3-(3,5-Dimethyl-4-methoxyphenyl)-1-propene-1-C^{14}, colorless liquid, b.p. 113–114° (11 mm.), n^{30}D 1.5182.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.10. Found: C, 81.8; H, 9.18.

Degradation of Rearrangement Products.—Chart III indicates the degradative route used to determine the distribution of radioactive carbon-14 after the rearrangement.

A. **Hydroxylation Reaction.**—The method described by Swern, Billen and Scanlan was used.[19] The oily products were dissolved in sufficient anhydrous ether to give a viscous, but not solid, mass at −80°. Crystallization was induced by scratching the walls of the container as the material was warmed slowly to room temperature. As soon as crystals formed, the solvent was removed at reduced pressure to prevent the solid from redissolving.

2,3-Dihydroxy-1-(2-methoxyphenyl)-propane-1-C^{14}, white needles, m.p. 62–63°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 66.0; H, 7.70. Found: C, 66.2; H, 8.21.

1,2-Dihydroxy-3-(3,5-dimethyl-4-methoxyphenyl)-propane-1-C^{14}, white needles, m.p. 81–82°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.6; H, 8.58. Found: C, 69.0; H, 8.79.

B. **Periodic Acid Cleavage of the Glycols.**—1-(2-Methoxyphenyl)-2-propene-1-C^{14}, HCOOH fraction, 5 ± 4 c./min. The corresponding methoxyphenylacetic acid was not isolated. $KMnO_4$ oxidation of 1-(2-methoxyphenyl)-2-propene-1-C^{14} yielded 2-methoxybenzoic-*carboxy*-C^{14} acid which was decarboxylated with copper chromite catalyst[25]: 3-(3,5-dimethyl-4-methoxyphenyl)-1-propene-1-C^{14}; HCOOH fraction, 504 ± 10 c./min.; 663 ± 10 c./min.; 3,5-dimethyl-4-methoxyphenylacetic acid, white needles, m.p. (sealed tube) 191–192°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.23. Found: C, 67.8; H, 7.14.

Decarboxylation of this acid with copper chromite gave the following counting rate: 4 ± 4 c./min.

$KMnO_4$ oxidation yielded methoxytrimesic acid (II); white powder, m.p. 235–250° dec. (lit. m.p. 248° dec.).[26] This compound was further characterized by preparation of its trimethyl ester using diazomethane; m.p. 85–86° (lit. m.p. 86°)[26]. Decarboxylation of II with copper chromite gave: 1 ± 4 c./min.

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(25) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 142.

(26) F. Ullmann and K. Brittner, *Ber.*, **42**, 2543 (1909).

MINNEAPOLIS 14, MINNESOTA

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

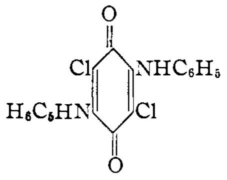
Quinone Imides. XXII. The Reaction of Primary Aromatic Amines with 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide[1]

BY ROGER ADAMS AND B. H. BRAUN[2]

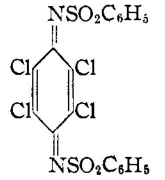
RECEIVED JULY 10, 1952

2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide (II) gives equimolar addition products with aniline, *o*-toluidine, *m*-toluidine and 2,6-dimethylaniline; it is reduced to the corresponding diamide by *p*-toluidine, 2,4-dimethylaniline and mesidine; no reaction occurs with 2,4,6-trichloroaniline. The addition products contain primary amino groups, as exemplified by reactions of the anilino compound; benzenesulfonation, diazotization and coupling to a dye with β-naphthol, replacement of the amino group with hydrogen. Confirmation that the *para* hydrogen to the amino group has taken part in the addition was obtained by the fact that dimethylaniline also added. The adducts appear to be *p,p'*-diaminodiphenylamine derivatives (III, IV) formed by 1,6-addition of the amines to the N,N conjugated system.

Chloranil reacts readily with aniline[3]; the chief product is 2,5-dianilino-3,6-dichloro-*p*-quinone (I). Other primary aromatic amines react similarly.[3,4]



I



II

2,3,5,6-Tetrachloro-*p*-phenylenedibenzenesulfonamide has been synthesized by successive oxidations and additions of hydrogen chloride to *p*-phenylenedibenzenesulfonamide[5] or more conveniently by chlorination of *p*-phenylenedibenzenesulfonamide in dimethylformamide.[6] By oxidation, the dibenzenesulfonimide analog of chloranil, 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide (II), is formed.

The reaction of II with aniline and other amines has been investigated. The results were unexpected; the course of the reaction is completely different from that of chloranil with the same amines.

When II and either one mole equivalent or excess of aniline were mixed in chloroform solution, a reaction occurred and a colorless addition product separated in good yield. It was an adduct of one molecule of aniline and one molecule of II, with chloroform of solvation. Acetone and acetic acid solvates were also prepared. The solvation did not interfere with the subsequent reactions of the compound. The product contained a primary amino group as revealed by diazotization and coupling with β-naphthol to form a dye, by benzenesulfonation, and by diazotization and replacement of the amino group by hydrogen. The infrared spectrum indicated the presence of three N–H groupings. The molecule, on the basis of these facts, was postulated as being a diphenylamine derivative of structure III. A 1,6 addition to the N,N conjugated system of II had occurred with a proton

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(1) For paper XXI, see R. Adams and W. Moje, THIS JOURNAL, **74**, 5562 (1952).

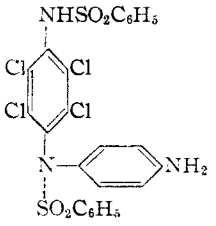
(2) An abstract of a portion of a thesis submitted by B. H. Braun to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) O. Hesse, *Ann.*, **114**, 292 (1860); H. von Knapp and G. Schultz, *ibid.*, **210**, (1881); M. Niemeyer, *ibid.*, **228**, 322 (1885); M. Andresen, *J. prakt. Chem.*, **136**, 422 (1883); A. W. Hofmann, *Jahresb.*, 416 (1863).

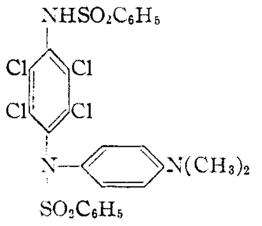
(4) H. Imbert and J. Pages, *Bull. soc. chim. France*, [3] **19**, 575 (1893); M. Martynoff and G. Tsatsas, *ibid.*, [5] **14**, 52 (1947); Swiss Patent 225,370, May 17, 1943 [*C. A.*, **43**, 5964 (1949)].

(5) R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).

(6) R. Adams and B. H. Braun, *ibid.*, **74**, 3171 (1952).



III



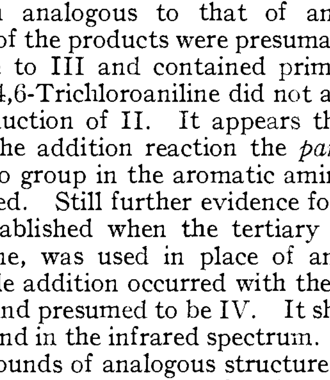
IV

from the *para* position of the aniline molecule taking part in the reaction. Further experimentation tended to confirm this structure.

p-Toluidine, 2,4-dimethylaniline or mesidine, when used in place of aniline, did not react similarly; 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide, the reduction product of II, was formed in good yields. However, when *o*-toluidine, *m*-toluidine or 2,6-dimethylaniline replaced aniline, an addition analogous to that of aniline took place. All of the products were presumably similar in structure to III and contained primary amino groups. 2,4,6-Trichloroaniline did not add nor did it cause reduction of II. It appears that for the success of the addition reaction the *para* position to the amino group in the aromatic amine must be unsubstituted. Still further evidence for structure III was established when the tertiary amine, dimethylaniline, was used in place of aniline. An equally facile addition occurred with the formation of a compound presumed to be IV. It showed only one N–H band in the infrared spectrum.

No compounds of analogous structure have been reported from the reaction of quinones and dialkylanilines.[7] Colored adducts, assumed to be of a quinhydrone type, have been noted and in one case analyzed,[7c] but the only colorless product observed was hydroquinone.[7a]

By the chlorination in dimethylformamide of the benzenesulfonamide of III, only a hexachloro compound resulted. The two entering chlorines are probably adjacent to the benzenesulfonamido group as shown in V.



V

It appears that perchlorination of benzenesulfonamides[6] in dimethylformamide may be successful only if a hydrogen atom is present on the nitrogen atom.

Experimental

All melting points are corrected.

2,3,5,6-Tetrachloro-*p*-phenylenedibenzenesulfonamide.—The preparation previously described[6] was modified. After the dimethylformamide solution had absorbed the required amount of chlorine at a temperature not exceeding 30°, dry hydrogen chloride was passed in. White crystals formed and the temperature rapidly rose. When the mixture was at 110° the stream of hydrogen chloride was discontinued and two volumes of boiling acetic acid added. The product was collected after cooling; m.p. 303–305° (dec.). The yield was 87%. The previously reported crude product[6] melted at 277–281° (dec.) and was formed in 68% yield.

2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide.—This compound was prepared by a modification of that previously described.[5] To a well-stirred suspension of 38.5 g. of 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide in 300 ml. of acetic anhydride 32.5 g. of dry lead tetraacetate was added. The mixture was heated to 60–70° on a water-bath and kept at this temperature 30 minutes; the color rapidly turned orange. The suspension was then cooled and filtered with suction, drying the cake as well as possible. The residue was washed with distilled water until the filtrate was free of lead. The bright orange product, after drying in a vacuum desiccator over phosphorus pentoxide, weighed 37.3 g. (97%); m.p. 242–244° (dec.) (lit. m.p. 240.5–241.5°).[5]

Recrystallization from glacial acetic acid, in which it is very sparingly soluble at the boiling point and practically insoluble at room temperature, gave very slender, brilliant orange needles, m.p. 247–249° (dec.).

Addition of Aniline to 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide: 2,3,5,6-Tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine Benzenesulfonamide (III).—To a suspension of 5.24 g. of 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide in 50 ml. of chloroform, 1.4 ml. of redistilled aniline was added. The reaction was rapid and moderately exothermic; the orange solid dissolved, forming a pale brown solution from which in a few seconds tan crystals began to deposit. The 6.35 g. of solid was filtered and washed with petroleum ether (b.p. 30–60°). An additional 0.73 g. was precipitated from the mother liquors with petroleum ether. The total yield was 7.08 g. (96%). The product is a solvate containing one molecule of chloroform. The chloroform is given off at 130–140° with very slight sintering if the compound is placed in a bath at room temperature and heated slowly; if the sample is placed in a bath at about 200°, it melts at once with vigorous evolution of gas and then resolidifies. Heated either way the dry solid melts at 227–228° (dec.).

Anal. A sample dried to constant weight at 180–190° (bath temperature). Calcd. loss of $CHCl_3$ from $C_{24}H_{17}Cl_4N_3O_4S_2 \cdot CHCl_3$: 16.22; found, 15.90.

The substance was recrystallized from acetone (Norit) with which it formed a solvate. This became dry at about 130° and melted at 234° (dec.). For analysis the sample was dried *in vacuo* at the temperature of refluxing xylene, but the solvent was not lost.

Anal. Calcd. for $C_{24}H_{17}Cl_4N_3O_4S_2 \cdot C_3H_6O$: C, 48.01; H, 3.43; O, 6.22; volatile (at 180–190°), 8.60. Found: C, 47.96; H, 3.20; N, 6.39; volatile, 8.63.

The infrared spectra of the two solvates were very similar, except for a strong carbonyl band at 1710 cm.$^{-1}$ of the acetone solvate; each showed three bands in the N–H region, at 3170, 3355 and 3460 cm.$^{-1}$ for the acetone and at 3170, 3363 and 3471 cm.$^{-1}$ for the chloroform adduct. The N–H band region of the acetic acid adduct was also studied and showed bands at 3180, 3368 and 3470 cm.$^{-1}$.

Diazotization and Coupling of 2,3,5,6-Tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine Benzenesulfonamide.—The procedure of Shriner and Fuson[8] was followed. Treatment of the amine with hydrochloric acid disintegrated the crystals without effecting solution. The diazonium chloride was also insoluble. Addition of the diazotized solution to sodium β-naphtholate caused the immediate formation of a heavy, bright red, amorphous precipitate (dark red when dry) for which no method of recrystallization was found.

Reductive Deamination of 2,3,5,6-Tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine Benzenesulfonamide: 2,3,5,6-Tetrachloro-4-benzenesulfonamidodiphenylamine Benzenesulfonamide.—A mixture of 2.0 g. of the chloroform solvate of 2,3,5,6-tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine benzenesulfonamide and 30 ml. of dilute hydrochloric acid (1:1) was warmed; the crystals disintegrated without dissolving and gave off a strong odor

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(7) (a) J. Schmidt and A. Sigwart, *Ber.*, **46**, 1491 (1913); (b) P. Monnel, F. Reverdin and E. Nolting, *ibid.*, **12**, 2305 (1879); (c) G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 256 (1929).

(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 114.

of chloroform. The suspension was cooled below 5° in an ice–salt-bath and a solution of 1.0 g. of sodium nitrite in 10 ml. of water was added with stirring over a period of 20 minutes. There was no visible evidence of reaction. Addition of 50 ml. of 50% hypophosphorous acid over a period of 15 minutes caused evolution of much gas and the mixture became stiff and paste-like. Stirring was continued for one hour, keeping the flask in the ice-bath. The liquid was then transferred to a large beaker and the copious foam which had formed was rinsed into the same beaker with *ca.* 100 ml. of water. The slurry was kept in the refrigerator for 20 hours, then warmed to room temperature and filtered. The precipitate weighed 1.88 g. and was a mixture of product and unreacted starting material. After two recrystallizations from glacial acetic acid (Norit), the product melted at 203–205° (dec.) and was free from starting material as shown by the analysis and by exhibiting in the infrared spectrum only one band in the N–H region, at 3259 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{16}Cl_4N_2O_4S_2$: C, 47.85; H, 2.68; N, 4.65. Found: C, 47.81; H, 2.85; N, 4.74.

Benzenesulfonation of 2,3,5,6-Tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine Benzenesulfonamide: 2,3,5,6-Tetrachloro-4,4′-dibenzenesulfonamidodiphenylamine Benzenesulfonamide.—To a solution of 4.90 g. of the chloroform solvate of 2,3,5,6-tetrachloro-4′-amino-4-benzenesulfonamidodiphenylamine benzenesulfonamide in 20 ml. of pyridine, 0.90 ml. of benzenesulfonyl chloride was added and the mixture refluxed for 30 minutes. The addition of the chloride caused a slight, exothermic reaction and the solution turned yellow. Upon boiling, the mixture became dark red temporarily, but rapidly turned pale again. Most of the solvent was removed by means of a stream of air and the viscous gum left was taken up in about 20 ml. of glacial acetic acid. The product crystallized and weighed 4.5 g. Dilution of the mother liquors furnished an additional crop of 0.45 g. The yield was 4.95 g. (94%). The product was recrystallized from glacial acetic acid (Norit), m.p. 249° (dec.).

Anal. Calcd. for $C_{30}H_{21}Cl_4N_3O_6S_3$: C, 47.56; H, 2.79; N, 5.55. Found: C, 47.55; H, 3.00; N, 5.58.

Chlorination of 2,3,5,6-Tetrachloro-4,4′-dibenzenesulfonamidodiphenylamine Benzenesulfonamide: 2,3,5,6,3′,5′-Hexachloro-4,4′-dibenzenesulfonamidodiphenylamine Benzenesulfonamide.—Into a solution of 1.01 g. of the tetrachloro compound in 4 ml. of dimethylformamide, a stream of chlorine was passed, keeping the temperature below 50°. When the mixture had gained 1.15 g. in weight it was cooled and slowly poured into excess of concd. hydrochloric acid and then diluted with water. The mixture was heated with stirring and the oil that separated soon solidified. The solid was filtered, dissolved in 10 ml. of warm dimethylformamide, and warm glacial acetic acid was added in small portions; no precipitate appeared even after 30 ml. had been added. To the warm solution warm water was then added in small portions; each portion caused formation of an amorphous precipitate which redissolved on swirling. After 23 ml. of water had been added crystals suddenly began to form. Cooling resulted in a yield of 0.65 g. (59%) of a microcrystalline powder. The product was once recrystallized from glacial acetic acid (Norit), m.p. 262–263° (dec.). It proved to be a hexachloro compound.

Anal. Calcd. for $C_{30}H_{19}Cl_6N_3O_6S_3$: C, 43.60; H, 2.32; N, 5.09. Found: C, 43.88; H, 2.55; N, 4.95.

Reaction of 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide with Mesidine: 2,3,5,6-Tetrachloro-*p*-phenylenedibenzenesulfonamide.—To a suspension of 5.24 g. of the diimide in 25 ml. of chloroform, 1.36 g. of mesidine was added dropwise, with swirling. There was a slight exothermic reaction and the red solid disappeared. After addition of 100 ml. of petroleum ether (b.p. 30–60°), the mixture was left overnight. Filtration gave a quantitative yield of a tan powder. For purification, this was dissolved in 5% aqueous sodium hydroxide, boiled with Darco, and reprecipitated with acid. The crude white product thus obtained melted at 295°. It was then recrystallized from glacial acetic acid, white crystals m.p. 273–274°.[6] By recrystallization from nitrobenzene, the product melted at 307–308°.[6] The reason for the differences in melting points depending on the solvent employed was not determined. Analysis and the infrared spectrum showed it to be 2,3,5,6-tetrachloro-*p*-phenylenedibenzenesulfonamide.

Anal. Calcd. for $C_{18}H_{12}Cl_4N_2O_4S_2$: C, 41.06; H, 2.28; N, 5.32. Found: C, 41.46; H, 2.62; N, 5.56.

Similar results were obtained using 2,4-dimethylaniline or *p*-toluidine.

Reaction of 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide with 2,6-Dimethylaniline: 2,3,5,6-Tetrachloro-4-benzenesulfonamido-3′,5′-dimethyl-4′-aminodiphenylamine Benzenesulfonamide.—This reaction was run like the previous one, but 1.21 g. of the 2,6-dimethylaniline was used. The white microcrystalline product weighed 6.5 g. (100%). It was soluble in acetone and dioxane and for analysis was recrystallized three times from dioxane and water, m.p. 249–250° (dec.). It did not form a solvate.

Anal. Calcd. for $C_{26}H_{21}Cl_4N_3O_4S_2$: C, 48.38; H, 3.28; N, 6.51. Found: C, 48.51; H, 3.38; N, 6.27.

Reaction of 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide with *o*-Toluidine: 2,3,5,6-Tetrachloro-4-benzenesulfonamido-3′-methyl-4′-aminodiphenylamine Benzenesulfonamide.—This was run like the mesidine experiment, except that 1.05 g. of *o*-toluidine was added to the suspension of the quinone diimide. The product, a pale cream microcrystalline powder, was a solvate. The solvent was driven off at about 130°. The product thus obtained melts at 238–240° (dec.). No satisfactory solvent for recrystallization was found; for purification it was dissolved in acetone, treated with Norit and precipitated with petroleum ether (b.p. 30–60°). Even after repetition of the process the melting point had not changed. The compound was prepared for analysis by drying at 100° *in vacuo*.

Anal. Calcd. for $C_{25}H_{19}Cl_4N_3O_4S_2$: C, 47.55; H, 3.03; N, 6.66. Found: C, 47.82; H, 3.33; N, 6.59.

Reaction of 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide with *m*-Toluidine: 2,3,5,6-Tetrachloro-4-benzenesulfonamido-2′-methyl-4′-aminodiphenylamine Benzenesulfonamide.—This reaction was run like the previous ones except that 1.07 g. of the *m*-toluidine was added to the quinone diimide. The product was decidedly yellow and weighed 6.14 g. (97%). It melted at 207–209° (dec.) and the melting point was unchanged after twice dissolving in acetone and precipitating with petroleum ether. A trace of colored impurities always remained. It did not form a solvate.

Anal. Calcd. for $C_{25}H_{19}Cl_4N_3O_4S_2$: C, 47.55; H, 3.03; N, 6.66. Found: C, 47.63; H, 3.26; N, 6.40.

The infrared spectra of the compounds formed with 2,6-dimethylaniline, *o*- and *m*-toluidine show the expected three bands in the N–H stretching region, respectively, at 3199, 3385 and 3482 cm.$^{-1}$; 3221, 3376 and 3485 cm.$^{-1}$; and at 3217, 3382 and 3482 cm.$^{-1}$. The chloroform–petroleum ether solvate of the compound formed from *o*-toluidine exhibited a striking shift in the bands, which were at 3172, 3360 and 3456 cm.$^{-1}$.

Trichloroaniline did not react under similar conditions with 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide.

Reaction of 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide with Dimethylaniline: 2,3,5,6-Tetrachloro-4-benzenesulfonamido-4′-dimethylaminodiphenylamine Benzenesulfonamide (IV).—This reaction was run like the one with mesidine. The product separated as a white microcrystalline powder and was a chloroform solvate, m.p. 221–222° (dec.), after becoming dry at 120–130°. The yield from 5.24 g. of diimide was 6.05 g. The compound was twice recrystallized from chloroform in which it is very soluble. For analysis it was dissolved in acetone, in which it is also very soluble, and precipitated with petroleum ether (b.p. 30–60°). The melting point and the temperature at which the solvent was released were unchanged. The infrared spectrum showed a single N–H band, at 3200 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{21}Cl_4N_3O_4S_2$: C, 48.38; H, 3.28; N, 6.51. Found: C, 48.68; H, 3.37; N, 6.43.

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