed solvates with several solvents from which it was crystallized. These solvated compounds could not be desolvated by drying *in vacuo* over phosphorus pentoxide; under these conditions they decomposed. However, by warming these compounds with acetic acid or formic acid, an unsolvated product resulted. Reduction of XIII with lithium aluminum hydride in tetrahydrofuran gave the deaminated bismethyl compound (XIV). This was oxidized with lead tetraacetate in acetic acid to the corresponding tetraimide (XV).

Acknowledgment.—The authors are indebted to Miss Emily Davis, Mrs. Esther 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.

Diethyl 1,4-naphthalenedibenzenesulfonamido-2-malonate (II).—To a solution of 1 g. of 1,4-naphthoquinonedibenzenesulfonimide⁵ in 25 ml. of benzene was added 0.4 ml. of diethyl malonate and one drop of triethylamine. After standing for one week the small gray crystals that had separated were filtered, washed with benzene and dried. The yield was 1.14 g. (83%). Recrystallization from aqueous ethanol gave white needles, m.p. 187–188° (dec.). The infrared spectrum showed the presence of the carbon-oxygen double bond and the -NH- linkage.

Anal. Calcd. for C₂₉H₂₈N₂O₆S₂: C, 58.37; H, 4.73; N, 4.69. Found: C, 58.28; H, 5.00; N, 4.68.

Ethyl 1,4-naphthalenedibenzenesulfonamido-2-benzoylacetate (III).—To a solution of 2 g. of 1,4-naphthoquinonedibenzenesulfonimide in 30 ml. of chloroform was added 1 ml. of ethyl benzoylacetate and one drop of triethylamine. After standing for 2 days the feathery white needles that had separated were collected, washed with chloroform and dried. Recrystallization from ethanol gave 2.68 g. (90%) of white needles, m.p. 123–124° (dec.) with previous softening at 118°. The infrared spectrum indicated the presence of the -NH- grouping and the carbon-oxygen double bond. The compound contained one-half a molecule of ethanol of crystallization as shown by analysis.

Anal. Calcd. for C₃₃H₂₈N₂O₇S₂·1/2C₂H₅OH: C, 62.65; H, 4.79; N, 4.30. Found: C, 62.46; H, 4.92; N, 4.28.

A sample was heated *in vacuo* at 121° for 12 hours; wt. of sample, 0.2787 g.; loss in weight, 0.0092 g.; calcd. loss in weight for one-half a mole of ethanol, 0.0099 g.

1,4-Naphthalenedibenzenesulfonamido-2-acetylacetone (IV).—To a solution of 2 g. of 1,4-naphthoquinonedibenzenesulfonimide in 25 ml. of chloroform was added 1 ml. of acetylacetone and one drop of triethylamine. After standing overnight the small pale yellow needles that had separated were filtered, washed with chloroform and dried. The yield was 2.05 g. (84%). Recrystallization from aqueous methanol gave white needles, m.p. 206–207° (dec.). The infrared spectrum indicated the presence of the -NH- linkage and the carbon-oxygen double bond.

Anal. Calcd. for C₂₇H₂₄N₂O₆S₂: C, 60.43; H, 4.51; N, 5.22. Found: C, 60.36; H, 4.60; N, 5.24.

1,4-Naphthalenedibenzenesulfonamido-2-acetic Acid (V).—A suspension of 0.77 g. of the malonate (II) in 10 ml. of 50% aqueous potassium hydroxide was boiled for 5 minutes. Addition of 5 ml. of water gave a clear solution which was boiled for 5 minutes longer. Acidification with dilute aqueous hydrochloric acid gave a gummy white precipitate which was filtered, washed with water and treated with saturated aqueous sodium bicarbonate. Acidification of the bicarbonate filtrate gave a white precipitate which was recrystallized from acetic acid. The yield was 0.56 g. (88%) of small feathery white needles, m.p. 231–232° (dec.), with previous darkening at 218°. The infrared spectrum showed the presence of the -NH- linkage and the carbon-oxygen double bond.

Anal. Calcd. for C₂₄H₂₀N₂O₆S₂: C, 58.05; H, 4.06; N, 5.64. Found: C, 57.98; H, 4.08; N, 5.38.

A solution of 0.50 g. of the benzoylacetate (III) in 10 ml. of 20% aqueous potassium hydroxide was refluxed for 5 minutes. After cooling, the solution was worked up as described above. The yield was 0.30 g. (82%). A melting point of a mixture of this compound and that described above showed no depression. Their infrared spectra were also identical.

1,4-Naphthalenedibenzenesulfonamido-2-acetylmethane (VI).—A solution of 1 g. of IV in 20 ml. of 5% aqueous sodium hydroxide was heated on the steam-bath for 15 minutes. The yellow solution was cooled, acidified with dilute aqueous hydrochloric acid, and the white solid that precipitated was filtered and washed with water. Recrystal-

(5) R. Adams and W. Moje, *THIS JOURNAL*, **74**, 2592 (1952).

lization from aqueous methanol gave 0.81 g. (88%) of small feathery white needles, m.p. 216–217° (dec.), with previous softening at 183°. The infrared spectrum showed the presence of the –NH– linkage and the carbon–oxygen double bond. This compound gave no color with aqueous ethanolic ferric chloride whereas IV gave a deep purple color.

Anal. Calcd. for $C_{23}H_{22}N_2O_6S_2$: C, 60.71; H, 4.48; N, 5.66. Found: C, 60.83; H, 4.56; N, 5.36.

α -(1,4-Naphthalenedibenzenesulfonamido-2)-nitroethane (VII).—To a solution of 1 g. of 1,4-naphthoquinonedibenzenesulfonamide in a mixture of 25 ml. of chloroform and 10 ml. of ethanol was added 1 ml. of nitroethane and 1 drop of triethylamine. After standing at room temperature for 24 hours, 1 ml. of acetic acid was added. After an additional 24 hours the small yellow crystals (10 mg.) that had separated were filtered and washed with chloroform. Evaporation of the filtrate to a volume of approximately 10 ml. gave a pale yellow solid which, after washing with ether, weighed 0.75 g. (64%). Recrystallization from aqueous ethanol gave small white needles, m.p. 211–212° (dec.). The infrared spectrum showed the presence of the –NH– linkage and the nitro grouping.

Anal. Calcd. for $C_{24}H_{21}N_3O_6S_2$: C, 56.34; H, 4.14; N, 8.21. Found: C, 56.60; H, 4.25; N, 8.17.

Recrystallization of the yellow solid by-product from cyclohexanone–ethanol gave yellow needles, m.p. 328–329° (dec.). The infrared spectrum showed the presence of the –NH– linkage and the nitro grouping.

No reaction took place between 2-nitropropane and 1,4-naphthoquinonedibenzenesulfonamide in chloroform alone or in a mixture of chloroform and ethanol with a drop of triethylamine as a catalyst.

α -(1,4-Naphthalenedibenzenesulfonamido-2)-ethylamine (VIII).—A suspension of 0.60 g. of VII in 30 ml. of ethanol was reduced catalytically with 1 g. of Raney nickel and hydrogen at atmospheric pressure. Dilution of the solution with water gave 0.49 g. (88%) of the crude amine. Recrystallization from acetonitrile gave small white prisms, m.p. 209–210° (dec.). The infrared spectrum showed the presence of the –NH– linkage and the NH_2 grouping.

Anal. Calcd. for $C_{24}H_{23}N_3O_4S_2$: C, 59.85; H, 4.81; N, 8.73. Found: C, 60.05; H, 4.63; N, 8.89.

Ethyl 1,4-naphthoquinonedibenzenesulfonimido-2-benzoylacetate (IX).—To a mechanically stirred solution of 2 g. of III in 20 ml. of acetic acid was added at room temperature 2.5 g. of lead tetraacetate. The product began to separate after 10 minutes. After the reaction had proceeded for 20 minutes, 1 ml. of ethylene glycol was added. The reaction mixture was then placed in an ice-bath for 30 minutes. The product was removed by filtration, washed with acetic acid and dried. The yield was 1.87 g. (97%). Recrystallization from chloroform–cyclohexane gave long yellow needles, m.p. 196–197° (dec.). The infrared spectrum showed the presence of the carbon–nitrogen and carbon–oxygen double bonds.

Anal. Calcd. for $C_{33}H_{26}N_2O_7S_2$: C, 63.24; H, 4.18; N, 4.47. Found: C, 63.51; H, 4.46; N, 4.43.

1,4-Naphthoquinonedibenzenesulfonimido-2-acetylacetone (X).—To a mechanically stirred suspension of 1.35 g. of IV in 10 ml. of acetic acid was added at room temperature 2.5 g. of lead tetraacetate. After the reaction had proceeded for 1.5 hours, 1 ml. of ethylene glycol was added. The product was removed by filtration, washed with acetic acid and dried. The yield was 1.16 g. (86%). Recrystallization from benzene gave small lemon-yellow plates, m.p. 180–181° (dec.). The infrared spectrum showed the presence of the carbon–nitrogen and carbon–oxygen double bonds.

Anal. Calcd. for $C_{27}H_{22}N_2O_6S_2$: C, 60.66; H, 4.15; N, 5.24. Found: C, 60.68; H, 4.30; N, 5.26.

α -(1,4-Naphthoquinonedibenzenesulfonimido-2)-nitroethane (XI).—To a suspension of 0.5 g. of VII in 10 ml. of acetic acid was added 1 g. of lead tetraacetate. The mixture was heated at the boiling point for one minute during which time the amide went into solution. After the yellow solution had cooled, 1 ml. of ethylene glycol was added. After cooling in an ice-bath for one hour the product was filtered, washed with acetic acid and dried. The yield was 0.40 g. (82%). Recrystallization from ethyl acetate–cyclohexane gave yellow needles, m.p. 178–179° (dec.).

The infrared spectrum showed the presence of the carbon–nitrogen double bond and the nitro grouping.

Anal. Calcd. for $C_{24}H_{19}N_3O_6S_2$: C, 56.57; H, 3.76; N, 8.25. Found: C, 56.63; H, 3.74; N, 7.97.

Diethyl (1-benzenesulfonimido-4-benzenesulfonamido-1,2-dihydronaphthylidene-2)-malonate (XII).—To a mechanically stirred solution of 1 g. of II in 20 ml. of acetic acid was added at room temperature 1.5 g. of lead tetraacetate. After the reaction had proceeded for 10 minutes, 1 ml. of ethylene glycol was added. The deep red solution was then placed in an ice-bath for 1 hour. The deep red solid that had separated was filtered, washed with acetic acid and dried. The yield was 0.87 g. (87%). Recrystallization from acetic acid gave ruby red needles, m.p. 173–174° (dec.). The infrared spectrum showed the presence of the carbon–nitrogen double bond, the –NH– linkage and the conjugated ester carbon–oxygen double bond.

Anal. Calcd. for $C_{29}H_{26}N_2O_8S_2$: C, 58.57; H, 4.41; N, 4.71. Found: C, 58.68; H, 4.50; N, 4.99.

Bis-(1,4-naphthalenedibenzenesulfonamido-2)-nitromethane (XIII).—To a solution of 5 g. of 1,4-naphthoquinonedibenzenesulfonamide in 60 ml. of chloroform was added 5 ml. of freshly distilled nitromethane and two drops of triethylamine. After standing for two days at room temperature the cream colored solid was collected, washed with chloroform and dried. The solid weighed 5.05 g. Recrystallization from aqueous tetrahydrofuran gave 4.80 g. (84%) of small white needles, m.p. 157–162° (dec.), with previous darkening at 142°. The crystals gradually turned pink on standing in the air.

Recrystallization from various solvents gave solvated products as described below. None showed perfect analyses, but they were indicative of solvation.

Ethanol: small white plates, m.p. 165–168° (dec.), with darkening at 150°.

Anal. Calcd. for $C_{45}H_{35}N_5O_{10}S_4 \cdot C_2H_5OH$: C, 57.59; H, 4.22; N, 7.15. Found: C, 57.03, 56.90; H, 4.01, 4.01; N, 7.44.

Ethyl acetate: small white needles, m.p. 165–167° (dec.) with darkening at 152°.

Anal. Calcd. for $C_{45}H_{35}N_5O_{10}S_4 \cdot C_4H_8O_2$: C, 57.95; H, 4.38; N, 6.76. Found: C, 57.44, 57.54; H, 4.67, 4.95; N, 6.03.

Aqueous acetone: small white needles, m.p. 157–162° (dec.), with darkening at 122°.

Anal. Calcd. for $C_{45}H_{35}N_5O_{10}S_4 \cdot C_3H_6O$: C, 58.11; H, 4.17; N, 7.06. Found: C, 57.18; H, 4.01; N, 7.23.

Tetrahydrofuran: small white needles, m.p. 157–162° (dec.), with darkening at 140°.

Anal. Calcd. for $C_{45}H_{35}N_5O_{10}S_4 \cdot C_4H_8O$: C, 58.49; H, 4.31; N, 6.96. Found: C, 57.04, 57.71, 57.72; H, 4.45, 4.53, 4.67; N, 7.24.

A solution of the compound from tetrahydrofuran in warm glacial acetic acid was cooled. The unsolvated compound was obtained as small colorless needles, m.p. 215–216° (dec.). This could be converted to the tetrahydrofuran solvated compound by recrystallization from tetrahydrofuran.

Anal. Calcd. for $C_{45}H_{35}N_5O_{10}S_4$: C, 57.87; H, 3.78; N, 7.49. Found: C, 57.52, 57.97; H, 3.65, 3.91; N, 7.17.

The infrared spectrum showed the presence of the –NH– linkage and the nitro grouping.

Evaporation of the filtrate from the crystallization of the main product of the reaction *in vacuo* to remove the tetrahydrofuran gave 0.20 g. of a pale yellow fluorescent solid. Recrystallization from cyclohexanone–ethanol gave yellow needles, m.p. 328–329° (dec.). The infrared spectrum showed the presence of the –NH– linkage and the nitro grouping. The spectrum of this compound and the yellow compound formed in the nitroethane reaction were almost identical.

Bis-(1,4-naphthalenedibenzenesulfonamido-2)-methane (XIV).—To a suspension of 3 g. of lithium aluminum hydride in 50 ml. of tetrahydrofuran was added portionwise 1.73 g. of XIII. After the addition was completed, the excess lithium aluminum hydride was destroyed with ethanol. Acidification with aqueous hydrochloric acid gave a cream-colored precipitate which was filtered, washed with water and dried. The colored impurities were removed by washing with 20 ml. of hot chloroform. Recrystallization from aqueous ethanol gave 1.0 g. (60%) of small white needles,

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

Anal. Calcd. for $C_{15}H_{16}N_4O_8S_2$: 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 $C_{15}H_{16}N_4O_8S_2$: C, 61.07; H, 3.64; N, 6.33. Found: C, 60.89; H, 3.63; N, 6.40.

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

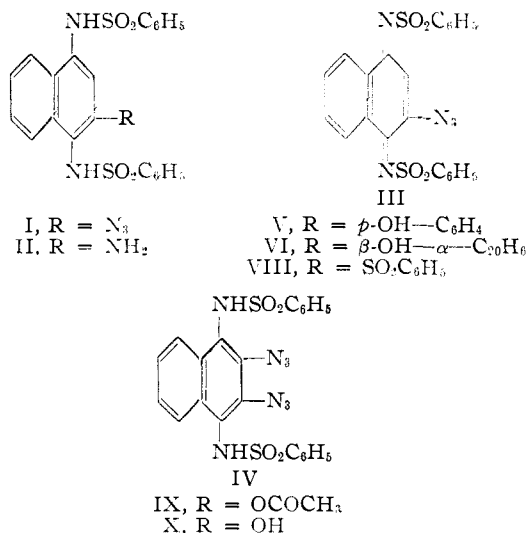
BY ROGER ADAMS AND WILLIAM MOJE

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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).

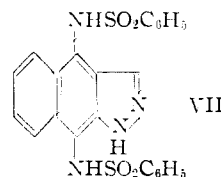


The 2-azido-1,4-naphthalenedibenzesulfonamide was readily oxidized in acetic acid to the orange 2-azido-1,4-naphthoquinonedibenzesulfonamide (III). This added a molecule of hydrazoic acid to give 2,3-diazido-1,4-naphthalenedibenzesulfonamide (IV). All of the azides prepared showed

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**, I, 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).