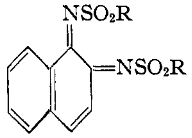
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Quinone Imides. VII. 1,2- and 2,6-Naphthoquinone Disulfonimides

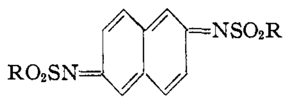
By Roger Adams and R. A. Wankel

It has been demonstrated that the 1,2- and 2,6-naphthylenedibenzenesulfonamides can be oxidized to the corresponding naphthoquinone dibenzenesulfonimides. Lead tetraacetate in benzene is the most satisfactory oxidizing agent for the former and purified lead dioxide in benzene for the latter. Both quinone diimides are readily reduced to the corresponding diamides and add various reagents such as hydrogen chloride, morpholine and thiophenol in a manner similar to other quinone diimides previously described.

The quinone imides previously described have been limited to the sulfonyl derivatives of various *p*-phenylenediamines,[1a] 1,4-naphthylenediamines[1c] and *p*-aminophenols[1d] as well as to certain acyl and aroyl derivatives of *p*-phenylenediamines.[1b] The study has now been extended to the benzenesulfonyl derivatives of 1,2- and 2,6-naphthylenediamines.



I



II

The 1,2-diimide (I) was formed preferably by the oxidation of the appropriate disulfonamide by means of lead tetraacetate in hot benzene, although lead tetraacetate in acetic acid or freshly prepared lead dioxide in hot benzene, achieved the same result but in lower yields. 1,2-Naphthoquinone dibenzenesulfonimide is an orange crystalline compound, stable under ordinary conditions. It exhibits the same reactions as the 1,4-isomer. It is reduced to the diamide by means of hydrogen and a platinum catalyst. Upon addition of hydrogen chloride in chloroform solution, 4-chloronaphthylene-1,2-dibenzenesulfonamide is formed, the structure of which was established by an independent synthesis from 4-chloro-2-nitro-1-naphthylamine through reduction to the diamine and benzenesulfonation. Morpholine also adds, presumably with formation of the 4-morpholinonaphthylene-1,2-dibenzenesulfonamide. Thiophenol, on the other hand, did not add to the 1,2-naphthoquinone dibenzenesulfonimide but was oxidized with simultaneous reduction of the quinone diimide to the naphthylenediamide. Oxidation of the 4-chloronaphthylene-1,2-dibenzenesulfonamide to the 4-chloro-1,2-naphthoquinone dibenzenesulfonimide took place readily but the latter compound failed to add hydrogen chloride and is apparently resistant to addition reactions under the conditions employed.

Naphthylene-2,6-dibenzenesulfonamide was oxidized by lead tetraacetate in benzene but the crystalline quinone diimide (II) decomposed rapidly on standing. Apparently this accelerated decomposition must be ascribed to the acetic acid or lead diacetate in the reaction mixture, for a stable deep orange crystalline product resulted when the oxidation was effected by means of freshly prepared lead dioxide in boiling benzene, a superb reagent recently described by Kuhn and Hammer.[2]

2,6-Naphthoquinone dibenzenesulfonimide is readily reduced to the corresponding naphthylenediamide. It adds hydrogen chloride, morpholine and thiophenol to give the chloro, morpholino and phenylmercapto derivatives, respectively, of naphthylene-2,6-dibenzenesulfonamide. The position of the groups was not established since no appropriate reference compounds were available.

An attempted oxidation of 1-benzenesulfonamido-2-naphthol to the corresponding monoimide failed.

Ultraviolet absorption spectra data on the 1,2-, the 1,4- and the 2,6-naphthoquinone dibenzenesulfonimides are shown in Table I. It is significant that all three have strong maxima at 219 mμ and at about 240 mμ.

Table I

Ultraviolet Absorption Spectra of Naphthoquinone Diimides

Naphthoquinone dibenzenesulfonimide	λ in mμ	$\epsilon \times 10^{-3}$ max.
1,2-	219	33.3
	240	27.0
	350	10.6
1,4-	219	33.9
	233	36.4
	273	6.3
	304	11.8
2,6-	219	27.8
	243	26.3

Experimental

2-Benzenesulfonamido-1-naphthylamine Hydrochloride.—The reduction of 15 g. of benzenesulfonyl-2-amino-1-nitronaphthalene[3] was carried out in 40 ml. of absolute ethanol with 0.3 g. of platinum oxide under hydrogen at 40 p.s.i. The reaction was complete after shaking for three hours. Filtration, followed by addition of 150 ml. of dry ether and saturation with dry hydrogen chloride, gave a brown precipitate which was collected on a filter. Recrystallization from methanol (Darco) and dry ether gave colorless crystals, m.p. 185–186° (cor.). The yield was 10.7 g. (71%).

Anal. Calcd. for $C_{16}H_{15}ClN_3O_2S$: C, 57.39; H, 4.52. Found: C, 57.38; H, 4.76.

Naphthylene-1,2-dibenzenesulfonamide.—Treatment of 8.0 g. of 2-benzenesulfonamido-1-naphthylamine hydrochloride with 20 ml. of pyridine and 3.1 g. of benzenesulfonyl chloride at refluxing temperature for one hour gave a brown precipitate when poured into 100 ml. of dilute hydrochloric acid. Filtration followed by recrystallization from 88% formic acid (Darco) gave colorless crystals, m.p. 160–161° (cor.). The yield was 7.3 g. (70%).

Anal. Calcd. for $C_{22}H_{18}N_2O_4S_2$: C, 60.25; H, 4.14; N, 6.39. Found: C, 60.38; H, 4.29; N, 6.21.

---

(1) (a) R. Adams and A. S. Nagarkatti, This Journal, **72**, 4601 (1950); (b) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); (c) R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); (d) R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951); (e) R. Adams and K. R. Eilar, *ibid.*, **73**, 1149 (1951); (f) R. Adams and C. R. Walter, *ibid.*, **73**, 1152 (1951).

(2) R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950); **84**, 91 (1951).

(3) G. T. Morgan and W. Godden, *J. Chem. Soc.*, **97**, 1714 (1910).

1,2-Naphthoquinone Dibenzenesulfonimide.—A suspension of 1.0 g. of naphthylene-1,2-dibenzenesulfonamide in 25 ml. of benzene was stirred for 2 hours at refluxing temperature with 1.0 g. of dry lead tetraacetate. After thorough cooling followed by filtration, the product was precipitated from the benzene filtrate by the addition of 125 ml. of petroleum ether (b.p. 35–40°). Recrystallization from benzene and cyclohexane or from glacial acetic acid gave orange needles, m.p. 171–172° (cor.). The yield was 0.71 g. (70%).

Anal. Calcd. for $C_{22}H_{16}N_2O_4S_2$: C, 60.53; H, 3.70. Found: C, 60.62; H, 3.58.

This diimide was also prepared by using lead tetraacetate in acetic acid and freshly prepared lead dioxide in refluxing benzene. The yields in both cases were lower.

A solution of 1,2-naphthoquinone dibenzenesulfonimide in methanol was reduced to naphthylene-1,2-dibenzenesulfonamide using platinum oxide catalyst and hydrogen at 40 p.s.i.

Two attempts to add thiophenol to 1,2-naphthoquinone dibenzenesulfonimide in glacial acetic acid and in chloroform gave only the reduced product, naphthylene-1,2-dibenzenesulfonamide.

4-Chloronaphthylene-1,2-dibenzenesulfonamide.—(A) A solution of 0.4 g. of 1,2-naphthoquinone dibenzenesulfonimide in 10 ml. of acetic acid was treated with dry hydrogen chloride. Decolorization took place immediately and after standing for one hour, the product was precipitated with water. Recrystallization from 88% formic acid gave white crystals, m.p. 225° (cor.). The yield was 0.4 g. (85%).

Anal. Calcd. for $C_{22}H_{17}ClN_2O_4S_2$: C, 55.87; H, 3.62; N, 5.92. Found: C, 56.06; H, 3.78; N, 5.79.

(B) A solution of 1.0 g. of 4-chloro-2-nitro-1-naphthylamine[4] in 10 ml. of glacial acetic acid was reduced catalytically with platinum oxide and hydrogen at 40 p.s.i. Filtration followed by addition of 50 ml. of dry ether and saturation with dry hydrogen chloride gave a brown precipitate which was collected on a filter. Recrystallization from methanol and ether gave 0.9 g. of the diamine hydrochloride. This salt was dissolved in 8 ml. of pyridine and treated with 1.2 g. of benzenesulfonyl chloride. After standing 12 hours, the brown solution was stirred into 50 ml. of dilute hydrochloric acid. After thorough cooling, the product was collected on a filter. After three recrystallizations from 88% formic acid, the white product melted at 225°. The melting point was not depressed when mixed with 20% of the compound prepared by method (A). The infrared spectra of the two products were identical.

4-Chloro-1,2-naphthoquinone Dibenzenesulfonimide.—A suspension of 0.5 g. of 4-chloronaphthylene-1,2-dibenzenesulfonimide and 0.5 g. of lead tetraacetate in 3 ml. of glacial acetic acid was stirred at 50° for 45 minutes. After thorough cooling, the product was collected on a filter and recrystallized from glacial acetic acid; orange needles, m.p. 193–194° (cor.). The yield was 0.27 g. (55%).

Anal. Calcd. for $C_{22}H_{15}ClN_2O_4S_2$: C, 56.10; H, 3.12; N, 5.95. Found: C, 55.86; H, 3.38; N, 5.78.

This compound did not add hydrogen chloride either in glacial acetic acid or chloroform as solvents.

4-Morpholinonaphthylene-1,2-dibenzenesulfonamide.—A solution of 0.5 g. of 1,2-naphthoquinone dibenzenesulfonimide in 5 ml. of glacial acetic acid was treated with 0.5 ml. of morpholine. After standing overnight, the crude product was precipitated by the addition of 10 ml. of water. After collecting on a filter the brown precipitate was dissolved in 10 ml. of 10% aqueous sodium hydroxide (Darco). Filtration, followed by acidification with acetic acid, gave a light gray product. Recrystallization from 60% ethanol–water gave white crystals, m.p. 74–75° (cor.). The yield was 0.47 g. (82%).

Anal. Calcd. for $C_{26}H_{25}N_3O_5S_2$: C, 59.63; H, 4.81; N, 8.02. Found: C, 59.53; H, 4.62; N, 7.92.

1-Benzenesulfonamido-2-naphthol.—A mixture of 10.0 g. of 1-amino-2-naphthol hydrochloride dissolved in 25 ml. of pyridine was treated with 9.1 g. of benzenesulfonyl chloride. Considerable heat was evolved and a dark brown coloration occurred. After standing at room temperature for 12 hours, the mixture was added to 100 ml. of dilute hydrochloric acid, stirred well, cooled and the crude product collected on a filter. Recrystallization from hot benzene (Darco) gave white needles, m.p. 168–169° (cor.). The yield was 11.0 g. (72%).

Anal. Calcd. for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38. Found: C, 64.24; H, 4.50.

This compound gives no precipitate with dry hydrogen chloride in ether, hence benzenesulfonyl chloride must have reacted with the amino group and not the hydroxyl group. Two attempts to oxidize 1-benzenesulfonamido-2-naphthol to the 1,2-naphthoquinone-1-monobenzenesulfonimide in boiling acetic acid with lead tetraacetate failed entirely; only the original amide was recovered unchanged.

Naphthylene-2,6-dibenzenesulfonamide.—A solution of 1.0 g. of 2,6-naphthylenediamine in 15 ml. of pyridine was treated with 2.3 g. of benzenesulfonyl chloride. Considerable heat was evolved and a dark purple coloration occurred. After standing at room temperature overnight, the solution was poured into 100 ml. of dilute hydrochloric acid, cooled in an ice-bath, and the purple product collected on a filter. Recrystallization from 95% ethanol (Darco) gave colorless crystals, m.p. 245–246° (cor.). The yield was 2.5 g. (90%).

Anal. Calcd. for $C_{22}H_{18}N_2O_4S_2$: C, 60.25; H, 4.14; N, 6.39. Found: C, 60.29; H, 4.25; N, 6.56.

2,6-Naphthoquinone Dibenzenesulfonimide.—A mixture of 0.50 g. of naphthylene-2,6-dibenzenesulfonamide and 2.0 g. of freshly prepared lead dioxide[2] was added to 25 ml. of boiling benzene. After stirring at refluxing temperature for 20 minutes, the solution was quickly cooled and filtered. Treatment of the filtrate with 100 ml. of petroleum ether (b.p. 35–40°) gave an orange-brown precipitate. Recrystallization from benzene and cyclohexane gave dark orange needles, m.p. 166–167° (cor.). The yield was 0.36 g. (73%).

Anal. Calcd. for $C_{22}H_{16}N_2O_4S_2$: C, 60.53; H, 3.70; N, 6.42. Found: C, 60.77; H, 3.85; N, 6.53.

Catalytic reduction of 2,6-naphthoquinone dibenzenesulfonimide in methanol, using platinum oxide and hydrogen at 40 p.s.i., gave naphthylene-2,6-dibenzenesulfonamide in 70% yield. Attempted addition of thiophenol in benzene as the solvent gave only a semi-solid from which no crystalline material could be isolated.

4(?)-Chloronaphthylene-2,6-dibenzenesulfonamide.—A solution of 0.3 g. of 2,6-naphthoquinone dibenzenesulfonimide in 25 ml. of benzene was treated with excess dry hydrogen chloride. Decolorization occurred in five minutes. After standing one hour, 100 ml. of petroleum ether (b.p. 35–40°) was added with stirring. Filtration, followed by recrystallization from 95% ethanol (Darco), gave a white product, m.p. 193–194° (cor.). The yield was 0.22 g. (67%).

Anal. Calcd. for $C_{22}H_{17}ClN_2O_4S_2$: C, 55.87; H, 3.62. Found: C, 55.68; H, 3.85.

4(?)-Morpholinonaphthylene-2,6-dibenzenesulfonamide.—A solution of 2,6-naphthoquinone dibenzenesulfonimide in 15 ml. of benzene was treated with 0.30 g. of morpholine. Decolorization occurred in two minutes. After standing 24 hours, the benzene was removed under reduced pressure and the residue dissolved in 10 ml. of acetic acid. After treatment with charcoal, the gray product was precipitated by the addition of 20 ml. of water. Recrystallization from 70% ethanol–water gave white crystals, m.p. 182–183° (cor.). The yield was 0.25 g. (69%).

Anal. Calcd. for $C_{26}H_{25}N_3O_5S_2$: C, 59.63; H, 4.81; N, 8.04. Found: C, 59.64; H, 5.04; N, 7.92.

URBANA, ILLINOIS

RECEIVED OCTOBER 27, 1950

---

(4) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 321 (1943).