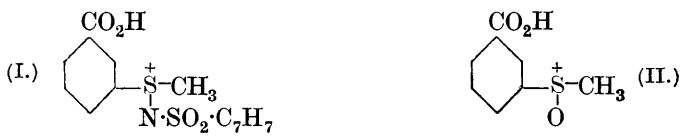


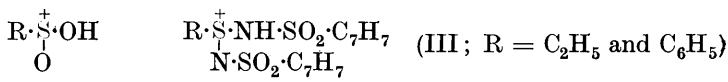
CLVI.—*The Preparation of Compounds analogous in Structure to Sulphinic Acids but containing p-Toluenesulphonimido-groups in Place of Oxygen Atoms. Phenyl- and Methyl-p-toluenesulphonimido-sulphine-p-toluenesulphonylimines.*

By SYDNEY GEORGE CLARKE, JOSEPH KENYON, and HENRY PHILLIPS.

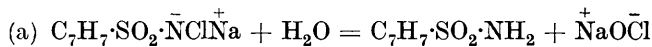
THE resolution of *dl-m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (I) (Clarke, Kenyon, and Phillips, J., 1927, 188), corresponding to the *dl*-sulphoxide (II) resolved by Harrison, Kenyon, and Phillips (J., 1926, 2079), provided experimental evidence that the *p*-toluenesulphonimido-group could become linked



with sulphur in the same manner as the oxygen atom of a sulphoxide. It has now been found that compounds can be prepared analogous in structure to sulphinic acids but containing two *p*-toluenesulphonimido-groups in place of the two oxygen atoms of the sulphinic acid group. Two examples of this new class of compound have been



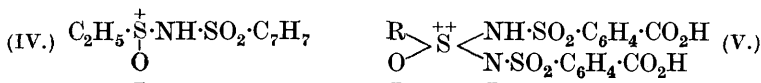
prepared in which R = C₂H₅ and C₆H₅ respectively. They can be obtained readily by the action of chloramine-T on solutions of sodium phenyl and ethyl mercaptides. The formation of these compounds, under the experimental conditions employed, provides evidence that in aqueous solution chloramine-T not only undergoes hydrolysis as in equation (a) but also dissociates to give a neutral *p*-toluenesulphonimido-radical as indicated in equation (b).



From a consideration of these equations it would be anticipated that, by the use of a suitable anhydrous solvent in which sodium chloride is insoluble, the production of the *p*-toluenesulphonimido-radical would be favoured and the hydrolysis of chloramine-T suppressed. This deduction receives support from the fact that

a greater yield of the phenyl compound is obtained from solutions of phenyl mercaptan in acetic acid or in pyridine than from solutions of the mercaptan (as sodium salt) in water. Even when a large excess of chloramine-T is employed in these reactions, the same two compounds are obtained, indicating that the sulphur atoms of the mercaptans show little or no tendency to combine with three *p*-toluenesulphonimido-groups to produce compounds analogous to sulphonic acids. The chemical properties of *phenyl*- and *ethyl*-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines are also in agreement with the view that the large *p*-toluenesulphonimido-groups exert a protective influence on the central sulphur atoms and cause them to be far less reactive than the corresponding sulphur atoms of sulphinic acids. For example, sulphinic acids react readily with bromine to yield sulphonyl bromides and condense with formaldehyde, benzoquinone (Hinsberg, *Ber.*, 1884, **27**, 3359) and azobenzene (Hantzsch and Glogauer, *Ber.*, 1897, **30**, 2565), but, under the same experimental conditions, ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines do not react with these reagents. A similar difference in behaviour exists between sulphilimines and sulphoxides; *m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (I) cannot be converted into a derivative of sexavalent sulphur, whereas the corresponding sulphoxide (II) readily forms a sulphone. When heated with concentrated hydrochloric acid, the new sulphonylimines slowly decompose, producing the corresponding disulphides, sulphonic acids, and *p*-toluenesulphonamide. The quantities of *p*-toluenesulphonamide obtained are in harmony with the view that two *p*-toluenesulphonimido-groups are present in each molecule.

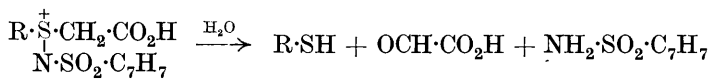
It was not found possible to replace the imido hydrogen atoms in these compounds by methyl groups by the agency of either methyl sulphate or methyl iodide under various experimental conditions. During such attempted methylations, the compounds decomposed, *p*-toluenesulphon-monomethyl- and -dimethyl-amides being the chief products. From the decomposition products of the methylation of ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, *ethyl*-*p*-toluenesulphonylsulphinamide (IV) was isolated.



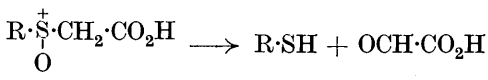
The sulphonylimines undergo oxidation much less readily than do the corresponding sulphinic acids. They are unaffected by perhydrol, but, in alkaline solution, they are converted by potassium permanganate into tribasic acids (V). These new acids yield

p-sulphonamidobenzoic acid on hydrolysis with concentrated acids, but the experimental evidence that they contain oxygen atoms linked to the central sulphur atoms is not conclusive.

Ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines were also isolated from the products of the interaction of ethyl- and phenyl-thiolacetates with chloramine-T. The failure to obtain the sulphilimines of these salts by this means can be attributed either to the instability of these sulphilimines in the presence of water, or, alternatively, to the preferential formation



of the corresponding sulfoxides, which decompose in a similar manner (Pummerer, *Ber.*, 1909, **42**, 2282; 1910, **43**, 1404):



The ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines isolated from these reactions doubtless arise from the interaction of the chloramine-T with the mercaptans produced during the decomposition of either the sulphilimine or the sulfoxide or both these compounds, as indicated in the above equations.

EXPERIMENTAL.

Ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine (III; R = Et).—(a) *From ethyl mercaptan.* Chloramine-T (58 g., 2 mols.) in warm water (150 c.c.) was added to a solution of ethyl mercaptan (6.2 g.) in sodium hydroxide (3*N*, 33 c.c.), and after an hour the solution was acidified with dilute sulphuric acid. The *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* (20 g.) produced was extracted from the precipitate obtained by means of dilute sodium carbonate solution, in which the *p*-toluenesulphonamide (12.8 g.) simultaneously precipitated was insoluble. By acidification of the sodium carbonate extract, the new compound was precipitated. After crystallisation from ethyl alcohol, it had m. p. 189° (decomp.), either alone or when mixed with the *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* prepared from ethylthiolacetic acid as described below.

(b) *From ethylthiolacetic acid.* A warm solution of chloramine-T (240 g.) in water (1000 c.c.) was added to an alkaline solution of ethylthiolacetic acid (48 g.) in sodium hydroxide (3*N*, 200 c.c.) After 3 days, the solid which had separated was removed by filtration, and, on acidification of the alkaline filtrate, *ethyl-p-toluenesulphonylimine* was precipitated.

sulphonimidodisulphine-*p*-toluenesulphonylimine was precipitated. It was purified as described above and then weighed 20.4 g. and had m. p. 189° (decomp.) [Found: C, 47.8; H, 5.0; N, 7.0; S, 23.7. $C_{16}H_{20}O_4N_2S_3$ requires C, 48.0; H, 5.0; N, 7.0; S, 24.0%. 0.4000 G. required 0.0400 g. of sodium hydroxide for neutralisation to phenolphthalein: equiv., 400. $(C_{16}H_{19}O_4N_2S_3)H$ requires equiv., 400. Found for the silver salt, after drying at 120—130°: Ag, 21.6. $C_{16}H_{19}O_4N_2S_3Ag$ requires Ag, 21.3%].

The solid which was removed by filtration was triturated with chloroform (150 c.c.); *p*-toluenesulphonamide (83 g., m. p. 138°) remained undissolved. From the chloroform extract a neutral substance (3.1 g.) was isolated which, after crystallisation from ethyl alcohol, had m. p. 128° (decomp.). This neutral compound decomposed at its m. p., yielding an inflammable vapour, and left a residue (97% of the original) which, after crystallisation from ether and light petroleum, had m. p. 108—112°. On hydrolysis with hot concentrated hydrochloric acid, the neutral compound gave 15% of its weight of *p*-toluenesulphonamide (Found: C, 34.4; H, 3.7; N, 4.1; S, 18.2; Cl, 20.9%, corresponding fairly closely with the empirical composition $C_{10}H_{12}O_4NCl_2S_2$).

*The Chemical Properties and Reactions of Ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine.—Hydrolysis.* Dilute sulphuric acid was without action on the compound, but the clear solution obtained by heating it (1.0 g.) with 50% sulphuric acid deposited *p*-toluenesulphonamide (0.82 g.) on cooling [Theoretical quantity for $C_2H_6S(C_7H_7O_2SN)_2$, 0.86 g.]. A similar result was obtained by the use of concentrated hydrochloric acid.

Oxidation. Formation of
$$\text{Et} \begin{array}{c} \text{O} \\ \text{S}^+ \\ \text{O} \end{array} \begin{array}{l} \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ \text{N} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \end{array}$$
 To

ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (8 g.) dissolved in dilute aqueous sodium hydroxide, small quantities of a saturated solution of potassium permanganate (in all, 13.6 g.) were added during 3 hours. After the passage of sulphur dioxide to dissolve the manganese dioxide, the resulting solution was acidified with dilute sulphuric acid; the new compound (8.2 g., m. p. 260—262°) was then precipitated. After three recrystallisations from alcohol, it had m. p. 275—276° (decomp.), which was unchanged by reprecipitation of the compound from its solution in sodium hydroxide solution and further recrystallisation from alcohol [Found: S, 20.6%. 0.5000 G. neutralised 0.1204 g. of sodium hydroxide: equiv., 166. $(C_{16}H_{13}O_9N_2S_3)H_3$ requires S, 20.2%; equiv., 159. $(C_{16}H_{13}O_8N_2S_3)H_3$ requires S, 20.8%; equiv., 154]. This acid (1.0 g.) was heated under reflux with concentrated hydrochloric acid (25 c.c.) for 1.5 hours. *p*-Sulphon-

amidobenzoic acid (0.68 g.), m. p. 284—285°, either alone or when mixed with an authentic specimen of that compound, was filtered from the cold reaction mixture (Found: S, 16.1. Calc. for $C_7H_7O_4NS$: S, 15.9%).

Action of methylating agents. Formation of ethyl-p-toluenesulphonylsulphinamide, $Et \cdot SO \cdot NH \cdot SO_2 \cdot C_7H_7$. The sulphonylimine (8 g.), dissolved in *N*-sodium hydroxide (40 c.c.), was treated with methyl sulphate and sufficient sodium hydroxide to maintain the solution alkaline, until the oily precipitate which separated from the hot reaction mixture ceased to increase in amount. On cooling, this oily precipitate solidified; after crystallisation from alcohol, it was obtained (1.8 g.) with m. p. 78—79°, either alone or when mixed with *p*-toluenesulphondimethylamide prepared by the action of methyl sulphate on an alkaline solution of *p*-toluenesulphonamide (Found: S, 16.1. $C_9H_{13}O_2NS$ requires S, 16.1%). The filtrate from this *p*-toluenesulphondimethylamide was concentrated, and, after several days, it deposited a crystalline sodium salt. On acidification of an aqueous solution of this salt, *ethyl-p-toluenesulphonylsulphinamide* (3.5 g.) was precipitated, and this, after crystallisation from alcohol, had m. p. 120° (Found: S, 25.6; N, 5.6. $C_9H_{13}O_3NS_2$ requires S, 25.9; N, 5.6%).

By treatment of ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine in boiling toluene containing anhydrous potassium carbonate with methyl sulphate, only a mixture of *p*-toluenesulphonmonomethyl- and -dimethyl-amides was obtained. Similarly, the silver salt of the sulphonylimine, when heated under reflux with methyl iodide, gave *p*-toluenesulphondimethylamide. Each of these methylation reactions yielded small quantities of other products which were not identified.

Phenyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine (III; R = Ph).—(a) *From thiophenol*. (i) *In water*. To thiophenol (5.5 g., 1 mol.), dissolved in dilute aqueous sodium hydroxide, a warm aqueous solution of chloramine-T (28.3 g., 2 mols.) in water (100 c.c.) was added. The granular precipitate which was thrown down consisted mainly of *p*-toluenesulphonamide, but gave some diphenyl disulphide (5 g.), m. p. 61—62°, when extracted with benzene. The warm filtrate, on cooling, deposited the crystalline sodium salt of phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, m. p. 226° (Found: Na, 4.8. $C_{20}H_{19}O_4N_2S_3Na$ requires Na, 4.9%). A warm aqueous solution of this salt gave, on acidification, *phenyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* which, after crystallisation from alcohol, had m. p. 152—153° [Found: C, 52.9; H, 4.6; N, 6.5; S, 21.3. $C_{20}H_{20}O_4N_2S_3$ requires C, 53.1; H, 4.5; N, 6.3; S, 21.4%. 0.2000 G. neutralised

0.0176 g. of sodium hydroxide : equiv., 455. ($C_{20}H_{19}O_4N_2S_3$)H requires equiv., 448]. The *silver* salt was a white curdy precipitate obtained by vigorously stirring a solution of the sodium salt to which silver nitrate had been added [Found (after drying at 110°) : Ag, 19.9. $C_{20}H_{19}O_4N_2S_3$ Ag requires Ag, 19.5%].

(ii) *In acetic acid.* Chloramine-T (280 g.) was shaken with a hot solution of thiophenol (55 g.) in glacial acetic acid (300 c.c.). After being heated on a steam-bath for 15 minutes, the mixture was poured into water. The solid material which separated was extracted with benzene to remove diphenyl disulphide, and then digested with hot dilute sulphuric acid. A heavy viscous oil remained which crystallised on cooling and, after recrystallisation, gave phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (40 g.), m. p. $152-153^\circ$. A further quantity of this compound (20 g.) was obtained by acidification of the filtrate from the solid material which separated when the reaction mixture was poured into water.

(iii) *In pyridine.* The reaction was carried out as described in (ii). When the reaction mixture was poured into water, only diphenyl disulphide separated. The sulphonylimine was precipitated by the addition of acid to the aqueous pyridine. Thiophenol (5 g.) gave 5 g. of the sulphonylimine.

(b) *From phenylthiolacetic acid.* Chloramine-T (85 g.) was shaken with a solution of the sodium salt of phenylthiolacetic acid (23.5 g.) in hot water. After being heated for 30 minutes on the steam-bath, the mixture was cooled and the water together with some crystalline material was decanted from the compact solid mass which had formed on the bottom of the flask. Diphenyl disulphide (12 g.), m. p. $60-61^\circ$, was extracted from this mass with benzene. The residual solid was recrystallised from alcohol and proved to be the sodium salt of phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (4 g.), m. p. $227-228^\circ$, either alone or when mixed with the sodium salt prepared directly from sodium thiophenoxide. The crystalline material, mentioned above, was dissolved in hot water and reprecipitated as an oil by the addition of acid. This oil solidified on cooling and proved to be the sulphonylimine, m. p. 153° , either alone or when mixed with the sulphonylimine prepared from sodium thiophenoxide.

The Chemical Properties and Reactions of Phenyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine.—Hydrolysis. When heated on a steam-bath for 30 minutes with concentrated hydrochloric acid (100 c.c.), the sulphonylimine (3 g.) gradually lost its crystalline character and gave place to an oil. The hot acid, decanted from the oil, deposited *p*-toluenesulphonamide (1.4 g.) on cooling : on con-

centration, the filtrate from this sulphonamide deposited a further quantity (0.3 g.) of this substance. The filtrate from this second crop of sulphonamide was taken to dryness in a vacuum; the residue (benzenesulphonic acid) gave benzenesulphonamide, after successive treatment with phosphorus pentachloride and ammonium carbonate.

The oil, obtained as described above, solidified on cooling. After being freed from *p*-toluenesulphonamide by extraction with sodium hydroxide solution and recrystallised from light petroleum, it gave diphenyl disulphide (0.7 g.), m. p. and mixed m. p. 60—61°.

Oxidation. The preparation of $\text{Ph} \begin{array}{l} \text{O} \\ \text{S} \end{array} \begin{array}{l} \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ \text{N} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \end{array}$.

Perhydrol was without action on hot aqueous solutions of either phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine or its sodium salt. The latter compound was, however, successfully oxidised with potassium permanganate. To a solution of the sodium salt (4.4 g.) in water (50 c.c.), heated on a steam-bath, a saturated aqueous solution of potassium permanganate was added during 3 hours. In all, 6.6 g. of permanganate (about 3 mols. oxygen) were added: a further small addition was not decolorised. After passage of sulphur dioxide to dissolve the manganese mud, hydrochloric acid was added; a colourless crystalline solid then separated. After three recrystallisations from alcohol, it (1.2 g.) was obtained with m. p. 201° (decomp.) (Found: N, 5.4; S, 17.9. $\text{C}_{20}\text{H}_{16}\text{O}_9\text{N}_2\text{S}_3$ requires N, 5.3; S, 18.3%. $\text{C}_{20}\text{H}_{16}\text{O}_8\text{N}_2\text{S}_3$ requires N, 5.5; S, 19.0%).

When a suspension of this compound (1.0 g.) in concentrated hydrochloric acid was heated under reflux for 1 hour, a silky crystalline compound was produced, m. p. 284—285°, either alone or when mixed with *p*-sulphonamidobenzoic acid.

Action of methylating agents. To a solution of the sulphonylimine (9 g.) in dilute aqueous sodium hydroxide heated to 90—95°, methyl sulphate (21 g., 9 mols.) was added gradually with vigorous shaking. During the addition an oil separated which solidified on cooling; after recrystallisation from alcohol, it had m. p. 79—80°, either alone or when mixed with *p*-toluenesulphondimethylamide. The aqueous filtrate from this sulphonamide gave, on evaporation, a small quantity of a basic oil which was not identified.

The finely divided sulphonylimine (4.5 g.) and potassium carbonate (4.0 g.) were heated under reflux in toluene containing methyl sulphate (2 g.) for 7 hours. The toluene was removed and the portion of the residue insoluble in water was proved to consist of a mixture of *p*-toluenesulphon-monomethyl- and -dimethyl-amides, together with some diphenyl disulphide and unchanged sulphonyl-

imine. The only product which could be isolated from the products of the interaction of the silver salt of the sulphonylimine with methyl iodide was diphenyl disulphide.

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