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Quinone Imides. XXXVI. Orientation of Groups in Adducts of Quinone Diimides with Different N-Substituents

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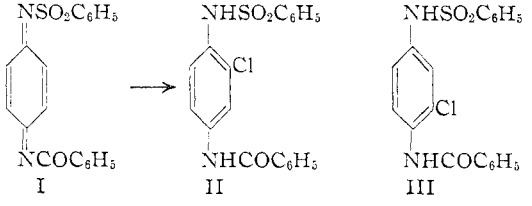
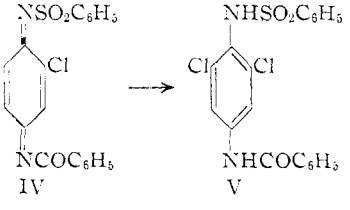
p-Quinonemonobenzimidemonobenzenesulfonimide adds hydrogen chloride to give exclusively 2-chloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide. Upon oxidation of this latter product to the diimide and subsequent addition of hydrogen chloride, 2,6-dichloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide is formed. In a similar manner *p*-quinonemonopivalimidemonobenzenesulfonimide reacts with hydrogen chloride to give 2-chloro-*p*-phenylene-4-pivalamide-1-benzenesulfonamide. The position of the chlorine atoms was determined by unequivocal syntheses of these compounds.

The addition of hydrogen chloride to *p*-quinonemonobenzimidemonobenzenesulfonimide (I) results in a single monochloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide, the constitution of which was not previously determined.[2] It may have one of two structures (II or III). Both compounds II and III have now been synthesized by unequivocal methods and the adduct has been shown to have structure II by melting point comparison and identical infrared spectra.



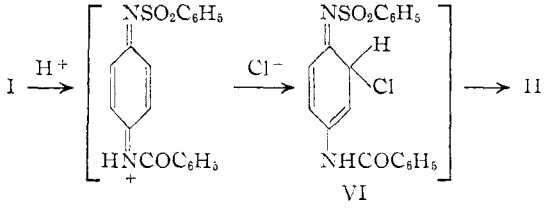
In a similar manner hydrogen chloride added to *p*-quinonemonopivalimidemonobenzenesulfonimide and the chlorine was shown to occupy the position in the diamide *meta* to the pivalamido group thus corresponding to compound II.

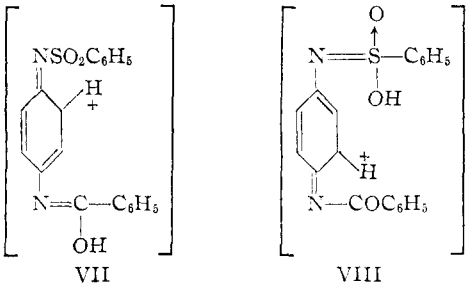
Oxidation of II provided the corresponding quinone diimide IV to which hydrogen chloride added with the exclusive formation of the 2,6-dichloro diamide V.



This orientation may be explained on the basis that the benzenesulfonyl is a more powerful electron-attracting group than the benzoyl and a greater electron density will therefore exist around the carbonyl nitrogen. When hydrogen chloride is added to *p*-quinonemonobenzimidemonobenzenesulfonimide, the proton should add to the benzimido nitrogen and the chloride anion should react in a normal manner to give VI which rearranges to II.

Another possible mechanism involves 1,6-addition with protonation of an oxygen atom as the first step. An intermediate VII would be formed that by addition of a chloride anion followed by a prototropic shift would result in the product found, II. An analogous protonation of the sulfonyl oxygen would be very unlikely since it would involve an enol nitrogen–sulfur double bond, VIII, and an expansion of the sulfur octet to ten electrons, thus requiring more energy to effect the transition state than in the case of the benzamido group.





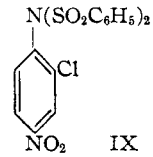
p-Quinonemonobenzimidemonobenzenesulfonimide is most conveniently made by oxidation of the corresponding diamide with lead tetraacetate in refluxing benzene solution. Without isolation of the diimide, the solution may be filtered from the precipitated lead diacetate and saturated with dry hydrogen chloride. The monochloro diamide is thus obtained in 70% yield. The oxidation of the monochloro diamide and subsequent addition of hydrogen chloride to the diimide was effected in a similar manner with a 50% over-all yield of the dichloro diamide.

The proposed unequivocal route to the synthesis of II was by the following steps: 2-chloro-4-nitroaniline, N-benzenesulfonyl-2-chloro-4-nitroaniline, N^1-benzenesulfonyl-2-chloro-*p*-phenylenediamine, 2-chloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide (II). The first reaction was complicated by the fact that the usual benzenesulfonation methods resulted in a dibenzenesulfonyl derivative IX even when a single mole of benzenesulfonyl chloride was used.

This product IX by the action of sodium ethoxide in absolute ethanol was converted to the monoben-

(1) An abstract of a thesis submitted by Richard S. Colgrove to the Graduate College of the University of Illinois, 1954, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; University of Illinois Fellow, 1950–1951; Minnesota Mining and Manufacturing Company Fellow, 1951–1952; American Cyanamid Company Fellow, 1952–1953.

(2) R. Adams and J. L. Anderson, THIS JOURNAL, **72**, 5154 (1950).



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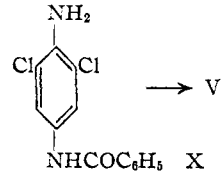
zenesulfonyl derivative which was readily reduced and benzoylated to give II. The dibenzenesulfonyl derivative was reduced to N^1,N^1-dibenzenesulfonyl-2-chloro-*p*-phenylenediamine and the amine benzoylated to give N^1,N^1-dibenzenesulfonyl-N^4-benzoyl-2-chloro-*p*-phenylenediamine. Upon monodebenzenesulfonation, II resulted. This second route is less satisfactory because of lower yields.

The structure of 2-chloro-*p*-phenylene-4-pivalamide-1-benzenesulfonamide was determined by synthesis in an analogous way.

Compound III was prepared by the following steps: 2-chloro-4-nitroaniline, N-benzoyl-2-chloro-4-nitroaniline, N^1-benzoyl-2-chloro-*p*-phenylenediamine, 3-chloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide (III).

To identify 2,6-dichloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide (V), an unequivocal synthesis was sought. 2,6-Dichloro-4-nitroaniline could not be benzenesulfonated by any of the methods in common use. This nitro compound was therefore reduced to 2,6-dichloro-*p*-phenylenediamine and benzoylated with one mole of benzoyl chloride. The monobenzoyl derivative was the N^1-benzoyl-3,5-dichloro-*p*-phenylenediamine (X) which upon benzenesulfonation gave a product identical with V. The position of the benzoyl group was established by the fact that in V one chlorine is known to be adjacent to the benzenesulfonamido group because V was synthesized from IV in which the chlorine position was proved. If one chlorine is adjacent to the benzenesulfonamido group then the other must be adjacent since the second synthesis of V started with 2,6-dichloro-4-nitroaniline.



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Acknowledgment.—The authors are indebted to Mr. Joseph Nemeth, Mrs. Esther Fett and Mrs. Lucy Chang for the microanalyses and to Miss Helen P. Miklas and Mrs. Rosemary F. Hill for the determination and interpretation of the infrared absorption spectra.

Experimental

All melting points are corrected.

The infrared spectra were run in Nujol mulls using a Perkin–Elmer model 21 double beam spectrophotometer.

The lead tetraacetate used in all oxidations was recrystallized from glacial acetic acid and dried over phosphorus pentoxide.

In all benzenesulfonations, benzoylations and pivalylations, pyridine (reagent grade) dried over potassium hydroxide was employed as a solvent.

***x*-Chloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide.**—This product was made by the general procedure previously described[2] but as a higher melting product and in superior yields when the diimide was not isolated. *p*-Nitroaniline was benzenesulfonated best at room temperature in pyridine[2,3] and the resulting compound reduced catalytically in ethanol with platinum oxide and hydrogen at room temperature.[2,4] Benzoylation of this amine was effected at room temperature.[2] The yields in each step were 88% or better.

A suspension of 5.30 g. of *p*-phenylenemonobenzamidemonobenzenesulfonamide and 6.65 g. of lead tetraacetate in 450 ml. of dry thiophene-free benzene (dried over sodium) was heated under reflux with stirring. After 8.5 hours, the insoluble lead diacetate was removed by filtration. Into the orange filtrate dry hydrogen chloride was bubbled for 30 minutes. The resulting amber solution was concentrated to a small volume and ethanol added to the boiling solution. When the odor of benzene was no longer detected the ethanol solution was poured into a large volume of water to give a semi-colloidal solution. It was concentrated on a steam-cone to *ca.* 200 ml. and allowed to stand overnight. There was obtained 4.09 g. (70.5%) of crude tan product. Three recrystallizations from ethanol–water (Darco) gave white needles, m.p. 181–182° (lit.[2] m.p. 177–178°).

Anal. Calcd. for $C_{19}H_{15}ClN_2O_5S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 58.94; H, 4.20; N, 7.25.

Infrared analysis indicated NH bands at 3250 and 3370 cm.$^{-1}$; amide C=O at 1684 cm.$^{-1}$; NH deformation band at 1532 cm.$^{-1}$; SO_2 bands at 1173 and 1330 cm.$^{-1}$.

N,N-Dibenzenesulfonyl-2-chloro-4-nitroaniline.—To 17.3 g. of 2-chloro-4-nitroaniline (m.p. 105–108°) dissolved in 50 ml. of dry pyridine was added a solution of 35.6 g. of benzenesulfonyl chloride in 50 ml. of dry pyridine. The reaction mixture was cooled under tap water with agitation until the initial warming had subsided (*ca.* 5 min.). After standing at room temperature for about a week, the solution was poured into 400 ml. of 1:1 hydrochloric acid containing crushed ice. The yellow precipitate which was washed on the filter with *ca.* 100 ml. of ether to remove starting material weighed 40.5 g. (89.5%). It was purified by recrystallization from glacial acetic acid; clusters of white needles, m.p. 212–214°.

Anal. Calcd. for $C_{18}H_{13}ClN_2O_6S_2$: C, 47.74; H, 2.89; N, 6.19. Found: C, 47.86; H, 3.08; N, 6.05.

Infrared analysis indicated NO_2 bands at 1533 and 1358 cm.$^{-1}$; SO_2 bands at 1170 and 1185 cm.$^{-1}$; no NH bands.

N-Benzenesulfonyl-2-chloro-4-nitroaniline.—To a sodium ethoxide solution prepared from 0.5 g. of sodium and 50 ml. of absolute ethanol was added 9.06 g. of N,N-dibenzenesulfonyl-2-chloro-4-nitroaniline and 50 ml. of absolute ethanol. The reaction mixture was heated under reflux for one hour. The resulting yellow solution was diluted with an equal volume of distilled water and acidified with concentrated hydrochloric acid to yield 6.15 g. (98%) of faintly yellow plates. One recrystallization from dioxane–water and two recrystallizations from ethanol–water gave a pure product; pale yellow microneedles, m.p. 163–164.5° (lit.[5] m.p. 161°).

Anal. Calcd. for $C_{12}H_9ClN_2O_4S$: C, 46.08; H, 2.90; N, 8.96. Found: C, 46.22; H, 2.89; N, 8.83.

Infrared analysis indicated an NH band at 3260 cm.$^{-1}$; NO_2 bands at 1523 and 1342 cm.$^{-1}$; SO_2 bands at 1342, 1176 and 1158 cm.$^{-1}$; the probable presence of monosubstituted benzene bands at 687, 743 or 760 cm.$^{-1}$.

The N^1-Benzenesulfonyl-2-chloro-*p*-phenylenediamine. Method A.—To a suspension of 1.34 g. of N-benzenesulfonyl-2-chloro-4-nitroaniline in 110 ml. of absolute ethanol was added *ca.* 0.05 g. of platinum oxide and the reduction effected at 3 atm. pressure (2 hours). After removing the catalyst the colorless filtrate was concentrated to *ca.* 50 ml., water was added to the cloud point and the solution allowed to stand overnight. The yield was 1.1 g. (91%). The product was purified by recrystallization once from benzene–petroleum ether (93–97.5°) and twice from ethanol–water; white platelets, m.p. 164.5–166°.

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2S$: C, 50.97; H, 3.92; N, 9.91. Found: C, 50.97; H, 3.75; N, 9.96.

Infrared analysis indicated NH bands at 3480, 3375 and

(3) E. Lellmann, *Ber.*, **16**, 595 (1883); S. Opolski, *ibid.*, **40**, 3534 (1907).

(4) G. T. Morgan and F. M. G. Micklethwait, *J. Chem. Soc.*, **87**, 80 (1905); R. S. Shreiber and R. L. Shriner, THIS JOURNAL, **57**, 1306 (1935).

(5) Aktien-Gesellschaft für Anilin-Fabrikation, German Patent 157,859; *Chem. Zentr.*, **76**, I, 415 (1905).

3290 cm.$^{-1}$; SO_2 bands at 1174 and 1333 cm.$^{-1}$; monosubstituted benzene at 687 and 757 cm.$^{-1}$; NH_2 deformation band at 1625 cm.$^{-1}$.

Method B.—A solution of 1.1 g. of N-benzenesulfonyl-2-chloro-4-nitroaniline in *ca.* 150 ml. of 95% ethanol was heated to boiling, water added to the cloud point and ethanol until clear. To the aqueous–alcoholic solution was added 1.85 g. of solid sodium hydrosulfite in small portions and boiling was continued for 30 minutes following the discharge of the yellow color. After filtration the solution was concentrated to the cloud point and allowed to stand overnight. There was obtained 0.51 g. (51%) of white platelets, m.p. 164.5–166.5°.

2-Chloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide. Method A.—To 0.5 g. of N^1-benzenesulfonyl-2-chloro-*p*-phenylenediamine dissolved in 15 ml. of dry pyridine was added a solution of 0.25 g. of benzoyl chloride in 10 ml. of dry pyridine. The mixture was shaken and allowed to stand for 11 hours at room temperature, then poured into 200 ml. of *ca.* 9% hydrochloric acid. The white gummy precipitate, after standing one hour, was removed by filtration and air-dried. It weighed 0.56 g. (82.5%). Three recrystallizations from ethanol–water gave white needles, m.p. 181–182°.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_3S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 59.10; H, 4.09; N, 7.05.

A *melting point of a mixture with x*-chloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide showed no depression. Infrared analyses of the two products were identical.

Method B.—To a solution of 0.25 g. of sodium in 20 ml. of absolute ethanol was added 1.33 g. of N^1,N^1-dibenzenesulfonyl-N^4-benzoyl-2-chloro-*p*-phenylenediamine together with another 20 ml. of absolute ethanol. The mixture was refluxed for one hour, then poured into *ca.* 200 ml. of water, filtered and acidified with concentrated hydrochloric acid. The orange gum, after drying, weighed 0.73 g. (74.5%). Four recrystallizations from ethanol–water (Darco) gave white needles, m.p. 181–182°.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_3S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 59.10; H, 4.12; N, 7.03.

A melting point of this product with that from method A gave no depression. The infrared analyses were identical.

N^1,N^1-Dibenzenesulfonyl-2-chloro-*p*-phenylenediamine. Method A.—To 12.75 g. of N,N-dibenzenesulfonyl-2-chloro-4-nitroaniline suspended in *ca.* 200 ml. of aqueous ethanol was added in small portions 14.8 g. of sodium hydrosulfite. After boiling for 15 minutes a colorless solution resulted which was filtered and concentrated until solid began to separate. After standing overnight at room temperature, the oil, which first formed, solidified. It weighed 4.22 g. (35.5%). Five recrystallizations from ethanol–water gave off-white platelets, m.p. 192.5–193.5° dec.

Anal. Calcd. for $C_{18}H_{13}ClN_2O_4S_2$: C, 51.12; H, 3.58; N, 6.63. Found: C, 51.24; H, 3.63; N, 6.50.

Infrared analysis indicated NH bands at 3485 and 3390 cm.$^{-1}$; SO_2 bands at 1170, 1182 and 1192 cm.$^{-1}$ and 1325 and 1360 cm.$^{-1}$ (wk.); NH_2 deformation band at 1632 cm.$^{-1}$.

Method B.—To 3.13 g. of N,N-dibenzenesulfonyl-2-chloro-4-nitroaniline suspended in 100 ml. of absolute ethanol was added *ca.* 0.05 g. of platinum oxide and reduction was effected at 3 atm. pressure (5 hours). The catalyst was removed by filtration and the filtrate concentrated to *ca.* 70 ml. Upon standing overnight 1.14 g. (39%) of pale yellow crystals was obtained. It was purified by recrystallization from ethanol–water to give off-white crystals, m.p. 189.5–191.5° dec.

N^1,N^1-Dibenzenesulfonyl-N^4-benzoyl-2-chloro-*p*-phenylenediamine.—A solution of 2.9 g of N^1,N^1-dibenzenesulfonyl-2-chloro-*p*-phenylenediamine in 50 ml. of dry pyridine was benzoylated as previously described for the monobenzenesulfonyl derivative. The product weighed 1.64 g. (45.5%). Three recrystallizations from ethanol–water (Darco) gave a white powder, m.p. 203.5–204.5°.

Anal. Calcd. for $C_{25}H_{19}ClN_2O_5S_2$: C, 56.97; H, 3.63; N, 5.32. Found: C, 56.81; H, 3.85; N, 5.17.

Infrared analysis indicated an NH band at 3285 cm.$^{-1}$; amide C=O band at 1685 cm.$^{-1}$; NH deformation band at 1527 cm.$^{-1}$; SO_2 bands at 1173, 1187, 1368 and 1314 cm.$^{-1}$ (wk.).

N-Benzoyl-2-chloro-4-nitroaniline.—A solution of 17.3 g. of 2-chloro-*p*-nitroaniline in 100 ml. of dry pyridine was benzoylated as described for the N^1-benzenesulfonyl-2-chloro-*p*-phenylenediamine. The product weighed 26.0 g. (94%). After four recrystallizations from 95% ethanol, one from carbon tetrachloride, one from methanol and a final recrystallization from absolute ethanol, there was obtained white needles, m.p. 159–161° (lit.[6] m.p. 161°).

Anal. Calcd. for $C_{13}H_9ClN_2O_3$: C, 56.43; H, 3.28; N, 10.13. Found: C, 56.51; H, 3.03; N, 9.83.

Infrared analysis indicated an NH band at 3305 cm.$^{-1}$; C=O at 1667 cm.$^{-1}$; NO_2 bands at 1512 and 1317 cm.$^{-1}$; monosubstituted benzene at 699 cm.$^{-1}$.

N^1-Benzoyl-2-chloro-*p*-phenylenediamine.—To a solution of 2.77 g. of N-benzoyl-2-chloro-4-nitroaniline in *ca.* 200 ml. of boiling 95% ethanol was added boiling water to the cloud point and ethanol until clear. To this solution was added 5.22 g. of sodium hydrosulfite portionwise and the boiling was continued for 30 minutes after the addition was complete. After filtration, concentration to *ca.* 100 ml., and standing overnight, a white product separated that weighed 0.86 g. (35%). One recrystallization from methanol–water and one from ethanol–water gave white needles, m.p. 150–152°.

Anal. Calcd. for $C_{13}H_{11}ClN_2O$: C, 63.29; H, 4.50; N, 11.36. Found: C, 63.26; H, 4.60; N, 11.14.

Infrared analysis indicated NH bands at 3430, 3310 and 3225 cm.$^{-1}$; amide C=O at 1652 cm.$^{-1}$; NH deformation band at 1526 cm.$^{-1}$; NH_2 deformation band at 1608 cm.$^{-1}$.

3-Chloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide.—To a solution of 2.87 g. of N^1-benzoyl-2-chloro-*p*-phenylenediamine in 50 ml. of dry pyridine was added 2.05 g. of benzenesulfonyl chloride dissolved in 20 ml. of dry pyridine and the reaction mixture was allowed to stand at room temperature for 40 hours. Upon pouring into *ca.* 200 ml. of 1:1 hydrochloric acid a tan precipitate formed which weighed 4.12 g. (92%). Recrystallization from ethanol–water (Darco) gave white plates, m.p. 174.5–175.5°.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_3S$: C, 58.99; H, 3.91; N, 7.24. Found: C, 58.95; H, 3.85; N, 7.22.

A melting point of a mixture of this product and *x*-chloro - *p* - phenylenemonobenzamidemonobenzenesulfonamide gave a 15° depression.

Infrared analysis indicated NH bands at 3340 and 3110 cm.$^{-1}$; amide C=O band at 1645 cm.$^{-1}$; SO_2 bands at 1313 and 1173 cm.$^{-1}$; NH deformation band at 1525 cm.$^{-1}$; monosubstituted benzene bands at 686 and 723 cm.$^{-1}$.

***x*-2-Dichloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide.**—A suspension of 3.4 g. of 2-chloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide and 3.9 g. of lead tetraacetate in 300 ml. of dry thiophene-free benzene was refluxed with stirring. After 2 hours no lead tetraacetate was detected, either by addition of a few drops of the reaction mixture to water or by iodide–starch test paper. The lead diacetate was removed by filtration, the benzene filtrate cooled to room temperature and treated with dry hydrogen chloride for 30 minutes. The reaction mixture was concentrated and the benzene replaced by 95% ethanol. It was treated with Darco, filtered and water added to the cloud point. The resulting semi-colloidal precipitate was coagulated on a steam-cone. The crude tan product weighed 1.85 g. (50%). Two recrystallizations from glacial acetic acid and three from ethanol–water yielded white needles, m.p. 235–236.5°.

Anal. Calcd. for $C_{19}H_{14}Cl_2N_2O_3S$: C, 54.17; H, 3.35; N, 6.65. Found: C, 54.24; H, 3.52; N, 6.57.

Infrared analysis indicated NH bands at 3335 and 3105 cm.$^{-1}$; amide C=O at 1662 cm.$^{-1}$; SO_2 bands at 1330 and 1167 cm.$^{-1}$; NH deformation band at 1523 cm.$^{-1}$; monosubstituted benzene at 705 and 753 cm.$^{-1}$.

N^1-Benzoyl-3,5-dichloro-*p*-phenylenediamine.—(2,6-Dichloro-*p*-nitroaniline could not be benzenesulfonated in pyridine or α-picoline at reflux temperature for many hours nor by heating with benzenesulfonyl chloride without solvent.)

The 2,6-dichloro-*p*-phenylenediamine used in this preparation was obtained either (1) by sodium hydrosulfite reduction of 2,6-dichloro-*p*-nitroaniline in ethanol (48.5% yield)

(6) P. Cohn, *Chem. Zentr.*, **73**, **I**, 752 (1902).

as described for other compounds in this paper or (2) by stannous chloride reduction in hydrochloric acid followed by treatment with alkali (98.5% yield).[7]

To 3.6 g. of 2,6-dichloro-*p*-phenylenediamine dissolved in 20 ml. of dry pyridine was added a solution of 2.8 g. of benzoyl chloride in 15 ml. of dry pyridine. After 4 days the pyridine solution was poured into *ca.* 100 ml. of 1:1 hydrochloric acid. The product weighed 5.1 g. (91%). Two recrystallizations from ethanol–water gave white microneedles, m.p. 185–186°.

Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O$: C, 55.53; H, 3.59; N, 9.97. Found: C, 55.36; H, 3.33; N, 10.09.

Infrared analysis indicated NH bands at 3445, 3345 and 3250 cm.$^{-1}$; amide C=O at 1630 cm.$^{-1}$; monosubstituted benzene at 689 and/or 704 cm.$^{-1}$; NH deformation band at 1535 cm.$^{-1}$; NH_2 deformation band at 1595 cm.$^{-1}$.

2,6-Dichloro-*p*-phenylene-4-benzamide-1-benzenesulfonamide.—To a solution of 5.1 g. of N^1-benzoyl-3,5-dichloro-*p*-phenylenediamine in 70 ml. of dry pyridine was added 3.2 g. of benzenesulfonyl chloride dissolved in 20 ml. of dry pyridine and the reaction was allowed to proceed at room temperature for 3 days. Upon pouring into *ca.* 200 ml. of 1:1 hydrochloric acid a cream-colored precipitate formed weighing 7.26 g. (95.5%). Two recrystallizations from ethanol–water gave white needles, m.p. 235.5–237°.

Anal. Calcd. for $C_{19}H_{14}Cl_2N_2O_3S$: C, 54.17; H, 3.35; N, 6.65. Found: C, 54.15; H, 3.23; N, 6.72.

A melting point of a mixture of this compound and the *x*,2-dichloro-*p*-phenylenemonobenzamidemonobenzenesulfonamide showed no depression. Infrared analyses were identical.

***p*-Phenylenemonopivalamidemonobenzenesulfonamide.**—To a solution of 17.7 g. of N-benzenesulfonyl-*p*-phenylenediamine in 80 ml. of dry pyridine was added 8.6 g. of pivalyl chloride in 20 ml. of dry pyridine. The mixture was cooled under running tap water until the initial warming had subsided (*ca.* 3 min.) and allowed to stand at room temperature overnight. After 17 hours the reaction mixture was poured into 200 ml. of concentrated hydrochloric acid containing crushed ice. A pale orange precipitate formed which after filtration and drying in a vacuum desiccator over calcium chloride weighed 22.4 g. (94.5%). Three recrystallizations from ethanol–water after treatment with Darco gave white needles, m.p. 190–191.5°.

(7) O. N. Witt, *Ber.*, **8**, 145 (1875); N. L. Drake, *et al.*, THIS JOURNAL, **68**, 1602 (1946).

Anal. Calcd. for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.30; H, 6.01; N, 8.38.

Infrared analysis indicated NH bands at 3365 and 3140 cm.$^{-1}$; amide C=O at 1650 cm.$^{-1}$; SO_2 bands at 1332 and 1165 cm.$^{-1}$; monosubstituted benzene at 690 and/or 725 cm.$^{-1}$; NH deformation band at 1525 cm.$^{-1}$.

***x*-Chloro-*p*-phenylenemonopivalamidemonobenzenesulfonamide.**—A suspension of 3.3 g. of *p*-phenylenemonopivalamidemonobenzenesulfonamide and 4.4 g. of lead tetraacetate in 300 ml. of dry thiophene-free benzene was heated under reflux with stirring for 2 hours. The insoluble lead diacetate was removed by filtration. Dry hydrogen chloride was passed into the orange benzene filtrate for *ca.* 30 minutes. The resulting amber solution was concentrated to *ca.* 50 ml. and ethanol added to displace the benzene. The ethanolic solution (Darco) was filtered, concentrated to *ca.* 50 ml., water added to the cloud point and the solution allowed to stand overnight. An oil separated which was taken up in acetone, poured into water and allowed to stand several days. There was obtained a crude pink product which weighed 3.02 g. (83%). Three recrystallizations from methanol–water and one from acetone–water gave white needles, m.p. 164.5–166°.

Anal. Calcd. for $C_{17}H_{19}ClN_2O_3S$: C, 55.65; H, 5.22; N, 7.64. Found: C, 55.88; H, 5.29; N, 7.41.

Infrared analysis indicated an NH band at 3260 cm.$^{-1}$; amide C=O at 1655 cm.$^{-1}$; SO_2 bands at 1337 and 1175 cm.$^{-1}$; monosubstituted benzene at 685 and/or 721 cm.$^{-1}$; NH deformation band at 1530 cm.$^{-1}$.

2-Chloro-*p*-phenylene-4-pivalamide-1-benzenesulfonamide.—To 2.27 g. of N^1-benzenesulfonyl-2-chloro-*p*-phenylenediamine dissolved in 10 ml. of dry pyridine was added 0.97 g. of pivalyl chloride dissolved in 5 ml. of dry pyridine. The mixture was cooled under running tap water for *ca.* 5 minutes with stirring and allowed to stand at room temperature. After 20 hours the pyridine solution was poured into 150 ml. of 1:1 hydrochloric acid to give a tan precipitate which, after filtration and air-drying, weighed 2.80 g. (95%). Two recrystallizations from methanol–water and one from acetone–water gave white needles, m.p. 164.5–166°.

Anal. Calcd. for $C_{17}H_{19}ClN_2O_3S$: C, 55.65; H, 5.22; N, 7.64. Found: C, 55.71; H, 5.16; N, 7.46.

A melting point of a mixture of this product with *x*-chloro-*p*-phenylenemonopivalamidemonobenzenesulfonamide showed no depression. Infrared analyses were identical.

URBANA, ILLINOIS

NOTES

Derivatives of Quinoline-3-carboxylic Acid

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Quinoline-3-carboxylic acid, was converted into its acid chloride hydrochloride and into β-diethylaminoethyl quinoline-3-carboxylate dihydrochloride and methobromide.

The acid chloride hydrochloride reacted with 2-aminopropanol and with 2-aminobutanol to form the 2-(1-hydroxy)-propyl- and the 2-(1-hydroxy)-butylamide of quinoline-3-carboxylic acid, respectively.

The 2-(1-hydroxy)-butylamide was tested for oxytocic activity in the Parke, Davis and Company laboratories; it was found to be inactive.

When ethyl quinoline-3-carboxylate was hydrogenated, in acetic acid–ethanol solution in the presence of platinum oxide catalyst, two atomic equivalents of hydrogen were absorbed. Although no proof of structure was obtained, it was assumed that this product was ethyl dihydroquinoline-3-carboxylate, possibly the 1,4-dihydro derivative. This ester was hydrolyzed to the corresponding 3-carboxylic acid which seemed to decarboxylate readily, and the acid chloride could not be obtained.

The ethyl ester of the dihydro compound reacted with hydrazine hydrate to produce the acid hydrazide which, when treated with nitrous acid, yielded the acid azide. This substance reacted with ammonia to form dihydroquinoline-3-carboxamide.

Experimental

β-Diethylaminoethyl Quinoline-3-carboxylate Dihydrochloride and Methobromide.—Quinoline-3-carboxylic acid[1]

(1) Prepared through 3-cyanoquinoline from 3-bromoquinoline. *Cf.* H. Gilman and S. M. Spatz, THIS JOURNAL, **63**, 1553 (1941), and Cl. Claisen and F. Collichonn, *Ber.*, **19**, 2763 (1886).