345. *The Isomerisation of Sulphidimines. Part III.* The Action of Chloramine-T on Cinnamyl Phenyl Sulphide, and the Hydrolysis and Oxidation of* N-*Substituted Toluene*-p-*Sulphonamides.*

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When cinnamyl phenyl sulphide and chloramine-T interact the sulphidimine † cannot be isolated, but immediately isomerises to *N*-1-phenylallyl-*N*-phenylthiotoluene-*p*-sulphonamide. The structure of this isomer follows from its alkaline hydrolysis to thiophenol and *N*-1-phenylallyltoluene-*p*-sulphonamide, identified by reduction to *N*-1-phenylpropyltoluene-*p*-sulphonamide. The isomerisation of the sulphidimine is therefore accompanied by inversion. The hydrolysis of several *N*-aralkyltoluene-*p*-sulphonamides with hydrochloric acid gives toluene-*p*-sulphonamide; the *N*-1-phenylethyl compound yields also styrene and 1-phenylethyl chloride. *N-iso*Propyltoluene-*p*-sulphonamide is almost unchanged, under comparable conditions, but the *tert.*-butyl derivative gives *tert.*-butyl chloride, *iso*butene, and toluene-*p*-sulphonamide. Oxidation of the *N-tert.*-butyl compound gives *N-tert.*-butyl-*p*-sulphamylbenzoic acid, *tert.*-butylamine, and 2-methyl-2-nitropropane. The mechanism of these reactions is discussed.

IN Parts I and II * it was shown that the sulphidimines prepared from diallyl sulphide ‡ and either *N*-chloro-*N*-sodiotoluene-*p*-sulphonamide (chloramine-T) or *N*-chloro-4-methyl-3-nitro-*N*-sodiobenzenesulphonamide undergo spontaneous isomerisation at room temperature, an allyl group migrating to nitrogen. The isomers have the structure $CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2{\cdot}CH{:}CH_2){\cdot}SO_2R$ because on boiling with alkali, $R{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, diallyl disulphide, hydrogen sulphide, and a resin arising from

* Part I, Ash, Challenger, and Greenwood, *J.*, 1951, 1877; Part II, Ash and Challenger, *J.*, 1952, 2792.

† Compounds of the type $\begin{matrix}R\\R'\end{matrix}\!>\!S{:}N{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p$ were named sulphilimines by Mann and Pope (*J.*, 1922, **121**, 1052) and this term has been used in Parts I and II. The modern nomenclature is *SS*-dialkyl-*N*-toluene-*p*-sulphonylsulphidimines (Editorial Report on Nomenclature, *J.*, 1952, 5058).

‡ The analyses recorded (*J.*, 1950, 29; 1951, 1879) for the sulphidimine from diallyl sulphide were performed on the liquid, isomerised product and not on the original, unstable sulphidimine. The isomerisation was shown to occur without loss in weight.

acraldehyde are produced. With *N*-chloro-*N*-sodionaphthalene-1-sulphonamide, the isomer is formed at once. Allyl benzyl sulphide and chloramine-T give a sulphidimine $(CH_2Ph)(CH_2{:}CH{\cdot}CH_2)S{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me$ which changes immediately at its m. p., or in a few days at room temperature, giving, by migration of the allyl group, the solid isomer $CH_2{:}CH{\cdot}CH_2{\cdot}N(S{\cdot}CH_2Ph){\cdot}SO_2{\cdot}C_6H_4Me$.

The similar conversion of *N*-crotyl-*N*-methylaniline oxide into *N*-methyl-*N*-(1-methylallyloxy)aniline proceeds with inversion of the crotyl group.[1] These changes resemble the Claisen rearrangements.[2] Mumm and Möller [3] found that crotyl α-phenyliminobenzyl ether (I) formed *N*-1-methylallyl-*N*-phenylbenzamide (II) at 210°, showing that inversion as well as rearrangement had occurred. The corresponding isomer (III) also rearranged giving (IV):

$$\underset{\text{(I)}}{Ph{\cdot}C(:NPh){\cdot}O{\cdot}CH_2{\cdot}CH{:}CHMe} \longrightarrow \underset{\text{(II)}}{Ph{\cdot}CO{\cdot}NPh{\cdot}CHMe{\cdot}CH{:}CH_2}$$

$$\underset{\text{(III)}}{Ph{\cdot}C(:NPh){\cdot}O{\cdot}CHMe{\cdot}CH{:}CH_2} \longrightarrow \underset{\text{(IV)}}{Ph{\cdot}CO{\cdot}NPh{\cdot}CH_2{\cdot}CH{:}CHMe}$$

With the sulphidimine from cinnamyl phenyl sulphide it might be possible to detect inversion should migration take place. Bergmann [4] showed that the isomerisation of cinnamyl thiocyanate to the *iso*thiocyanate is not accompanied by inversion, though crotyl thiocyanate was found by Mumm and Richter [5] to give 1-methylallyl *iso*thiocyanate after 2—3 days at room temperature, inversion having occurred:

$$Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}S{\cdot}CN \longrightarrow CH_2{:}CH{\cdot}CHMe{\cdot}N{:}C{:}S$$

These authors suggested that the steric effect of the phenyl group might be responsible for the absence of inversion in the case of cinnamyl thiocyanate.

No sulphidimine (V) could be isolated from cinnamyl phenyl sulphide and chloramine-T in aqueous acetone at room temperature or at 0°. At room temperature, migration and inversion of the cinnamyl group occurred; thus:

$$\underset{\text{(V)}}{CHPh{:}CH{\cdot}CH_2{\cdot}SPh{\rightarrow}N{\cdot}SO_2{\cdot}C_6H_4Me} \longrightarrow \underset{\text{(VI)}}{Ph{\cdot}S{\cdot}N(CHPh{\cdot}CH{:}CH_2){\cdot}SO_2{\cdot}C_6H_4Me}$$

The structure of the product (VI) follows from its decomposition with aqueous sodium hydroxide, whereby thiophenol, diphenyl disulphide, and *N*-1-phenylallyltoluene-*p*-sulphonamide $CH_2{:}CH{\cdot}CHPh{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$ (VII) were obtained. The synthesis of the sulphonamide (VII) from toluene-*p*-sulphonamide and 1-phenylallyl bromide was impossible since the action of phosphorus tribromide on 1-phenylallyl alcohol yields cinnamyl bromide.[6] It was therefore reduced catalytically to *N*-1-phenylpropyltoluene-*p*-sulphonamide which was synthesised from 1-phenylpropylamine and toluene-*p*-sulphonyl chloride. An attempt to prepare it from toluene-*p*-sulphonamide, sodium hydroxide, and 1-phenylpropyl bromide yielded only β-methylstyrene; this was also obtained by Errera [7] from 1-phenylpropyl chloride and alcoholic potassium hydroxide. In order further to confirm the structure of (VII) and the occurrence of inversion during spontaneous isomerisation of the sulphidimine, the isomeric *N*-cinnamyltoluene-*p*-sulphonamide was prepared from cinnamyl bromide, toluene-*p*-sulphonamide, and alcoholic potassium hydroxide. *NN*-Dicinnamyltoluene-*p*-sulphonamide was obtained as a by-product and was also formed from the monocinnamyl-compound with cinnamyl bromide and alcoholic sodium hydroxide. The monocinnamyl derivative was different from *N*-1-phenylallyltoluene-*p*-sulphonamide (VII).

To confirm the structure of the *N*-monocinnamyltoluene-*p*-sulphonamide and to

[1] Kleinschmidt and Cope, *J. Amer. Chem. Soc.*, 1944, **66**, 1929.
[2] Claisen and Tietze, *Ber.*, 1925, 58, 275; 1926, **59**, 2344; Hurd and Cohen, *J. Amer. Chem. Soc.*, 1931, **53**, 1917.
[3] Mumm and Möller, *Ber.*, 1937, **70**, 2214.
[4] Bergmann, *J.*, 1935, 1361.
[5] Mumm and Richter, *Ber.*, 1940, **73**, 843.
[6] Moureu and Gallagher, *Bull. Soc. chim. France*, 1921, **29**, 1009.
[7] Errera, *Gazzetta*, 1886, **16**, 323.

exclude the possibility of a three-carbon isomerisation during the interaction of cinnamyl bromide with toluene-*p*-sulphonamide, the cinnamyl derivative was reduced with hydrogen and palladium–charcoal. The product was identical with that obtained from 3-phenylpropylamine and toluene-*p*-sulphonyl chloride.

Phenyl 1-phenylpropyl sulphide was converted into the sulphone, but the sulphide's reaction with chloramine-T appears to be abnormal and is under investigation.

Acid Hydrolysis of Sulphonamides.—Hydrolysis of the various *N*-aralkyltoluene-*p*-sulphonamides might afford further proof of their structure by formation of an amine and toluene-*p*-sulphonic acid, as in the hydrolysis of the *N*-substituted arenesulphonamides obtained in Hinsberg's process for the separation of amines, in which, however, concentrated hydrochloric acid at 150—170° is usually employed. We found that hot aqueous hydrochloric acid (1 : 1) and *N*-cinnamyl-, *N*-1-phenylallyl-, and *N*-1-phenylpropyl-toluene-*p*-sulphonamides gave toluene-*p*-sulphonamide. Odours of the aralkyl chlorides were always present. The *N*-3-phenylpropyl derivative was not hydrolysed by the hot concentrated acid. *N*-Benzyltoluene-*p*-sulphonamide is completely stable to the boiling aqueous acid (1 : 1), and *N*-allyltoluene-*p*-sulphonamide was only very slowly attacked, giving unidentified products. The stability of the allyl–nitrogen bond was to be expected in view of the formation of *N*-allyl*iso*butylamine from *N*-allyl-*N*-*iso*butyltoluene-*p*-sulphonamide and hydrochloric acid at 130° [8] and the stability of the similar bond in *N*-allyl-*N*-allylthiotoluene-*p*-sulphonamide to hot hydrochloric acid.[9]

There are very few recorded instances of the elimination of a sulphonamide on hydrolysis of a *N*-substituted derivative: (1) arenesulphonyl derivatives of *S*-alkyl*iso*thioureas give the arenesulphonamide and alkanethiol with strong acids; [10] (2) tritoluene-*p*-sulphonylmelamine gives cyanuric acid and toluene-*p*-sulphonamide with ethanolic hydrogen chloride, though hot sulphuric acid gives melamine and the sulphonic acid; [11] (3) *N*-phenyl-*N*-vinyltoluene-*p*-sulphonamide with 50% sulphuric acid gives *N*-phenyltoluene-*p*-sulphonamide and acetaldehyde.[12] The first two cases are not closely related to the abnormal hydrolyses examined by us, and the third probably involves the hydration of the vinyl group, giving an unstable 1-hydroxyethylamino-grouping.

The fission of the N–C bond by acid, in the cases of *N*-cinnamyl- and *N*-1-phenylallyltoluene-*p*-sulphonamides is probably associated with the relatively high stability of the aralkenyl groups as mesomeric carbonium ions.[13] If the first step in acid hydrolysis of sulphonamides is a protonisation of the nitrogen atom, the resulting ammonium ion might decompose by the splitting off of such a carbonium ion, rather than by separation of the arenesulphonyl cation, which presumably occurs, under more vigorous conditions, during normal hydrolysis:

$$Ar\cdot SO_2\cdot NHR \xrightarrow{H^+} Ar\cdot SO_2\cdot \overset{+}{N}H_2R \xrightarrow[H_2O]{\text{normal}} Ar\cdot SO_2\cdot OH + R\cdot NH_2 + H^+$$

$$\Big\downarrow \text{abnormal}$$

$$Ar\cdot SO_2\cdot NH_2 + R^+$$

The carbonium ion, $Ph\cdot CH{:}CH\cdot \overset{+}{C}H_2 \longleftrightarrow Ph\cdot \overset{+}{C}H\cdot CH{:}CH_2$, can become stabilised either by capture of a chlorine ion, giving cinnamyl chloride, or by ejection of a proton, giving phenylallene; in either case, cationic polymerisation may follow.

The abnormal hydrolysis of *N*-1-phenylpropyltoluene-*p*-sulphonamide (see above) is explicable on similar lines, since there is evidence that 1-phenylalkyl groups have considerable stability as cations.[13] To confirm this view, *N*-1-phenylethyltoluene-*p*-sulphonamide was boiled with aqueous (1 : 1) hydrochloric acid. As expected, the products were toluene-*p*-sulphonamide, 1-phenylethyl chloride, and styrene. When hydrolysis was

[8] Wedekind, *Ber.*, 1909, **42**, 3941.
[9] Ash, Challenger, and Greenwood, *J.*, 1951, 1877.
[10] Bergmann, Israelashvili, and Weinberg, *J. Amer. Chem. Soc.*, 1946, **68**, 761.
[11] Kurzer and Powell, *J.*, 1953, 2536.
[12] Clemo and Perkin, *J.*, 1924, **125**, 1808.
[13] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 324, 586.

effected with phosphoric acid at 100°, the products were toluene-*p*-sulphonamide and an oily mixture of distyrene and higher polymers which was almost identical with the mixture of liquid polymers obtained from styrene and phosphoric acid [14] and from styrene and sulphuric acid.[15]

Ingold [16] points out that the stability of the 1-phenylethyl cation is comparable with that of trialkylmethyl cations. Hickinbottom's results [17] are relevant. He found that *N-tert.*-butyl-*N*-phenyltoluene-*p*-sulphonamide with 15N-sulphuric at 135—145° gave *N*-phenyltoluene-*p*-sulphonamide in 85% yield. *N-tert.*-Butyl-, *N-tert.*-pentyl-, and *N-tert.*-hexyl-anilines with strong acids at 110—145° slowly gave low yields of aniline.

The hydrolysis of *N-tert.*-butyltoluene-*p*-sulphonamide might therefore be expected to be abnormal and to give toluene-*p*-sulphonamide and reaction products of the *tert.*-butyl cation. We obtained the arenesulphonamide, *tert.*-butyl chloride, and *iso*butene. If the *tert.*-butyl chloride is continuously removed, little *iso*butene is produced, suggesting that the chloride is the primary product. In contrast, *N-iso*propyltoluene-*p*-sulphonamide was recovered in high yield after prolonged boiling with hydrochloric acid.

N-tert.-Butyltoluene-*p*-sulphonamide is almost insoluble in hot dilute alkali, in contrast with the solubility in cold alkali of most *N*-monoalkyl-sulphonamides, including the *N-iso*propyl compound. In this respect the *N-tert.*-butyl compound resembles *N*-benzylbenzenesulphonamide and *N*-benzyltoluene-*p*-sulphonamide.[18] *N*-1-Phenylethyl-, *N*-cinnamyl-, *N*-1-phenylallyl-, and *N*-1-phenylpropyl-toluene-*p*-sulphonamide dissolve in hot aqueous sodium hydroxide, but separate again when the solution is cooled.

Oxidation of Sulphonamides.—In Part II it was shown that *N*-allyltoluene-*p*-sulphonamide is oxidised by excess of boiling alkaline permanganate to *p*-sulphamylbenzoic acid. This acid is also obtained with toluene-*p*-sulphonamide when the corresponding *N*-methyl and *N*-ethyl derivatives are similarly oxidised. We are aware of only one other recorded oxidative dealkylation of *N*-alkylsulphonamides. Verkade [19] found that *N-o*-methoxyphenyl-*N*-methyltoluene-*p*-sulphonamide gives *N*-2-methoxy-4-nitrophenyltoluene-*p*-sulphonamide with 10% nitric acid at 80°. Under milder conditions, however, the *N*-methyl-sulphonamido-group is not attacked. Remsen and Clark [20] prepared *o*-carboxy-*N*-methylbenzenesulphonamide from *N*-methyltoluene-*o*-sulphonamide and alkaline permanganate below 10°. Oxidative dealkylation of amines by permanganate has, however, been observed with tropine and scopoline,[21] and with dibutylamine.[22]

The oxidation of primary and secondary amines probably involves a preliminary dehydrogenation to the imine. This has been isolated from benzylaniline and its substitution products [23] and aminofluorene.[24] Usually, however, a carbonyl derivative is produced, presumably by hydrolysis of the imine.[25,26] We have detected acetone, *p*-sulphamylbenzoic acid, and toluene-*p*-sulphonamide on permanganate oxidation of *N-iso*propyltoluene-*p*-sulphonamide in either neutral or alkaline solution. With limited quantities of permanganate, oxidation of the methyl group of the toluene-*p*-sulphonyl residue and of the *N*-alkyl group occurs simultaneously. Such dealkylations do not require the presence of a hydrogen atom on the nitrogen since *NN*-dimethyltoluene-*p*-sulphonamide is readily dealkylated by alkaline permanganate, giving *p*-sulphamylbenzoic acid. This reaction may be compared with the easy oxidation of tertiary amines.

Vorländer [27] and Goldschmidt and Beuschel [24] found that *tert.*-butylamine, which contains no hydrogen on the α-carbon atom, was not oxidised by permanganate under

[14] Cf. Dumontet, *Compt. rend.*, 1952, **234**, 1173.
[15] Risi and Gauvin, *Canad. J. Res.*, 1936, **14**, *B*, 255.
[16] Ingold, *op. cit.*, ref. 13, pp. 316, 325.
[17] Hickinbottom, *J.*, 1933, 1070.
[18] Carothers, Bickford, and Hurwitz, *J. Amer. Chem. Soc.*, 1927, **49**, 2913.
[19] Verkade, *Rec. Trav. chim.*, 1948, **67**, 241.
[20] Remsen and Clark, *Amer. Chem. J.*, 1903, **30**, 281.
[21] Houben-Weyl, "Die Methoden der Organischen Chemie," Thieme, Leipzig, 1925, Vol. II, p. 21.
[22] Smirnow and Shklyaruk, *J. Gen. Chem., U.S.S.R.*, 1950, **20**, 331 (*Chem. Abs.*, 1950, **44**, 3689).
[23] Ref. 21, p. 96.
[24] Goldschmidt and Beuschel, *Annalen*, 1926, **447**, 197.
[25] Wallach and Claisen, *Ber.*, 1875, **8**, 1237.
[26] Goldschmidt and Voeth, *Annalen*, 1924, **435**, 265.
[27] Vorländer, *ibid.*, 1906, **345**, 251.

conditions where other amines were rapidly oxidised. The behaviour of *N-tert.*-butyltoluene-*p*-sulphonamide towards alkaline permanganate was therefore examined. Under conditions (*A*) where other *N*-alkyltoluene-*p*-sulphonamides give approximately 50% yields of *p*-sulphamylbenzoic acid, the *N-tert.*-butyl compound gave in 68% yield *N-tert.*-butyl-*p*-sulphamylbenzoic acid free from any other sulphonamide or carboxylic acid. The minor products of the permanganate oxidation (*A*) were *tert.*-butylamine and 2-methyl-2-nitropropane. These compounds were also obtained with oxalic acid on prolonged oxidation (*B*) of *N-tert.*-butyl-*p*-sulphamylbenzoic acid. The nitro-compound was identical with a specimen prepared by permanganate oxidation of *tert.*-butylamine.[28] The 2-methyl-2-nitropropane produced in reactions (*A*) and (*B*) presumably arises by the same oxidation. It is, however, unlikely that *tert.*-butylamine is formed by simple alkaline hydrolysis of its toluene-*p*-sulphonyl or *p*-carboxybenzenesulphonyl derivatives because these compounds were almost completely unaffected by boiling 2N-sodium hydroxide.[29]

A second possible mechanism for reactions (*A*) and (*B*) would involve oxidation of the sulphonamide to a hydroxylamine derivative, $p\text{-}CO_2H\cdot C_6H_4\cdot SO_2\cdot N(OH)Bu^t$. Such compounds are hydrolysed by alkali to a nitroso-compound and a sulphinic acid thus:[30] $Ph\cdot SO_2\cdot N(OH)Ph + NaOH = Ph\cdot SO_2Na + Ph\cdot NO + H_2O$. The nitro-compound could presumably arise by oxidation of the nitroso-derivative, but this mechanism does not explain the formation of the amine which is also produced in reactions (*A*) and (*B*). Furthermore, the sulphinic acid should yield the sulphonic acid on further oxidation; *p*-sulphobenzoic acid could not be detected. Finally, the attachment of oxygen to amine nitrogen is particularly facilitated by such reagents as Caro's acid, benzoyl peroxide, and hydrogen peroxide.[26,31] *N-tert.*-Butyl-*p*-sulphamylbenzoic acid was unchanged after treatment with neutral sodium monopersulphate, ethereal monoperphthalic acid, hydrogen peroxide in acetic acid or in sodium hydroxide, or sodium peroxide. Caro's acid at 40° gave *p*-sulphamylbenzoic acid. The intermediate formation of a hydroxylamine derivative is therefore unlikely.

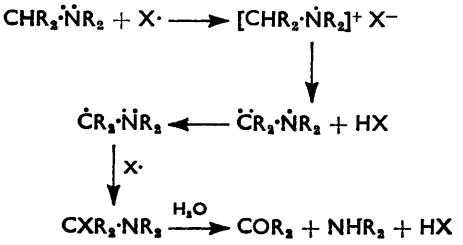
Probably, oxidative degradation of the aromatic ring gives oxalic acid (which was detected) and *tert.*-butylsulphamic acid. The literature contains very little clear information concerning the alkaline hydrolysis of *N*-alkylsulphamic acids. There is, however, some evidence that electron access to the nitrogen atom facilitates hydrolytic fission of the N–S link, phenylsulphamic acid being stable to hot strong alkali whereas the *p*-ethoxyphenyl compound readily gives *p*-phenetidine.[32] *tert.*-Butylsulphamic acid might therefore, under the conditions of our experiments, give *tert.*-butylamine and sulphate, both of which were detected. The amine would then yield 2-methyl-2-nitropropane on oxidation. The high consumption of permanganate (24 equiv. per mole) during the oxidation is also consistent with this assumption. Formation of oxalic acid and the other products mentioned above requires 26 equiv. Under identical conditions *p*-sulphamylbenzoic acid is slowly oxidised, giving oxalic acid and sulphate.

Analogy with *N-tert.*-butyltoluene-*p*-sulphonamide would suggest that toluene-*p*-sulphonanilide would be oxidised to *p*-carboxybenzenesulphonanilide and oxidation products of aniline. However, when an excess of 6% neutral or alkaline permanganate is used, the main product is *p*-sulphamylbenzoic acid, and we have not been able to detect nitrobenzene. With a limited quantity of 3% neutral ($MgSO_4$) permanganate, toluene-*p*-sulphonamide can be isolated, as reported by Troeger and Uhlmann.[33] These products must be formed by oxidative degradation of the *N*-phenyl ring. This degradation occurs far more rapidly with the sulphonanilide than with acetanilide.

No decision has yet been reached regarding the mechanism of oxidation of amines by alkaline permanganate. Drummond and Waters[34] consider that the first step is the removal of a single electron from the amine by the MnO_4^- ion and that attack occurs

[28] Kornblum and Clutter, *J. Amer. Chem. Soc.*, 1954, **76**, 4494.
[29] See also Sidgwick, "Organic Chemistry of Nitrogen," Univ. Press, Oxford, 1937, p. 157.
[30] Piloty, *Ber.*, 1896, **29**, 1559; Angeli, Angelico, and Scurti, *Chem. Zentr.*, 1902, II, 691.
[31] Ref. 29, p. 25.
[32] Audrieth *et al.*, *Chem. Rev.*, 1940, **26**, 68; Weil and Moser, *Ber.*, 1922, **55**, 732.
[33] Troeger and Uhlmann, *J. prakt. Chem.*, 1895, **51**, 435.
[34] Drummond and Waters, *J.*, 1953, 435.

vicinally to the nitrogen atom. Horner and Betzel [35] suggest that oxidation of tertiary amines by benzoyl peroxide also involves extraction of a single electron from the substrate, by means of a free radical. They suggest that this electron is removed from the unshared pair of the nitrogen atom and put forward the following scheme which might also apply to oxidation of tertiary amines or *N*-dialkylsulphonamides by permanganate (X· is a free radical) :



A slightly modified scheme could be suggested for oxidation of primary and secondary amines and of *N*-monoalkyl-sulphonamides. However, this mechanism would appear inapplicable to the oxidation of *N-tert.*-butyltoluene-*p*-sulphonamide. Removal of one electron from the nitrogen would give the radical-ion $[RSO_2\cdot\dot{N}H\cdot CMe_3]^+$, which might be expected to lose a proton giving $RSO_2\cdot\dot{N}\cdot CMe_3$. This free radical would then presumably dimerise to give the tetrasubstituted hydrazine $RSO_2\cdot N(CMe_3)\cdot N(CMe_3)\cdot SO_2R$.[24, 26] The oxidation products observed by us could hardly arise from further oxidation of such a hydrazine. To this extent our results support the conclusions of Drummond and Waters.[34]

Experimental

Preparation of Cinnamyl Phenyl Sulphide.—Cinnamyl bromide was prepared by a modification of Bouis's method [36] which yielded a purer product. Cinnamyl alcohol is added to phosphorus tribromide and pyridine in an ice-bath, and the cinnamyl bromide separated from phosphorus compounds by ether extraction followed by distillation; it had b. p. 127—129°/12 mm. (yield 74%). The method described by Tarbell and McCall [37] for the preparation of similar sulphides was then employed. Thiophenol (28·8 g.) was stirred into ethanolic sodium ethoxide [from sodium (6 g.) and ethanol (125 c.c.)]. Cinnamyl bromide (51·5 g.) was added slowly so as to keep the mixture warm but to avoid refluxing. After 3 hours' stirring the mixture was added to water (800 c.c.), and the precipitate crystallised from ethanol. It had m. p. 78·5° (yield, 47·2 g., 80%) (Found : C, 79·25, 79·25; H, 6·35, 6·15; S, 13·95, 14·15. Calc. for $C_{15}H_{14}S$: C, 79·65; H, 6·2; S, 14·15%). Barnard and Hargrave [38] prepared cinnamyl phenyl sulphide but gave no experimental details. Their sample had m. p. and mixed m. p. with the above specimen, 78°.

Dr. R. W. Saville, of the British Rubber Producers' Research Association, has determined the infrared spectrum of Barnard's sample and reports that : " The spectrum shows a band at 960 cm.$^{-1}$ indicating unsaturation of the type *trans*-R·CH:CHR. The band is not affected by conjugation, stilbene and other compounds with this type of unsaturation all showing the 960 cm.$^{-1}$ band. Vinylidene unsaturation $CH_2{=}C{:}$ is indicated by a band at 890 cm.$^{-1}$ and this band is not present in this case. Although, here, conjugation may alter the position of the 890 cm.$^{-1}$ band, it could not become as high as 960 cm.$^{-1}$. It appears that none of the isomer $CH_2{:}CH\cdot CHPh\cdot SPh$ is present, infrared evidence thus favouring the structure $Ph\cdot CH{:}CH\cdot CH_2\cdot SPh$." See also Bellamy.[39]

Cinnamyl Phenyl Sulphone.—Cinnamyl phenyl sulphide (2·5 g.) was dissolved in warm glacial acetic acid (40 c.c.). Hydrogen peroxide (30%; 1·6 c.c.) was then added, and the mixture gently warmed to keep the sulphide in solution, left at room temperature for 24 hr., and then poured into water (100 c.c.). Extraction with chloroform and washing with aqueous

[35] Horner and Betzel, *Annalen*, 1953, **579**, 175.
[36] Bouis, *Bull. Soc. chim. France*, 1927, **41**, 1160.
[37] Tarbell and McCall, *J. Amer. Chem. Soc.*, 1952, **74**, 48.
[38] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 543.
[39] Bellamy, " Infra-Red Spectra of Complex Molecules," Methuen, London, 1954, p. 31.

sodium hydrogen carbonate and crystallisation from light petroleum containing 5% of chloroform yielded needles, m. p. 115° (Found: C, 70·2; H, 5·2; S, 12·4. Calc. for $C_{15}H_{14}O_2S$: C, 69·8; H, 5·4; S, 12·4%). Barnard [40] gives the m. p. of the sulphone as 112—112·5°.

Cinnamyl Phenyl Sulphide and Chloramine-T: Attempted Preparation of a Sulphidimine.—This reaction was carried out under various conditions: (1) in water alone, (2) in acetone containing different proportions of water at room temperature and at 0°, and (3) in boiling alcohol for 1 hr.; the yield of product was then very low. The best yield was obtained as follows: The sulphide (8 g.) in acetone (130 c.c.) was treated with chloramine-T (16 g.) in water (30 c.c.), and the mixture shaken for 1 hr. and poured into water (400 c.c.). The resulting white solid was separated, washed with water to remove chloramine-T, and with dilute sodium hydroxide to remove toluene-*p*-sulphonamide and finally with water. It was then dried and recrystallised from alcohol to constant m. p. 88° [yield 10·4 g., 71·5% calculated as the sulphidimine (V)]. The m. p. was unchanged after the substance had been kept for several months or recrystallised from a different solvent, or when kept at its m. p. for 3 hr. [Found: C, 66·6; H, 5·3; N, 3·5; S, 16·0%; *M* (camphor), 315. $C_{22}H_{21}O_2NS_2$ requires C, 66·85; H, 5·3; N, 3·55; S, 16·2%; *M*, 395].

When the sulphide and chloramine-T were stirred for 3 hr. at −10°, samples of solid removed at intervals and freed from toluene-*p*-sulphonamide with sodium hydroxide contained much unchanged sulphide.

Reactions of N-1-*Phenylallyl*-N-*phenylthiotoluene*-p-*sulphonamide* (VI), *m. p.* 88°.—(1) *With hydrochloric acid.* The compound (2 g.) was refluxed with the concentrated acid (25 c.c.) for 1½ hr., giving a yellow oil and a strong odour of cinnamyl chloride. On cooling, an oil (*A*) and a crystalline solid separated. After being washed with benzene the crystals melted at 138° alone or in admixture with toluene-*p*-sulphonamide, m. p. 138°. The benzene yielded an oil which gave an odour of benzaldehyde with hot acidified potassium permanganate. The oil (*A*) was washed with alkali, shaken with ether, and the extract washed with water and evaporated; the residue did not distil below 160°/22 mm. (cinnamyl chloride boils at 98°/18 mm.). The oil contained much chlorine and some nitrogen and sulphur and was probably mainly a polymer of cinnamyl chloride.

(2) *With sodium hydroxide.* The compound (VI) (2 g.) was refluxed for 2 hr. with aqueous 25% sodium hydroxide (10 c.c.), giving an oil which solidified on cooling. Several recrystallisations from aqueous methanol (1 : 1) gave crystals, m. p. 103°, of the *sulphonamide* (VII) (Found: C, 67·15; H, 5·95; N, 5·1; S, 11·1. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 5·9; N, 4·9; S, 11·15%).

The alkaline solution had an odour of thiophenol. Acidification gave an oil and intensified the odour. Lead acetate paper turned yellow, and a drop of mercuric cyanide gave a white precipitate when exposed to the vapour. Hydrogen sulphide was absent. The acid solution when kept for 24 hr. deposited a solid (0·2 g.) which after recrystallisation from ethanol had m. p. 62° alone and when mixed with authentic diphenyl disulphide.

(3) *Oxidation of the toluene*-p-*sulphonamide* (VI) *with alkaline potassium permanganate.* The compound (VI) (3 g.) was refluxed with water (15 c.c.), potassium permanganate (14 g.), and potassium carbonate (4 g.). The odour of benzaldehyde was detected. When no further reduction occurred, sulphur dioxide was passed in; the clear liquid contained some suspended solid (*S*) which was mainly diphenyl disulphide, m. p. and mixed m. p. 60°. Acidification of the filtrate gave a white solid, m. p. 280—283° (decomp.). The m. p. of *p*-sulphamylbenzoic acid is given in the literature as 280—281° (decomp.). One of us (P. A. B.) finds that crystallisation raises the m. p. to 292—293° (see p. 1766). In a second experiment steam distillation of the solid (*S*) yielded benzoic acid, m. p. and mixed m. p. 119—122°.

(4) *Reduction of the toluene*-p-*sulphonamide* (VI), *with zinc and hydrochloric acid.* The compound (VI) (1 g.) was mixed with successive quantities of zinc dust and the acid, a strong odour of thiophenol being produced. Solids were then separated and extracted with ether, yielding a white solid, m. p. 103—104° after recrystallisation from aqueous alcohol. An admixture with *N*-1-phenylallyltoluene-*p*-sulphonamide, m. p. 103°, had the same m. p. The m. p. of the *N*-cinnamyl-sulphonamide, m. p. 110°, was depressed to 80—90°. Reduction of compound (VI) (3 g.) with palladium gave an odour of thiophenol, much unchanged material, and a mixture which appeared to contain a small amount of *N*-1-phenylallyltoluene-*p*-sulphonamide.

Reactions of N-1-*Phenylallyltoluene*-p-*sulphonamide.*—Hydrolysis with hot 2N-sulphuric acid yielded a small amount of toluene-*p*-sulphonamide (m. p. and mixed m. p.); 1 g. of (VII) was boiled with syrupy phosphoric acid (1 c.c.) in diethylene glycol (2 c.c.) for 2 min., and the

[40] Barnard, personal communication.

product cooled, acidified with hydrochloric acid, and filtered, giving toluene-*p*-sulphonamide, m. p. and mixed m. p. 138°. The acid filtrate when made alkaline and extracted with ether did not yield amine. The *N*-1-phenylallyl compound was recovered unchanged after treatment in aqueous alcoholic suspension with sodium amalgam.

Hydrogenation of N-1-*Phenylallyltoluene*-p-*sulphonamide with* 5% *Palladium–Charcoal.*—The compound (VII) (2 g.) in ethanol (60 c.c.) with the catalyst (4·5 g.) absorbed 170 c.c. of hydrogen in 10 min. (Calc. for $C_{16}H_{17}O_2NS$: 160 c.c.). Separation of the catalyst and concentration gave N-1-*phenylpropyltoluene*-p-*sulphonamide*, m. p. 108° after repeated crystallisation from aqueous ethanol.

The m. p. of a mixture with the phenylallyl compound (m. p. 103°) was 96—100° (Found : C, 66·35; H, 6·1. $C_{16}H_{19}O_2NS$ requires C, 66·4; H, 6·65; N, 4·85; S, 11·05%).

Synthesis of N-1-*Phenylpropyltoluene*-p-*sulphonamide.*—Propiophenone oxime, m. p. 54—55° (lit. 53—54°), was reduced with sodium and alcohol to 1-phenylpropylamine, b. p. 97·5°/30 mm. Billon [41] gives 100—105°/35 mm. The benzoyl derivative and the hydrochloride melted at 116—117° and 192°, respectively (lit. 115—116° and 194°). The base (2·8 g.), suspended in aqueous sodium hydroxide (50 c.c.), was added to toluene-*p*-sulphonyl chloride (4 g.) in the minimum quantity of acetone. The mixture was shaken for 10 min., the emulsion filtered, and the filtrate acidified and shaken. The precipitate (5·7 g., m. p. 103°) was recrystallised (aqueous ethanol) to m. p. 106—107° (Found : C, 66·45; H, 6·35; N, 5·15; S, 11·05%). The mixed m. p. with the product (m. p. 108°) of the previous experiment was 106—108°. An attempt to prepare this compound by refluxing toluene-*p*-sulphonamide (8·6 g.) and 1-phenylpropyl bromide (10 g.) in alcohol with alcoholic sodium hydroxide (2 g. in 80 c.c.) for 7 hr. yielded β-methylstyrene (b. p. 84—86°/25 mm.; lit. 76—78°/19 mm.) and unchanged sulphonamide.

Hydrolysis of N-1-*Phenylpropyltoluene*-p-*sulphonamide.*—The sulphonamide (0·5 g.) was refluxed with hydrochloric acid (60 c.c.) for 10 hr. A strong odour resembling that of 1-phenylpropyl bromide was produced, and on cooling, toluene-*p*-sulphonamide (0·1 g.; m. p. and mixed m. p. 136—138°) separated. The acid, when freed from oil, concentrated and made alkaline, gave no odour of an amine. Repetition of this experiment for 6 hr. with 1·5 g. of the sulphonamide gave the same result; some unchanged material was recovered, and amine not detected.

Hydrogenation of N-*Cinnamyltoluene*-p-*sulphonamide.*—The *N*-cinnamyl compound (2 g.) in ethanol (50 c.c.) in presence of palladium–charcoal catalyst (4 g.) absorbed 170 c.c. of hydrogen (Calc. : 160 c.c.). The filtered and evaporated solution left a solid, m. p. 66—67° [after crystallisation from aqueous methanol (1 : 1)] (Found : C, 66·2; H, 6·5; N, 4·75; S, 11·15. Calc. for $C_{16}H_{15}O_2NS$: C, 66·4; H, 6·65; N, 4·85; S, 11·1%). The mixed m. p. with an authentic sample of *N*-3-phenylpropyltoluene-*p*-sulphonamide, m. p. 66—67°, was the same.

Synthesis of N-3-*Phenylpropyltoluene*-p-*sulphonamide.*—3-Phenylpropylamine was prepared by Tafel's method.[42] About 0·5 g. was mixed with dilute sodium hydroxide (5 c.c.), and the mixture added to toluene-*p*-sulphonyl chloride in the minimum of acetone and shaken. After 30 min., hydrochloric acid (5 c.c.) was added to the emulsion. A brown oil separated which soon solidified to needles, m. p. 66—67° [after recrystallisation from aqueous methanol (1 : 1)]. Coke and McElvain [43] give m. p. 65·5°. The amide (0·4 g., prepared by hydrogenation, see above) was boiled with hydrochloric acid (20 c.c.) for 4 hr. Most of it was unchanged, and toluene-*p*-sulphonamide was not obtained.

N-*Mono- and* NN-*Di-cinnamyltoluene*-p-*sulphonamides.*—The following method is based on that of de Montmollin and Matile [44] for the preparation of the mono- and di-2-β-naphthyloxyethyl derivatives of toluene-*p*-sulphonamide. Cinnamyl bromide (5·9 g., 0·05 mole) and toluene-*p*-sulphonamide (8·6 g., 0·05 mole) in alcohol (60 c.c.) were treated with a solution of potassium hydroxide (2·9 g., 0·05 mole) in alcohol (25 c.c.) containing a few drops of water. The mixture was refluxed for 6 hr., the solvent removed, and water (100 c.c.) added. The resulting oily solid was washed with ether and shown to be unchanged sulphonamide. The ether was shaken with alkali to remove toluene-*p*-sulphonamide, then with water, and dried, yielding a yellow oil (6·6 g.), which was dissolved in methanol. Needles of NN-*dicinnamyl compound* separated, m. p. 95° (after recrystallisation from methanol) (Found : C, 74·45; H, 6·2; N, 4·65; S, 8·65. $C_{25}H_{25}O_2NS$ requires C, 74·45; H, 6·2; N, 4·65; S, 7·9%). Concentration of the methanol

[41] Billon, *Compt. rend.*, 1926, **182**, 472.
[42] Tafel, *Ber.*, 1886, **19**, 1930.
[43] Coke and McElvain, *J. Amer. Chem. Soc.*, 1931, **53**, 1589.
[44] de Montmollin and Matile, *Helv. Chim. Acta*, 1929, **12**, 871.

mother-liquors gave the *mono-derivative*, m. p. 110° (after recrystallisation from acetone–light petroleum) (Found: C, 66·8; H, 6·2; N, 4·65; S, 11·3. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 5·9; N, 4·9; S, 11·15%).

Conversion of the mono- into the di-cinnamyl derivative. The monocinnamyl compound (0·9 g.) was warmed with sodium hydroxide (0·18 g.) in ethanol (20 c.c.), cinnamyl bromide (0·6 g.) added, and the mixture refluxed for 3 hr. The solid which separated on cooling was washed with water. Recrystallisation from methanol gave the dicinnamyl compound, m. p. and mixed m. p. 92—95°.

Neither compound gave any odour with cold acidified potassium permanganate but, when warmed, benzaldehyde was detected in both cases. The di-derivative was insoluble in aqueous sodium hydroxide, hot or cold; the mono-derivative was insoluble in the cold but dissolved on being warmed and separated again on cooling. The monocinnamyl derivative (1 g.), when boiled for 7 hr. with diluted hydrochloric acid (1 : 1, 30 c.c.), gave an odour of cinnamyl chloride, and a deposit of toluene-*p*-sulphonamide on cooling. A black resin was also produced but the acid solution gave no amine odour when made alkaline.

Phenyl 1-*Phenylpropyl Sulphide.*—Thiophenol (2·9 g.) was added to a solution of sodium ethoxide [from sodium (0·6 g.) and ethanol (30 c.c.)], the mixture warmed, and 1-phenylpropyl bromide (5·75 g.) slowly added. After refluxing for 3 hr. the mixture was poured into water (500 c.c.), excess of alcohol removed, and the suspended oil extracted with ether and dried (Na_2SO_4). The *sulphide* distilled at 186—187°/25 mm., solidified on cooling, and after crystallisation from aqueous ethanol (1 : 1) formed needles, m. p. 42° (Found: C, 79·05; H, 7·0; S, 13·8. $C_{15}H_{16}S$ requires C, 78·9; H, 7·1; S, 14·05%).

Phenyl 1-*Phenylpropyl Sulphone.*—The sulphide (0·2 g.) in the minimum of glacial acetic acid was treated with 3% aqueous potassium permanganate in slight excess, sulphur dioxide passed in, and the colourless solution poured into water (100 c.c.). The resulting white *sulphone* (m. p. 94—97°) crystallised from ethanol in needles, m. p. 101° (Found: C, 68·95; H, 6·2; S, 12·4. $C_{15}H_{16}O_2S$ requires C, 69·2; H, 6·2; S, 12·3%).

Attempted Preparation of S-*Phenyl*-S-1-*phenylpropyl*-N-*toluene*-p-*sulphonylsulphidimine.*—Phenyl 1-phenylpropyl sulphide (3 g.) in acetone (30 c.c.) and chloramine-T (6 g.) in water (50 c.c.) were shaken together for 1 hr. and poured into water (250 c.c.). Evaporation of acetone left a wax which, after being washed with sodium hydroxide and then with water, had m. p. 99—111°; after repeated crystallisation from acetone–light petroleum the m. p. was finally raised to 116—117° (Found: C, 56·85; H, 4·60; N, 3·6; S, 23·05. $C_{13}H_{13}O_2NS_2$ requires C, 55·9; H, 4·7; N, 5·0; S, 22·95%). The N-*phenylthio-compound* will be studied in detail later. The aqueous filtrate from this reaction was extracted with ether, the resulting solid added to that from the mother-liquors of the compound, m. p. 116—117°, and the whole dissolved in acetone and shaken for 2 hr. with more chloramine-T in 20 c.c. of water. Distillation of the acetone left a solid which, after removal of toluene-*p*-sulphonamide with dilute sodium hydroxide, had m. p. 96—98° (0·1 g.).

The alkaline washings and the filtrates from the two treatments with chloramine-T were united and concentrated. A white solid (1·0 g.) separated; it had m. p. 228—229° after crystallisation from ethanol. A mixed m. p. with the sodium salt of *S*-phenyltoluene-*p*-sulphonamidosulphinetoluene-*p*-sulphonylimine, m. p. 231°, prepared by Clarke, Kenyon, and Phillips's method,[45] was 228—229°. Acidification gave the corresponding acid which was impure (m. p. 96—150°) after one crystallisation from alcohol (see below). Acidification of the alkaline filtrate from the salt of m. p. 228—229° gave toluene-*p*-sulphonamide.

Examination of the Residues from the Interaction of Chloramine-T and Cinnamyl Phenyl Sulphide.—After the identification of the compound (VI), m. p. 88°, arising from this reaction (see p. 1761) as *N*-1-phenylallyl-*N*-phenylthiotoluene-*p*-sulphonamide the aqueous acetone liquors were combined with the alkaline washings from the solid of m. p. 88° and concentrated to about two-thirds of their volume in an open dish on the steam-bath. A brown colour quickly developed and traces of solid formed. The alkaline solution (S) on extraction with ether yielded a brown oil with a strong odour of cinnamaldehyde and white crystals. The crystals were drained and washed with ethanol. They melted at 102—103° alone and in admixture with *N*-1-phenylallyltoluene-*p*-sulphonamide, m. p. 103°. The alkaline solution (S) was acidified with hydrochloric acid, and odours of cinnamyl chloride and thiophenol were detected. Extraction with ether yielded a brown solid which dissolved almost completely in warm dilute sodium hydroxide, but was mostly deposited on cooling; after two crystallisations from acetone–light petroleum it had 228—230° alone and in admixture with the sodium salt, m. p. 231° (see

[45] Clarke, Kenyon, and Phillips, *J.*, 1930, 1230.

above). Acidification of the alkaline extract gave a slight odour of thiophenol and a precipitate of toluene-*p*-sulphonamide, m. p. and mixed m. p. 137°.

N-tert.-*Butyltoluene*-p-*sulphonamide*.—Toluene-*p*-sulphonyl chloride (57·2 g., 0·3 mole) in pyridine (70 c.c.) was added during 25 min. to a stirred solution of *tert.*-butylamine (21·9 g., 0·3 mole) in pyridine (25 c.c.). The temperature was kept at 35—40°. After 30 min. on the steam-bath, followed by addition of ice, the mixture was diluted to 1200 c.c. with water, and the precipitated solid was washed with dilute hydrochloric acid and water. Two crystallisations from aqueous ethanol (1 : 1) (charcoal) gave short white needles, sintering at 111°, m. p. 113—114° (Found: C, 58·1; H, 7·3; N, 6·2; S, 14·1. $C_{11}H_{17}O_2NS$ requires C, 58·1; H, 7·5; N, 6·2; S, 14·1%). The *sulphonamide* is sparingly soluble (less than 2%) in boiling 2N-sodium hydroxide, but soluble in a cold ethanol–water (5 : 3) solution of sodium hydroxide.

Hydrolysis of N-tert.-*butyltoluene*-p-*sulphonamide*. (1) Aqueous hydrochloric acid (1 : 1; 50 c.c.) and the sulphonamide (12·0 g.) were refluxed, and volatile matter escaping from the water-cooled condenser was collected in a trap cooled in methanol–solid carbon dioxide. The sulphonamide quickly melted, and after 10 min. the gases escaping from the condenser decolorised bromine in carbon tetrachloride, indicating the presence of *iso*butene. After about 1 hr. an oil, b. p. about 50° (presumably *tert.*-butyl chloride), began to reflux, and a solid separated. After 5 hr. the solid had mostly redissolved and oil had almost ceased to reflux. On distillation through a lagged 6-in. Vigreux column no arrest in temperature rise was detected at 50° (*tert.*-butyl chloride) or at 80° (*tert.*-butanol–water), steady distillation first occurring at 100°. On being cooled and made alkaline, a clear solution was obtained (indicating the absence of unchanged sulphonamide). Acidification then precipitated toluene-*p*-sulphonamide (7·55 g., 83·5% yield), m. p. and mixed m. p. 137—137·5° after recrystallisation from water.

The trap contained 2 c.c. of material liquid at −78° (*iso*butene melts at −140°). This was treated with sulphuric acid (1 : 1; 20 c.c.) at −78°, and the trap closed and shaken at −10° for 3 hr. About 0·3 c.c. of oil remained. This had a strong odour of *tert.*-butyl chloride, did not decolorise bromine in carbon tetrachloride, and solidified at −78°. The acid layer was separated and slowly added to stirred ice-cold sodium hydroxide (25 g.) in water (50 c.c.).[46] Distillation of the alkaline liquid gave 2 c.c. of material, b. p. 80—83° (the *tert.*-butanol–water azeotrope, b. p. 80°, containing 70% of butanol). Treatment of the distillate with anhydrous potassium carbonate gave *tert.*-butanol (1 g.) (*p*-nitrobenzoyl ester, m. p. and mixed m. p. 115—116·5°; 3 : 5-dinitrobenzoyl ester, m. p. and mixed m. p. 140·5—141·5°).

(2) Experiment (1) was repeated under different conditions. The sulphonamide (22·7 g.; 0·1 mole) and hydrochloric acid (1 : 1; 125 c.c.) were refluxed under a partial condenser with a cooling tube containing ethyl formate (b. p. 54°). Uncondensed material was passed successively through two traps at 0° and −78°. Steady distillation at 47° lasted for 20 min. After 50 min. the colourless liquid in the first trap was removed (7·8 g.), dried ($CaSO_4$), and distilled; b. p. 50—51°. Some dissolved *iso*butene escaped during the distillation. The liquid, b. p. 50—51°, was characterised as *tert.*-butyl chloride (yield 84·5%) by formation of its Grignard compound and reaction with α-naphthyl *iso*cyanate giving *N*-trimethylacetyl-1-naphthylamine, m. p. and mixed m. p. 147·5°. The second trap (−78°) contained 0·2 c.c. of liquid, presumably *iso*butene. With sulphuric acid and alkali as in (1) an odour of *tert.*-butanol was produced. From the original acid reaction mixture toluene-*p*-sulphonamide (17·1 g.) was obtained in quantitative yield; m. p. and mixed m. p. 136·5—137·5°. The acid had a faint odour of *tert.*-butanol but none was obtained on distillation before or after neutralisation.

N-Benzyltoluene-*p*-sulphonamide (0·1 g.; m. p. 114—115°; Chattaway[47] gives m. p. 115°) was unchanged when refluxed with diluted hydrochloric acid (1 : 1; 4 c.c.) for 5 hr.

N-1-*Phenylethyltoluene*-p-*sulphonamide*.—Toluene-*p*-sulphonyl chloride (19·1 g.; 0·1 mole) in pyridine (30 c.c.) was slowly added to a cooled, stirred solution of 1-phenylethylamine (12·1 g.; 0·1 mole) in pyridine (20 c.c.), kept for 1 hr. at 100°, and poured into water. Recrystallisation of the product from 50% alcohol (charcoal) gave white needles (14·9 g., 54%), m. p. 81—82° (Found: C, 65·3; H, 5·9; N, 5·1; S, 11·5. $C_{15}H_{17}O_2NS$ requires C, 65·4; H, 6·2; N, 5·1; S, 11·6%). The *sulphonamide* is only sparingly soluble in cold, but readily soluble in hot 2N-sodium hydroxide solution, from which it separates unchanged on cooling.

Hydrolysis with hydrochloric acid. The sulphonamide (6·9 g.) and aqueous hydrochloric acid (1 : 1; 80 c.c.) were slowly distilled in nitrogen through an 18-in. vertical air condenser into a tap-funnel containing light petroleum (b. p. 40—60°; 40 c.c.) and a few crystals of quinol. The aqueous layer of the distillate was periodically returned to the reaction flask. After 4 hr. the

[46] Read, *J. Amer. Chem. Soc.*, 1924, **46**, 1514.
[47] Chattaway, *J.*, 1905, **87**, 159.

clear aqueous mixture was cooled (deposit), made alkaline, and washed with ether to remove traces of resin. The alkaline solution on acidification gave toluene-*p*-sulphonamide, m. p. 136—137° (3·52 g., 82%) and mixed m. p. 136·5—137·5°. The light petroleum in the distillate was washed with alkali and with water and dried, yielding an oil (2·1 g.), b. p. 50—67°/12 mm. Redistillation gave two fractions: (*A*) b. p. 35—45°/12 mm. (0·6 g.), and (*B*) b. p. 66—67°/12 mm. (1·17 g.). Fraction (*A*) in carbon tetrachloride with bromine gave styrene dibromide which, when recrystallised from alcohol–water (4 : 1), had m. p. and mixed m. p. 73·5—74°. Fraction (*B*) had an odour of an aralkyl halide. Authentic 1-phenylethyl chloride,[48] purified by Ward's method,[49] had b. p. 67—68°/13 mm. and a similar odour. Fraction *B* was converted into *S*-1-phenylethylthiuronium picrate, m. p. and mixed m. p. 168—169° with an authentic sample of the same m. p. Levy and Campbell[50] give m. p. 167° (Found: C, 43·6; H, 3·6; N, 16·8. Calc. for $C_{15}H_{15}O_7N_5S$: C, 44·0; H, 3·7; N, 17·1%).

Hydrolysis with 90% *phosphoric acid.* *N*-1-Phenylethyltoluene-*p*-sulphonamide (5·5 g.) and phosphoric acid (*d* 1·75; 10 c.c.) were slowly distilled at 14 mm. from a bath at 100°. The distillate (1·6 g.) collected at −80° was water with one drop of an oil having an odour of styrene. The residue was diluted with water and extracted with ether, from which sodium hydroxide removed toluene-*p*-sulphonamide, m. p. 136·5—137° (2·8 g., 87%). The ether then yielded an oil which gave two fractions on distillation: (*A*) a mobile liquid (1·0 g.) and (*B*) a very viscous oil (0·45 g.). After two fractionations (*A*) had b. p. 155—157°/13 mm., 114—115°/0·4 mm., n_D^{20} 1·5880, and (*B*) boiled at 168—185°/0·15 mm. Analysis showed them to be polymers of styrene. Molecular weight (Rast) determinations were not reproducible, but a semimicro-ebullioscopic determination in benzene showed fraction (*A*) to be dimeric [Found for (*A*): C, 92·3; H, 7·6%; *M*, 214, 213. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%; *M*, 208. Found for (*B*): C, 92·3; H, 7·7%].

Attempted addition of bromine to fraction (*A*) under Stobbe and Posnjak's conditions[51] gave a viscous oil. Stoermer and Kootz[52] showed that distyrenes, containing only a small proportion of 1 : 3-diphenylbut-1-ene, give oils on bromination. Fraction (*A*) contained 30% of diphenylbutene (determined by the modified Wijs method[53]). The infrared spectrum of fraction (*A*) was compared with that of a distyrene (*C*), obtained from styrene and sulphuric acid and containing 10% of 1 : 3-diphenylbut-1-ene.[15] The spectra differed only in the lower intensity of a band at 964 cm.$^{-1}$ in the case of material (*C*). This would be expected if the specimens differed in their content of a diphenylbutene having a *trans*-CH:CH group.

Styrene and phosphoric acid. Freshly-distilled styrene (20 g.) and phosphoric acid (*d* 1·75; 100 c.c.) were heated on the steam-bath for 30 min., with vigorous stirring. The resulting oil (19 g.), extracted by ether, contained no unchanged styrene; on distillation it yielded a dimer (13·5 g.), b. p. 147—152°/0·6 mm., 125—132°/0·1 mm., n_D^{20} 1·5865 (Found: C, 92·4; H, 7·8%; *M*, 195, 199. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%; *M*, 208), which contained 38% of diphenylbutene (determined by the modified Wijs method). A trimer (2·4 g.), b. p. 190—207°/0·15 mm., n_D^{20} 1·5946, was also obtained (Found: C, 92·3; H. 7·8%; *M*, 299, 308. Calc. for $C_{24}H_{24}$: C, 92·3; H, 7·7%; *M*, 312).

Oxidation of N-tert.-*Butyltoluene*-p-*sulphonamide to* N-tert.-*Butyl*-p-*sulphamylbenzoic Acid.*—The sulphonamide (6 g.) was refluxed with potassium permanganate (16 g.) and anhydrous sodium carbonate (9 g.) in water (300 c.c.) for 1 hr. The cooled mixture was then treated with excess of sulphur dioxide, and the resulting white solid separated. It dissolved completely in cold 2N-sodium hydrogen carbonate (50 c.c.). On passing excess of carbon dioxide through the solution there was no precipitate, but on acidification to Congo-red material was precipitated having m. p. 182—183°, unchanged after two recrystallisation from water–ethanol (10 : 1). The *acid* (yield 5·5 g., 68%) formed long needles (Found: C, 51·7; H, 6·0; N, 5·4; S, 12·6. $C_{11}H_{15}O_4NS$ requires C, 51·3; H, 5·9; N, 5·4; S, 12·5%). The *methyl ester* was obtained by use of ethereal diazomethane and had m. p. 124—124·5° (constant) after crystallisation from benzene–light petroleum (b. p. 60—80°) (Found: C, 53·2; H, 6·1; N, 5·1; S, 11·6. $C_{12}H_{17}O_4NS$ requires C, 53·1; H, 6·3; N, 5·2; S, 11·8%). The ester (1 g.) was refluxed with aqueous hydrochloric acid (1 : 1; 20 c.c.) for 10 min.; an odour of *tert.*-butyl chloride was noticed. A solid which formed was completely soluble in aqueous sodium hydrogen carbonate,

[48] McKenzie and Clough, *J.*, 1913, **103**, 678.
[49] Ward, *J.*, 1927, 445.
[50] Levy and Campbell, *J.*, 1939, 1442.
[51] Stobbe and Posnjak, *Annalen*, 1909, **371**, 287.
[52] Stoermer and Kootz, *Ber.*, 1928, **61**, 2330.
[53] Wild, "Estimation of Organic Compounds," Univ. Press, Cambridge, 1953; Williams and Thomas, *J.*, 1948, 1867.

and after precipitation with hydrochloric acid it had m. p. and mixed m. p. 292—293° with *p*-sulphamylbenzoic acid.

Hydrolysis of N-tert.-*butyl*-p-*sulphamylbenzoic acid.* The acid (12·85 g., 0·05 mole) was heated for 1 hr. with aqueous hydrochloric acid (1 : 1; 120 c.c.) under a partial condenser at 54°. *tert.*-Butyl chloride, b. p. 50—52°, distilled and was characterised by conversion into *N*-trimethylacetyl-1-naphthylamine which when crystallised from ether–light petroleum (b. p. 40—60°) had m. p. and mixed m. p. 147—148°. During the hydrolysis *p*-sulphamylbenzoic acid (9·9 g., 93·5%) separated which, when crystallised from ethanol, melted at 293—294°, not depressing the m. p. (292—293°) of authentic material. The acid (1 g.) was treated in ether (15 c.c.) with a twofold excess of ethereal diazomethane. The ester (0·87 g.; 87·5%) when recrystallised from water–ethanol (5 : 1) had m. p. 180—181·5; the m. p. of a mixture with authentic ester was 180·5—182°.

p-*Sulphamylbenzoic acid.* This was prepared by oxidation of toluene-*p*-sulphonamide with potassium permanganate and was recrystallised from water.[9] It sintered slightly from 275° and melted at 292—293°. The m. p. was the same when the apparatus was slowly heated from room temperature or when the m. p. tube was inserted at 250°. Ash *et al.*[9] give m. p. 283° (decomp.). Other workers record m. p.s ranging from 280° to 286° (Found : C, 41·8; H, 3·8; N, 6·7; S, 15·7. Calc. for $C_7H_7O_4NS$: C, 41·8; H, 3·5; N, 7·0; S, 15·9%).

The acid [2 g. in ether (25 c.c.) or in benzene] reacted only sluggishly with ethereal diazomethane and methanol (1 c.c.) during 24 hr. Extraction of unchanged acid (0·41 g.) with aqueous sodium hydrogen carbonate gave the *ester* (1·3 g., 61%) which, recrystallised twice from alcohol, had m. p. 180·5—182° (Found : C, 44·6; H, 4·1; N, 6·7; S, 14·9. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5; S, 14·9%).

Oxidation of N-tert.-*Butyltoluene*-p-*sulphonamide* : *Identification of* 2-*Methyl*-2-*nitropropane and* tert.-*Butylamine.*—The sulphonamide (18·2 g.) was refluxed with excess of 6% aqueous permanganate containing 3% of sodium carbonate for 1 hr. Distillation yielded an alkaline aqueous liquid (see below) and a very volatile solid, m. p. 23°, identified as 2-methyl-2-nitropropane by its m. p. and infrared spectrum, which was identical with that of a specimen prepared by permanganate oxidation of *tert.*-butylamine.[28] *N-tert.*-Butyl-*p*-sulphamylbenzoic acid (15·7 g.) was obtained as before.

The spectrum of 2-methyl-2-nitropropane had maxima ($cm.^{-1}$) at : 2967 (s), 2924 (m, sh), 2874 (w, sh), 1548 (vs, sh), 1538 (vs), 1479 (s), 1458 (s), 1408 (s), 1376 (vs), 1348 (vs), 1256—1247 (m, broad), 1186 (m), 1017 (w), 858 (s), 801 (w), (intensities : vs, very strong; s, strong; m, medium; w, weak; sh, shoulder). The strong bands at about 1545 and 1348 $cm.^{-1}$ may be ascribed to the nitro-group, and the bands at 1408, 1376, *ca.* 1250, and 1186 $cm.^{-1}$ to the *tert.*-butyl group.[54]

In another experiment the sulphonamide (8 g.) was refluxed with potassium permanganate (11·13 g.) and anhydrous sodium carbonate (5·5 g.) in water (186 c.c.) (the calculated quantities for oxidation of a methyl to a carboxyl group) for 1·5 hr., the colour of the permanganate then being discharged. 20 C.c. of the mixture were distilled into dilute hydrochloric acid, which was then evaporated, thus removing 2-methyl-2-nitropropane. The residue was identified as *tert.*-butylamine hydrochloride by conversion into the picrate (m. p. and mixed m. p. 198—200°) and into *N-tert.*-butyltoluene-*p*-sulphonamide, m. p. and mixed m. p. 113—114°. The original alkaline mixture was filtered. Extraction of the manganese dioxide yielded unchanged sulphonamide (1·2 g., m. p. 113—114°), and acidification of the filtrate gave *N-tert.*-butyl-*p*-sulphamylbenzoic acid, m. p. 181·5—182°; yield, calc. on the sulphonamide which had reacted, 91%. Concentration of the acid filtrate, which contained sulphate, gave no sodium hydrogen *p*-sulphobenzoate. As this readily separates from acidified salt solutions[55] it was presumably absent.

Oxidation of N-tert.-*butyl*-p-*sulphamylbenzoic acid.* The acid (7 g.) was refluxed with potassium permanganate (21 g.) and anhydrous sodium carbonate (10·5 g.) in water (350 c.c.) until the permanganate was decolorised (9 hr.). A white solid formed in the condenser; this was treated with water, leaving some insoluble 2-methyl-2-nitropropane. Evaporation of the aqueous extract gave a solid which was insoluble in ether and sublimed above 120° without melting (sealed capillary tube). With dilute hydrochloric acid it gave carbon dioxide and *tert.*-butylamine hydrochloride (picrate, m. p. and mixed m. p. 198—200°). The solid was therefore the corresponding carbonate or carbamate. Passage of carbon dioxide into *tert.*-butylamine in moist ether gave a product with the same properties. 2-Methyl-2-nitropropane

[54] Ref. 39, pp. 13, 250.
[55] Smiles and Harrison, *J.*, 1922, **121**, 2022.

and *tert.*-butylamine were again obtained from the mixture. The nitro-compound had m. p. 23°, n_D^{28} 1·3980. Kornblum and Clutter [28] give m. p. 25—26°, n_D^{28} 1·3980. A specimen prepared by their method, dried [$Mg(ClO_4)_2$], and sublimed, had m. p. 23—25°, n_D^{28} 1·3980. Unchanged *N-tert.*-butylsulphamylbenzoic acid (2·8 g.) was removed as before. From the filtrate, faintly acid to Congo-red, sodium hydrogen oxalate separated, identified by the usual reactions and by conversion into its *S*-benzyl*iso*thiuronium salt, m. p. and mixed m. p. 195—196° (decomp.). The concentrated mother-liquors contained sulphate, but no sodium hydrogen *p*-sulphobenzoate could be detected.

Oxidation of p-*sulphamylbenzoic acid.* The acid (5·47 g.; equivalent to 7·0 g. of the *N-tert.*-butylsulphamylbenzoic acid) was oxidised with the same quantity of reagents as in the previous experiment. Decolorisation was complete (14 hr.) and 2·36 g. of unchanged acid were recovered. Concentration of the mixture and treatment as above gave approximately 1 g. of sodium hydrogen oxalate, identified as before [*S*-benzyl*iso*thiuronium salt, m. p. 195—196° (decomp.)].

N-iso*Propyltoluene*-p-*sulphonamide.* This was prepared from *iso*propylamine (17 c.c., 0·2 mole) and toluene-*p*-sulphonyl chloride (38·1 g., 0·2 mole) in pyridine as described for the *N-tert.*-butyl compound. It was purified by solution in warm aqueous sodium hydroxide, precipitation with hydrochloric acid, and crystallisation from aqueous alcohol (charcoal). The *amide* (28·5 g.; 67·5%) had m. p. 49·5—51°. The m. p. does not appear in the literature but is quoted as 51° [56] (Found: C, 56·3; H, 6·8; N, 6·6; S, 14·9. $C_{10}H_{15}O_2NS$ requires C, 56·3; H, 7·1; N, 6·6; S, 15·0%). When it was boiled for 14 hr. with aqueous hydrochloric acid (1 : 1; 230 c.c.) no volatile organic compound distilled and 90% of the sulphonamide was recovered unchanged. The aqueous layer when made alkaline gave a slight ammoniacal odour, presumably due to *iso*propylamine since aspiration through Nessler's solution gave a white precipitate but no brown colour.

Oxidation of N-iso*propyltoluene*-p-*sulphonamide.* A mixture of the sulphonamide (6 g.), potassium permanganate (30 g., 20 equiv. of O per mole), and anhydrous sodium carbonate (15 g.) in water (500 c.c.) was distilled in steam for 1 hr. The acetone in the distillate yielded 0·2 g. of 2 : 4-dinitrophenylhydrazone which, recrystallised from methanol, had m. p. and mixed m. p. 125—125·5°. Treatment of the main reaction mixture with sulphur dioxide and hydrochloric acid yielded *p*-sulphamylbenzoic acid (3·9 g., 68%) which, after recrystallisation from weak aqueous ethanol, had m. p. and mixed m. p. 292—293°. The amount of permanganate required for complete oxidation of the *N-iso*propyltoluene-*p*-sulphonamide to *p*-sulphamylbenzoic acid, carbon dioxide, and water is 25 equiv. per mole. When only 10 equiv. were used (reflux) and all permanganate was reduced, about one-third of the sulphonamide was recovered unchanged, and some toluene-*p*-sulphonamide and *p*-sulphamylbenzoic acid were obtained. By using only 2 equiv. of permanganate in presence of magnesium sulphate the yield of acetone 2 : 4-dinitrophenylhydrazone was 25%, original sulphonamide (67%) was recovered after treatment with sodium hydrogen carbonate, and a crude acid, m. p. 216—217°, which appeared to be a mixture of *p*-sulphamylbenzoic acid and its *N-iso*propyl derivative, was obtained.

Preparation and Oxidation of NN-*Dimethyltoluene*-p-*sulphonamide.*—Aqueous dimethylamine (25%; 20 c.c., 0·11 mole), toluene-*p*-sulphonyl chloride (28·5 g.; 0·15 mole), and 2N-sodium hydroxide (200 c.c.) were warmed for ½ hr. and boiled for ½ hr. The insoluble sulphonamide (18·1 g., 82%) when crystallised from aqueous alcohol (50%) had m. p. 80—81·5°. Chaplin and Hunter [57] give m. p. 80—81° without preparative details. With excess of hot aqueous permanganate–sodium carbonate mixture no aldehyde was evolved. The product (yield, 77·5%), isolated as before, was *p*-sulphamylbenzoic acid, m. p. and mixed m. p. 292—293°. By using 67% of the amount of permanganate required for oxidation to *p*-sulphamylbenzoic acid, carbon dioxide, and water, no toluene-*p*-sulphonamide was obtained; about 10% of the original sulphonamide was recovered and the crude *p*-sulphamylbenzoic acid had m. p. 255—260° and probably contained some of its *NN*-dimethyl derivative.

Oxidation of N-*Methyl- and* N-*Ethyl-toluene*-p-*sulphonamides.*—The sulphonamides were boiled for 1 hr. with excess of alkaline potassium permanganate. In the case of the *N*-methyl compound (5 g.) decolorisation with sulphur dioxide, collection of the precipitate, and concentration of the filtrate yielded a product which, on extraction with aqueous sodium hydrogen carbonate, left 1·2 g. of toluene-*p*-sulphonamide, m. p. and mixed m. p. 136—137°. Acidification and concentration of the extract gave a solid (m. p. 259°; 2·0 g.) which after two

[56] "Organic Reagents for Organic Analysis," Hopkin and Williams, Chadwell Heath, 1950.
[57] Chaplin and Hunter, *J.*, 1937, 1114.

crystallisations from water had m. p. and mixed m. p. 280—281° with authentic *p*-sulphamylbenzoic acid, m. p. 280—281°. The correct m. p. has now been found to be 292—293° (see p. 1761). Similar results were obtained with *N*-ethyltoluene-*p*-sulphonamide.

Oxidation of Toluene-p-*sulphonanilide.*—The sulphonanilide (4·94 g., 0·02 mole) was refluxed with potassium permanganate (42 g.) and magnesium sulphate (42 g.) in water (700 c.c.) for 1 hr. The mixture was treated as before, and yielded *p*-sulphamylbenzoic acid (3·4 g., 84·5%), m. p. and mixed m. p. 292—293° (Found: C, 41·7; H, 3·6. Calc. for $C_7H_7O_4NS$: C, 41·8; H, 3·5%); methyl ester, m. p. and mixed m. p. 181—182°. The same product was obtained in good yield when sodium carbonate replaced magnesium sulphate in the oxidation mixture.

Comparison of the Oxidation of Acetanilide and Toluene-p-*sulphonanilide with Potassium Permanganate.*—Acetanilide (2·7 g., 0·02 mole), potassium permanganate (8 g.), magnesium sulphate heptahydrate (8 g.), and water (270 c.c.) were boiled for ½ hr. Excess of permanganate was still present. Treatment with sulphur dioxide, filtration, and addition of ammonium sulphate to the filtrate yielded unchanged acetanilide (1·3 g.; recovery 48%). Toluene-*p*-sulphonanilide (4·94 g., 0·02 mole) was oxidised with the same quantities of materials. No permanganate remained after 3 minutes' boiling. After sulphur dioxide treatment and acidification, the resulting solid (3·6 g.) on extraction with aqueous sodium hydrogen carbonate was shown by m. p. and mixed m. p. (99—101°) to be the unchanged anilide (recovery 72%). Acidification of the extract gave only a trace of material, m. p. >250°. Concentration of the original filtrate yielded toluene-*p*-sulphonamide (0·1 g.; m. p. and mixed m. p. 137—137·5°). These results clearly show that toluene-*p*-sulphonanilide is much more susceptible to destructive oxidation than is acetanilide.

We thank Imperial Chemical Industries Limited for a research grant and Drs. E. Rothstein and R. W. Saville for carrying out the infrared measurements.

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[*Received, September 9th,* 1955.]