dicated by the yellow color of the filtrates likewise could not be isolated pure.

The filtrates were concentrated to dryness and chromatographed on alumina. The benzene eluate yielded the acyloin, m.p. 123–124° from ethanol.

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57. Found: C, 82.91; H, 8.75.

The Kolbe Electrolysis of Potassium 1-Phenylcyclopentanecarboxylate.—The method of Fichter and Stenzl[13] was used. In a 50-ml. beaker 1.5 g. of acid was dissolved in 30 ml. of anhydrous methanol containing 0.3 g. of potassium hydroxide and 10 ml. of dry pyridine. The solution was electrolyzed at 0.3 amp. and 6 volts for four hours. The resulting dark brown solution was evaporated to dryness, dissolved in water and extracted with ether. The ether layer was washed with dilute hydrochloric acid, then water, and finally evaporated to dryness. The residue was recrystallized several times from ethanol–water, m.p. 137–138°. The mixed melting point with V was 136–138°.

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[13] F. R. Fichter and H. Stenzl, *Helv. Chim. Acta*, **22**, 970 (1939).

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

Cleavage of Sulfonamides with Aqueous Hydrobromic Acid and Phenol. II

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The cleavage of sulfonamides by aqueous hydrobromic acid is an oxidation–reduction process in which disulfides are produced. When phenol is present in the reaction mixture disulfides are not formed. β-Naphthalenesulfonanilide reacts with phenol and hydrobromic acid to yield a hydroxyphenyl β-naphthyl sulfide as the principal sulfur-containing product. A mechanism for the process is discussed.

In the previous communication[2] a rapid cleavage of sulfonamides by hydrobromic acid and phenol was described. It was shown that the presence of phenol protected aromatic amines, when these were liberated in the cleavage, from bromination, presumably by reacting with a brominating agent formed in an oxidation–reduction process involving the sulfonyl function and the hydrobromic acid. The fate of the sulfur atom was not determined. In a somewhat similar cleavage of *p*-toluenesulfonamides by anhydrous hydrogen bromide and acetic acid Ohle and his associates[3] found di-*p*-tolyl disulfide as the reduction product. However in their studies bromine acceptors were not added, and the aromatic amines liberated in the cleavage were brominated. The present study was undertaken to determine the fate of the sulfur atom in cleavage by aqueous hydrobromic acid in the presence of phenol.

In the first experiments benzenesulfonanilide and *p*-toluenesulfonanilide were cleaved with 48% aqueous hydrobromic acid alone. Diphenyl disulfide and di-*p*-tolyl disulfide, respectively, were found among the reaction products; pure aniline was not isolated, but instead a mixture of aniline and its bromination products was obtained. There was no indication of the presence of a thiophenol in any of these reaction mixtures. Cleavages of benzenesulfonanilide were carried out in the presence of phenol, added in successive experiments in successively greater concentrations, up to a weight amount equal to that of the sulfonanilide. It was found that the amount of disulfide formed decreased with increasing phenol concentration; no disulfide was detected at the highest concentration of phenol. In these experiments it was noted that the purity of the aniline formed increased with the concentration of the phenol. Examination of the alkali-soluble fraction in the reaction mixture in which the largest amount of phenol was employed revealed that *p*-bromophenol was a major product.

None of the above reaction mixtures had the characteristic odor of thiophenols. Nevertheless, chemical tests for thiophenols were conducted. When they proved to be negative a cleavage of methanesulfonanilide in the presence of phenol was carried out. If methyl mercaptan (b.p. 6°) were an intermediate it should have been evolved during the cleavage. No liquid condensed in a Dry Ice trap connected to the apparatus used, and only a very faint odor, which might have been due to traces of this mercaptan, could be detected.

The results of the above experiments indicated that the reduction products containing sulfur were removed from the reaction mixtures along with the phenol. It was observed in the distillation of samples of recovered phenol that high-boiling residues were present; decomposition occurred near the end of such distillations, and the odors of the decomposition products suggested the presence of sulfur-containing compounds. In cleavages of β-naphthalenesulfonanilide with hydrobromic acid the phenolic fraction was found to contain a crystalline material which could be separated easily from phenol and bromophenols. This substance had the composition of a hydroxyphenyl β-naphthyl sulfide; it is probably the *p*-hydroxy compound. The yield of the pure compound was as high as 63%, based on the sulfonanilide cleaved. Thus it appears that in the cleavage in the presence of the phenol the major, and perhaps the only, sulfur-containing reduction product is a sulfide containing one group derived from the sulfonamide and one derived from phenol.

Ohle[3] proposed that the first step in the hydrogen bromide–acetic acid cleavage is the formation of the amine hydrobromide and the sulfonyl bromide, and that the sulfonyl bromide is reduced to the disulfide by further action of hydrogen bromide. This view is supported by the fact that sulfonyl

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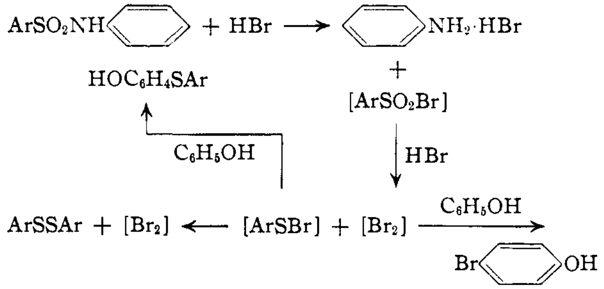
[1] Minnesota Mining and Manufacturing Co. Fellow, 1950–1951.

[2] H. R. Snyder and R. E. Heckert, THIS JOURNAL, **74**, 2006 (1952). See also D. I. Weisblat, B. J. Magerlein and D. R. Myers, U. S. Patent 2,562,222 (July 31, 1951), and D. I. Weisblat, Abstracts of the Twelfth International Congress of Pure and Applied Chemistry (Sept., 1951), p. 76.

[3] H. Ohle, H. Friedeberg and G. Haeseler, *Ber.*, **69**, 2311 (1936).

halides are known to be reduced by hydrogen bromide[4] to disulfides. The present work suggests that sulfenyl bromides (ArSBr) also may be intermediates. Their occurrence would account both for the formation of disulfides in the absence of phenol and for the production of a hydroxyphenyl sulfide in the presence of this reagent. Fries and Schürmann[5] found that 2-nitro-4-chlorobenzenesulfenyl bromide decomposes to the disulfide and bromine in boiling acetic acid containing a trace of hydrogen bromide. Kharasch[6] has found that 2,4-dinitrobenzenesulfenyl chloride reacts with resorcinol to yield a sulfide.



An alternative mechanism in which a free mercaptide radical (RS· or ArS·) attacks phenol might be written for the reaction leading to the hydroxy sulfide. If this were the true mechanism one would expect that the oxidation of a thiophenol in the presence of phenol also would yield a hydroxy sulfide. However, when *p*-thiocresol was oxidized with bromine in the presence of a large quantity of phenol no such sulfide was formed; the disulfide was isolated in 81% yield.

In several of the cleavage experiments searches were made for sulfonic acids formed by hydrolysis, since the similar cleavages with hydrogen iodide[7] have been regarded[8] as combinations of hydrolysis and reduction. Only in the cleavage of mesitylenesulfonanilide was there any indication of significant hydrolysis. In this instance both mesitylene and sulfuric acid were detected in 8% yield, based on the sulfonamide destroyed. These products may have resulted from the hydrolysis of mesitylenesulfonic acid. However, it is possible that mesitylene and phenylsulfamic acid are produced to a minor extent, and that the sulfuric acid arises by hydrolysis of the phenylsulfamic acid.

Experimental

General Procedure.—(Step A): The sulfonamide, 48% hydrobromic acid and phenol, if any was used, were heated under reflux in all-glass apparatus for the period indicated. (Step B): The mixture then was cooled rapidly and washed into a separatory funnel with ether or carbon tetrachloride. The organic layer was separated and combined with one or more similar extracts of the acid solution (the combined extract is referred to as extract B). (Step C): The acid solution remaining was carefully treated with an excess of sodium hydroxide, and the resulting alkaline solution (aqueous solution C) was extracted with ether, to give ether solution C. (Step D): The dried ether solution C was saturated with dry hydrogen chloride to cause the separation of solid amine hydrochloride, or mixture of amine hydrochlorides (precipitate D).

1. **Cleavage of Benzenesulfonanilide with Hydrobromic Acid Alone.**—In step A, 10.0 g. of the sulfonanilide and 75 ml. of 48% hydrobromic acid were refluxed for 30 minutes. The ether extract B was concentrated to an oil which was dissolved in hot 95% ethanol; cooling caused the separation of a solid which was washed successively with 10% sodium hydroxide, water, 5% hydrochloric acid and water. The remaining solid was recrystallized from 95% ethanol as 1.49 g. (30%) of white needles melting at 57.5–58.5°. After a second recrystallization the melting point was 60.1–60.6°, alone or mixed with authentic diphenyl disulfide.[9]

The precipitate D did not melt, but sintered at about 200°; it undoubtedly consisted of hydrochlorides of brominated anilines (see experiment 3).

2. **Cleavage of Benzenesulfonanilide in the Presence of Phenol.**—Repetition of the preceding experiment with addition of 5.0 g. of phenol at step A resulted in the formation of 0.5 g. (11%) of diphenyl disulfide, isolated from extract B by removal of acidic materials with dilute sodium hydroxide, evaporation of the solvent (CCl_4) and recrystallization of the residue from ethanol. Precipitate D (3.4 g., 61%, reckoned as aniline hydrochloride) melted at 165–175°; recrystallization from absolute ethanol by the addition of ether raised the melting point to 189–191° (aniline hydrochloride, m.p. 192°,[10] 198°[11]).

Repetition of the experiment with 7 g. of phenol added at step A also resulted in the formation of the disulfide in 11% yield. The weight of precipitate D was the same (3.4 g.), but the melting point was higher (176–180°); recrystallization as before raised the melting point to 188–190°.

In similar experiments in which 10 g. of phenol was added at step A, no diphenyl disulfide was obtained. In such an experiment ether solution B after extraction with dilute alkali and evaporation yielded only a trace of neutral material. Aniline hydrochloride (precipitate D) from this experiment amounted to 69% yield and melted at 190–192°.

The last experiment was repeated, and the carbon tetrachloride extract B, *without* preliminary washing with dilute alkali, was concentrated and the residue was distilled under diminished pressure. The main fraction, collected at 90–105° (4.5–5.0 mm.), was a pale yellow oil of phenolic odor; redistillation gave 2.3 g. of a colorless oil, b.p. 78–80° (2 mm.). Although this oil did not crystallize it was shown to be essentially *p*-bromophenol by conversion to the benzoate, melting at 102–102.5° (*p*-bromophenyl benzoate,[12] m.p. 102°).

3. **Cleavage of *p*-Toluenesulfonanilide.**—In an experiment in which 50 g. of the sulfonamide was refluxed 1.5 hours with 250 ml. of 48% hydrobromic acid, the ether extract B on concentration gave an orange-colored oil which partially crystallized on cold storage but melted quickly on removal from the refrigerator. When a 5-g. portion of this oil was subjected to sublimation at 0.2 mm., bath temperature 60–120°, 1.2 g. of a white waxy sublimate was obtained. Recrystallization first from ethanol and then from low boiling petroleum ether gave 0.4 g. of *sym*-tribromoaniline, m.p., alone or mixed with an authentic sample, 119–120°. Concentration of the ethanolic mother liquor gave a solid which, after recrystallization from petroleum ether, melted at 80–82° and gave a benzoyl derivative melting at 135–136.5°. 2,4-Dibromoaniline melts at 79° and yields a benzoyl derivative of m.p. 134°.[13] The residue from the sublimation partially crystallized after several days, and 0.83 g. of material melting at 36–41° was collected by filtration. Recrystallization from dilute ethanol raised the melting point to 45–46°, and admixture of di-*p*-tolyl disulfide did not cause any depression.

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(4) F. Challenger, S. Miller and G. Gibson, *J. Chem. Soc.*, 769 (1948).

(5) K. Fries and G. Schürmann, *Ber.*, **47**, 1195 (1914).

(6) C. Buess and N. Kharasch, THIS JOURNAL, **72**, 3529 (1950). See also N. Kharasch and T. Bruice, *ibid.*, **73**, 3240 (1951), and N. Kharasch, S. Potempa and H. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

(7) E. Fischer, *Ber.*, **48**, 93 (1915); K. Miescher and J. Billeter, *Helv. Chim. Acta*, **22**, 601 (1939).

(8) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 583.

(9) J. Stenhouse, *Ann.*, **149**, 251 (1869).

(10) A. Pinner, *Ber.*, **14**, 1083 (1881).

(11) F. Ullmann, *ibid.*, **31**, 1699 (1898).

(12) R. Shriner and R. Fuson, "The Systematic Identification of Organic Compounds," ed. 3, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 272.

(13) Reference 12, p. 239.

Steam-distillation of the major portion of the orange oil caused the volatilization of a little tribromoaniline and 2,4-dibromoaniline, but the residual oil did not crystallize on cooling. The oil was dried and distilled under diminished pressure; small further quantities of the amines which sublimed first were rejected, and di-*p*-tolyl disulfide was collected at 133–135° (0.1 mm.) as an oil which crystallized on standing. Recrystallization from ethanol gave material of m.p. 45–46.5°, alone or mixed with a known sample. The total yield of the disulfide was 10.0 g. (41%).

Precipitate D, weight 30.2 g., from this experiment evidently was a mixture of aniline hydrochloride and bromoaniline hydrochlorides. It sintered at about 200°, but melting was not complete at 225°. No attempt to separate this mixture was made.

4. **Cleavage of Methanesulfonanilide with Hydrobromic Acid and Phenol.**—In step A 15 g. of the anilide, 20 g. of phenol and 100 ml. of 48% hydrobromic acid were refluxed for one hour under a condenser which was connected to a Dry Ice cooled trap. At the end of the reflux period the trap contained only a trace of liquid; the presence of methylmercaptan (b.p. 6°) was suggested by the odor, but the minute quantity of material was insufficient for chemical tests.

The acidic reaction mixture was extracted with three 100-ml. portions of ether in a separatory funnel and with a fourth portion in a continuous extractor for 24 hours. Evaporation of the combined extracts left an oil, with the odor of phenol, from which no dimethyl disulfide (b.p. 116–118°) could be obtained by distillation.

Aniline hydrochloride melting at 191–194° was isolated in a yield of 8.7 g. (77%) by treating the extracted acidic solution as described above.

5. **Cleavage of β-Naphthalenesulfonanilide with Hydrobromic Acid and Phenol; Isolation of Hydroxyphenyl β-Naphthyl Sulfide.**—A mixture of 5 g. of the sulfonanilide, 10 g. of phenol and 60 ml. of 48% hydrobromic acid was refluxed for 40 minutes. Heating was discontinued and the mixture was left to cool in the air for one hour. The mixture was washed with 250 ml. of water into a 500-ml. flask which was then immersed in ice–salt for 30 minutes, during which time the organic layer solidified. The mixture was stored in the refrigerator for several hours and then filtered. The solid was washed seven times with 20-ml. portions of water to remove the greater part of the phenol. The solid then was dried in a desiccator over sulfuric acid. The dried solid still contained much phenol. It was dissolved in 200 ml. of 5% sodium hydroxide, the solution was extracted with ether, and the acidic material was regenerated by acidification of the aqueous solution. The solid was collected as before, washed with five 20-ml. portions of water, and recrystallized from dilute ethanol, yielding a first crop of 1.86 g. of a white substance melting at 117–118° and a second crop of 0.41 g. of a brown material melting at 109–111°. Recrystallization of the second crop raised the melting point to 118–119°; the total of material melting above 117° was 2.2 g. (50%). The analytical sample, prepared by three recrystallizations of material from the first crop from dilute ethanol, melted at 119.5–120°.

Anal. Calcd. for $C_{16}H_{12}OS$: C, 76.16; H, 4.79; S, 12.71. Found: C, 75.87; H, 4.88; S, 12.81.

The filtered original reaction mixture yielded 1.81 g. (79%) of aniline hydrochloride, melting at 198–199°, isolated in the usual manner.

6. **Cleavage of Mesitylenesulfonanilide with Phenol and Hydrobromic Acid.**—After a mixture of 9.2 g. of the sulfonanilide, 7.8 g. of phenol and 60 ml. of 48% hydrobromic acid had been refluxed for one hour it was steam distilled until about 2 l. of distillate had collected. The distillate was extracted with ether, and the ether extracts were washed with alkali, dried and concentrated to give 0.21 g. (5%) of a liquid, boiling at 159–161°, which possessed the characteristic odor of mesitylene.

The residue from the steam distillation was extracted with ether and the aqueous solution was made alkaline to cause the separation of aniline, which was isolated as the hydrochloride (2.5 g., 58%, m.p. 189–191.5°) in the usual manner. The alkaline solution from which the aniline was separated was reacidified with 43 ml. of 48% hydrobromic acid and boiled under reflux for 21 hours, to complete the hydrolysis of any mesitylenesulfonic acid which might not have been cleaved during the steam distillation. The addition of barium chloride caused the precipitation of 0.3748 g. of solid presumed to be barium sulfate. This amount of barium sulfate corresponds to 5% yield based on mesitylenesulfonanilide employed, or to 8% of the amount cleaved to aniline.

7. **Search for Benzenesulfonic Acid in Mixtures from the Cleavage of Benzenesulfonanilide.**—Only one of several experiments carried out is described. After being refluxed for 30 minutes, a mixture originally containing 44.6 g. of benzenesulfonanilide, 44 g. of phenol and 220 ml. of 48% hydrobromic acid was washed into a separatory funnel with 160 ml. of water and extracted with three 100-ml. portions of benzene. The aqueous layer was made alkaline by the addition of a solution of 68.5 g. of sodium hydroxide in 225 ml. of water, and the aniline which separated was collected in ether and isolated as the hydrochloride (16.4 g., 66%, m.p. 190–192°) in the usual manner. The alkaline solution remaining after removal of the aniline was neutralized to *p*H 6 by the addition of hydrobromic acid and then was evaporated to dryness. The residual salt was ground and dried for four hours at 140°. It was then placed in a 300-ml. flask fitted with a glass-joined condenser, 22 g. of phosphorus pentachloride was added, and the mixture was heated at 170–180° for 18 hours. The odor of free chlorine was evident, and the reaction mixture took on the color of free bromine. The mixture finally was cooled and added to a mixture of 1 kg. each of ice and water. The resulting mixture was extracted three times with 100-ml. portions of benzene, and the combined extract was concentrated to 20 ml. and then stirred vigorously with 20 ml. of concentrated ammonia. Acidification of the ammoniacal layer produced 0.2 g. of pure, white crystals melting at 179–180°. This substance probably is 2,5-dichlorobenzenesulfonamide (m.p. 181°[14]) in a yield of less than 0.5%. Evidently the very small amount of benzenesulfonyl chloride formed in the reaction with phosphorus pentachloride was chlorinated by the excess reagent.

8. **Formation of Di-*p*-tolyl Disulfide by the Action of Bromine on *p*-Thiocresol in the Presence of Phenol.**—To a solution of 2 g. (0.016 mole) of *p*-thiocresol and 10 g. (0.10 mole) of phenol in 10 ml. of carbon tetrachloride was added over a period of 10–15 minutes a solution of 2 g. (0.013 mole) of bromine in 10 ml. of the same solvent. The bromine color was discharged rapidly and hydrogen bromide was evolved. The solution was warmed on the steam-bath to drive out the residual hydrogen bromide, and it was then extracted with two 50-ml. portions of 5% sodium hydroxide. Acidification of the extracts caused the separation of an oil which did not deposit any crystalline solid when stored in the refrigerator in contact with sufficient water to prevent the crystallization of the phenol itself. The remaining carbon tetrachloride solution was evaporated to dryness; the residue crystallized on cooling and melted at 45.5–47°. It weighed 1.29 g. (81%). Recrystallization from dilute ethanol raised the melting point to 46–47.5°. A mixed melting point with di-*p*-tolyl disulfide was 46–48°.

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(14) Reference 12, p. 274.