714. *The Decomposition of Arylthiolsulphonic Acids. Identification of Thiolsulphonic and Sulphinic Acids as Benzylthiuronium Derivatives.*

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When liberated from their alkali salts with mineral acids, arylthiolsulphonic acids are rapidly decomposed into diarylsulphonyl trisulphide, aryl arylthiolsulphonate, and sulphur. A possible mechanism of this reaction is discussed. Both thiolsulphonic and sulphinic acids are conveniently characterised as benzylthiuronium salts.

ARYLTHIOLSULPHONIC acids are well known in the form of their salts, but are not stable in the free state. Blomstrand (*Ber.*, 1870, **3**, 963) and Otto and Tröger (*ibid.*, 1891, **24**, 492) reported that thiolsulphonic acids, when set free from their salts with mineral acids, decomposed almost immediately into the corresponding sulphinic acids and sulphur (equation 1), the latter giving rise to unspecified by-products; experimental details, however, were not given.

When postulating the intermediate formation of arylthiolsulphonic acids in a reaction involving arylthioureas, we (*J.*, 1950, 3269) referred to experiments on the decomposition of arylthiolsulphonic acids. The present paper records more detailed observations, arising from this work, on the instability of arylthiolsulphonic acids in strongly acid media.

When an arylthiolsulphonic acid was liberated from its salt under a variety of conditions, a diarylsulphonyl trisulphide, an aryl arylthiolsulphonate, and sulphur were obtained in approximately equivalent quantities. The addition of a large excess of hydrochloric acid to sodium toluene-*p*-thiolsulphonate, for example, produced an abundant precipitate, which was readily separated into ditoluene-*p*-sulphonyl trisulphide, *p*-tolyl toluene-*p*-thiolsulphonate, and sulphur. Varying small quantities of toluene-*p*-sulphinic acid were also formed. The same products resulted when the decomposition was carried out more slowly in stages. Comparable results were obtained with naphthalene-2-thiolsulphonic acid. The predominating reaction is satisfactorily represented by the overall equation (2) which agrees well with the observed yields of the individual products.

$$R{\cdot}SO_2{\cdot}SH \longrightarrow R{\cdot}SO_2H + S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$4R{\cdot}SO_2{\cdot}SH \longrightarrow (R{\cdot}SO_2)_2S_3 + R{\cdot}SO_2{\cdot}SR + 2H_2O + S \quad . \quad . \quad . \quad (2)$$

Smaller concentrations of mineral acids also caused decomposition according to equation (2), but affected only part of the thiolsulphonic acid present, the remainder being unchanged. An aqueous solution of sodium toluene-*p*-thiolsulphonate, for example, when treated with 1 equiv. of hydrochloric acid and stored at room temperature for 12 hours, gave a mixture which, though acid to Congo-red, decomposed according to equation (2) to the extent of only 25—30%. The bulk of unchanged thiolsulphonic acid was readily recovered as the benzylthiuronium derivative. In the presence of a weak acid, such as acetic acid, the thiolsulphonate entity was stable on short heating to 100°; solutions of pH 3·8—3·4 remained unchanged indefinitely at room temperature. Free arylthiolsulphonic acids thus possess some stability, provided that the concentration of the added mineral acid is not excessive and temperatures are fairly low.

Since the decomposition of arylthiolsulphonic acids (equation 2) proceeds rapidly under appropriate conditions, a mechanism involving ionic species may be considered. The experimental observations suggest that the thiolsulphonate ion is directly concerned in the reaction. Although a detailed mechanism cannot be decided upon with certainty, the following sequence of changes appears to account satisfactorily for the observed results :

$$3\mathrm{R{\cdot}SO_2{\cdot}SH} \dashrightarrow 3\mathrm{R{\cdot}SO_2H} + 3\mathrm{S} \quad \ldots\ldots \quad (3)$$

$$\longrightarrow \mathrm{R{\cdot}SO_2^-} + \mathrm{H^+} + 2\mathrm{R{\cdot}SO^+} + 2\mathrm{OH^-} + 3\mathrm{S} \quad \ldots\ldots \quad (4)$$

$$\text{or} \quad \left\{ \begin{aligned} &\longrightarrow \mathrm{R{\cdot}SO_2^-} + \mathrm{H^+} + \mathrm{R{\cdot}S^+} + \mathrm{R{\cdot}SO_2^+} + 2\mathrm{OH^-} + 3\mathrm{S} \quad \ldots \quad (5) \\ &\dashrightarrow \mathrm{R{\cdot}S^-} + \mathrm{H^+} + 2\mathrm{R{\cdot}SO_2^+} + 2\mathrm{OH^-} + 3\mathrm{S} \quad \ldots\ldots \quad (5a) \end{aligned} \right.$$

$$\mathrm{R{\cdot}SO_2SH} \longrightarrow \mathrm{R{\cdot}SO_2{\cdot}S^-} + \mathrm{H^+} \quad \ldots\ldots \quad (6)$$

From (5) and (6)

$$\left. \begin{aligned} \mathrm{R{\cdot}SO_2{\cdot}S^-} + \mathrm{R{\cdot}SO_2^+} + 3\mathrm{S} &\longrightarrow \mathrm{(R{\cdot}SO_2)_2S_3} + \mathrm{S} \\ \mathrm{R{\cdot}SO_2^-} + \mathrm{R{\cdot}S^+}\ (\text{or } \mathrm{R{\cdot}SO_2^+} + \mathrm{R{\cdot}S^-};\ \text{cf. equation } 5a) &\longrightarrow \mathrm{R{\cdot}SO_2{\cdot}SR} \\ 2\mathrm{H^+} + 2\mathrm{OH^-} &\longrightarrow 2\mathrm{H_2O} \end{aligned} \right\} \quad . \quad (7)$$

In this scheme the reaction is initiated by the fission of thiolsulphonic acid into sulphur and sulphinic acid (3); the sulphinyl ions ($\mathrm{RSO^+}$) arising therefrom (4) undergo an oxidation–reduction process to form sulphenyl and sulphonyl cations (5). The latter react with the excess of thiolsulphonate ions and yield, by simultaneous addition of two of the available sulphur atoms, the disulphonyl trisulphide. The remarkably ready conversion of disulphonyl monosulphides into trisulphides is well known (Tröger *et al.*, *Ber.*, 1891, **24**, 1125; *J. pr. Chem.*, 1899, **60**, 113). At the same time equivalent amounts of sulphenyl and sulphinate ions furnish aryl arylthiolsulphonate. Combination of these processes (7) results in the overall reaction (2). The oxidation–reduction stage of the above mechanism may occur, with identical final results, by different modes of oxygen transfer between the individual ions, but a definite choice cannot be made at present. One alternative in which the sulphinate ion gives up one atom of oxygen to each of the sulphinyl ions (*i.e.*, equations 4 and 5*a*), has the advantage of excluding the possibility of disulphone formation.

The suggested simultaneous ionisation of sulphinic acids in *two* distinct ways appears justifiable, when their well-known disarrangement into sulphonic acids and aryl arylthiolsulphonates is considered; this is generally accepted to proceed by the intermediate formation of sulphenic acids (Kharasch *et al.*, *Chem. Reviews*, 1946, **39**, 269) :

$$2\mathrm{R{\cdot}SO_2H} \longrightarrow \mathrm{R{\cdot}SO_3H} + \mathrm{R{\cdot}S{\cdot}OH} \quad \ldots \quad (8)$$

$$\mathrm{R{\cdot}SO_2H} + \mathrm{R{\cdot}S{\cdot}OH} \longrightarrow \mathrm{R{\cdot}SO_2{\cdot}SR} + \mathrm{H_2O} \quad \ldots\ldots \quad (9)$$

An ionic representation of this reaction, which occurs rapidly under suitable conditions, necessitates the presence of the organic residues in the form of both positive *and* negative ions. The second and third stage (4 and 5) of the mechanism for the decomposition of arylthiolsulphonic acids suggested above is in fact identical with one alternative by which the disarrangement of sulphinic acids may proceed; the eventual formation of diarylsulphonyl trisulphide instead of sulphonic acid is then ascribed simply to the presence of thiolsulphonate ion and sulphur.

The postulated direct participation of thiolsulphonate ions in the above reaction is indirectly supported by some observations on the interaction of arylsulphinic acids and sulphur in aqueous acids. Although diarylsulphonyl trisulphide and aryl arylthiolsulphonate were again the products of this reaction, it occurred considerably more slowly and failed to produce yields of diarylsulphonyl trisulphide comparable with those obtained in the decomposition of arylthiolsulphonic acids, even though the conditions of the two reactions were chosen as nearly identical as possible (*e.g.*, by supplying the sulphur in the colloidal state from acetone solution; cf. p. 3732). Varying quantities of unchanged sulphur and sulphinic acid were also recovered. The slower and incomplete formation of the trisulphide may here be due to the fact that thiolsulphonate ions are not immediately available at the beginning of the reaction, but are only formed comparatively slowly; a large proportion of the sulphinic acid may be expected to disarrange according to equations (8) and (9) before all the theoretically possible trisulphide has been formed, the yields of which are consequently lowered.

Further support for the above mechanism was finally obtained as follows: if arylthiolsulphonate ions are directly concerned in the decomposition of aromatic thiolsulphonic acids, the interaction, in acid media, of 3 equivs. of sulphinic acid and 2 equivs. of sulphur in the presence of 1 equiv. of thiolsulphonic acid (*i.e.*, in the proportions suggested by equations 3—7) should produce higher yields of diarylsulphonyl trisulphide than the sum of the yields that are *independently* obtainable, *under identical conditions*, by (*a*) the reaction between 3 equivs. each of sulphinic acid and sulphur, and (*b*) the decomposition of 1 equiv. of thiolsulphonic acid. Experiments showed that this requirement was fulfilled.

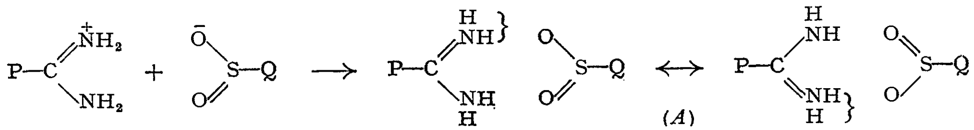
The above results appear to support the view that the decomposition of arylthiolsulphonic acids is unlikely to consist of a complete preliminary fission into sulphinic acid and sulphur, followed by their recombination to the final products, but that the thiolsulphonate entity takes part directly in the reaction.

Of other alternative mechanisms, brief reference will only be made to the possible initial simultaneous ionisation of thiolsulphonic acids into thiolsulphonate and hydrogen ions on the one hand, and sulphonyl and hydrosulphide ions on the other. This dissociation, however, should produce hydrogen sulphide, of which at least small quantities might be expected to escape from the strongly acid media employed, before undergoing further reaction. Since no trace of this substance was observed in any of the decomposition experiments, the intermediate occurrence of hydrosulphide ions appears unlikely.

The above experiments—and other work now being carried out—made it desirable to have available a method which facilitated the isolation and identification of sulphinic acids, and more particularly thiolsulphonic acids, for which suitable derivatives appeared to be lacking. We have found their benzylthiuronium salts useful for this purpose. With one exception (*viz.*, *p*-fluorobenzenesulphinic acid; Hann, *J. Amer. Chem. Soc.*, 1935, **57**, 2167), the applicability of this method to the sulphinic and thiolsulphonic acid series has not been previously examined. The benzylthiuronium derivatives of a few typical representatives of the two series are therefore now described. They were readily prepared, in excellent yields, by the general procedure (Donleavy and Johnson, *Science*, 1923, **57**, 753; Donleavy, *J. Amer. Chem. Soc.*, 1936, **58**, 1004), which was equally applicable to aliphatic and aromatic sulphinic and thiolsulphonic acids.

Although this method makes it possible to recover the above acids in the form of highly crystalline derivatives, even from dilute solutions, the properties of the benzylthiuronium salts impose some limitations on their use. One disadvantage is the difficulty of recovering the original acids: acid hydrolysis converts the liberated sulphinic acids into the thiolsulphonate esters ($R\cdot SO_2\cdot SR$), whereas thiolsulphonic acids are decomposed according to equation (2); alkaline hydrolysis, on the other hand, produces the disagreeable toluene-ω-thiol as by-product. As previously observed with carboxylic acids, the m. p.s of the sulphinic acid derivatives fall within a small temperature range. Moreover, melting-point depressions due to admixture of different derivatives (particularly when the sulphinic acids concerned are of analogous structure) are sometimes small. In establishing the identity of a given specimen by mixed m. p. determination with authentic material, very close agreement between the m. p. and the mixed m. p. is therefore essential. The m. p.s of the benzylthiuronium derivatives of thiolsulphonic acids cover a wider range, and mixtures of these salts give rise to more distinct melting-point depressions.

Walker (*J.*, 1949, 1997) in discussing the power of compounds containing an unsubstituted amidino-group to form sparingly soluble salts with certain acids, has adduced reasons, on structural grounds, for the general observation that the m. p.s of benzylthiuronium salts of carboxylic acids cover only a small temperature range whereas those of sulphonic acid derivatives show a wider distribution. In view of the formal structural analogies of sulphinic and thiolsulphonic with carboxylic and sulphonic acids, respectively, it seems possible to explain the similar observations now made in the former two series, and to provide at the same time, further examples in support of the original hypothesis. Thus, following Walker's arguments (*loc. cit.*), the observed distribution of the m. p.s may be accounted for, in the present case, by representing the benzylthiuronium salts of sulphinic acids by the resonance structure (*A*).



(*A*)

The aromatic thiolsulphonic acids required in this work were prepared by an improvement in the classical method (Spring, *Ber.*, 1874, **7**, 1158; Otto, *ibid.*, 1882, **15**, 127) by addition of a hot saturated solution of sulphur in acetone to aqueous sodium sulphinate, the former solvent being simultaneously removed under reduced pressure. In this way the uptake of the element was found to occur more readily than by simply stirring the sulphinate solution with sulphur. Owing to the limited solubility of sulphur in acetone, however, the procedure is most useful for the rapid preparation of small samples of thiolsulphonic acids. A second convenient method of preparing these acids, in the form of their pyridinium salts, consisted of the addition of sulphur to the pyridine solution of the corresponding sulphinic acid (cf. Kurzer, *J.*, 1950, 3269). Benzylthiuronium derivatives were directly obtained from the aqueous solutions of the pyridinium salts, thus confirming the general applicability of this synthesis of arylthiolsulphonic acids.

Another illustration of the usefulness of the benzylthiuronium derivatives may be given. The interaction of aromatic thioureas and sulphonyl chlorides has been shown (Kurzer, *loc. cit.*) to proceed by a mechanism involving the intermediate formation of unstable *S*-sulphonyl*iso*thioureas, which decompose into cyanamides and thiolsulphonic acids, but the occurrence of the latter products was only inferred indirectly. It has now been possible to isolate the intermediate thiolsulphonic acid in the form of its benzylthiuronium derivative. This test was again carried out with an *as*-disubstituted thiourea to avoid the complication of side reactions (*loc. cit.*): the products of the interaction of *as*-diphenylthiourea and toluene-*p*-sulphonyl chloride were *NN*-diphenylcyanamide and toluene-*p*-thiolsulphonic acid (equation 10). Additional more direct evidence for the mechanism previously suggested is thus provided.

$$\begin{aligned} Ph_2N{\cdot}CS{\cdot}NH_2 + R'{\cdot}SO_2Cl &\longrightarrow [Ph_2N{\cdot}C(S{\cdot}SO_2R'){:}NH] + HCl \\ &\longrightarrow Ph_2N{\cdot}CN + R'{\cdot}SO_2{\cdot}SH \quad . \; . \; . \quad (10) \end{aligned}$$

EXPERIMENTAL

M. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford. The yields of products obtained in the decomposition of arylthiolsulphonic acids are calculated on the basis of equation (2). Sodium toluene-*p*-sulphinate was employed in the form of the crystalline dihydrate throughout.

*Decomposition of Toluene-*p*-thiolsulphonic Acid.*—(i) To a solution of sodium toluene-*p*-thiolsulphonate dihydrate (7·4 g., 0·03 mole) in water (100 ml.) at 35°, an excess of concentrated hydrochloric acid (30 ml.) was added in one portion. A semicrystalline, almost white mass separated instantly, filling the whole volume of liquid. After 3 hours, the solid was filtered off and washed with water (filtrate: A), and the dried pale yellow powder (5·64 g.) extracted with boiling ethanol (2 × 20 ml.) (extracts: B). The residue (3·15 g.) was crystallised from benzene (50 ml.)–ethanol (10 ml.) and deposited minute, lustrous prisms of ditoluene-*p*-sulphonyl trisulphide, m. p. 184—186° (slight sintering at 160°) undepressed in admixture with authentic material (Found: C, 41·5; H, 3·5. Calc. for $C_{14}H_{14}O_4S_5$: C, 41·4; H, 3·5%). The mother-liquors therefrom deposited more trisulphide, m. p. 182—184° (total yield: 2·7 g., 88%), together with a few compact prisms of sulphur (0·15 g., 62%). The combined alcoholic extracts (B), evaporated to small volume (12 ml.) and decanted from a trace of insoluble material, deposited lustrous prisms of *p*-tolyl toluene-*p*-thiolsulphonate, m. p. 77—78° (total yield: 1·85 g., 88%).

The aqueous filtrate (A) was evaporated on the steam-bath to small volume and heated for 4 hours; it deposited a little oil, which solidified on cooling and consisted of *p*-tolyl toluene-*p*-thiolsulphonate, m. p. 76—78° (0·2 g.; accounting for 7% of the starting material *not* reacting according to equation 2). The aqueous filtrate therefrom, adjusted to pH 8 with sodium hydroxide and treated with *S*-benzylthiuronium chloride (2·0 g.), gave the benzylthiuronium salt of toluene-*p*-sulphonic acid, m. p. 180—181° (undepressed by authentic material) (0·44 g.; accounting for another 2% of the starting material not reacting according to equation 2).

(ii) The same results were obtained when a solution of equivalent quantities of sodium toluene-*p*-thiolsulphonate and hydrochloric acid (0·03 mol.) in water (200 ml.) was slowly evaporated on the steam-bath during 3 hours.

(iii) A solution of sodium toluene-*p*-thiolsulphonate (4·9 g., 0·02 mole) in water (70 ml.) at room temperature was treated with hydrochloric acid (5·5 ml.; 10% w/v; 0·015 mol.). The liquid (which was acid to Congo-red) deposited, overnight, a pale yellow solid (A; 1·25 g.). The filtrate therefrom was treated with a saturated warm aqueous solution of *S*-benzylthiuronium chloride (4·0 g., 0·02 mole), giving a white crystalline precipitate (4·35 g., 62%) of the corresponding *derivative* of toluene-*p*-thiolsulphonic acid, m. p. 121—123° (from ethanol–light petroleum) (undepressed in admixture with material prepared as described below). Solid A, consisting of ditoluene-*p*-sulphonyl trisulphide, *p*-tolyl toluene-*p*-thiolsulphonate, and sulphur, was separated into its constituents as before; the yields corresponded to a conversion of 29% of the starting material according to equation (2).

*Stability of Toluene-*p*-thiolsulphonic Acid in Acetic Acid Solution* (*at* pH 3·6).—A solution of sodium toluene-*p*-thiolsulphonate (5·25 g., 0·025 mole) in water (100 ml.) was treated with acetic acid (2·25 g., 0·0375 mole), and a slight turbidity filtered off. The liquid (pH 3·40) was slowly evaporated nearly to dryness on the steam-bath; addition of water (200 ml.) gave once again a clear liquid (pH 3·58). One-half of this solution was treated with aqueous silver nitrate (2·55 g., 0·015 mole), yielding white semicrystalline silver toluene-*p*-thiolsulphonate (Found: C, 29·1; H, 2·6; Ag, 36·2. Calc. for $C_7H_7O_2S_2Ag$: C, 28·5; H, 2·4; Ag, 36·6%). The other half of the solution was made just alkaline to phenolphthalein with sodium hydroxide; addition, at 40°, of *S*-benzylthiuronium chloride (5·06 g., 0·025 mole) in water (10 ml.) and immediate removal of the crude oily product by decantation (to avoid contamination with the corresponding derivative of acetic acid which separates slowly on cooling) gave the benzylthiuronium derivative of toluene-*p*-thiolsulphonic acid, m. p. 121—123° (from ethanol–light petroleum) (undepressed in admixture with authentic material, prepared as described below.)

Storage of aqueous solutions of equimolecular proportions of sodium toluene-*p*-thiolsulphonate and acetic acid at 0° (for at least 6 months) caused no decomposition of the thiolsulphonic acid.

Decomposition of Naphthalene-2-thiolsulphonic Acid.—Addition of concentrated hydrochloric acid (10 ml.) to an aqueous solution of sodium naphthalene-2-thiolsulphonate (2·26 g., 0·008 mole) precipitated a pale yellow viscous material, which solidified on short storage. This was dissolved in boiling ethanol (4 × 12 ml.): the undissolved residue was sulphur (0·03 g., 47%). Fractional evaporation of the ethanolic extracts and repeated crystallisation from ethanol gave the less soluble dinaphthalene-2-sulphonyl trisulphide, m. p. 141—142° (slight sintering at 136°) [undepressed in admixture with material prepared by method of Tröger and Hornung (*J. pr. Chem.*, 1899, **60**, 113) who report m. p. 130—132°] (0·71 g., 74%) (Found: C, 49·7; H, 2·8. Calc. for $C_{20}H_{14}O_4S_5$: C, 50·2; H, 2·9%). The more soluble fraction gave 2-naphthyl napthalene-2-thiolsulphonate, m. p. 102—103° (0·36 g., 52%).

*Interaction of Toluene-*p*-sulphinic Acid and Sulphur.*—(i) Flowers of sulphur (0·35 g., 0·011 g.-atom) were suspended in a solution of sodium toluene-*p*-sulphinate (2·14 g., 0·01 mole) in hydrochloric acid (3N; 30 ml.) and the mixture stirred at 90—100° for 3 hours. The filtered solid (1·1 g.) consisted of ditoluene-*p*-sulphonyl trisulphide (0·15 g.), *p*-tolyl toluene-*p*-thiolsulphonate (0·40 g.), and unchanged sulphur. Prolonged stirring of the above reaction mixture at room temperature did not result in interaction to any measurable extent. Repeated evaporation of the mixture to small volume during 8 hours raised the yield of disulphonyl trisulphide (0·35 g.). Supplying the sulphur in the colloidal form by the addition of its saturated acetone solution (the solvent being simultaneously removed) did not substantially improve the yields of disulphonyl trisulphide (see below).

(ii) *In the presence of toluene-*p*-thiolsulphonic acid.* To hydrochloric acid (3N; 25 ml.), at 75°, a solution of sodium toluene-*p*-sulphinate (3·21 g., 0·015 mole) and sodium toluene-*p*-thiolsulphonate (1·23 g., 0·005 mole) in water (30 ml.), and a saturated boiling solution of sulphur (0·35 g., 0·011 g.-atom) in acetone, were slowly added side by side during 1 hour, the acetone being removed simultaneously under reduced pressure. The solidified product, separated as previously described, gave ditoluene-*p*-sulphonyl trisulphide (1·40 g., 70%) and *p*-tolyl toluene-*p*-thiolsulphonate (1·15 g., 82%).

A control experiment, carried out under identical conditions but in the absence of sodium toluene-*p*-thiolsulphonate, gave only low yields of the trisulphide (0·14 g., 9%), much of the sulphinic acid being recovered unchanged (as the benzylthiuronium derivative; 2·9 g., 60%). (Since the quantity of sodium toluene-*p*-thiolsulphonate employed above would produce, independently, only approx. 0·50 g. of trisulphide, the present experiment shows that thiolsulphonate ions participate in the formation of the disulphonyl trisulphide.)

Arylthiolsulphonic Acids.—(a) *Sodium salts.* A solution of the sodium arylsulphinate (0·01 mole) in water (30 ml.)–acetone (20 ml.), to which 2 drops of aqueous sodium hydroxide had been added, was treated, during 1—2 hours, with a saturated solution of sulphur (0·011 g.-atom) in boiling acetone, the added solvent being simultaneously removed (at 40—45°) by distillation under reduced pressure. When all the sulphur had been added, the pale yellow liquid was diluted with more water (20 ml.), the acetone removed in a vacuum, and traces of unchanged sulphur removed by filtration with carbon. Evaporation in a vacuum-desiccator gave lustrous platelets of the sodium arylthiolsulphonate. For the preparation of benzylthiuronium derivatives the sodium salt solution was directly used.

(b) *Pyridinium salts.* A solution of the arylsulphinic acid (0·01 mole) in pyridine (12 ml.), treated with sulphur (0·011 g.-atom), was kept at 80° for 15 minutes, and poured into water (60 ml.). Traces of separated sulphur were removed by filtration with carbon. The resulting solutions of the pyridinium salt of arylthiolsulphonic acids in aqueous pyridine were directly used in preparing benzylthiuronium derivatives.

S-*Benzylthiuronium Derivatives of Acids.*—(i) *Sulphinic acids.* The well-stirred solution of the sodium sulphinate (0·01 mole) in water (80—100 ml.) was made acid (phenolphthalein) by dropwise addition of dilute hydrochloric acid. Separation of free sulphinic acid (in the case of the less soluble members of the series) was prevented by warming the solution gently if necessary. Addition of a warm (40°) saturated aqueous solution of *S*-benzylthiuronium chloride (3·0 g., 0·015 mole) gave immediately a crystalline precipitate of the *derivative*; the mixture was set aside at 0° for 2 hours, and the product filtered off and air-dried. Two or three crystallisations from ethanol–light petroleum (usual ratio 3 : 1) or from ethanol alone (in the case of the less soluble derivatives) gave the product, of constant m. p., in lustrous plates,

Benzylthiuronium derivatives of various sulphur acids.

Acid	M. p.	Yield,[1] %	Solvents [2] used and no. of recrystns.[3]	Formula of derivative	N, % Found	N, % Reqd.
Methanesulphinic	136—137°	50	III,[4] 3	$C_9H_{14}O_2N_2S_2$	11·3	11·4
Toluene-ω-sulphinic	152—153	60	II, 2	$C_{15}H_{18}O_2N_2S_2$	†	
Benzenesulphinic	154—155	85	I, 1	$C_{14}H_{16}O_2N_2S_2$	9·5	9·1
Toluene-*p*-sulphinic	167—168	84	I, 2	$C_{15}H_{18}O_2N_2S_2$	8·4	8·7 [5]
Toluene-*o*-sulphinic	178—179	90	I, 4	$C_{15}H_{18}O_2N_2S_2$	8·6	8·7
Naphthalene-2-sulphinic	168—169	76	II, 2	$C_{18}H_{18}O_2N_2S_2$	7·4	7·8
p-Bromobenzenesulphinic	171—172	60	II, 2	$C_{14}H_{15}O_2N_2S_2Br$	7·1	7·2
3 : 4-Dichlorobenzenesulphinic ...	170—171	90	II, 1	$C_{14}H_{14}O_2N_2S_2Cl_2$	7·2	7·4
Methanethiolsulphonic	141—142	52	III, 3	$C_9H_{14}O_2N_2S_3$	33·5	34·5 *
Benzenethiolsulphonic	91—93	77	III, 3	$C_{14}H_{16}O_2N_2S_3$	8·5	8·2
Toluene-*p*-thiolsulphonic	120—121	95	I, 3	$C_{15}H_{18}O_2N_2S_3$	7·4	7·9
Toluene-*o*-thiolsulphonic	137—138	66	II, 1	$C_{15}H_{18}O_2N_2S_3$	8·0	7·9
Naphthalene-2-thiolsulphonic	171—172	82	II, 3	$C_{18}H_{18}O_2N_2S_3$	23·9	24·6 *
p-Bromobenzenethiolsulphonic ...	146—147	73	II, 1	$C_{14}H_{15}O_2N_2S_3Br$	21·9	22·9 *
Methanesulphonic	148—149	63	I, 2	$C_9H_{14}O_3N_2S_2$	10·5	10·7

Note added in Proof.—Our attention has been drawn to the following three sulphinic acid derivatives prepared from other thiuronium chlorides: *p*-bromobenzylthiuronium salts of α-benzylthio-*p*-bromotoluene-α-sulphinic acid (m. p. 211°) and of the corresponding α-methylthio-acid (m. p. 220° [Snyder and Handrick, *J. Amer. Chem. Soc.*, 1944, **66**, 1860]; 1-naphthylmethylthiuronium salt of benzenesulphinic acid (m. p. 177°) [Bonner, *ibid.*, 1948, **70**, 3509].

* Analyses relate to sulphur.

† The derivative decomposed on storage, yielding benzaldehyde, and was not analysed.

[1] The yields of sulphinic acid derivatives are based on the quantity of sulphonyl chloride originally reduced to the sulphinic acid; those of thiolsulphonic acid derivatives are calculated from the quantity of sulphinic acid used in the conversion into the thiolsulphonic acid.

[2] Solvents: (I) ethanol–light petroleum; (II) ethanol; (III) water, followed by crystallisation from ethanol–light petroleum.

[3] The number of crystallisations required to give a product of constant m. p. is recorded.

[4] Owing to its high solubility, this derivative was crystallised from fairly concentrated solution.

[5] Found: C, 55·6; H, 5·9. $C_{15}H_{18}O_2N_2S_2$ requires C, 55·9; H, 5·6%.

usually freely soluble in warm acetone and ethanol, sparingly soluble in benzene, light petroleum, and cold water.

(ii) *Thiolsulphonic acids.* These derivatives were similarly prepared from the sodium or pyridinium salt solution of the thiolsulphonic acid (see above). The isolated product was usually crystallised once from hot (80°) water, and twice from ethanol–light petroleum (with the addition of a little charcoal to remove traces of separated colloidal sulphur, if necessary), giving lustrous plates of the *derivative*, of constant m. p. The solubilities resembled those under (i).

Interaction of as-*Diphenylthiourea and Toluene*-p-*sulphonyl Chloride : Isolation of Toluene*-p-*thiolsulphonic Acid.*—A solution of *as*-diphenylthiourea (3·40 g., 0·015 mole) in pyridine (15 ml.) was treated with toluene-*p*-sulphonyl chloride (2·90 g., 0·015 mole) and heated at 100° for 15 minutes. The liquid was stirred into ice-water (80 ml.) and acidified (to Congo-red) with concentrated acid. The supernatant aqueous layer was immediately decanted from the semi-solid deposit (A), treated with aqueous sodium hydroxide until just acid to litmus, and filtered with a little charcoal. Addition of *S*-benzylthiuronium chloride (3·05 g., 0·015 mole) and storage at 0° for several hours gave crystalline plates (m. p. 110—120°; 1·59 g., 30%); recrystallisation from ethanol–light petroleum yielded the benzylthiuronium derivative of toluene-*p*-thiolsulphonic acid, m. p. 121—123° (undepressed in admixture with authentic material). (Spontaneous evaporation, at room temperature, of the aqueous filtrates raised the yield to 42%.)

The solidified deposit (A) (2·2 g.) was *NN*-diphenylcyanamide, m. p. 70—72°, which was separated from small quantities of unchanged *as*-diphenylthiourea with cold acetone.

The authors gratefully acknowledge a grant from the Research Fund of the Chemical Society. Thanks are due to Dr. A. Lawson for advice and support, and to Professor H. Burton and Dr. J. Walker for valuable discussions.

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[*Received, April 3rd,* 1952.]