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 $C_{28}H_{22}N_2O_6S_3$: 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 $C_{22}H_{18}N_2O_5S_2$: C, 58.13; H, 3.99; N, 6.16. Found: C, 58.03; H, 4.05; N, 6.04.

URBANA, ILLINOIS

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

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

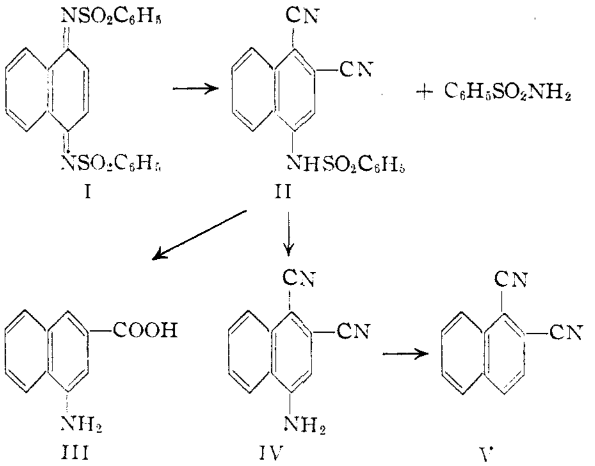
BY ROGER ADAMS AND WILLIAM MOJE

RECEIVED JULY 3, 1952

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-aminophthalic acid decarboxylates on treatment with hydrochloric acid to give 3-aminobenzoic acid.[3] On the other hand, treatment of II with warm con-



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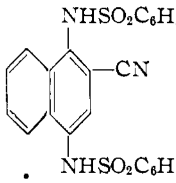
(1) J. Thiele and J. Meisenheimer, *Ber.*, **33**, 675 (1900); C. F. H. Allen and C. V. Wilson, THIS JOURNAL, **63**, 1756 (1941).

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

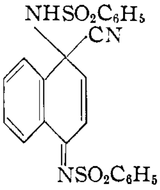
(3) M. T. Bogert and R. R. Renshaw, *ibid.*, **30**, 1135 (1908).

centrated sulfuric acid gave 3,4-dicyano-1-naphthylamine (IV). This was deaminated by diazotization and treatment with hypophosphorus acid to yield the known 1,2-dicyanonaphthalene (V).[4] All of the compounds (II, III, IV and V) in this series show bright fluorescence when examined under ultraviolet light.

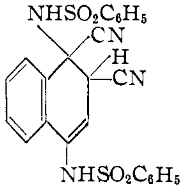
The formation of 3,4-dicyano-1-naphthalenebenzenesulfonamide may proceed by 1,4-addition of hydrogen cyanide to give an intermediate such as VI followed by displacement of the sulfonamido group by cyanide ion, or more likely by 1,2-addition of hydrogen cyanide to give an intermediate such as VII, then 1,4-addition to form VIII, followed by aromatization through elimination of benzenesulfonamide.



VI



VII



VIII

Attempts to prepare II by the addition of glacial acetic acid to a suspension of I in chloroform containing potassium cyanide gave only a small amount of II plus a large amount of 2-acetoxy-1,4-naphthalenedibenzenesulfonamide.[5] The latter compound was almost the sole product when a mixture of I and sodium acetate in acetic acid was treated with potassium cyanide.

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.

3,4-Dicyano-1-naphthalenebenzenesulfonamide.—To a suspension of 10 g. of 1,4-naphthoquinonedibenzenesulfonimide in 200 ml. of benzene was added 15 ml. of commercial 97% liquid hydrogen cyanide. The mixture was cooled in an ice-bath and treated with 2 ml. of triethylamine. The quinone gradually dissolved. After standing for 4 days at 0° white crystals had separated. The mixture was allowed to stand at room temperature for 6 hours, treated with 20 ml. of glacial acetic acid and allowed to stand for an additional hour. The product was collected on a filter and washed with benzene. Recrystallization from nitromethane gave 6.50 g. (85%) of small white prisms, m.p. 254–255°. The infrared spectrum indicated the presence of the carbon–nitrogen triple bond and the –NH– linkage.

Anal. Calcd. for $C_{18}H_{11}O_2N_3S$: C, 64.85; H, 3.33; N, 12.61. Found: C, 64.66; H, 3.46; N, 12.33.

The original benzene filtrate was evaporated on the steam-bath to a volume of 100 ml. After thorough cooling, the product was collected on a filter. Recrystallization from water gave white plates, m.p. 152–153°. The yield was 1.0 g. (28%). There was no depression when a melting point was taken of this compound mixed with an authentic sample of benzenesulfonamide.

3,4-Dicyano-N-methyl-1-naphthalenebenzenesulfonamide.—To a solution of 1 g. of 3,4-dicyano-1-naphthalenebenzenesulfonamide in 50 ml. of anhydrous acetone was added 3 ml. of dimethyl sulfate and 8 g. of anhydrous potassium carbonate. After refluxing the suspension for 24 hours it was filtered and the solid washed with acetone. Dilution of the acetone filtrate with water gave a white solid which was washed first with dilute aqueous alkali then with water and dried. The yield was 1.02 g. (98%). Recrystallization from acetic acid gave small white needles, m.p. 208–209°. The infrared spectrum showed the presence of the carbon–nitrogen triple bond and no –NH– linkage.

Anal. Calcd. for $C_{19}H_{13}N_3S_2O$: C, 65.69; H, 3.77; N, 12.10. Found: C, 65.71; H, 3.77; N, 12.23.

4-Amino-2-naphthoic Acid.—A suspension of 2 g. of 3,4-dicyano-1-naphthalenebenzenesulfonamide in a mixture of 50 ml. of acetic acid and 50 ml. of concentrated hydrochloric acid was refluxed for 5 days. After cooling the small gray needles that had separated were filtered and washed with acetic acid. The yield was 1.30 g. (97%). The solid was dissolved in aqueous ammonia (Darco), filtered, and acidified with acetic acid. After standing overnight at 0°, the product was collected, washed with water and dried. Recrystallization from toluene gave 0.69 g. (67%) of colorless needles, m.p. 215–216°. A melting point of a mixture of this compound with that prepared by Cason[2] showed no depression. Their infrared spectra were also identical and showed the presence of the –NH– grouping and the carbon–oxygen double bond.

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.54; H, 4.94; N, 7.31.

The acetate formed colorless crystals, m.p. 321–322° (dec.).

Anal. Calcd. for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.09; H, 4.98; N, 6.07.

3,4-Dicyano-1-naphthylamine.—A suspension of 1 g. of 3,4-dicyano-1-naphthalenebenzenesulfonamide in 10 ml. of concentrated sulfuric acid was heated to 65° on the steam-bath. The compound dissolved giving a pale red solution which gradually turned pale yellow. The solution was then cooled in an ice-bath and poured into ice-water. The pink precipitate was collected on a filter and washed with water. Recrystallization from ethanol gave 0.50 g. (86%) of pale yellow feathery needles, m.p. 295–296° (dec.). The infrared spectrum showed the presence of the carbon–nitrogen triple bond and the –NH– linkage.

Anal. Calcd. for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.83; H, 3.65; N, 21.74.

1,2-Dicyanonaphthalene.—To 0.5 g. of sodium nitrite in 50 ml. of concentrated sulfuric acid at 0° was added 50 ml. of 30% hypophosphorous acid. To this solution with stirring at 0° was added 0.20 g. of 3,4-dicyano-1-naphthylamine suspended in 50 ml. of acetic acid. The suspension was stirred for 1 hour at 0° and then placed in the refrigerator for 48 hours. The pale yellow suspension was poured into 300 ml. of cold water. The solid was collected on a filter, washed with water, dried and extracted with 25 ml. of hot benzene. The benzene filtrate was evaporated to 5 ml. and allowed to crystallize. The yield was 0.10 g. (55%) of small colorless needles, m.p. 190–191°. The reported melting point is 190°.[4] The infrared spectrum showed the presence of the carbon–nitrogen triple bond.

Anal. Calcd. for $C_{12}H_6N_2$: C, 80.88; H, 3.39; N, 15.72. Found: C, 80.87; H, 3.40; N, 15.63.

URBANA, ILLINOIS

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[4] P. T. Cleve, *Ber.*, **25**, 2475 (1892); E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).

[5] R. Adams and W. Moje, THIS JOURNAL, **74**, 5560 (1952).