atmospheres in presence of one gram of palladium–strontium carbonate catalyst (6%). After 3 hours one mole of hydrogen was absorbed. The catalyst was filtered off, washed with warm ethanol and the filtrate taken to dryness under reduced pressure. The residue was crystallized from 95% ethanol. The product, 1.0 g. (33%), was recrystallized from the same solvent; prisms, m.p. 197°. The mother liquors from the crystallization of the crude product left on evaporation an oil which resisted crystallization.

*Anal.* Calcd. for $C_{18}H_{25}O_6N$: C, 61.53; H, 7.12; N, 3.99. Found: C, 61.97; H, 6.85; N, 3.95.

**Rotation.**—9.0 mg. made up to 1.60 ml. with water at 28° gave $\alpha_D$ +0.125°; $l$ 1, $[\alpha]^{28}_D$ +22.3° (±1.0°).

**Lead Tetraacetate Oxidation of Dihydroriddelliine; Determination of Carbon Dioxide.**—A solution of 0.40 g. of dihydroriddelliine in 10 ml. of water saturated with sodium chloride was treated with 1.0 g. of lead tetraacetate. After a short induction period carbon dioxide was steadily evolved and collected in a gas buret as described above. After 30 minutes no more gas was evolved. The reaction vessel was heated for 5 minutes at 60° and allowed to cool to room temperature.

Calcd. for one mole of $CO_2$ from $C_{18}H_{22}O_6N$: 25.6 ml. at S.T.P. Found: 19.00 ml. at S.T.P.

URBANA, ILLINOIS

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

# Quinone Imides. XXX. Addition of Primary and Secondary Aromatic Amines

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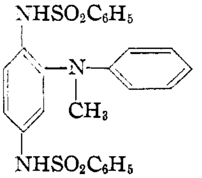
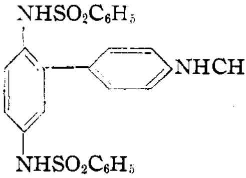
Methylaniline, dimethylaniline and diethylaniline add to *p*-quinonedibenzenesulfonimide and its 2-methyl derivatives differently from aniline, ring substituted anilines or aliphatic and alicyclic amines. They add 1,4 by the proton in the *p*-position to the amino groups reacting with one of the benzenesulfonimide nitrogens and the aminophenyl residue entering the quinone imide ring, thus resulting in biphenyl derivatives. The methylaniline adduct was converted to the dimethylaniline adduct by methylation. Aromatic primary and secondary amines add to 1,4-naphthoquinonedibenzenesulfonimide, however, by separation of the proton from the nitrogen atom; dimethylaniline merely causes reduction to the diamide.

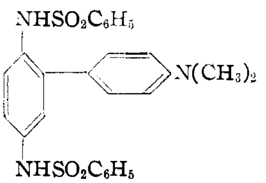
In the study of the reactions of amines with *p*-quinonedibenzenesulfonimide,[1] it was noted that monomethylaniline reacted differently from the other secondary amines and aniline. No succession of reactions occurred and the product in good yield was an adduct of the amine to the quinone diimide in mole to mole ratio. The structure assigned to it is shown in I and was originally accepted on the basis of analogy to the initial product obtained by the addition of morpholine to the diimide.[1]



I



II



III

Aniline and dimethylaniline add to tetrachloro-*p*-quinonedibenzenesulfonimide[2] in an unexpected fashion. A 1,6-addition to the two imide nitrogens occurs with the proton from the position para to the amino or dimethylamino group attacking one imide nitrogen and the aminophenyl residue the other. The difference in properties of the methylaniline from the other amine adducts with the unsubstituted quinone diimide and the character of the products of the aromatic amines with the tetrachloro diimide suggested a restudy of the methylaniline and *p*-quinonedibenzenesulfonimide adduct to determine whether it might not have structure II.

The methylaniline adduct (I or II) was methylated with excess methyl iodide in dimethylformamide as solvent. One methyl group was introduced. The infrared absorption spectrum of the methylated product showed marked similarities to that of the product from which it was formed. The methylaniline adduct has two N–H bands, one of medium intensity at 3178 cm.$^{-1}$ and one weak at 3386 cm.$^{-1}$; the methylated product has a single band of medium intensity at 3184 cm.$^{-1}$.

The addition of dimethylaniline to *p*-quinonedibenzenesulfonimide was next attempted. The reaction proceeded smoothly and the resulting product (III) was found to be identical with the methylated methylaniline adduct by infrared spectra and by a melting point of the mixture of the two. This not only established the constitution of the dimethylaniline adduct, but also confirmed the structure of the monomethylaniline derivative as II. Diethylaniline was found to add in similar fashion.

Dimethylaniline was added successfully to 2-methyl-1,4-benzoquinonedibenzenesulfonimide with the formation of a product in 75% yield which was formulated as IV, with the dimethylaniline group in the 5-position by analogy to the addition of other molecules to 2-methyl-*p*-quinonedibenzenesulfonimide.

The addition of aniline and morpholine in glacial acetic acid to 1,4-naphthoquinonedibenzenesulfonimide has been previously described.[3] The complicated reactions occurring in the corresponding benzene series[1] were not encountered, and the addition of one mole of amine to one mole of diimide resulted. The aniline derivative was assigned the structure V. When monomethyl-

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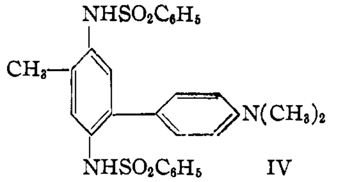
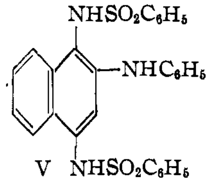
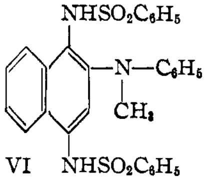
(1) R. Adams and K. A. Schowalter, THIS JOURNAL, **74**, 2597 (1952).

(2) R. Adams and B. H. Braun, *ibid.*, **74**, 5869 (1952).

(3) R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951).


IV


V

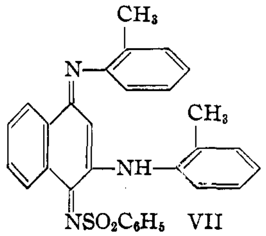

VI

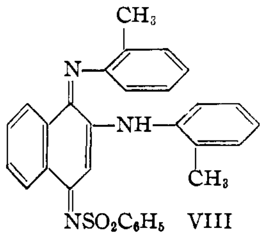
aniline was substituted for aniline, the chief product in 81% yield was a 1:1 adduct, assigned formula VI. Support for this structure was afforded by the infrared spectrum which showed a single broad N–H band at 3240–3280 cm.$^{-1}$ but no absorption in the 800–850 cm.$^{-1}$ region where *p*-disubstituted benzene derivatives strongly absorb. If the proton had come from the position para to the methylamino group to form 2-(*p*-aminophenyl-1,4-naphthalenedibenzenesulfonamide, a band would be expected in the 800–850 cm.$^{-1}$ region. The infrared spectrum of the aniline adduct was very similar to that of the monomethylaniline adduct, except that two N–H bands at 3310 and 3220 cm.$^{-1}$ were present in the former.

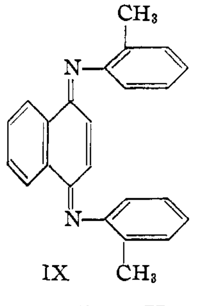
*p*-Toluidine also added to 1,4-naphthalenedibenzenesulfonimide in a manner similar to aniline (type V). Its infrared absorption spectrum showed two N–H bands (3220 and 3340 cm.$^{-1}$) and a band of medium intensity at 815 cm.$^{-1}$, in the region where *p*-disubstituted benzene derivatives absorb.

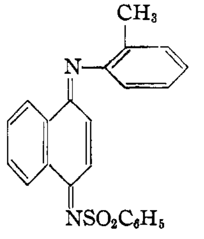
When *o*-toluidine reacted with 1,4-naphthoquinonedibenzenesulfonimide in acetic acid as solvent, reduction to 1,4-naphthalenedibenzenesulfonamide occurred, together with the formation of benzenesulfonamide and a dark red compound which, from its analysis and infrared spectrum, has been postulated as VII or VIII. The compound has an N–H band at 3230 cm.$^{-1}$ and a band at 1565 cm.$^{-1}$, characteristic of quinone diimides. By carrying out the same reaction in chloroform as solvent, an orange-red compound postulated as IX was formed, together with benzenesulfonamide and a small amount of 1,4-naphthalenedibenzenesulfonamide. The infrared spectrum of IX shows no band in the N–H region and a weak band at 1577 cm.$^{-1}$ in the C═N region.

The formation of VII or VIII may be explained by a 1,4-addition to 1,4-naphthoquinonedibenzenesulfonimide followed by oxidation and then 1,2-addition and elimination of benzenesulfonamide, as suggested for the course of the morpholine addition to *p*-quinonedibenzenesulfonimide.[1] By following this mechanism, either VII or VIII could be formed, although VII would probably be favored because of steric considerations. 1,2-Addition to the oxidized 1,4-adduct would probably occur more readily at the 1-carbon because the 4-carbon is partially blocked by the *o*-toluidino group.


VII


VIII


IX


X

Alternatively, the reaction may proceed by a 1,2-addition followed by elimination of benzenesulfonamide and oxidation to form an unisolated intermediate, X, and then 1,4-addition and oxidation to the imide VII or VIII. Using this mechanism, VII would be the expected product because the anil nitrogen in X is much more basic than the benzenesulfonimide nitrogen. In view of the fact that IX can be isolated from the reaction in chloroform solution, it would appear that this latter mechanism is more likely, since IX must be formed through the intermediate X by a 1,2-addition and elimination of benzenesulfonamide.

The compound (VII or VIII) was reduced with zinc and acetic acid to the corresponding amide. The infrared spectrum of the reduced compound showed two N–H bands at 3260 and 3330 cm.$^{-1}$. There was no absorption in the 1560 cm.$^{-1}$ region where imide absorption characteristically appears.

1,4-Naphthoquinonedi-*o*-methylanil (IX) was hydrogenated with platinum oxide to N,N′-di-(*o*-methylphenyl)-1,4-diaminonaphthalene. The infrared spectrum of this compound showed an N–H band at 3390 cm.$^{-1}$.

Dimethylaniline could not be added to 1,4-naphthoquinonedibenzenesulfonimide in chloroform, benzene or glacial acetic acid as solvents. Only reduction of the diimide to the diamide occurred. No other products could be isolated.

It is thus obvious that the reaction of aniline and its derivatives take quite a different course in their reactions with *p*-quinonedibenzenesulfonimide and with 1,4-naphthoquinonedibenzenesulfonimide. This may be due to the difference in the stability of the intermediate ions formed in the naphthalene and benzene series.

**Acknowledgment.**—The authors are indebted to Mr. J. Nemeth, Mrs. K. Pih and Mrs. Esther Fett for the microanalyses and Mrs. R. Hill and Miss Helen Miklas for the infrared spectra.

## Experimental[4]

**Reaction of *p*-Quinonedibenzenesulfonimide with Dimethylaniline. 2-(*p*-Dimethylaminophenyl)-*p*-phenylenedibenzenesulfonamide.** A.—To a solution of 19.16 g. of the diimide in 100 ml. of dioxane, 6.01 g. of dimethylaniline was added. The green solution was evaporated to a total volume of 50 ml., cooled and filtered. The precipitate was washed with chloroform. It weighed 19.83 g. From the

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[4] All melting points are corrected.

mother liquor another crop of 4.90 g. was recovered; total yield 24.73 g. (98%). The product was purified by crystallization from dioxane and acetone; m.p. 223–225° (dec.).

*Anal.* Calcd. for $C_{26}H_{25}N_3O_4S_2$: C, 61.51; H, 4.96; N, 8.28. Found: C, 61.46; H, 5.16; N, 8.48.

B.—To a solution of 0.5 g. of 2-(*p*-methylaminophenyl)-*p*-phenylenedibenzenesulfonamide in 10 ml. of dimethylformamide, 10 ml. of methyl iodide was added and the mixture refluxed overnight. The excess methyl iodide was distilled off and water was added to the warm residue; upon cooling, white crystals resulted, which were probably the hydroiodide of the product. The crystals were taken up in dioxane, the solution was made strongly basic with ammonia, and water was added until the beginning of turbidity. Heating this mixture caused the formation of a crystalline precipitate, m.p. 222° (dec.), 0.30 g. (58%). A melting point of a mixture with an authentic sample of 2-(*p*-dimethylaminophenyl)-*p*-phenylenedibenzenesulfonamide was 222°. The infrared spectra of the two samples were identical.

**2-(*p*-Diethylaminophenyl)-*p*-phenylenedibenzenesulfonamide.**—To a solution of 0.50 g. of the diimide in 5 ml. of purified dioxane, 0.20 g. of redistilled diethylaniline was added. The mixture turned green. The solution was boiled for a few moments and then cooled. The solution was evaporated to dryness and the gummy residue was crystallized from aqueous ethanol. The yield was 0.50 g. (71%). The compound was purified by recrystallization from ethanol; m.p. 186.5–188° (dec.).

*Anal.* Calcd. for $C_{28}H_{19}N_3O_4S_2$: C, 62.78; H, 5.45; N, 7.85. Found: C, 62.31; H, 5.52; N, 7.98.

**2-Methylanilino-1,4-naphthalenedibenzenesulfonamide.**—To a suspension of 0.50 g. of the diimide in 15 ml. of glacial acetic acid, 2.0 g. of methylaniline was added. The mixture became green and then red in color and most of the material dissolved. After 3 days, the mixture was filtered and a very small amount of solid, m.p. 258–261° (dec.), was obtained. This was identified as 1,4-naphthalenedibenzenesulfonamide. The filtrate was evaporated to a small volume and the solid was filtered. The yield was 0.50 g. (81%). The sample was purified by two recrystallizations from ethanol; m.p. 210.5–212.5° (dec.).

*Anal.* Calcd. for $C_{29}H_{25}N_3O_4S_2$: C, 64.07; H, 4.64; N, 7.73. Found: C, 64.07; H, 4.70; N, 7.72.

**Reaction of 1,4-Naphthoquinonedibenzenesulfonimide with Dimethylaniline in Various Solvents.**—Several experiments were carried out with 0.50-g. quantities of the diimide with an excess of redistilled dimethylaniline in chloroform, benzene and acetic acid. In each case about 0.40 to 0.47 g. of 1,4-naphthalenedibenzenesulfonamide was isolated.

**2-*p*-Toluidino-1,4-naphthalenedibenzenesulfonamide.**—To a suspension of 0.50 g. of the diimide in 15 ml. of glacial acetic acid, 2.0 g. of *p*-toluidine was added. The mixture was set aside for 24 hours and the pink solid was filtered; 0.51 g. (82%). Several recrystallizations from acetic acid gave a pure product, m.p. 229–231° (dec.).

*Anal.* Calcd. for $C_{29}H_{25}N_3O_4S_2$: C, 64.07; H, 4.64; N, 7.73. Found: C, 64.07; H, 4.72; N, 7.73.

**Reaction of 1,4-Naphthoquinonedibenzenesulfonimide with *o*-Toluidine. A. Acetic Acid as Solvent.**—To a suspension of 1.00 g. of the diimide in 20 ml. of glacial acetic acid, 4.0 g. of *o*-toluidine was added. In several experiments the reaction mixture was set aside for varying periods of time from 24 hours to 15 days in an attempt to isolate intermediate products. There was no significant difference in the yields of products, except that on longer standing more acet-*o*-toluidide was formed. In a 15-day experiment, the mixture was first filtered (fraction A); it weighed 0.79 g. Fraction A was dissolved in aqueous sodium hydroxide and filtered from a red crystalline solid (fraction B). The filtrate from B was acidified with dilute hydrochloric acid and filtered. The white solid weighed 0.41 g., m.p. 254–258° (dec.). This was identified as 1,4-naphthalenedibenzenesulfonamide.

Fraction B weighed 0.36 g. It was purified from ethanol and formed red-brown needles which decomposed at about 246°.

*Anal.* Calcd. for $C_{30}H_{25}N_3O_2S$: C, 73.29; H, 5.12; N, 8.55. Found: C, 73.25; H, 5.36; N, 8.72, 8.52.

The compound is insoluble in dilute aqueous sodium hydroxide and very slightly soluble in hot dilute hydrochloric acid. The infrared spectrum of the compound shows an N-H band at 3230 cm.$^{-1}$ and a band at 1565 cm.$^{-1}$, characteristic of quinone imides. The compound is probably either 2- or 3-*o*-toluidino-1,4-naphthoquinone-1-benzenesulfonimide-4-*o*-methylanil.

The filtrate from A was evaporated to an oily solid which was mixed with aqueous sodium hydroxide and extracted with chloroform. The aqueous layer was acidified and 0.12 g. of solid separated. This solid was recrystallized from tetrachloroethylene and chloroform to give a pure product, m.p. 151–152°. This was identified as benzenesulfonamide.

The chloroform layer was evaporated and the oily solid recrystallized from cyclohexane, m.p. 96–103°. A pure product was obtained on further recrystallization from cyclohexane and was identified as acet-*o*-toluidide.

**B. Chloroform as Solvent.**—To a solution of 0.50 g. of the diimide in 20 ml. of reagent chloroform was added 1 ml. of *o*-toluidine dissolved in 5 ml. of chloroform. The color became blue immediately and then after a few minutes, dark red. No precipitate appeared for several days. After 12 days, the mixture was filtered to give a white solid, weighing 0.11 g. This was recrystallized from chloroform to give a pure product, m.p. 150.5–151.5°. It was identified as benzenesulfonamide.

The reaction filtrate was evaporated to dryness in a stream of air, and the red residue crystallized from ethanol. The mixture was filtered and the orange-red solid weighed 0.31 g. It was purified by several recrystallizations from acetonitrile to give orange-red needles, m.p. 147–148°. It is 1,4-naphthoquinonedi-(*o*-methylanil).

*Anal.* Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.65; H, 6.12; N, 8.56.

The infrared spectrum of the compound shows a weak C=N band at 1577 cm.$^{-1}$.

On evaporation, the ethanol filtrate deposited a small amount of solid (0.02 g.) identified as 1,4-naphthalenedibenzenesulfonamide.

**Reduction of 2- or 3-*o*-Toluidino-1,4-naphthoquinone-1-benzenesulfonimide-4-*o*-methylanil.**—To a solution of 0.27 g. of 2- or 3-*o*-toluidinonaphthoquinone-1-benzenesulfonimide-4-*o*-methylanil in 20 ml. of boiling glacial acetic acid, zinc dust was added in small portions until the dark red solution became orange. Dilute hydrochloric acid was added to decompose all of the zinc. The solution was cooled and the resultant rose-colored precipitate was filtered. It weighed 0.14 g. Purification from ethanol gave a pure product, m.p. 168–169.5° (dec.).

*Anal.* Calcd. for $C_{30}H_{27}N_3O_2S$: C, 72.99; H, 5.52; N, 8.52. Found: C, 73.11; H, 5.56; N, 8.54.

The infrared spectrum of the compound showed two N-H bands at 3330 and 3260 cm.$^{-1}$.

**N,N'-Di-(*o*-methylphenyl)-1,4-diaminonaphthalene.**—A mixture of 0.12 g. of 1,4-naphthoquinonedi-(*o*-methylanil) and 100 ml. of ethanol was hydrogenated at 26 lb. pressure over platinum oxide. The mixture became colorless. The solution was filtered and the filtrate evaporated in a stream of air. The residual red-brown oil was crystallized from *n*-hexane and weighed 0.08 g. (67%). The white solid was recrystallized from *n*-hexane to give a pure product, m.p. 102–103°.

*Anal.* Calcd. for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55. Found: C, 84.87; H, 6.50.

**Reaction of 2-Methyl-*p*-quinonedibenzenesulfonimide with Dimethylaniline. 2-Methyl-x-(*p*-dimethylanilino)-*p*-phenylenedibenzenesulfonamide.**—To a solution of 0.40 g. of the diimide in 25 ml. of chloroform, 1 ml. of redistilled dimethylaniline was added. The solution immediately turned green in color, and after about 3 hours the color was a light green-brown. The solution was colored a light pink-brown when it was evaporated after 24 hours. The residual oil was crystallized readily from ethanol to give a white solid, 0.39 g. (75%). After 3 crystallizations from ethanol it was pure, m.p. 184.5–186.5° (dec.).

*Anal.* Calcd. for $C_{27}H_{27}N_3O_4S_2$: C, 62.16; H, 5.22; N, 8.06. Found: C, 62.03; H, 5.26; N, 8.25.

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