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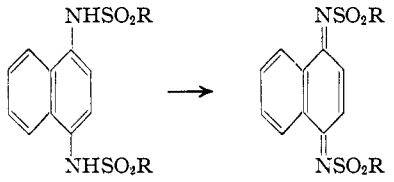
Quinone Imides. III. 1,4-Naphthoquinone Disulfonimides

BY ROGER ADAMS AND R. A. WANKEL

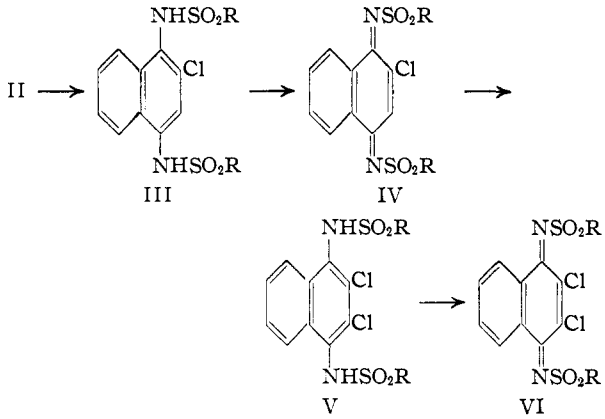
A description of the synthesis and reactions of certain *p*-quinone disulfonamides has been given in a previous paper.[1] Various disulfonyl derivatives of 1,4-naphthylenediamine (I) have now been oxidized with lead tetraacetate to the corresponding 1,4-naphthoquinone disulfonimides (II) and the reactions of these compounds studied. The benzenesulfonyl, *p*-toluenesulfonyl and methanesulfonyl derivatives of 1,4-naphthylenediamine are as readily oxidized to quinone diimides as the derivatives of *p*-phenylenediamine. The yellow crystalline products are stable under ordinary conditions.



I II

R = phenyl, *p*-tolyl, methyl

Reduction of 1,4-naphthoquinone dibenzenesulfonimide to the diamide from which it was produced was effected by hydrogen in presence of platinum catalyst. Boiling with dilute aqueous sodium hydroxide also led to reduction; this compound was much less readily reduced by this means than the *p*-quinone dibenzenesulfonimides. Hydrogen chloride reacted slowly in glacial acetic acid as solvent with formation of the expected 2-chloro compound III, which upon oxidation to the quinone diimide (IV) and treatment with hydrogen chloride yielded the 2,3-dichloro compound V. This, in

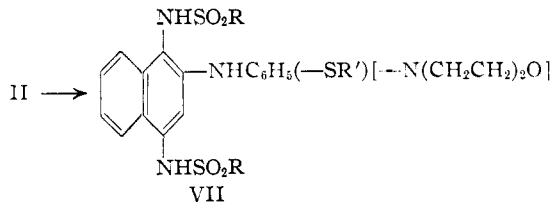


III IV V VI

turn, was oxidized to the corresponding quinone diimide (VI) which was stable to hydrogen chloride.

A 2-methyl group in the naphthalene ring had no effect upon the ease with which oxidation took place. The dibenzenesulfonyl derivative of 2-methyl-1,4-naphthylenediamine was readily converted to 2-methyl-1,4-naphthoquinone dibenzenesulfonimide. This product added hydrogen chloride to give 2-methyl-3-chloronaphthalene-1,4-dibenzenesulfonamide which in turn was oxidized to the corresponding quinone diimide.

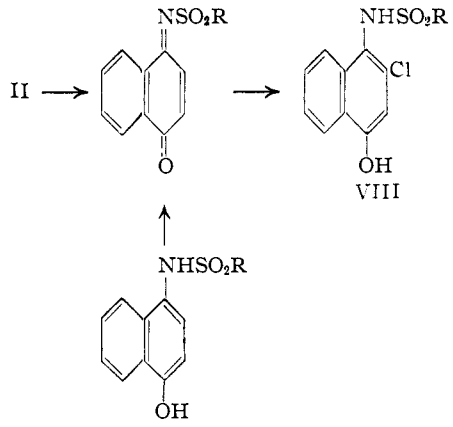
The addition of thiophenol, aniline and morpholine to II took place with formation of compounds shown by formula VII. The phenylmercapto derivative was oxidized to the corresponding naphthoquinone diimide by means of lead tetraacetate. Upon addition of hydrogen chloride to this product, 2-phenylmercapto-3-chloronaphthylene-1,4-dibenzenesulfonamide was formed. On the other hand, attempts to add thiophenol to 2-chloro-1,4-naphthoquinone dibenzenesulfonimide to give the same product always resulted in oxidation of the thiophenol and simultaneous reduction of the quinone diimide to 2-chloronaphthalene-1,4-dibenzenesulfonamide. Attempted addition of thiophenol to 2-phenylmercapto-1,4-naphthoquinone dibenzenesulfonimide also resulted merely in oxidation of the thiophenol and reduction of the quinone diimide.



VII

The 2-morpholinonaphthalene-1,4-dibenzenesulfonamide was oxidized readily to the corresponding quinone diimide. Preliminary experiments indicated that addition products of this latter compound could not be formed readily.

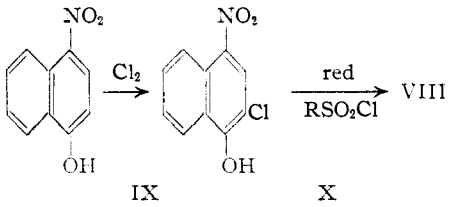
Attempts to hydrolyze 1,4-naphthoquinone dibenzenesulfonimide (II) with dilute sulfuric acid failed. It was found, however, that upon boiling with concentrated hydrochloric acid and glacial acetic acid 1,4-naphthoquinone dibenzenesulfonimide was converted to 4-benzenesulfonamido-2-chloro-1-naphthol (VIII) presumably by initial hydrolysis of one benzenesulfonimido group followed by addition of hydrogen chloride. This mechanism was established through preparation of the identical compound by oxidation of the benzene-



VIII

(1) Adams and Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); see also Adams and Anderson, *ibid.*, **72**, 5154 (1950).

sulfonyl derivative of 4-aminonaphthol and addition of hydrogen chloride. A mixture of boiling concentrated hydrochloric and glacial acetic acid had no effect on 2-chloronaphthalene-1,4-dibenzenesulfonamide, hence hydrogen chloride addition is not the first step in this reaction. The location of the chlorine in the 2-position was demonstrated by synthesis of the chloro compound by an unequivocal method. 4-Nitro-1-naphthol was chlorinated, then reduced to the chloro aminonaphthol followed by benzenesulfonation as shown in IX-X-VIII. Several attempts to prepare X by the



method described by Hodgson and Elliot[2] were unsuccessful.

The 1,4-naphthoquinone disulfonimides are thus convenient raw materials for the synthesis of many 1,4-naphthalenediamine derivatives.

Experimental

The melting points of many of the sulfonamides prepared in these experiments varied considerably according to the rate of elevation of the temperature. All melting points reported in this paper were taken starting at room temperature and raising the temperature at the rate of 3° per minute.

Naphthalene-1,4-dibenzenesulfonamide.—A solution of 5 g. of 4-nitro-1-naphthylamine[3] in 25 ml. of 95% ethanol was reduced catalytically with 0.2 g. of platinum oxide and hydrogen at 40 p.s.i. Saturation of the solution with dry hydrogen chloride, followed by addition of 100 ml. of ether, gave 6.0 g. of the crude diamine hydrochloride. Treatment of this salt in 30 ml. of benzene with 9.9 g. of benzenesulfonyl chloride and 8.7 g. of pyridine on a steam-bath for one hour gave a brown solid. This was stirred well with 25 ml. of petroleum ether (b. p. 30–40°) and 50 ml. of dilute hydrochloric acid. The resulting solid was collected on a filter, dissolved in 100 ml. of 5% sodium hydroxide (Darco), filtered and acidified with acetic acid. The white solid was recrystallized from glacial acetic acid; needles, m. p. 253–254° (cor.). The yield was 8.4 g. (70%).

Anal. Calcd. for $C_{22}H_{18}N_2O_4S_2$: C, 60.25; H, 4.14; N, 6.39. Found: C, 60.31; H, 4.18; N, 6.45.

Naphthalene-1,4-di-*p*-toluenesulfonamide and -1,4-Dimethanesulfonamide.—Treatment of the diamine hydrochloride with two molecular equivalents of methanesulfonyl chloride or *p*-toluenesulfonyl chloride in a similar manner gave naphthalene-1,4-dimethanesulfonamide, m. p. 261–262° (cor.) in 86% yield and naphthalene-1,4-di-*p*-toluenesulfonamide, m. p. 241–242° (cor.) in 38% yield. Both were purified from glacial acetic acid.

Anal. Calcd. for $C_{12}H_{14}N_2O_4S_2$ (methanesulfonyl derivative): C, 45.84; H, 4.49; N, 8.91. Found: C, 45.82; H, 4.62; N, 8.83. Calcd. for $C_{24}H_{22}N_2O_4S_2$ (*p*-toluenesulfonyl derivative): C, 61.78; H, 4.75; N, 6.01. Found: C, 61.69; H, 4.80; N, 6.16.

1,4-Naphthoquinone Dibenzenesulfonimide.—A mixture of 1.0 g. of naphthalene-1,4-dibenzenesulfonamide, 15 ml. of glacial acetic acid and 1.0 g. of lead tetraacetate, was stirred vigorously for one hour, while the temperature was kept at 45–50°. After cooling thoroughly, the yellow product was collected on a filter. Recrystallization from boiling glacial acetic acid gave needles, m. p. 213–214° (cor.). The yield was 0.8 g. (83%).

Anal. Calcd. for $C_{22}H_{16}N_2O_4S_2$: C, 60.53; H, 3.70; N, 6.42. Found: C, 60.46; H, 3.74; N, 6.29.

(2) Hodgson and Elliot, *J. Chem. Soc.*, 1705 (1934).

(3) Price and Voong, *Organic Syntheses*, **28**, 80 (1948).

Reduction of 1,4-naphthoquinone dibenzenesulfonimide in 95% ethanol with platinum oxide and hydrogen at 40 lb. pressure gave naphthalene-1,4-dibenzenesulfonamide in 96% yield.

1,4-Naphthoquinone Di-*p*-toluenesulfonimide and Dimethanesulfonimide.—1,4-Naphthoquinone dimethanesulfonimide, m.p. 218–219° (cor.) in 85% yield, and 1,4-naphthoquinone di-*p*-toluenesulfonimide, m. p. 222–223° (cor.) in 84% yield were prepared from the corresponding amides in a similar manner. Both compounds formed yellow needles and were purified from glacial acetic acid.

Anal. Calcd. for $C_{12}H_{12}N_2O_4S_2$ (methanesulfonyl derivative): C, 46.14; H, 3.87; N, 8.97. Found: C, 46.32; H, 4.04; N, 9.10. Calcd. for $C_{24}H_{20}N_2O_4S_2$ (*p*-toluenesulfonyl derivative): C, 62.05; H, 4.34; N, 6.03. Found: C, 61.91; H, 4.38; N, 6.16.

2-Chloronaphthylene-1,4-dibenzenesulfonamide.—Into a suspension of 1.0 g. of 1,4-naphthoquinone dibenzenesulfonimide in 15 ml. of glacial acetic acid dry hydrogen chloride was introduced rapidly. The solution became warm; in 20 minutes the yellow color had disappeared and a white precipitate separated. After addition of 100 ml. of water, the product was collected by filtration and recrystallized from glacial acetic acid; white needles, m. p. 228° (cor.). The yield was 1.05 g. (96%).

Anal. Calcd. for $C_{22}H_{17}ClN_2O_4S_2$: C, 55.87; H, 3.62; N, 5.92. Found: C, 56.04; H, 3.76; N, 5.88.

This product was recovered unchanged after boiling for 3 hours in glacial acetic acid with 4% concentrated hydrochloric acid.

2-Chloro-1,4-naphthoquinone Dibenzenesulfonimide.—A solution of 0.50 g. of 2-chloronaphthylene-1,4-dibenzenesulfonamide in 3 ml. of glacial acetic acid was oxidized with one molecular equivalent of lead tetraacetate by heating with stirring until everything was in solution. After thorough cooling the product separated. It was purified by recrystallization from glacial acetic acid, giving yellow needles, m. p. 171–173° (cor.). The yield was 0.37 g. (75%).

Anal. Calcd. for $C_{22}H_{15}ClN_2O_4S_2$: C, 56.10; H, 3.21; N, 5.95. Found: C, 56.18; H, 3.42; N, 5.90.

2,3-Dichloronaphthylene-1,4-dibenzenesulfonamide.—Into a suspension of 0.30 g. of 2-chloro-1,4-naphthoquinone dibenzenesulfonimide in 5 ml. of glacial acetic acid, dry hydrogen chloride was introduced. An immediate decolorization occurred and a heavy white precipitate separated. About 50 ml. of water was added, the product collected by filtration and recrystallized from glacial acetic acid, giving white needles, m. p. 276–277° (cor.). The yield was 0.29 g. (90%).

Anal. Calcd. for $C_{22}H_{16}ClN_2O_4S_2$: C, 52.07; H, 3.18. Found: C, 52.30; H, 3.44.

2,3-Dichloro-1,4-naphthoquinone Dibenzenesulfonimide.—A mixture of 0.50 g. of 2,3-dichloronaphthalene-1,4-dibenzenesulfonamide and 0.50 g. of lead tetraacetate in 5 ml. of glacial acetic acid was stirred vigorously at 90° for one hour. The product separated on cooling. It was purified by recrystallization from glacial acetic acid; light yellow needles, m. p. 205–206° (cor.). The yield was 0.39 g. (77%).

Anal. Calcd. for $C_{22}H_{14}Cl_2N_2O_4S_2$: C, 52.28; H, 2.79; N, 5.54. Found: C, 52.36; H, 2.95; N, 5.62.

2-Anilinonaphthalene-1,4-dibenzenesulfonamide.—A suspension of 0.5 g. of 1,4-naphthoquinone dibenzenesulfonimide in 15 ml. of glacial acetic acid was treated with 2.0 g. of aniline. An immediate red color developed and considerable heat was evolved. After standing at room temperature for 24 hours the reddish precipitate was removed by filtration. Recrystallization from dimethylformamide and ether gave a white solid, m. p. 247–248° (cor.). The yield was 0.55 g. (91%).

Anal. Calcd. for $C_{28}H_{23}N_3O_4S_2$: C, 63.49; H, 4.38; N, 7.94. Found: C, 63.38; H, 4.36; N, 8.09.

2-Morpholinonaphthalene-1,4-dibenzenesulfonamide.—A suspension of 0.5 g. of 1,4-naphthoquinone dibenzenesulfonimide in 3 ml. of glacial acetic acid was treated with 0.5 g. of morpholine. The mixture developed a red color and became warm spontaneously. After warming on a steam-bath for several minutes the mixture was allowed to stand at room temperature for 12 hours. The product that

separated was purified by recrystallization from acetone and petroleum ether (b. p. 30–40°); white crystals, m. p. 201–202° (cor.). The yield was 0.41 g. (70%).

Anal. Calcd. for $C_{26}H_{25}N_3O_5S_2$: C, 59.63; H, 4.81; N, 8.04. Found: C, 59.73; H, 5.05; N, 7.89.

2-Morpholino-1,4-naphthoquinone Dibenzenesulfonimide.—A solution of 1.0 g. of 2-morpholinonaphthalene-1,4-dibenzenesulfonamide in 20 ml. of benzene was treated with 0.84 g. of lead tetraacetate. An immediate red coloration developed and the mixture was warmed on a hot-plate for 5 minutes. After filtration, 100 ml. of petroleum ether was added to the filtrate and a flocculent red precipitate separated. It was purified by recrystallization from ether and petroleum ether (b. p. 30–40°); red needles, m. p. 109–110° (cor.). The yield was 0.71 g. (72%).

Anal. Calcd. for $C_{26}H_{23}N_3O_5S_2$: C, 59.87; H, 4.44; N, 8.06. Found: C, 59.59; H, 4.66; N, 7.83.

Attempted addition to this product of hydrogen chloride by a solution in glacial acetic acid gave only a tar from which no solid could be isolated.

2-Phenylmercaptonaphthalene-1,4-dibenzenesulfonamide.—A suspension of 0.5 g. of 1,4-naphthoquinone dibenzenesulfonimide in 10 ml. of glacial acetic acid was treated with 0.2 g. of thiophenol. After stirring vigorously for 30 minutes at room temperature, the yellow color had entirely disappeared and a heavy white precipitate separated. The product was purified by recrystallization from glacial acetic acid; white needles, m. p. 205–206° (cor.).

Anal. Calcd. for $C_{28}H_{22}N_2O_4S_2$: C, 61.51; H, 4.06; N, 5.13. Found: C, 61.27; H, 4.20; N, 4.88.

When this reaction was carried out at about 80° approximately 60% of the product was naphthalene-1,4-dibenzenesulfonamide.

2-Phenylmercapto-1,4-naphthoquinone Dibenzenesulfonimide.—A mixture of 0.25 g. of 2-phenylmercaptonaphthalene-1,4-dibenzenesulfonamide, 2 ml. of glacial acetic acid and 0.25 g. of lead tetraacetate was heated to 40° with vigorous stirring. After further stirring at room temperature for 30 minutes a heavy red precipitate had separated. It was purified by recrystallization from glacial acetic acid; red plates, m. p. 193–194° (cor.). The yield was 0.13 g. (53%).

Anal. Calcd. for $C_{28}H_{20}N_2O_4S_3$: C, 61.74; H, 3.70; N, 5.15. Found: C, 61.93; H, 3.84; N, 5.04.

Two attempts to add thiophenol to this naphthoquinone diimide, one in acetic acid and one in chloroform, gave only the reduced product, 2-phenylmercaptonaphthalene-1,4-dibenzenesulfonamide.

2-Phenylmercapto-3-chloronaphthalene-1,4-dibenzenesulfonamide.—Into a mixture of 0.2 g. of 2-phenylmercapto-1,4-naphthoquinone dibenzenesulfonimide and 5 ml. of glacial acetic acid, dry hydrogen chloride was bubbled slowly. A slow decolorization took place and a flocculent white precipitate formed. The product was purified by recrystallization from glacial acetic acid; white needles, m. p. 235° (cor.). The yield was 0.17 g. (78%).

Anal. Calcd. for $C_{28}H_{21}ClN_2O_4S_3$: C, 57.87; H, 3.64; N, 4.82. Found: C, 57.93; H, 3.98; N, 4.91.

In an attempt to prepare this compound by adding thiophenol to 2-chloro-1,4-naphthoquinone dibenzenesulfonimide in glacial acetic acid at room temperature, a quantitative yield of the reduced product, 2-chloronaphthalene-1,4-dibenzenesulfonamide, resulted.

2-Methyl-1,4-naphthoquinone Dibenzenesulfonimide.—Oxidation of 0.5 g. of 2-methylnaphthalene-1,4-dibenzenesulfonamide[4] with 0.5 g. of lead tetraacetate in glacial acetic acid was effected in a manner identical to that given for the preparation of 2-chloro-1,4-naphthoquinonedibenzenesulfonimide. The product formed yellow needles from glacial acetic acid; m. p. 139° (cor.). The yield was 0.36 g. (73%).

Anal. Calcd. for $C_{23}H_{18}N_2O_4S_2$: C, 61.32; H, 4.03; N, 6.22. Found: C, 61.26; H, 4.25; N, 6.01.

2-Methyl-3-chloronaphthalene-1,4-dibenzenesulfonamide.—Into a solution of 0.4 g. of 2-methyl-1,4-naphthoquinone dibenzenesulfonimide in 5 ml. of acetic acid, dry hydrogen chloride was passed. Immediate decolorization occurred and a heavy white precipitate was formed. It was purified by recrystallization from glacial acetic acid; white needles, m. p. 249–250° (cor.). The yield was 0.39 g. (89%).

Anal. Calcd. for $C_{23}H_{19}ClN_2O_4S_2$: C, 56.72; H, 3.93; N, 5.75. Found: C, 56.77; H, 3.96; N, 5.64.

2-Methyl-3-chloro-1,4-naphthoquinone Dibenzenesulfonimide.—A mixture of 0.5 g. of 2-methyl-3-chloronaphthalene-1,4-dibenzenesulfonamide, 2 ml. of glacial acetic acid and 0.5 g. of lead tetraacetate was stirred for 2 hours at 100°. After cooling, yellow crystals deposited. They were washed twice with 3-ml. portions of acetic acid and recrystallized from glacial acetic acid; yellow needles, m. p. 171–172° (cor.). The yield was 0.37 g. (73%).

Anal. Calcd. for $C_{23}H_{17}ClN_2O_4S_2$: C, 59.96; H, 3.53; N, 5.78. Found: C, 56.94; H, 3.74; N, 5.63.

4-Benzenesulfonamido-2-chloro-1-naphthol.—(A) A suspension of 1.0 g. of 1,4-naphthoquinone dibenzenesulfonimide in 10 ml. of glacial acetic acid was warmed with stirring with 1.0 ml. of concentrated hydrochloric acid until a colorless solution resulted (one hour). Addition of 25 ml. of water gave a crude brown product which after two recrystallizations from 88% formic acid melted at 187–188° (cor.). The yield was 0.57 g. (74%). A melting point of a mixture of this compound with those described below showed no depression.

Anal. Calcd. for $C_{16}H_{12}ClNO_3S$: C, 57.57; H, 3.63; N, 4.19. Found: C, 57.66; H, 3.90; N, 4.14.

The synthesis of this compound by two unequivocal methods (B) and (C) are given below.

4-Benzenesulfonamido-1-naphthol.—A solution of 10 g. of recrystallized 4-amino-1-naphthol hydrochloride in 25 ml. of pyridine was treated with 9.1 g. of benzenesulfonyl chloride with vigorous stirring. Considerable heat was evolved and coloration occurred. After standing one hour, the mixture was poured into 50 ml. of dilute hydrochloric acid, stirred well and filtered. The crude product was recrystallized from boiling acetic acid; white crystals, m. p. 193–194° (cor.). The yield was 9.7 g. (64%).

Anal. Calcd. for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.32; H, 4.40; N, 4.59.

1,4-Naphthoquinone Monobenzenesulfonimide.—A suspension of 0.6 g. of 4-benzenesulfonamido-1-naphthol in 3 ml. of acetic acid was treated with 0.9 g. of lead tetraacetate. Upon stirring vigorously and warming, a complete solution resulted. After thorough cooling the product separated and was recrystallized from hot glacial acetic acid; yellow needles, m. p. 148–149° (cor.). The yield was 0.3 g. (51%).

Anal. Calcd. for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71. Found: C, 64.69; H, 3.88; N, 4.80.

4-Benzenesulfonamido-2-chloro-1-naphthol.—(B) Dry hydrogen chloride was passed into a solution of 1,4-naphthoquinonemonobenzenesulfonimide in glacial acetic acid. After saturation, complete decolorization took place and the product was precipitated by the addition of water. Recrystallization from 88% formic acid gave the desired product, m. p. 187–188° (cor.), in 71% yield. The infrared spectrum of this product and that of the substance obtained by the action of hydrochloric acid in acetic acid on 1,4-naphthoquinone dibenzenesulfonamide were identical.

4-Nitro-2-chloro-1-naphthol.—A stream of chlorine gas was slowly introduced into a solution of 3 g. of 4-nitro-1-naphthol[5] in 15 ml. of acetic acid over a period of 2 hours. Upon addition of 50 ml. of water and thorough stirring a yellow flocculent precipitate formed. It was recrystallized twice from 80% ethanol-water; white crystals, m. p. 179–180° (cor.). The yield was 1.75 g. (50%).

Anal. Calcd. for $C_{10}H_6ClNO_3$: C, 53.71; H, 2.71. Found: C, 53.53; H, 2.45.

Three attempts to prepare this compound according to the method of Hodgson and Elliot[2] from 4-nitro-1-acetonaphthalide failed. Upon chlorination of 4-nitro-1-acetonaphthalide a product melting at 231° as described by them was isolated, but its analysis was not correct for 4-nitro-2-chloro-1-acetonaphthalide. When the chlorinated product in our hands, m. p. 231°, was hydrolyzed a substance m. p. 93–106° resulted. No material melting at the same point, 231°, as reported by Hodgson and Elliot could be obtained. Since the authentic 4-nitro-2-chloro-1-naphthol

(4) Adams and Mattson, unpublished work.

(5) Andreoni and Biederman, *Ber.*, **6**, 342 (1873).

melts at 179–180°, it is obvious that these authors did not have the product reported.

4-Benzenesulfonamido-2-chloro-1-naphthol.—(C) A solution of 1.5 g. of 4-nitro-2-chloro-1-naphthol in 15 ml. of methanol was treated with 0.1 g. of platinum oxide and shaken with hydrogen at 40 p.s.i. for 2 hours. After filtration, 50 ml. of dry ether was added and the solution was saturated with dry hydrogen chloride. A gray hydrochloride salt separated. This was dissolved in 5 ml. of methanol and precipitated by the slow addition of 50 ml. of dry ether. Treatment of the white hydrochloride in 10 ml. of pyridine with 0.9 g. of benzenesulfonyl chloride caused evolution of considerable heat and a dark coloration developed. The solution was poured into 50 ml. of dilute hydrochloric acid, stirred well and filtered. The dark brown precipitate was recrystallized twice from 88% formic acid (Darco), then three times from 88% formic acid alone, to yield a white product, m. p. 187–188° (cor.). The yield was 0.2 g. (9%).

3-Chloro-1,4-naphthoquinone 1- Benzenesulfonimide.—4-Benzenesulfonamido-2-chloro-1-naphthol was oxidized by gently warming and stirring in a minimum amount of glacial acetic acid with one molecular equivalent of lead tetraacetate. After thorough cooling, the yellow product was collected on a filter and recrystallized from glacial acetic acid; yellow needles, m. p. 180–181° (cor.). The yields varied from 45 to 75%.

Anal. Calcd. for $C_{16}H_{10}ClNO_3S$: C, 57.92; H, 3.04; N, 4.22. Found: C, 57.86; H, 3.11; N, 4.48.

Reaction of 1,4-Naphthoquinone Dibenzenesulfonimide with Sodium Hydroxide.—A suspension of 0.5 g. of 1,4-naphthoquinone dibenzenesulfonimide in 10 ml. of 5% sodium hydroxide was heated with vigorous stirring for one hour. Most of the naphthoquinone diimide went into solution, giving a dark coloration. After neutralization with acetic acid, the brown precipitate was collected on a filter. Recrystallization from glacial acetic acid gave 0.37 g. of naphthylene-1,4-dibenzenesulfonamide, m. p. 250–251° (cor.).

Summary

1. The dibenzenesulfonimido, dimethanesulfonimido and di-*p*-toluenesulfonimido derivatives of 1,4-naphthoquinone have been prepared from the corresponding diamides by oxidation with lead tetraacetate.

2. These compounds add in glacial acetic acid as solvent hydrogen chloride, aniline, morpholine and thiophenol with formation in excellent yield of the corresponding 2-substituted naphthalene-1,4-disulfonamides. These adducts, with the exception of the anilino compound, were oxidized to the substituted 1,4-naphthoquinone diimides. The 1,4-naphthoquinone disulfonimides are stable under ordinary conditions.

3. The 2-chloro-1,4-naphthoquinone dibenzenesulfonimide adds hydrogen chloride to give 2,3-dichloronaphthalene - 1,4 - dibenzenesulfonamide. Thiophenol, however, does not add but is merely oxidized with resulting reduction of the quinone diimide. 2-Phenylmercapto-1,4-naphthoquinone dibenzenesulfonimide similarly adds hydrogen chloride and is reduced by thiophenol.

4. 1,4-Naphthoquinone dibenzenesulfonimide is reduced to the corresponding dibenzenesulfonamide by means of platinum and hydrogen. It is also reduced slowly to the diamide by boiling with dilute aqueous sodium hydroxide. Upon boiling with concentrated hydrochloric acid in glacial acetic acid, partial hydrolysis occurs, followed by addition of hydrogen chloride. The structure of the resulting product, 4-benzenesulfonamido-2-chloro-1-naphthol, was proved through synthesis by an unequivocal method.

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The Identity of α-Longilobine and Seneciphylline

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The difficulty of purification of many *Senecio* alkaloids has frequently been encountered by investigators in this field, and the presence usually of more than one closely related alkaloid in a single plant has been established. Minute quantities of impurities of related substances modify markedly the optical rotation and melting points of the products. The identification and separation of four alkaloids from *Senecio longilobus* and two or more of the same alkaloids from several other *Senecio* species have been achieved.[1] These results are indicative that certain *Senecio* alkaloids already described may be mixtures of one or more of these same four but have not been immediately recognized from the reported constants. Warren, *et al.*,[2] have established the identity of retrorsine with β-longilobine.

A comparison has now been made of seneciphylline and α-longilobine. Seneciphylline was first isolated by Orekhov and Tiedebel, from *Senecio platyphyllus*,[3] and later from *Senecio stenocephalus*.[4] Manske has shown this alkaloid to be the principal base occurring in *Senecio spartioides*.[5] Quite recently a structural study of seneciphylline[6] has shown that the hydrolysis products of this alkaloid, $C_{18}H_{23}O_5N$, are retronecine, the structure of which is well established,[7] and a dibasic acid of molecular formula $C_{10}H_{14}O_5$. The melting point of the acid depends upon the mode of hydrolysis; aqueous alkali results in isoseneciphyllic acid, m. p. 105–108°, whereas ethanolic potassium hydroxide gives seneciphyllic acid, m. p. 144–145°. The possibility of *cis–trans* isomerism has been postulated to account for the isomeric acids, and the conversion of isoseneciphyllic acid to seneciphyllic acid under the influence of hydrochloric acid supports this theory. Seneciphylline is thus an ester, in which in all probability the two hydroxyl groups of retronecine are esterified by the two carboxyl groups of isoseneciphyllic acid. Recent work by Warren and co-workers indicates that the action of aqueous potassium hydroxide parallels that of barium hydroxide in the hy-

(1) Adams and Govindachari, THIS JOURNAL, **71**, 1956 (1949).

(2) Warren, Kropman, Adams, Govindachari and Looker, *ibid.*, **72**, 1421 (1950).

(3) Orekhov and Tiedebel, *Ber.*, **68**, 650 (1935).

(4) Konovalova and Orekhov, *Bull. soc. chim.*, [5] **4**, 2037 (1937).

(5) Manske, *Can. J. Research*, **B17**, 1 (1939).

(6) Konovalova and Danilova, *Zhur. Obshchei Khim.*, **18**, 1198 (1948).

(7) Adams and Leonard, THIS JOURNAL, **66**, 257 (1944).