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DERIVATIVES OF SULFENIC ACIDS. XV. A NEW SYNTHESIS OF THIOPHENOLS

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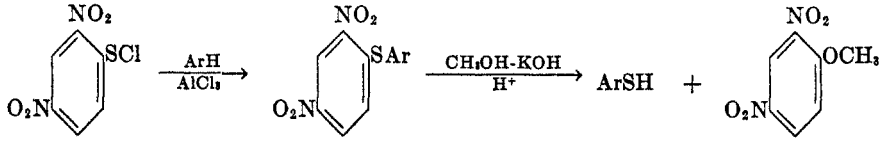
Herz and Tarbell (1), as well as Bordwell, Andersen, and Pitt (2) have recently reported interesting new syntheses of thiophenols. The purpose of the present communication is to report still another novel and essentially simple method for preparing thiophenols. The original work was completed in this laboratory a few years ago (3), and has subsequently proved useful in certain of our studies.

The new thiophenol synthesis involves a two step sequence, wherein (*a*) the reaction of 2,4-dinitrobenzenesulfenyl chloride (I) with an aromatic substance yields a corresponding aryl 2,4-dinitrophenyl sulfide (II); and (*b*) the sulfide is cleaved by alkali, and the mixture is acidified to yield the desired thiophenol (III). Thus, scission of the appropriate examples of II (*Cf.* the experimental



I II III

part) leads to thiophenol (80%, isolated as the lead salt), *p*-thiocresol (80%), *p*-xenylthiol (70%), *p*-bromothiophenol (79%), and *p*-chlorothiophenol (76%).

Since the reaction of I with aromatic systems promises to be a very general one (4), the aryl 2,4-dinitrophenyl sulfides should prove to be readily obtained, easily stored, and useful intermediates for the preparation of the thiophenols by the above sequence. The synthesis is especially convenient for the preparation of small amounts of thiophenols, although it can be easily scaled up, and the yields appear comparable to or better than those obtained by other methods. The success of the new synthesis depends, of course, on the easy displacement of the ArS^- group, by nucleophilic attack of the base on II. Sodium methoxide in methanol solution may also be used, in place of potassium hydroxide, as the base in the conversion of II to III.

The possibility of extending the above synthesis of thiols to the preparation of corresponding sulfinic acids is suggested by the rapid cleavage of phenyl 2,4-dinitrophenyl sulfone (easily available by oxidizing the sulfide) with methanolic alkali, and isolation of benzenesulfinic acid (79% crude yield) from the acidified reaction mixture. Backer (5) has recently reported a similar scission of this sulfone with ammonia and with benzylamine. The syntheses of three new aryl 2,4-dinitrophenyl sulfides (Ar = 2,4-dimethylphenyl, 2,4,6-trimethylphenyl, and *p*-diethylaminophenyl), *via* I and the appropriate aromatic systems, are also recorded in the experimental part.

Acknowledgment. We are indebted to Dr. Charles M. Buess for carrying out preliminary studies of the above method for the synthesis of thiophenols and to Dr. Maurice B. Sparke for checking the utility of the synthesis in the case of *p*-chlorothiophenol.

EXPERIMENTAL[1]

Aryl 2,4-dinitrophenyl sulfides. The sulfides required for the preparation of the thiols reported above had been synthesized previously (4) in about 1-g. lots for characterization purposes. They were now prepared in 10–20 g. amounts, or sometimes larger, as follows.

p-Xenyl 2,4-dinitrophenyl sulfide. Biphenyl (7.2 g., 0.05 mole) and I (9.4 g., 0.04 mole) were dissolved in 100 ml. of dry ethylene chloride, in a 3-necked flask equipped with a stirrer and thermometer. The mixture was cooled to −20° in a calcium chloride-ice bath, and 16 g. (0.12 mole) of reagent grade aluminum chloride was added at once. The solution turned red, hydrogen chloride was evolved, and the temperature of the mixture rose to −10°. After stirring 5 minutes at −10°, 20 ml. of absolute alcohol was added slowly, keeping the temperature below 0°. The orange mixture was extracted with two 100-ml. portions of 6 *N* hydrochloric acid, the clear organic layer was separated, and the volume of the latter was reduced to 35 ml. by aspirating the solvent from the heated solution. Petroleum ether (*ca.* 100 ml., boiling 63–69°) was added, the mixture was thoroughly chilled, and the precipitate was collected and dried. The product consisted of yellow plates; 12.8 g. (91%), melting at 143–147°, and raised to 146–147° by recrystallization from absolute alcohol. The higher-melting value corresponds to that recorded by Bost, *et al.* (6). The lower-melting product was cleaved to 4-mercaptobiphenyl (see below).

The *p*-xenyl sulfide was also prepared (86%; m.p. 143–145°), using a molar ratio of aluminum chloride to I of 1:1, and a reaction period of 30 minutes, at 0°. To assure that the above product was the *para* isomer, it was compared with the analytically pure *ortho* isomer (m.p. 130–132°). The two products gave a sharp depression in melting point when admixed.[2]

p-Bromophenyl 2,4-dinitrophenyl sulfide, melting at 137–139°, was prepared at 20°, in 80% yield, by the above detailed procedure for the *p*-xenyl sulfide; and 2,4-dinitrophenyl phenyl sulfide (m.p. of product directly from reaction mixture, 116–118.5°) was also thus prepared in 91% yield. *p-Chlorophenyl 2,4-dinitrophenyl sulfide* was prepared (94% crude yield), starting with 0.25 mole of I, 0.75 mole of aluminum chloride, and 0.25 mole of chlorobenzene, at 0°, for 30 minutes. These sulfides were used for the cleavages without further purification, although a single crystallization from absolute alcohol raised the melting points to the recorded values (4) of 140–141°, 120–120.5°, and 123–124°, respectively.

2,4-Dinitrophenyl p-tolyl sulfide was prepared at −10° (92% crude product, melting at 76–85°). The product, m.p. 99–100.5°, used for cleavage to *p*-thiocresol, resulted in 70% over-all yield by recrystallizing from a benzene-methanol mixture (1:5 by volume). That the crude product from toluene contained some *ortho* isomer was shown as follows. The mother liquor from the above preparation was evaporated and the residue was oxidized (hydrogen peroxide-glacial acetic acid) to a mixture of the isomeric sulfones. Fractionation from methanol led to low recovery (*ca.* 1%) of 2,4-dinitrophenyl *o*-tolyl sulfone, m.p. 152–154°, which did not depress the melting point of the authentic sulfone (m.p. 154–155°) prepared by the method of Bost, *et al.* (6); *Cf.* also Bost, Turner, and Conn (7). The isomeric *p*-tolyl sulfone was also isolated; m.p. 185–187°, compared to the corrected recorded value (6) of 189.5°.

p-Diethylaminophenyl phenyl sulfide was prepared by reaction of I (2.3 g.) and 5 g. of diethylaniline (b.p. 93–95°, 10 mm.), in 75 ml. of glacial acetic acid, at 100° for 5 minutes. The mixture was cooled to room temperature and poured on 300 g. of ice. Recrystallization from absolute ethanol-acetone (1:1 by volume) gave 2.8 g. of red crystals, melting at 141–

[1] The analyses were made by Mr. J. V. Pirie. Melting points are uncorrected.

[2] The *ortho* isomer, previously unreported, was kindly supplied by Mr. S. J. Assony.

143° (81% yield). Recrystallization from chloroform-methanol (1:1 by volume) gave 2.4 g.; 70% over-all yield, m.p. 146–147°.

Anal. Calcd for $C_{16}H_{17}N_3O_4S$: C, 55.32; H, 4.93.

Found: C, 55.21; H, 5.11.

The products from *m*-xylene and mesitylene were obtained in good yields by the method of Buess and Kharasch (4), using aluminum chloride. The products melted at 141–142° and 171–172°, respectively.

Anal. Calc'd for *2,4-dimethylphenyl 2',4'-dinitrophenyl sulfide* ($C_{14}H_{12}N_2O_4S$): C, 55.25; H, 3.98.

Found: C, 55.31; H, 4.03.

Anal. Calc'd for *2,4,6-trimethylphenyl 2',4'-dinitrophenyl sulfide* ($C_{15}H_{15}N_2O_4S$): C, 56.60; H, 4.43.

Found: C, 56.74; H, 4.08.

Cleavage of aryl 2,4-dinitrophenyl sulfides to thiophenols. The general procedure is exemplified for the case of *p*-thiocresol. To a solution of 5.6 g. (0.1 mole) of C.P. potassium hydroxide in 250 ml. of methanol (the C.P. reagent was generally used, but is not strictly necessary) was added 14.6 g. (0.05 mole) of 2,4-dinitrophenyl *p*-tolyl sulfide (m.p. 99–100.5°). The suspension was heated to reflux, forming a blood-red solution. After 30 minutes, 150 ml. of solvent was distilled from the mixture, the residue was thoroughly cooled, and crushed ice was added to bring the volume to 400 ml. The precipitated product, collected and recrystallized from hot methanol (using charcoal), melted at 93–95° and did not depress the melting point of authentic 2,4-dinitroanisole. The filtrate from the major reaction mixture was acidified with concentrated hydrochloric acid to precipitate crude *p*-thiocresol. This was purified by steam-distillation, and dried in *vacuo* over sulfuric acid, giving white plates; 5 g., 80%, m.p. 41–43°. Lit. (8), 43–44°. The product was identified by reconversion to 2,4-dinitrophenyl *p*-tolyl sulfide (m.p. 102–103°), by reaction with 2,4-dinitrochlorobenzene.

Similar procedures, using 0.05 mole of the appropriate aryl 2,4-dinitrophenyl sulfide were used in the other cases. *p*-Xenylthiol was obtained in 70% yield; m.p. 107–110°. The recorded value (9) is 110–111°. Refluxing for 90 minutes was required in this case for complete solution of the sulfide. *p*-Bromothiophenol (79%), m.p. 71–73° [Lit. (10), 70–71° and 74–75°] resulted after a 40-minute reflux period; and thiophenol (80% yield) was isolated as the lead salt, by adding lead acetate to the steam-distillate. The identity of each of these thiophenols was established by reconversion to the respective aryl 2,4-dinitrophenyl sulfides, through reaction with 2,4-dinitrochlorobenzene. *p*-Chlorothiophenol was obtained on a somewhat larger scale, in 76% yield, from 71 g. of crude *p*-chlorophenyl 2,4-dinitrophenyl sulfide, by heating with 28.0 g. (0.5 mole) of potassium hydroxide in 1.25 liters of methanol, at reflux for 30 minutes, acidifying and steam-distilling the product. Identity of the latter was confirmed by conversion to the sulfenyl chloride and preparation of derivatives of the latter (11).

Benzenesulfinic acid from 2,4-dinitrophenyl phenyl sulfone. The sulfone was obtained in 98% yield by reaction of 15.5 g. (0.056 mole) of 2,4-dinitrophenyl phenyl sulfide with 15 ml. of 30% hydrogen peroxide, in 250 ml. of glacial acetic acid, at 100°, until the yellow color of the sulfide disappeared entirely (*ca.* two hours). The product, precipitated by diluting the reaction mixture with water, had m.p. 157.5–158.5° and was used as such for the cleavage. The pure sulfone, prepared by permanganate oxidation melts (6) at 161°, corr. The sulfone, 10.6 g. (0.034 mole) was suspended in a solution of 3.3 g. (0.06 mole) of potassium hydroxide in 300 ml. of methanol, and refluxed for one hour. The methanol was completely removed from the resulting solution by distillation at reduced pressure, and the residue was extracted with 200 ml. of warm water. The remaining solid melted at 87–90°, and was judged to be crude 2,4-dinitroanisole. The alkaline extract was cooled to 0° and the solution just acidified with concentrated hydrochloric acid. The white crystals were collected and purified by dissolving in alkali and reprecipitating by acidification (twice repeated). The product was dried *in vacuo* over sulfuric acid for 15 hours; 3.9 g. (79%),

melting at 79–82°; Lit. (12), 83°. In another run, a final purified product, melting at 82–84°, was isolated in 41% yield. The acid was characterized by conversion to *phenyl picryl sulfone*, dec. 233–235°; Lit. (13), 233°.

SUMMARY

A new two step synthesis of thiophenols is described. The method consists of preparing the appropriate aryl 2,4-dinitrophenyl sulfide, by reaction of 2,4-dinitrobenzenesulfenyl chloride and an aromatic substance, and subsequent cleavage of the sulfide with alkali.

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