of the hydrogenation and not present in the initial cholesterol.

Cholestanyl acetate was undoubtedly formed by ester interchange of either the starting material or of the product with the ethyl acetate.

The formation of coprostanol is another example of the formation of significant amounts of a coprostane derivative in the catalytic hydrogenation of a $\Delta^{5,6}$-double bond.[9]

The hydrogenolysis of a hydroxyl group in the presence of hydrogen, platinum and perchloric acid has been noted before[10] and this may explain the presence of cholestane.

## Experimental[11]

### Hydrogenation of Cholesterol

In order to make a comparison of the products of the hydrogenation of cholesterol with the starting material a large lot of cholesterol was carefully crystallized from ethyl acetate. The material obtained melted at 148.6–149.8°, $[\alpha]^{24}D$ −40.26°. Upon chromatographic analysis of a 20-g. sample using a column of Florosil there was obtained only 0.12 g. of material melting at 139–145° (0.6%) while the remainder was substantially pure cholesterol.

A solution of 1250 g. of this purified cholesterol in 17 l. of C.P. ethyl acetate at 40–50° was hydrogenated in a reciprocating type hydrogenator with the aid of 25 g. of platinum oxide catalyst[12] and 2.0 cc. of 70–72% perchloric acid. The initial pressure was 15 lb./sq. in. and the hydrogenation was complete in approximately 30 minutes.[13] The heat of hydrogenation kept the solution at about the starting temperature. After displacing the hydrogen with nitrogen the solution was treated with 1 cc. of 50% sodium hydroxide solution, filtered with suction to remove the catalyst, cooled to 10° and held overnight at this temperature. There was thus obtained 579 g. of β-cholestanol, m.p. 139–141°, $[\alpha]^{24}D$ +22.3°. The mother liquors were evaporated to dryness under reduced pressure and the residue was recrystallized from 17 l. of methanol. Two more crops were obtained which weighed 526.5 g., m.p. 139–142°, thus givng a total yield of 1105.5 g. (88.0%) of cholestanol. The same yield was obtained from different samples of unrecrystallized U.S.P. cholesterol using this procedure. Further concentration of the mother liquors gave material melting below 100°.

In order to separate this residue into its components the methanolic mother liquors were evaporated to dryness leaving 143 g. of light brown material, m.p. 75–88°. A 20-g. sample was dissolved in 200 ml. of hexane and adsorbed onto a 1-meter column of 100–200 mesh Florosil. Successive elutions with hexane, hexane–chloroform (95:5), hexane–chloroform (85:15), and chloroform gave four fractions. From the hexane eluate there were obtained three fractions. The first, 1.6 g., m.p. 63.4–72.8°, gave cholestane m.p. 79.8–81.6°, $[\alpha]^{23}D$ +27.3°, after one crystallization from acetone.

*Anal.* Calcd. for $C_{27}H_{48}$: C, 87.02; H, 12.98. Found: C, 87.14; H, 13.00.

The next fraction, 2.04 g., reached a maximum melting point at 104° and ranged from m.p. 85–104–98°. It was crystallized from acetone and from methanol and gave cholestanyl acetate m.p. 109.0–110.0°, $[\alpha]^{22}D$ +12.34°.

*Anal.* Calcd. for $C_{29}H_{50}O_2$: C, 80.87; H, 11.70. Found: C, 80.73; H, 11.55.

The third and last fraction from the hexane eluate weighed 4.26 g., m.p. 73–103–83°. Three crystallizations of this fraction from methanol gave coprostanol, m.p. 99.2–100.4°, $[\alpha]^{22}D$ +23.84°

*Anal.* Calcd. for $C_{27}H_{48}O$: C, 83.43; H, 12.45. Found: C, 83.45; H, 12.10.

Each of the above three compounds was compared with authentic samples by mixture melting point and by direct comparisons of the infrared spectra. In each case no differences were observed.

From the hexane–chloroform eluates there was obtained 8.1 g. of substantially pure cholestanol. Allowing for the cholestanol in the residue the over-all yield obtained from the hydrogenation was 92.5%, while approximately 1–2% of cholestane, 1–2% of cholestanyl acetate and 2.5–3.5% of coprostanol were formed as by-products.

BLOOMFIELD, NEW JERSEY RECEIVED AUGUST 18, 1950

(9) T. Reichstein and A. Lardon, *Helv. Chim. Acta*, **24**, 955 (1941).

(10) K. Kindler and D. Kwok, *Ann.*, **554**, 9 (1943); K. Rosenmund and E. Karg, *Ber.*, **75**, 1850 (1942).

(11) All melting points are corrected. Optical rotations were determined in a 1% chloroform solution. The optical data and microanalyses were determined by Mr. W. Tarpley, Mr. Edwin Conner and their Staff.

(12) Baker and Company, Newark, New Jersey.

(13) FOOTNOTE ADDED IN PROOF.—Only 20 minutes was required in a rotary hydrogenator [E. B. Hershberg, F. Bertsch, H. Kaplan and H. Brown, *Ind. Eng. Chem.*, **42**, 2336 (1950)].

---

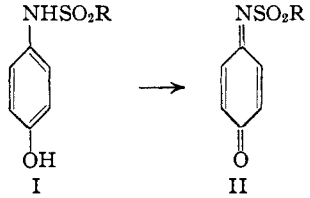
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Quinone Imides. IV. p-Quinone Monosulfonimides

BY ROGER ADAMS AND J. H. LOOKER

Lead tetraacetate oxidation of the benzenesulfonyl, *p*-toluenesulfonyl and methanesulfonyl derivatives of *p*-aminophenol give the corresponding *p*-quinone imides. The 2-methyl, 3-methyl, 2-chloro, 3-chloro and 2,6-dichloro derivatives of 4-benzenesulfonamidophenol have been oxidized similarly. The *p*-quinone imides are (1) readily reduced, (2) hydrolyzed by hot water to the quinone and sulfonamide and (3) add hydrogen chloride or thiophenol to give the corresponding chloro- or phenylmercapto-4-sulfonamidophenol. The primary products of the addition reactions have the entering groups ortho to the hydroxyl. The sulfonamidophenols are best prepared from the aminophenols and sulfonyl chlorides in pyridine.

The conversion of the disulfonamides of *p*-phenylenediamine, 1,4-naphthylenediamine and their derivatives to *p*-quinone disulfonimides by oxidation with lead tetraacetate has been described in previous papers.[1] The identical procedure is equally adaptable to the sulfonamides of *p*-aminophenol and its derivatives and leads to the formation of *p*-quinone monosulfonimides. Thus, the benzenesulfonyl, *p*-toluenesulfonyl and methanesulfonyl derivatives of *p*-aminophenol (I) are oxidized to the corresponding *p*-quinone imides II.




I II

R = phenyl, *p*-tolyl, methyl

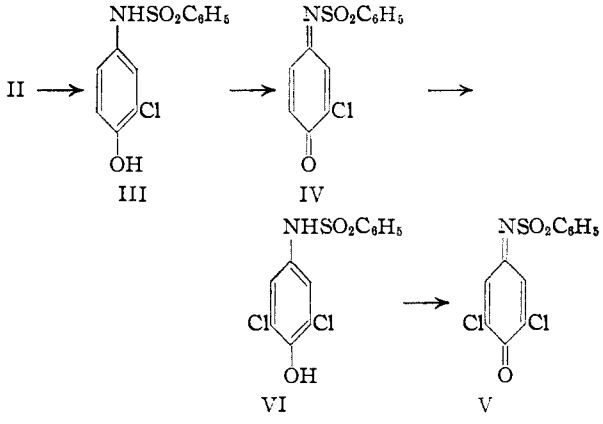
The benzenesulfonyl derivatives of 2-chloro-, 2,6-

(1) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); see also R. Adams and J. H. Anderson, *ibid.*, **72**, 5154 (1950).

dichloro-, 3-chloro-, 2-methyl- and 3-methyl-4-aminophenols were also converted to the *p*-quinone monoimides and it is thus probable that a sulfonamide of any *p*-aminophenol which does not contain groups sensitive to lead tetraacetate will exhibit the same characteristics.

The crystalline *p*-quinone monoimides are yellow or orange-yellow and stable at room temperature over a period of at least several months. They are more soluble in ordinary organic solvents than the benzene derivatives from which they are formed and much more soluble than the *p*-quinone disulfonimides. There seems to be a correlation between the type and number of substituents in the benzenesulfonamidophenol and the yield of the oxidation product obtained. *p*-Quinone monobenzenesulfonimide and its monochloro derivatives are formed in yields of approximately 60%, whereas the monomethyl and dichloro derivatives are obtained in yields in excess of 84%. The dichloro derivative is a bright lemon-yellow color, in contrast to the orange-yellow of the other quinone monoimides.

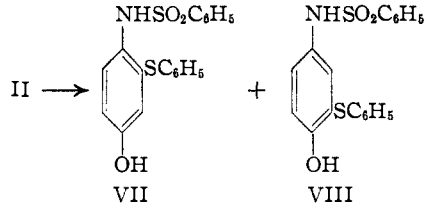
The lead tetraacetate oxidation products of the sulfonamidophenols, the *p*-quinone monosulfonimides, resemble *p*-quinones and *p*-quinone disulfonimides in many of their reactions. They are readily reduced to the corresponding *p*-aminophenol either by hydriodic acid or sodium hydrosulfite. Aqueous alkali in the cold converts them to tars. Hydrogen chloride in chloroform or water adds readily to *p*-quinone benzenesulfonimide with formation of 2-chloro-4-benzenesulfonamidophenol (III) as the principal product. III may be oxidized to the corresponding *p*-quinone imide IV to which a second molecule of hydrogen chloride adds to give 2,6-dichloro-4-benzenesulfonamidophenol (V). Compound V is readily oxidized to the compound VI.




The position of the chlorine in III was established both by showing its identity with an authentic sample of 2-chloro-4-benzenesulfonamidophenol, prepared by benzenesulfonation of 2-chloro-4-aminophenol, and indirectly by its non-identity to 3-chloro-4-benzenesulfonamidophenol, made by an analogous procedure. The second chlorine entered the 6-position since the product was identical with that formed by benzenesulfonating the known 2,6-dichloro-4-aminophenol. It appears that the nitrogen preferentially accepts the proton from the hydrogen chloride and the chlorine in the 1,4-addition enters next to the quinone carbonyl group.

The addition of one mole of dry hydrogen chloride to *p*-quinone benzenesulfonimide gave, in addition to III, a very small yield of a lower melting compound. This substance has not been obtained in a state of purity, but has been identified as *p*-benzenesulfonamidophenol by examination of the infrared spectrum of a fraction containing it. It is apparent that a small amount of reduction occurred during the reaction with hydrogen chloride. No 3-chloro-4-benzenesulfonamidophenol could be detected.

*p*-Quinone benzenesulfonimide adds thiophenol to give a mixture of the two isomers VII and VIII. Only the higher melting isomer has been obtained in a pure condition. Which of the two structures VII or VIII should be assigned to this molecule has not been determined, although by analogy to the hydrogen chloride adduct, formula VIII would appear the more likely. *p*-Quinone benzenesulfonimide




and morpholine react in chloroform solution but no crystalline reaction product could be isolated.

The most striking difference between the *p*-quinone monobenzenesulfonimides and *p*-quinone dibenzenesulfonimides lies in their relative susceptibility to hydrolysis. The latter, with one exception in the naphthalene series which will be described in another communication, are not hydrolyzed by boiling with mineral acids. The former, however, are hydrolyzed to a *p*-quinone and benzenesulfonamide by the action of boiling water alone.

The preparation of the sulfonyl derivatives of the *p*-aminophenols was not as facile as that of the sulfonyl derivatives of the *p*-phenylenediamines, the yields usually being lower. The reported methods, by the reaction of two moles of the aminophenol with one mole of the sulfonyl chloride,[2] and the treatment of the aminophenol hydrochloride with one mole of the sulfonyl chloride in presence of aqueous alkali,[3] proved in our hands to be very inferior procedures. A more convenient and satisfactory general method is the reaction of equimolar quantities of the free aminophenol, the hydrochloride, or acid sulfate, with the sulfonyl chloride in pyridine at room temperature. The sulfonamidophenols prepared and the yields obtained are listed in Table I.

When methanesulfonyl chloride was used in excess with *p*-aminophenol in pyridine, and the resulting solution heated, both the amino and hydroxyl groups were methanesulfonated with formation of IX. This replacement of the hydrogen of the hydroxyl by the methanesulfonyl group has been previously observed[4] when anhydrous conditions are used.

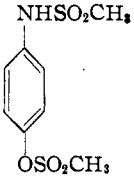
(2) J. Troeger and P. W. Uhlmann, *J. prakt. Chem.*, **159**, 438 (1895).
(3) J. B. Tingle and L. F. Williams, *Am. Chem. J.*, **37**, 69 (1907).
(4) B. Helferich and P. Papalambrou, *Ann.*, **551**, 235 (1942).

TABLE I

SULFONAMIDOPHENOLS

| Compound | M. p., °C. (cor.) pure | % yield of crude | Solvent for purif. | Analyses, % Calcd. | Found |
|---|---|---|---|---|---|
| *p*-Benzenesulfonamidophenol,[3,a] | 156 | 78 | Ethyl acetate | ..... | ... |
| 2-Chloro-4-benzenesulfonamidophenol[b] | 168–168.5 | 50 | EtOAc–Bz | C, 50.79 | 51.04 |
| | | | | H, 3.55 | 3.71 |
| | | | | N, 4.74 | 4.98 |
| 3-Chloro-4-benzenesulfonamidophenol[c] | 149.5–150.5 | 75 | Ethyl acetate | C, 50.79 | 50.95 |
| | | | | H, 3.55 | 3.61 |
| | | | | N, 4.74 | 4.63 |
| 2-Methyl-4-benzenesulfonamidophenol[a] | 198–199 | 100[d] | EtOAc–Bz | C, 59.30 | 58.93 |
| | | | | H, 4.98 | 4.98 |
| | | | | N, 5.32 | 5.10 |
| 3-Methyl-4-benzenesulfonamidophenol[a] | 132.5–133.5 | 48[e] | EtOAc–Bz | C, 59.30 | 59.13 |
| | | | | H, 4.98 | 5.07 |
| | | | | N, 5.32 | 5.17 |
| 2,6-Dichloro-4-benzenesulfonamidophenol[a] | 150.5–151.5 | 94 | EtOAc–$CHCl_3$ | C, 45.29 | 45.41 |
| | | | | H, 2.85 | 2.82 |
| | | | | N, 4.40 | 4.56 |

[a] The aminophenols used were obtained from Eastman Kodak Company. [b] 2-Chloroaminophenol was made from the nitro compound by reduction using the method of W. G. Christiansen, THIS JOURNAL, **45**, 2192 (1923). [c] 3-Chloronitrophenol (H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, **127**, 1600 (1925), was reduced by the method of Christiansen (see *b*). [d] Corrected for recovered starting material (2-methyl-4-aminophenol sulfate). [e] Based on material purified from sodium hydroxide as found in Experimental part.




IX

By using the calculated amount of reagent, and avoiding heating, this difficulty was eliminated and only an amino hydrogen reacted.

**Acknowledgment.**—The authors acknowledge with thanks the contribution of Miss Emily Davis and Miss Rachel Kopel for microanalyses and of Miss Elizabeth Petersen for infrared spectra.

## Experimental

All melting points are corrected.

**2,6-Dichloro-4-aminophenol.**—A solution of 50 g. of 2,6-dichloro-4-nitrophenol in 1 l. of 5% aqueous sodium hydroxide was heated to boiling and solid sodium hydrosulfite added until the red color of the alkaline solution was discharged. Upon cooling, the aminophenol crystallized and was collected by filtration, washed with water and dried in the air; yield 37.5 g. (88%); m. p. 166–167° (lit.[5] m. p. 167°). This material was used without recrystallization for further reactions.

**General Method for Preparing Benzenesulfonamides from *p*-Aminophenols.**—To 0.1 mole of the aminophenol (or the sulfate or hydrochloride), suspended or dissolved in approximately 40 ml. of medicinal pyridine, was added 0.1 mole of benzenesulfonyl chloride in 6–7 ml. of pyridine. The red solution was cooled under running tap water until initial reaction heat subsided, and was permitted to stand at room temperature 24 hours. The reaction mixture was then poured into a large volume of ice-water containing a quantity of hydrochloric acid considerably in excess of that required to neutralize the pyridine. The aqueous suspension, sometimes containing some tar, was permitted to stand overnight and the crude benzenesulfonamide derivative filtered and washed with water. The total quantity of crude product was dissolved in 5% aqueous sodium hydroxide, treated with decolorizing charcoal (Darco), and the sulfonamide recovered by adding 1:1 hydrochloric acid slowly, with vigorous stirring, until an acid reaction to litmus was obtained. Two recrystallizations (including one decolorization with charcoal) from ethyl acetate, ethyl acetate–benzene or ethyl acetate–chloroform gave the pure, colorless benzenesulfonamide derivative. The compounds prepared by this procedure, together with other pertinent data, are listed in Table I.

***p*-Methanesulfonamidophenol.**—To 5.4 g. of *p*-aminophenol, dissolved in 40 ml. of pyridine, was added a solution of 5.7 g. of pure methanesulfonyl chloride in approximately 12 ml. of pyridine. The resulting mixture was permitted to stand at room temperature 96 hours, and was then poured into 1.5 l. of ice-water containing sufficient hydrochloric acid to neutralize completely the pyridine. No material precipitated, even after standing several days. The aqueous mixture was extracted exhaustively with ethyl acetate (total volume 500 ml.). Concentration of the ethyl acetate to about 50 ml., followed by slow evaporation gave 7 g. of crude, crystalline material (75%). Solution in 10% aqueous sodium hydroxide (Darco) and reprecipitation by concentrated hydrochloric acid gave a cream-colored product. This material was recrystallized twice from ethyl acetate to give the colorless and pure methanesulfonamide derivative, m. p. 154.5–155.5°. The compound was dried 12 hours *in vacuo* over boiling xylene prior to analysis.

*Anal.* Calcd. for $C_7H_9NO_3S$: C, 44.91; H, 4.84; N, 7.48. Found: C, 44.82; H, 4.87; N, 7.71.

***p*-Methanesulfonamidophenyl Methanesulfonate.**—A solution of 5.4 g. of *p*-aminophenol in 40 ml. of pyridine was allowed to react with 12 g. of methanesulfonyl chloride in 12 ml. of pyridine. The reaction mixture was heated to boiling several times over a 3-hour period, cooled and poured into 250 ml. of an ice-water mixture containing enough hydrochloric acid to neutralize the pyridine. The crude product was filtered, washed with water and dried in the air; yield 11 g. (82%). The crude material was dissolved in 350 ml. of 10% aqueous sodium carbonate, a small quantity of insoluble material removed by filtration, and the compound reprecipitated from the filtrate with dilute hydrochloric acid. Filtration, washing with water and air-drying gave 6.1 g. of a light buff solid, which was recrystallized from 175 ml. of hot absolute ethanol (Darco) to which sufficient acetone was added to effect complete solution. This colorless material was recrystallized from absolute ethanol–acetone, and finally from acetone–water; m. p. 162–163°. This product gave a negative ferric chloride test and a negative phosphomolybdic acid test.

*Anal.* Calcd. for $C_8H_{11}NO_5S_2$: C, 36.22; H, 4.18; N, 5.28. Found: C, 36.23; H, 4.20; N, 5.03.

***p*-Quinone Monobenzenesulfonimide.**[6]—To a mechanically stirred suspension of 10 g. of finely powdered *p*-benzene-

(5) A. Kollrepp, *Ann.*, **234**, 10 (1886).

(6) Preliminary work with this compound was performed by A. S. Nagarkatti in this Laboratory.

TABLE II

*p*-QUINONE MONOSULFONIMIDES[a]

| Sulfonamidophenol | Wt. of phenol, g. | Vol. solv. in ml. | Wt. $PbAc_4$ | Reacn. temp., °C. | Reacn. time in min. | Solv. for crystn. | Yield, of crude, g. | M. p. of pure, °C., with dec.[b] | Analyses, % Calcd. | Found |
|---|---|---|---|---|---|---|---|---|---|---|
| 4-(*p*-Toluenesulfonamido)[c] | 2 | 20 | 3.4 | 50<br>Room | 40<br>120 | $CHCl_3$ | 0.8 | 126–127.5 | C, 59.75<br>H, 4.24<br>N, 5.36 | 60.02<br>4.44<br>5.20 |
| Methanesulfonamido | 1.9 | 7 | 4.4 | Room | 25 plus 45 | $CHCl_3$,[d] room t. | 1.3 | 134 | C, 45.40<br>H, 3.81<br>N, 7.56 | 45.30<br>3.76<br>7.88 |
| 2-Chloro-4-benzenesulfonamido | 5.6 | 22 | 8.8 | Room | 75 | $CHCl_3$, addn. of pet. ether | 3.2 | 116–117 | C, 51.15<br>H, 2.86<br>N, 4.97 | 51.27<br>2.98<br>4.84 |
| 3-Chloro-4-benzenesulfonamido | 0.8 | 3 | 1.3 | Room | 25 | EtAc, cyclohexane–$CHCl_3$ | 0.5 | 141–142 | C, 51.15<br>H, 2.86<br>N, 4.97 | 51.27<br>2.98<br>4.84 |
| 2-Methyl-4-benzenesulfonamido | 5.2 | 20 | 4.4[e] | Room | 120 | $CHCl_3$,[d] room t. with addn. few drops EtAc | 4.4 | 108.5–109 | C, 59.75<br>H, 4.24<br>N, 5.36 | 59.40<br>4.56<br>5.09 |
| 3-Methyl-4-benzenesulfonamido | 1.3 | 5 | 2.2 | Room | 20 plus 55 | $CHCl_3$, room t. $CHCl_3$–pet. ether | 1.2 | 136 | C, 59.75<br>N, 4.24<br>N, 5.36 | 59.80<br>4.38<br>5.44 |
| 2,6-Dichloro-4-benzenesulfonamido | 4.8 | 18 | 6.6 | Room | 60 plus 60 | EtAc | 4.3 | 162–163 | C, 45.58<br>H, 2.23<br>N, 4.43 | 45.38<br>2.42<br>4.53 |

[a] Oxidation with lead tetraacetate, following the procedure described for *p*-quinone monobenzenesulfonamide, was used. Ethylene glycol in small amounts was advantageously added in most of the experiments to remove excess of lead tetraacetate before working up the reaction mixture; when added, stirring is continued at room temperature for a half hour to an hour. The *p*-quinone monoimides are yellow or orange-yellow crystalline products. [b] The melting point bath was preheated to 20° below the m.p. to get values reported. [c] Reference 2. [d] The procedure was to dissolve in $CHCl_3$ at room temperature, filter from small amounts of amorphous material and cool to −15° in a hydrochloric acid and ice-bath. [e] After 20 minutes a second 4.4 g. was added and after another hour 0.5 g.

sulfonamidophenol in 40 ml. of glacial acetic acid was added at room temperature 17.6 g. of solid lead tetraacetate[7] (slightly moist with acetic acid) over a 15-minute period. The quinone imide began to crystallize after about 10 minutes. After the reaction had proceeded 30 minutes, two drops of ethylene glycol was added and after 15 more minutes an additional 0.5 ml. of ethylene glycol was added. Stirring was continued 10 minutes and the reaction mixture was then placed in an ice-bath prior to filtration of the crystalline quinone imide; yield of crude product after drying *in vacuo* over potassium hydroxide, 5.7 g. (58%). Recrystallization was effected by suspending the crude material in approximately 200 ml. of cyclohexane, heating to boiling on the steam-bath, adding sufficient chloroform to effect solution (except for a small quantity of amorphous material which was removed by filtration), and permitting the resulting solution to stand at room temperature overnight; yield of pure orange-yellow product, 4.3 g., m. p. 134° (dec.). The quinone imide was dried *in vacuo* at room temperature for 24 hours.

*Anal.* Calcd. for $C_{12}H_9NO_3S$: C, 58.28; H. 3.67; N, 5.67. Found: C, 58.55; H, 3.82; N, 5.95.

This product is immediately converted to a tar by the action of cold 5% aqueous sodium hydroxide.

Other *p*-quinone monoimides are listed in Table II.

**2-Chloro-4-benzenesulfonamidophenol from *p*-Quinone Monobenzenesulfonimide.**—(A) A suspension of 4 g. of the *p*-quinone monobenzenesulfonimide in 30 ml. of 12% hydrochloric acid was heated to boiling several times over a 90-minute interval. An additional 10-ml. portion of hydrochloric acid was added and intermittent heating continued for an additional 90 minutes. The mixture was cooled and the crude buff reaction product was removed by filtration, washed with water and dried in the air; yield 4.2 g. (91%). Three crystallizations from ethyl acetate–benzene gave pure, colorless 2-chloro-4-benzenesulfonamidophenol (see Table I), m. p. 166–167°.

*Anal.* Calcd. for $C_{12}H_{10}ClNO_3S$: C, 50.79; H, 3.55; N, 4.94. Found: C, 50.89; H, 3.70; N, 4.94.

(7) Lead tetraacetate obtained from Arapahoe Chemicals, Inc., or prepared by the method of O. Dimroth and R. Schweitzer, *Ber.*, **56**, 1375 (1923), was used.

(B) A solution of 40 g. of *p*-quinone monobenzenesulfonimide in 350 ml. of chloroform was subjected to the action of a dry hydrogen chloride stream. After several minutes, the reaction product crystallized from solution and was removed by filtration. The chloroform filtrate was again subjected to the action of hydrogen chloride, this time for approximately 30 minutes. The filtrate was concentrated to a small volume and the crude sulfonamide was collected by filtration. The total yield of crude chloro-*p*-benzenesulfonamidophenol was 38.5 g. (84%). By careful fractionation from ethyl acetate–benzene mixture a total of 20.1 g. of quite pure 2-chloro-4-benzenesulfonamidophenol was obtained. After two subsequent recrystallizations from ethyl acetate, a product, m. p. 166–167°, resulted, not depressed upon admixture with authentic 2-chloro-4-benzenesulfonamidophenol (see Table I). The infrared absorption spectra of the two samples were identical.

From filtrates of the ethyl acetate–benzene crystallizations a product was obtained, the infrared absorption spectrum of which showed it to be a mixture consisting principally of 2-chloro-4-benzenesulfonamidophenol (characteristic bands at 3354, 3257, 1512, 1388, 1317, 1158, 754 and 686 $cm.^{-1}$) and a minute quantity of *p*-benzenesulfonamidophenol (characteristic bands at 3410, 1271, 1213 and 796 $cm.^{-1}$). None of the bands characteristic of pure 3-chloro-4-benzenesulfonamidophenol could be detected.

**2,6-Dichloro-4-benzenesulfonamidophenol from 3-Chloro-*p*-quinone 1-Benzenesulfonimide.**—Dry hydrogen chloride was bubbled through a solution of 3.2 g. of 3-chloro-*p*-quinone 1-benzenesulfonimide in 40 ml. of chloroform until the orange-yellow color of the solution was discharged. Concentration of the mixture to a small volume, followed by addition of petroleum ether (b. p. 40–50°) to turbidity gave 3.0 g. (89%) of crude crystalline material. Two recrystallizations from ethyl acetate–chloroform gave pure 2,6-dichloro-4-benzenesulfonamidophenol (see Table I), m. p. 150–151°, not depressed upon admixture with authentic material (m. p. 150.5–151.5°). The infrared absorption spectra of the two samples were identical.

**2(?)-Phenylmercapto-*p*-benzenesulfonamidophenol.**—To a solution of 1 g. of the *p*-quinone monobenzenesulfonimide in 10 ml. of dry chloroform, contained in a 50-ml. erlenmeyer flask, was added all at once a solution of 0.5 g. of thiophenol

n 2 ml. of dry chloroform. The flask was stoppered immediately and shaken vigorously. After about twenty minutes, the adduct began to crystallize. The reaction mixture was permitted to stand at room temperature for 48 hours. The crystalline material present was collected by filtration and dried in the air; yield 1.25 g. (87%). This product was washed with two 7–8 ml. portions of boiling dry chloroform and was then recrystallized from hot dry chloroform to which sufficient dry ethyl acetate was added to effect complete solution. Further recrystallization from chloroform–ethyl acetate gave the analytically pure thiophenol adduct, m. p. 189–190.5°, with softening at 187°.

*Anal.* Calcd. for $C_{18}H_{15}NO_2S$: C, 60.48; H, 4.23; N, 3.92. Found: C, 60.74; H, 4.51; N, 3.78.

**Attempted Addition of Morpholine to *p*-Quinone Monobenzenesulfonimide.**—To a solution of 1 g. of the quinone imide in 10 ml. of dry chloroform was added a chloroform solution of 0.4 g. of morpholine. The resulting mixture became violet in color, then greenish-black. The reaction mixture was permitted to stand 48 hours and was then evaporated to dryness. The tarry residue was dissolved in 5% aqueous sodium hydroxide (Darco). Dilute hydrochloric acid was added dropwise with stirring to the alkaline solution, until a *p*H of approximately 7.5 was reached. A tar resulted, which resisted all attempts at crystallization.

**Reduction of *p*-Quinone Monobenzenesulfonimide with Sodium Hydrosulfite.**—To an absolute ethanolic solution of 0.5 g. of the quinone imide was added sufficient 10% aqueous sodium hydrosulfite to effect decolorization. Inorganic material was removed by filtration and the filtrate was evaporated to dryness. The residue was washed with water, filtered and dried in the air; yield 0.4 g. Recrystallization from ethyl acetate gave *p*-benzenesulfonamidophenol, m. p. 154–155°, not depressed upon admixture with authentic material.

**Hydriodic Acid Reduction of *p*-Quinone Monobenzenesulfonimide.**—To 5 ml. of concd. hydriodic acid (sp. gr. 1.50) was added 0.5 g. of solid *p*-quinone monobenzenesulfonimide. An instant liberation of iodine occurred. The reaction mixture was heated on the steam-bath for 30 minutes. The crude product was collected by filtration, washed with water, dried in the air and washed with chloroform; yield 0.3 g. Recrystallization from ethyl acetate gave pure *p*-benzenesulfonamidophenol, m. p. 155–156°, unchanged upon admixture with authentic material.

**Hydrolysis of *p*-Quinone Monobenzenesulfonimide.**—A suspension of 0.5 g. of the quinone imide in 20 ml. of water was heated under reflux over a low flame for 45 minutes. The reaction mixture was cooled and the crystalline material present was collected by filtration and dried in the air; yield 0.2 g. Recrystallization from dilute ethanol gave a virtually colorless compound, m. p. 151–152°, not depressed upon admixture with authentic benzenesulfonamide, m. p. 152–153°. A depression of 30° was obtained upon admixture with *p*-benzenesulfonamidophenol, m. p. 156°.

A small quantity of *p*-benzoquinone, m. p. 110–114°, collected in the lower part of the condenser tube. Further evidence for the presence of quinone was found in the detection of its characteristic odor in the reaction mixture and in the steam volatility of the reaction product remaining in the reaction mixture after removal of the benzenesulfonamide.

**Hydrolysis of 3-Methyl-*p*-quinone 1-Benzenesulfonimide.**—A suspension of 1.0 g. of the quinone imide in 40 ml. of water was heated under reflux for 15 minutes. A quantity of *p*-toluquinone, m. p. 67–68°, collected in the lower part of the condenser. Upon cooling, solid material separated from the reaction mixture. Recrystallization from benzene gave nicely crystalline material, m. p. 148–150°, not depressed upon admixture with authentic benzenesulfonamide.

URBANA, ILL. RECEIVED JULY 27, 1950

---

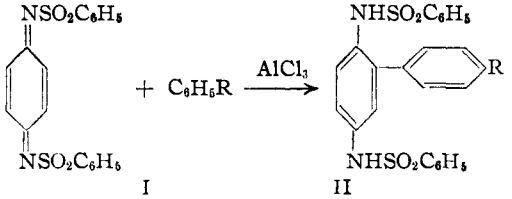
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Quinone Imides. V. Aluminum Chloride-catalyzed Arylations of *p*-Quinone Dibenzenesulfonimides

BY ROGER ADAMS AND KENDRICK R. EILAR

Aromatic hydrocarbons, phenols and phenolic ethers in the presence of aluminum chloride react with *p*-quinone dibenzenesulfonimides to give 2-aryl-*p*-phenylenedibenzenesulfonamides in yields of 26 to 67%. In the addition of hydrocarbons, it is essential that the quinone diimide be added to the aluminum chloride in the hydrocarbon; addition of the aluminum chloride to the hydrocarbon solution of the quinone diimide results in quantitative reduction of the quinone diimide to *p*-phenylenedibenzenesulfonamide. Boron trifluoride, as catalyst, is effective in the addition of phenolic compounds and phenol ethers but not of the hydrocarbons regardless of the order of addition of reactants. Attempted oxidation of the 2-aryl-*p*-phenylenedibenzenesulfonamides to the corresponding quinones was successful only in the case of 2-(β-hydroxy-α-naphthyl) compound; the other sulfonamides either resisted oxidation or were degraded to *p*-quinone dibenzenesulfonimide.

Pummerer and co-workers discovered that a variety of aromatic compounds in the presence of aluminum chloride will add, presumably by a 1,4 process, to *p*-benzoquinone to give 2,5-diarylhydroquinones.[1] This reaction has now been extended to *p*-quinone dibenzenesulfonimide (I).[2] The arylation




I II

of the quinone diimide terminates with the monosubstituted *p*-phenylenediamine derivative; thus, reaction of *p*-quinone dibenzenesulfonimide (I) with benzene gives 2-phenyl-*p*-phenylenedibenzenesulfonamide (II, R = H) in 67% yield, when the quinone diimide is added to a mixture of aluminum chloride in benzene. When the addition is reversed, the introduction of aluminum chloride to a solution of the quinone diimide in benzene, reduction takes place quantitatively with formation of the parent *p*-phenylenedibenzenesulfonamide. The oxidation product of the benzene in the latter reaction was presumably biphenyl, although it was not isolated and identified.

The reaction of *m*-xylene with I, carried out by adding the quinone diimide to a mixture of aluminum chloride in *m*-xylene, gives a mixture of products. Three were isolated; one was the expected adduct (III), the second, *p*-phenylenedibenzenesulfonamide formed by reduction of the quinone di-

(1) R. Pummerer and E. Prell, *Ber.*, **55**, 3105 (1922); R. Pummerer and H. Fiedler, *ibid.*, **60**, 1439 (1927); R. Pummerer and G. Huppmann, *ibid.*, **60**, 1442 (1927); R. Pummerer, M. Dally and S. Reissinger, *ibid.*, **66**, 792 (1933).

(2) R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950); see also R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950); R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951); R. Adams and J. H. Looker, *ibid.*, **73**, 1145 (1951).