*Additive Compounds as Possible Intermediates in Substitution Processes. Part II.**

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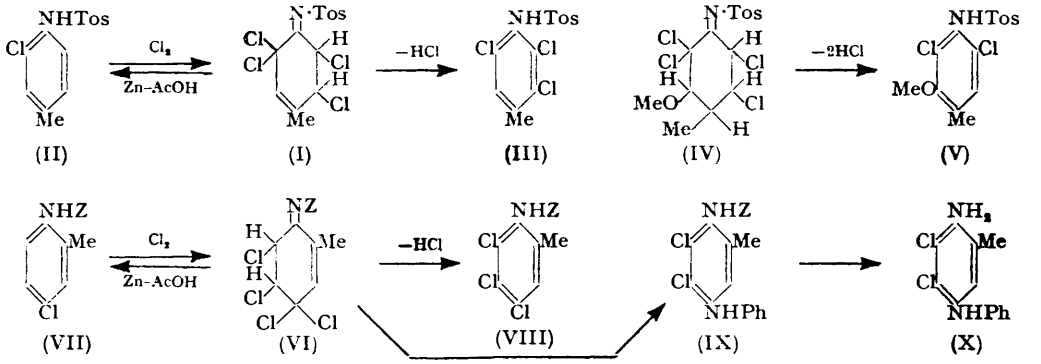
Derivatives of *cyclo*hexene are readily produced by the chlorination of many sulphonanilides. The reactions of these compounds are described. Observations are recorded on the halogenation of 3 : 4 : 1-xylidine.

SCHULOFF, POLLAK, AND RIESS (*Ber.*, 1929, **62**, 1849), by the treatment of toluene-*p*-sulphonyl-*p*-toluidine with excess of chlorine, obtained a compound, m. p. 176°, which was not analysed but was found to yield with 80% sulphuric acid a trichloro-*p*-toluidine, m. p. 59—60°. Bell (*J.*, 1953, 4182) recorded that the analysis of the above compound, after purification, corresponded to that of a tetrachloro-derivative but it is now confirmed that hydrolysis yields a trichloro-base. More detailed examination leads to the unusual constitution (I) for this compound and not *N* : 2 : 3 : 6-tetrachloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine ($NH_2 = 1$) (see Chattaway, *J.*, 1904, **85**, 1185, for properties of *N*-chlorosulphonamides). The compound reacts vigorously with piperidine or aniline, indicating the presence of reactive chlorine. On reduction with zinc and acetic acid it gives 2-chloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine (II), whereas related nuclear halogenated compounds, such as 2-bromo-6-chloro- and 2 : 6-dibromo-*N*-(toluene-*p*-sulphonyl)-*p*-toluidines, are unchanged under the same conditions. The tetrachloro-compound is smoothly decomposed by heat to yield 2 : 3 : 6-trichloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine (III), also obtained, but in small yield, by dissolving the tetrachloro-compound in pyridine. When boiled with alcohols the tetrachloro-compound gave the trichloro-compound (III) together with addition products, probably of type (IV) (position of OMe uncertain), which were converted almost quantitatively into compounds of type (V) by dissolution in pyridine.

The trichloro-compound (III) was smoothly hydrolysed to 2 : 3 : 6-trichloro-*p*-toluidine, m. p. 60—62°, which formed an acetyl derivative, m. p. 196°. As Cohen and Dakin (*J.*, 1902, **81**, 1337) give m. p. 179° for the trichloro-derivative formed by the prolonged action of sodium chlorate and hydrochloric acid on aceto-*p*-toluidide and this value appears to be confirmed by Mannino and Di-Donato (*Gazzetta*, 1908, **38**, 22), who used a mixture of concentrated hydrochloric acid and nitric acid to chlorinate aceto-*p*-toluidide, both processes were re-examined. Cohen and Dakin's method gave material of rather indefinite

* Part I, *J.*, 1955, 24.

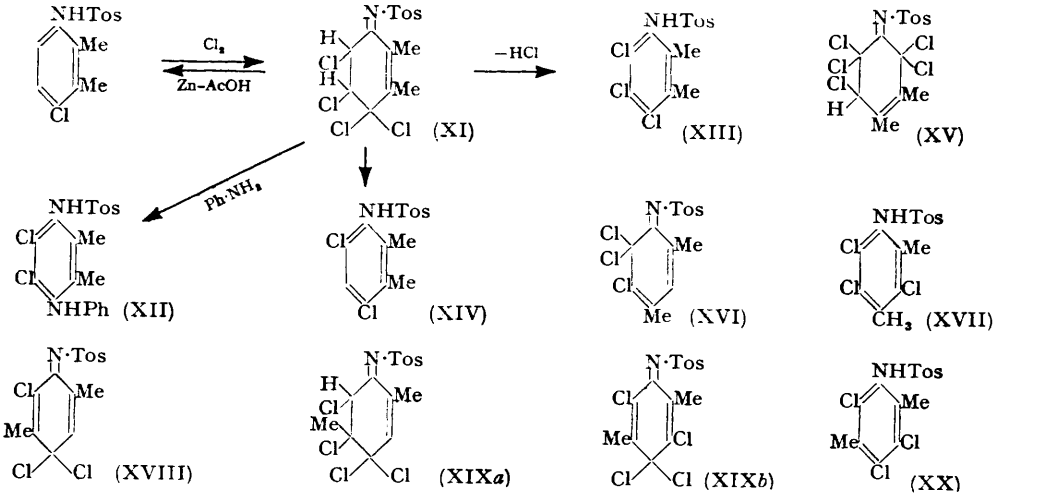
m. p., which on hydrolysis gave a base requiring purification by recrystallisation. The pure base gave an acetyl derivative, m. p. 196°, identical with the above. Mannino and Di-Donato's method yielded in our hands none of the desired trichloro-derivative although it is clear that the authors themselves handled the pure trichloro-base.



(Tos = *p*-$C_6H_4Me{\cdot}SO_2^-$. Z = $Ph{\cdot}SO_2^-$.)

Chlorination of benzenesulphonyl-*p*-toluidine gave a compound analogous to (I), and of benzenesulphonyl-*o*-toluidine a compound to which is ascribed formula (VI). The latter product was decomposed by heat to the trichloro-compound (VIII), and was smoothly reduced to *N*-benzenesulphonyl-4-chloro-*o*-toluidine ($NH_2 = 1$) (VII); with aniline it gave the derivative (IX), which was readily hydrolysed to the dichlorodiamine (X).

Similar results were obtained with certain xylidines. 2 : 3 : 1-Xylidine gave the compound to which is ascribed formula (XI), and the reactions of which are set out. The



smooth reaction with aniline to yield the compound (XII), the conversion into the trichloro-derivative by boiling alcohol, and the production of both the trichloro- (XIII) and the dichloro-derivative (XIV) by dissolution in pyridine are worthy of note. 3 : 4 : 1-Xylidine gave in very small yield a compound, probably (XV), which was not examined in detail. 1 : 3 : 2-Xylidine gave substitution products together with uncrystallisable oils. 2 : 4 : 1-Xylidine gave in small yield a reactive trichloro-compound, probably (XVI), together with the aromatic isomer (XVII). *p*-Xylidine gave a mixture of a trichloro- and a tetrachloro-compound. The trichloro-compound, probably (XVIII), passed rapidly in

hot ethanol into the aromatic product (XX). The tetrachloro-compound, probably (XIX *a* or *b*), was stable under the same conditions. It appears from these results that a methyl group in the benzene nucleus usually opposes the addition of chlorine to the carbon atom to which it is itself attached.

Several authors have recorded difficulty in the preparation of a pure monochloro-derivative from aceto-*p*-toluidide (Lellmann and Klotz, *Annalen*, 1885, **231**, 308; Wynne, *J.*, 1892, **61**, 1053; Cohen and Dakin, *loc. cit.*), higher chloro-derivatives being always produced although the monochloro-derivative itself is not particularly easy to chlorinate further. The above results suggest that the trichloroaceto-*p*-toluidide may be formed by an addition-elimination mechanism (cf. Bell, *J.*, 1953, 3035).

Although *N*-acetyl-3 : 4 : 1-xylidine ($NH_2 = 1$) undergoes chlorination at positions 2 and 6 (Crossley, *J.*, 1904, **85**, 277) bromination in acetic acid is said to occur in positions 2 and 5 (Jaeger and Blanksma, *Rec. Trav. chim.*, 1906, **25**, 354). The evidence rests on hydrolysis to a base, which was converted by the Sandmeyer reaction into a bromoxylene, m. p. 86°, presumed to be 3 : 4 : 6-tribromo-1 : 2-xylene. No analyses were given. The bromination of *N*-acetyl-3 : 4 : 1-xylidine in acetic acid was examined by Mills and Nixon (*J.*, 1930, 2524), who make no reference to the above paper. By use of one molecular proportion of bromine in the cold a 6-bromo-derivative was obtained, which was oriented by hydrolysis and subsequent conversion into 4 : 5-dibromo-1 : 2-xylene, m. p. 88°. As it is not possible to reconcile these two statements the reaction was re-examined. It was found that the 6-bromo-derivative was the only product even when a very large excess of bromine was employed. *N*-Toluene-*p*-sulphonyl-3 : 4 : 1-xylidine behaved similarly, and only in pyridine did it undergo dibromination, then giving the 2 : 6-dibromo-derivative. It is concluded the Jaeger and Blanksma's " 3 : 4 : 6-tribromo-1 : 2-xylene " was in fact 4 : 5-dibromo-1 : 2-xylene, and that bromination of derivatives of 3 : 4 : 1-xylidine follows the same course as chlorination, but that the 2-position is entered with considerably greater difficulty.

Experimental

3 : 3 : 5 : 6-*Tetrachloro*-1-*methyl*-4-*toluene*-p-*sulphonyliminocyclohexene* (I) was prepared from toluene-*p*-sulphonyl-*p*-toluidine by interaction with chlorine in either acetic acid or chloroform, or with sulphuryl chloride alone or in chloroform. The following method gives reproducible results and smoothly achieves the separation from the monochloro-derivative. The amide (10 g.) was added slowly to excess of sulphuryl chloride and after the brisk reaction the excess of chloride was removed under diminished pressure. The residual oil was dissolved in warm acetic acid and reprecipitated by dilution with an equal volume of water. After decantation of the aqueous layer the oil was rubbed with warm ethanol. Solid immediately separated (4·7 g.; m. p. 175—179°). This after recrystallisation from acetic acid or benzene gave the pure *compound*, m. p. 184° (Found: C, 42·3; H, 3·3; Cl, 35·4. $C_{14}H_{13}O_2NSCl_4$ requires C, 41·9; H, 3·2; Cl, 35·4%), which underwent the following reactions: (*a*) It reacted readily with piperdine but no definite compound could be isolated. (*b*) Excess of zinc dust was added gradually to a solution of the compound in boiling acetic acid, and the solution filtered. On slight dilution 2-chloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidide (II) crystallised (Schuloff, Pollak, and Riess, *loc. cit.*). (*c*) The compound was heated at 200° until gas evolution ceased, and the residue crystallised from acetic acid. 2 : 3 : 6-*Trichloro*-N-(*toluene*-p-*sulphonyl*)-p-*toluidide* was obtained in needles, m. p. 160° (Found: C, 45·8; H, 3·2. $C_{14}H_{12}O_2NSCl_3$ requires C, 46·1; H, 3·3%). On dissolution in cold sulphuric acid this gave 2 : 3 : 6-trichloro-*p*-toluidine almost quantitatively. The base formed needles, m. p. 60—62°, from methanol, and on acetylation with cold acetic anhydride–concentrated sulphuric acid gave the acetyl or in the hot the *diacetyl derivative*, crystallising from acetic acid in needles, m. p. 196° (Found: C, 43·0; H, 3·4. Calc. for $C_9H_8ONCl_3$: C, 42·8; H, 3·2%) and 150° (Found: C, 45·2; H, 3·3. $C_{11}H_{10}O_2NCl_3$ requires C, 44·8; H, 3·4%) respectively. (*d*) The compound reacted vigorously with pyridine. On acidification of the solution 2 : 3 : 6-trichloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine (above) was precipitated but in poor yield. (*e*) The compound (2 g.) was heated at 150° for 1½ hr. with sulphuric acid (4 c.c.) and water (4 c.c.), and the aqueous layer decanted from the black tar. Excess of aqueous ammomia was added and the product crystallised from aqueous methanol, to give trichlorotoluidine as above

(confirmed by preparation of acetyl and diacetyl derivatives). (*f*) On addition to aniline there was a very brisk reaction and the mixture set to a paste. Excess of aniline was removed by dilute hydrochloric acid, and the resultant pale yellow precipitate filtered off and dried. The product was extremely soluble in benzene or ethanol; it gave a clear solution in cold acetic acid which soon deposited a white solid. This recrystallised from acetic acid as needles, m. p. *ca.* 135°, but was not obtained pure. (*g*) The compound slowly dissolved in boiling ethanol (3 hr.). The solution was evaporated to small bulk. The crop obtained on cooling was purified by repeated recrystallisation. 1 : 1 : 3 : 4-*Tetrachloro*-6(?)*ethoxy*-5-*methyl*-2-*toluene*-p-*sulphon*-*imido*cyclo*hexane* was obtained in lustrous plates, m. p. 195° (Found: C, 43·1; H, 3·9; Cl, 32·4. $C_{16}H_{19}O_3NSCl_4$ requires C, 43·0; H, 4·2; Cl, 31·8%). The mother-liquors yielded trichloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine (above). (*h*) A similar reaction with methanol gave the *methoxy-analogue* (IV), prisms (from ethanol), m. p. 187° (Found: C, 41·6; H, 3·7. $C_{15}H_{17}O_3NSCl_4$ requires C, 41·6; H, 3·9%). Reduction of this by zinc dust and acetic acid gave 2-chloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine; decomposition at 220° until gas evolution ceased gave much tar and some trichloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine. Dissolution in warm pyridine resulted in almost quantitative conversion into 2 : 6-*dichloro*-3-*methoxy*-N-(*toluene-p-sulphonyl*)-p-*toluidine* (V), which crystallised from acetic acid in prisms, m. p. 190° (Found: C, 50·1; H, 4·2. $C_{15}H_{15}O_3NSCl_2$ requires C, 50·0; H, 4·2%); this compound was obtained also by use of aniline in place of pyridine but was accompanied by sticky, red decomposition products.

Trichloro-p-*toluidine*.—Aceto-*p*-toluidide was chlorinated by Cohen and Dakin's method (*loc. cit.*). The product had m. p. *ca.* 179° after crystallisation from acetic acid or chloroform (Cohen and Dakin give 179°) but was not pure. On hydrolysis in ethanol by hydrochloric acid it gave a base with a melting range 35—47°. This was purified by recrystallisation from light petroleum and then methanol, and then on re-acetylation gave trichloroaceto-*p*-toluidide, m. p. 196° (diacetyl derivative, m. p. 150°), identical with that described above. The base with toluene-*p*-sulphonyl chloride gave material which, after being freed from any ditoluene-*p*-sulphonyl derivative by dissolution in piperdine, crystallised from acetic acid to yield 2 : 3 : 6-trichloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine as prisms, m. p. 160° (above). Similarly there was obtained 2 : 3 : 6-*trichloro*-N-*benzenesulphonyl*-p-*toluidine*, which crystallised from ethanol in needles, m. p. 169° (Found: Cl, 30·2. $C_{13}H_{10}O_2NSCl_3$ requires Cl, 30·4%).

Attempted Preparation of Trichloro-aceto-p-*toluidide by Mannino and Di-Donato's Method* (loc. cit.).—In a typical experiment 5 g. of aceto-*p*-toluidide gave the 2 : 6-dinitro-derivative (1·9 g.), m. p. 190° (corresponding base, m. p. 168°), as the only crystalline product. Various proportions of nitric and hydrochloric acid were employed but in no case was any of the trichloro-derivative isolated.

N-*Benzenesulphonyl*-2 : 6-*dichloro*-p-*toluidine*, from 2 : 6-dichloro-*p*-toluidine (Lellmann and Klotz, *loc. cit.*), formed needles, m. p. 169°, from acetic acid (Found: C, 48·9; H, 3·8. $C_{13}H_{11}O_2NSCl_2$ requires C, 49·4; H, 3·5%). 2 : 6-*Dichloro*-N-(*toluene*-p-*sulphonyl*)-p-*toluidine* crystallised from benzene in prisms, m. p. 180° (Found: C, 50·7; H, 3·9. $C_{14}H_{13}O_2NSCl_2$ requires C, 50·9; H, 3·9%).

2-*Bromo*-6-*chloro*-N-(*toluene*-p-*sulphonyl*)-p-*toluidine*, obtained by addition of *N*-bromo-succinimide (1 mol.) to a pyridine solution of 2-chloro-*N*-(toluene-*p*-sulphonyl)-*p*-toluidine, crystallised from acetic acid in needles, m. p. 180° (Found: C, 44·2; H, 3·3. $C_{14}H_{13}O_2NSClBr$ requires C, 44·8; H, 3·5%). It was unchanged after treatment with zinc dust in boiling acetic acid.

2-*Bromo*-N-(*toluene*-p-*sulphonyl*)-p-*toluidine*, obtained by the addition of bromine (1 mol.) to a solution of the anilide in chloroform, crystallised from ethanol in prisms, m. p. 118° (Found: C, 49·7; H, 4·3. $C_{14}H_{14}O_2NSBr$ requires C, 49·4; H, 4·1%). It was unchanged after treatment in chloroform with chlorine.

2 : 6-*Dibromo*-N-(*toluene*-p-*sulphonyl*)-p-*toluidine*, obtained by the addition of *N*-bromo-succinimide (2 mols.) to a pyridine solution of toluene-*p*-sulphonyl-*p*-toluidine, crystallised from acetic acid in needles, m. p. 179—180° (Found: Br, 38·7. $C_{14}H_{13}O_2NSBr_2$ requires Br, 38·2%), and was unchanged by zinc dust in acetic acid.

p-Toluidine treated with chlorine in acetic acid or under the conditions of D.R.-P. 400,254 gave thick, dark oils.

4-*Benzenesulphonylimino*-3 : 3 : 5 : 6-*tetrachloro*-1-*methyl*cyclo*hexene* (as I).—Excess chlorine was passed into a solution of benzenesulphonyl-*p*-toluidine in chloroform, and the solution diluted with light petroleum. The precipitated oil did not solidify for several days and was, therefore, separated and dissolved in ethanol. Crystals were soon formed and after recrystallisation from acetic acid gave the *tetrachloro-compound* as prisms, m. p. 164° (Found: Cl, 37·4.

$C_{13}H_{11}O_2NSCl_4$ requires Cl, 36·7%) (yield *ca.* 1 g. from 5 g.). This reacted vigorously with pyridine to give *N*-benzenesulphonyl-2 : 3 : 6-trichloro-*p*-toluidine (above) in small yield and with aniline to give a mixture from which was isolated a grey, crystalline powder, m. p. 158° (decomp.), by recrystallisation from acetic acid (Found : Cl, 30·4%); the latter appears to have been produced by removal of hydrogen chloride ($C_{13}H_{10}O_2NSCl_3$ requires Cl, 30·4%), but the product was of doubtful purity.

6-*Benzenesulphonylimino*-3 : 3 : 4 : 5-*tetrachloro*-1-*methyl*cyclo*hexene* (VI).—Excess of chlorine was passed into a solution of benzenesulphonyl-*o*-toluidine (4 g.) in chloroform, and the solution, after concentration, diluted with light petroleum. The crop (1·6 g.), after recrystallisation from acetic acid, gave the tetrachloro-compound as prisms, m. p. 166° (Found : Cl, 37·4. $C_{13}H_{11}O_2NSCl_4$ requires Cl, 36·7%). The yield was not improved by using *N*-benzenesulphonyl-4-chloro-*o*-toluidine as starting material. By zinc in acetic acid the tetrachloro-compound was smoothly converted into benzenesulphonyl-4-chloro-*o*-toluidine (VII). With aniline it reacted briskly to give 4-*anilino*-N-*benzenesulphonyl*-5 : 6-*dichloro*-o-*toluidine* (IX), which formed prisms, m. p. 207°, from acetic acid (Found : C, 56·1; H, 3·8; Cl, 18·0. $C_{19}H_{16}O_2N_2SCl_2$ requires C, 56·0; H, 3·9; Cl, 17·4%), and was hydrolysed by cold sulphuric acid to 4-*anilino*-5 : 6-*dichloro*-o-*toluidine* (X), which crystallised from ethanol in prisms, m. p. 115° (Found : C, 57·6; H, 4·1; Cl, 27·0. $C_{13}H_{12}N_2Cl_2$ requires C, 58·4; H, 4·5; Cl, 26·6%). When heated above the m. p., the tetrachloro-compound gave N-*benzenesulphonyl*-4 : 5 : 6-*trichloro*-o-*toluidine* (VIII), which crystallised from acetic acid in prisms, m. p. 159° (Found : Cl, 29·6. $C_{13}H_{10}O_2NSCl_3$ requires Cl, 30·4%).

Toluene-*p*-sulphonyl-*o*-toluidine (14 g.), submitted to the same process, gave the 4-chloro-derivative (4 g.) and an oil.

N-Acetyl-2-chloro-*p*-toluidine (4 g.) similarly gave the 2 : 6-dichloro-amide (1 g.) and an uncrystallisable oil.

Interaction of Arenesulphonamides with Sulphuryl Chloride.—Excess of sulphuryl chloride was added to the sulphonamide and, after the initial reaction, the excess of sulphuryl chloride was removed under diminished pressure and the residue (usually a glass) dissolved in ethanol or acetic acid.

The following results were obtained :

(*a*) Toluene-*p*-sulphonyl-*o*-toluidine (5 g.) gave the 4-chloro-derivative (4 g.), m. p. 144° (Schuloff, Pollak, and Riess, *loc. cit.*).

(*b*) Benzenesulphonyl-*o*-toluidine (4 g.) gave the 4-chloro-derivative (2·6 g.) and a small yield of the compound (VI), m. p. 166° (above).

(*c*) Benzenesulphonyl-*m*-toluidine gave an almost quantitative yield of the dichloro-derivative, m. p. 116° (Raper, Thompson, and Cohen, *J.*, 1904, **85**, 374).

(*d*) Toluene-*p*-sulphonyl-*m*-toluidine gave crude 2 : 4-*dichloro*-N-*toluene*-p-*sulphonyl*-m-*toluidine*. The pure compound, prepared from 2 : 4-dichloro-*p*-toluidine, crystallised from acetic acid in prisms, m. p. 145° (Found : C, 50·3; H, 3·6. $C_{14}H_{13}O_2NSCl_2$ requires C, 50·9; H, 3·9%).

(*e*) Benzenesulphonyl-*p*-toluidine (5 g.) gave the 2-chloro-derivative (2·5 g.) and an oil.

(*f*) Toluene-*p*-sulphonyl-*p*-anisidine gave *dichloro*-N-*toluene*-p-*sulphonyl*-p-*anisidine*, which formed large prisms, m. p. 166°, from acetic acid (Found : Cl, 21·3. $C_{14}H_{13}O_3NSCl_2$ requires Cl, 20·5%). It was smoothly hydrolysed by cold sulphuric acid to the dichloro-base, needles (from aqueous methanol), m. p. 75° (Hodgson and Wignall, *J.*, 1927, 2219, give the m. p. of 2 : 6-dichloro-4-methoxyaniline as 71°; the 2 : 5-isomeride is not known.

Toluene-p-*sulphonyl*-2 : 3 : 1-*xylidine*, obtained by the interaction of 2 : 3 : 1-xylidine with toluene-*p*-sulphonyl chloride in pyridine, crystallised from ethanol in needles, m. p. 147° (Found : C, 65·6; H, 6·2. $C_{15}H_{17}O_2NS$ requires C, 65·4; H, 6·2%).

Chlorination of Toluene-p-*sulphonyl*-2 : 3 : 1-*xylidine*.—(*a*) By passage of chlorine (1 mol.) into a solution of the sulphonamide in chloroform there was obtained an almost quantitative yield of 4-*chloro*-N-*toluene*-p-*sulphonyl*-2 : 3 : 1-*xylidine*, which crystallised from ethanol in large prisms, m. p. 142° (Found : Cl, 11·5. $C_{15}H_{16}O_2NSCl$ requires Cl, 11·5%). This was alternatively prepared from 4-chloro-2 : 3 : 1-xylidine (Hinkel, Collins, and Ayling, *J.*, 1923, **123**, 2972) by interaction with toluene-*p*-sulphonyl chloride in pyridine; it was unchanged after 2 days in concentrated sulphuric acid.

(*b*) Excess of sulphuryl chloride was added to the amide and after the vigorous reaction the excess was removed and the residue dissolved in acetic acid. The small first crop, m. p. 169—172°, recrystallised from acetic acid, gave 4 : 6-*dichloro*-N-*toluene*-p-*sulphonyl*-2 : 3 : 1-*xylidine* (XIV) as needles, m. p. 174° (Found : Cl, 21·2. $C_{15}H_{15}O_2NSCl_2$ requires Cl, 20·7%).

The main crop after recrystallisation formed rosettes, m. p. 128—130° (Found: Cl, 33·9. $C_{15}H_{15}O_2NSCl_4$ requires Cl, 34·2%), regarded as 3 : 3 : 4 : 5-*tetrachloro*-1 : 2-*dimethyl*-6-*toluene*-p-*sulphonimido*cyclo*hexene* (XI), for by boiling in ethanolic solution for 3 hr., by dissolution in pyridine, or at 190° it gave 4 : 5 : 6-*trichloro*-N-*toluene*-p-*sulphonyl*-2 : 3 : 1-*xylidine* (XIII), which crystallised from acetic acid in needles, m. p. 206° (Found: Cl, 28·1. $C_{15}H_{14}O_2NSCl_3$ requires Cl, 28·2%). On reduction in acetic acid with zinc dust it gave 4-chloro-*N*-toluene-*p*-sulphonyl-2 : 3 : 1-xylidine (above), and with aniline it reacted briskly to give 4-*anilino*-5 : 6-*dichloro*-N-*toluene*-p-*sulphonyl*-2 : 3 : 1-*xylidine* (XII), which crystallised from acetic acid in prisms, m. p. 205° (Found: C, 57·2; H, 4·2; Cl, 16·3. $C_{21}H_{20}O_2N_2SCl_2$ requires C, 57·9; H, 4·6; Cl, 16·3%).

Chlorination of Toluene-p-*sulphonyl*-3 : 4 : 1-*xylidine*.—(*a*) Chlorine (2 mols.) was passed into the sulphonamide dissolved in chloroform, and the solution then concentrated and diluted with light petroleum. The small crop consisted of toluene-*p*-sulphonamide; the remainder of the material had been converted into an oil.

(*b*) The sulphonamide (5 g.) was treated in the usual way with sulphuryl chloride. The residual oil was very soluble in acetic acid, ethanol, and chloroform, but the solution in the last slowly deposited crystals (0·6 g.), which after two recrystallisations from acetic acid formed needles, m. p. 187° (decomp.) (Found: C, 40·5; H, 2·8; Cl, 38·5. $C_{15}H_{14}O_2NSCl_5$ requires C, 40·0; H, 3·1; Cl, 39·5%). This compound is probably 3 : 3 : 5 : 5 : 6-*pentachloro*-4-*toluene*-p-*sulphonimido*-1 : 2-*dimethyl*cyclo*hexene* (XV), since *N*-acetyl-3 : 4 : 1-xylidine is known to be chlorinated in the 2 : 6-positions (Crossley, *J.*, 1904, **85**, 277). It yielded uncrystallisable material on thermal decomposition, and on reduction with zinc in acetic acid a complex mixture.

Chlorination of N-*Acetyl*-3 : 4 : 1-*xylidine* (method of Crossley, *loc. cit.*).—The mother-liquor remaining after removal of the main crop, on slight dilution, gave a sticky precipitate, which after repeated recrystallisation from acetic acid gave a *monochloro*-derivative in needles, m. p. 153° (Found: Cl, 18·5. $C_{10}H_{12}ONCl$ requires Cl, 18·0%).

Passage of excess of chlorine into a chloroform solution of acetyl-3 : 4 : 1-xylidine led to oils.

Toluene-p-*sulphonyl*-2 : 4 : 1-*xylidine*, obtained by the interaction of 2 : 4 : 1-xylidine with toluene-*p*-sulphonyl chloride in pyridine, crystallised from ethanol in prisms, m. p. 109° (Found: C, 65·4; H, 6·2. $C_{15}H_{17}O_2NS$ requires C, 65·4; H, 6·2%).

Chlorination of Toluene-p-*sulphonyl*-2 : 4 : 1-*xylidine*.—(*a*) Excess of sulphuryl chloride was added to the amide and the residue, after removal of excess of reagent, dissolved in acetic acid. No crystallisation occurred, so the product was precipitated with water and dissolved in ethanol. On cooling, a small crop was obtained, which after recrystallisation from acetic acid formed prisms, m. p. 163° (decomp.) (yield 0·2 g. from 4 g.). This *trichloro-compound* (Found: Cl, 28·4. $C_{15}H_{14}O_2NSCl_3$ requires Cl, 28·2%) may be (XVI) as it contains reactive chlorine, shown by very vigorous reaction with pyridine.

(*b*) Chlorine (2 mols.) was passed into the sulphonamide dissolved in chloroform, and the solution concentrated and diluted with light petroleum. First a very small crop of the compound described under (*a*) was obtained and then a small crop of 3 : 5 : 6-*trichloro*-N-*toluene*-p-*sulphonyl*-2 : 4 : 1-*xylidine* (XVII), which formed needles, m. p. 152°, after recrystallisation from acetic acid (Found: Cl, 28·4%).

(*c*) Commercial sodium hypochlorite solution (20 c.c.) was added to the sulphonamide (5 g.) in acetic acid (50 c.c.) at 50°. The crop obtained on cooling was treated with warm dilute hydrochloric acid, filtered, and repeatedly recrystallised from acetic acid. 6-*Chloro*-N-*toluene*-p-*sulphonyl*-2 : 4 : 1-*xylidine* was obtained in needles, m. p. 158° (Found: C, 57·7; H, 4·9 $C_{15}H_{16}O_2NSCl$ requires C, 58·2; H, 5·2%).

Chlorination of Benzenesulphonyl-2 : 4 : 1-*xylidine*.—(*a*) The amide (8 g.) with sulphuryl chloride gave a viscous mass which was dissolved in benzene. The solution slowly deposited crystals (1·9 g.), m. p. *ca.* 160°, and the mother-liquor on dilution with light petroleum deposited a thick oil of camphory odour. Recrystallisation of the crop from ethanol, acetic acid, or chloroform gave crystals of rather indefinite m. p., the highest being 198—202°. A highly crystalline crop, m. p. 190—193°, was essentially a *trichloro-derivative* (Found: C, 47·5; H, 3·5. $C_{15}H_{14}O_2NSCl_3$ requires C, 47·5; H, 3·7%).

(*b*) Chlorination of the sulphonamide in chloroform led to a similar result.

Chlorination of Toluene-p-*sulphonyl*-2 : 5 : 1-*xylidine*.—(*a*) The sulphonamide was dissolved in sulphuryl chloride, and the oil remaining after removal of excess of reagent was dissolved in acetic acid. The crop, A, m. p. *ca.* 125° (1·5 g. from 4 g.), was filtered off and the filtrate treated with water. The sticky mass remaining after decantation of the aqueous layer was repeatedly recrystallised from ethanol and gave pale yellow needles, m. p. 152° (Found: C, 43·4; H, 3·6;

Cl, 34·0. $C_{15}H_{13}O_2NSCl_4$ requires C, 43·6; H, 3·2; Cl, 34·4%). This *tetrachloro-derivative* is probably (XIX), for on reduction by zinc dust in acetic acid it gave 4-*chloro*-N-*toluene*-p-*sulphonyl*-2 : 5 : 1-*xylidine*, which crystallised from ethanol in plates, m. p. 145° (Found : C, 57·6; H, 4·9. $C_{15}H_{16}O_2NSCl$ requires C, 58·2; H, 5·2%); its vigorous reaction with pyridine gave no recognisable compound; in cold concentrated sulphuric acid it dissolved with evolution of hydrogen chloride, and the solution on precipitation gave a brown resin. The main crop (A) after recrystallisation from acetic acid gave prisms, m. p. 132° (Found : C, 47·6; H, 4·1; Cl, 28·0. $C_{15}H_{14}O_2NSCl_3$ requires C, 47·5; H, 3·7; Cl, 28·2%), regarded as 3 : 3 : 5-*trichloro*-6-*toluene*-p-*sulphonimido*-1 : 4-*dimethyl*cyclo*hexa*-1 : 4-*diene* (XVIII), for on solution in hot ethanol it was immediately transformed into 3 : 4 : 6-*trichloro*-N-*toluene*-p-*sulphonyl*-2 : 5 : 1-*xylidine* (XX), needles, m. p. 167° (from ethanol) (Found : C, 48·0; H, 3·6; Cl, 27·9%); the same compound was obtained in small yield from the products of thermal decomposition (bath at 160°), and also on suspension in cold sulphuric acid although here the majority of the compound underwent complete decomposition with free evolution of hydrogen chloride. On addition of the diene (XVIII) to pyridine there was produced momentarily a bright yellow colour which faded as the compound dissolved with evolution of considerable heat. On addition of dilute hydrochloric acid there was precipitated 4 : 6-*dichloro*-N-*toluene*-p-*sulphonyl*-2 : 5 : 1-*xylidine*, which crystallised from ethanol in prisms, m. p. 125—126° (Found : C, 52·0; H, 4·3. $C_{15}H_{15}O_2NSCl_2$ requires C, 52·3; H, 4·4%), and was hydrolysed by solution in cold sulphuric acid to the dichloro-base, needles, m. p. 45—48° (from aqueous methanol). This without further purification was acetylated by dissolution in warm acetic anhydride and gave *N*-acetyl-4 : 6-dichloro-2 : 5 : 1-xylidine, needles, m. p. 166—168° (from ethanol) (Wheeler and Morse, *J. Amer. Chem. Soc.*, 1924, **46**, 2573, give m. p. 167°), and was alternatively prepared by dissolution of acetyl-2 : 5 : 1-xylidine in sulphuryl chloride. It was only partly converted into the dichloro-base by several hours' boiling with ethanol–hydrochloric acid. By reduction of the diene (XVIII) in boiling acetic acid with zinc dust there was produced material which crystallised from ethanol in needles, m. p. 117—120°, unchanged after reprecipitation from pyridine (Found : Cl, 20·3%). This appears to be a mixture of mono- and tri-chloro-derivatives, for after dissolution in sulphuric acid, precipitation with water, and recrystallisation from ethanol it yielded pure 4-chloro-*N*-toluene-*p*-sulphonyl-2 : 5 : 1-xylidine, m. p. 145° (above).

3 : 4 : 6-Trichloro-*N*-toluene-*p*-sulphonyl-2 : 5 : 1-xylidine was unchanged after treatment in boiling acetic acid with zinc dust, but on dissolution in sulphuric acid readily gave the amine, which formed needles, m. p. 206°, from ethanol (Bureš and Rubeš, *Č. čsl. Lékárn.*, 1928, **8**, 258, give m. p. 206°).

(*b*) Addition of sulphuryl chloride (1 mol.) to the sulphonamide, dissolved in chloroform, gave an almost theoretical yield of 4-chloro-*N*-toluene-*p*-sulphonyl-2 : 5 : 1-xylidine. The same compound was produced but in slightly diminished yield by use of 2 mols. of sulphuryl chloride.

(*c*) Chlorine (2 mols.) was passed into a solution of the sulphonamide (5 g.) in chloroform, and the solution concentrated and diluted with light petroleum. After 24 hr. the first crop (1·2 g.) was collected, and recrystallised from acetic acid and then three times from ethanol to give 4-chloro-*N*-toluene-*p*-sulphonyl-2 : 5 : 1-xylidine. The second crop was recrystallised from acetic acid, to give the trichloro-compound, m. p. 132° (XVIII) (1 g.).

(*d*) Excess of commercial sodium hypochlorite solution was added to the sulphonamide (2 g.) in acetic acid (20 c.c.) at 50°. The crop which separated on cooling was the 4-chloro-derivative contaminated by difficultly removable unchanged material.

Chlorination of Toluene-p-*sulphonyl*-2 : 6 : 1-*xylidine*.—(*a*) Chlorine (2·2 mols.) was passed into a solution of the sulphonamide (Wepster, *Rec. Trav. chim.*, 1954, **73**, 814) in chloroform, and the solution concentrated and diluted with light petroleum. The crop, after repeated recrystallisation from acetic acid or ethanol, gave the *monochloro-derivative* as prisms, m. p. 158° (Found : C, 58·0; H, 4·9. $C_{15}H_{16}O_2NSCl$ requires C, 58·2; H, 5·2%).

(*b*) The sulphonamide (4 g.) with excess of sulphuryl chloride gave the above monochloro-derivative (1·9 g.) and a thick oil.

Bromination of Acetyl-3 : 4 : 1-*xylidine*.—Addition of bromine (2 mols.) in acetic acid to the compound in acetic acid (10 parts) produced a thick yellow paste which had passed completely into solution before the addition was complete. After 24 hr. the mixture was poured into water, and the precipitate washed free from bromine and dried. It had m. p. 155—160° and was essentially *N*-acetyl-6-bromo-3 : 4 : 1-xylidine free from dibromo-derivative (Found : Br, 33·7. Calc : Br, 33·0%). Recrystallisation from ethanol raised the m. p. to 164° (Mills and Nixon give 164°). Hydrolysis was brought about by ½ hour's heating with an ethanol–concentrated hydrochloric acid (2 : 1). The resultant 6-bromo-3 : 4 : 1-xylidine gave a *toluene*-p-*sulphonyl*

derivative, which crystallised from ethanol in prisms, m. p. 122° (Found: Br, 24·0. $C_{15}H_{16}O_2NSBr$ requires Br, 23·9%).

Bromination of Toluene-p-sulphonyl-3 : 4 : 1-xylidine.—(*a*) Addition of bromine (1 mol.) in chloroform to the compound in chloroform gave the 6-bromo-derivative (above) in almost quantitative yield. Heating in chloroform with bromine (2 mols.) led to the same compound together with a variable amount of the hydrobromide of 2 : 6-dibromo-3 : 4 : 1-xylidine.

(*b*) Addition of bromine (2 mols.) to the sulphonamide in cold pyridine gave in high yield the 2 : 6-***dibromo-derivative***, which formed needles, m. p. 165°, from ethanol (Found: Br, 38·0. $C_{15}H_{15}O_2NSBr_2$ requires Br, 38·7%). By dissolution in cold sulphuric acid this gave the 2 : 6-dibromo-amine (Jaeger and Blanksma, *loc. cit.*), which gave an ***acetyl derivative***, m. p. 198° (Found: C, 36·9; H, 3·5. $C_{10}H_{11}ONBr_2$ requires C, 37·4; H, 3·4%). This compound crystallised from ethanol in needles, which in contact with the solvent were slowly transformed into prisms.

Passage of chlorine (1—2 mols.) into either *N*-acetyl-6-bromo- or 6-bromo-*N*-toluene-*p*-sulphonyl-3 : 4 : 1-xylidine in chloroform led to no crystallisable material other than the initial compounds. 6-Bromo-*N*-toluene-*p*-sulphonyl-3 : 4 : 1-xylidine was unchanged after treatment in pyridine solution with iodine.

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