## 199. *Some Further Derivatives of Sulphanilohydrazide.*

By R. J. W. Cremlyn.

In a search for new fungicides, more sulphanilylhydrazones have been prepared, including those from aldose sugars and certain dicarbonyl compounds. A study has also been made of the bromination, nitration, and nitrosation of $N^4$-acetylsulphanilohydrazide. The last reaction affords a useful method for the preparation of sulphonyl azides, *e.g.*, $N^4$-acetylsulphanilyl azide; and some of the reactions of this azide are described.

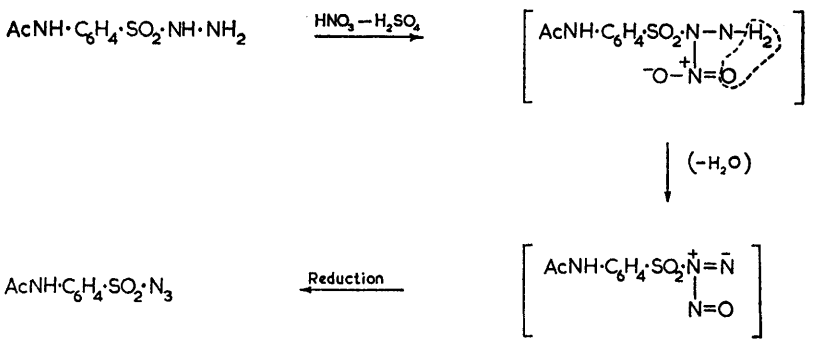


The various derivatives of $N^4$-acetylsulphanilyl hydrazide now described (cf. ref. 10) can be divided into the following classes: hydrazones from monocarbonyl compounds (Table 1); dicarbonyl compounds (Table 2); and certain $N'$-acyl derivatives (Table 3). A wide range of trichloromethylthio-derivatives are fungicidal,[1] and in particular good activity has been reported [2] for certain aryloxy-compounds of type $ArO{\cdot}S{\cdot}CCl_3$. Accordingly several hydroxysulphonylhydrazones have been condensed with trichloromethanesulphenyl chloride and the products examined for fungitoxicity.

Some electrophilic substitution reactions of $N^4$-acetylsulphanilyl hydrazide were investigated:

(a) *Bromination.* This always resulted in loss of the sulphonyl hydrazide group and its replacement by bromine, giving either 2,4-dibromoacetanilide or 2,4,6-tribromoaniline. This behaviour was not entirely unexpected, since Schmitt [3] has shown that during bromination of sulphanilic acid the sulphonic acid group is replaced by bromine.

(b) "*Nitration.*" This yielded the corresponding sulphonyl azide (cf. nitrosation): a surprising result because, by analogy with the nitration of sulphanilic acid,[4] it was expected that the sulphonyl hydrazide group would be replaced by a nitro-group, giving *p*-nitroacetanilide. A similar result was also obtained with toluene-*p*-sulphonyl hydrazide. Possibly the course of " nitration " may be explained as follows:




The last stage may be effected by the sulphinic acid, which is known to be formed in the decomposition of sulphonyl hydrazides.[5]

(c) *Nitrosation.* Treatment with nitrous acid gave $N^4$-acetylsulphanilyl azide (I).

The azide (I) was remarkably stable and could be heated up to 150° before vigorous decomposition occurred; also it was substantially unaffected by boiling ethanol or butanol.

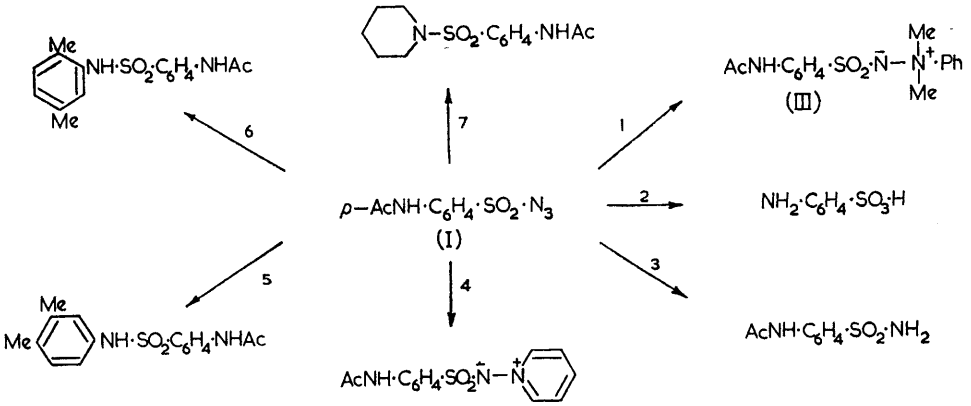
[1] Kittleson, *Science*, 1952, **115**, 84; Johnston, Rueggeberg, and Block, *J. Sci. Food Agric.*, 1957, **5**, 672; Pfleger, *Angew. Chem.*, 1953, **65**, 415.
[2] Fawcett, Spencer, and Wain, *Ann. Appl. Biol.*, 1958, **46**, 651.
[3] Schmitt, *Annalen*, 1861, **120**, 136.
[4] Zincke and Kuchenbecker, *Annalen*, 1905, **339**, 226.
[5] Deavin and Rees, *J.*, 1961, 4970.

The reactions shown indicate that the azide can react by either of two main mechanisms:

(i) $AcNH{\cdot}C_6H_4{\cdot}SO_2N_3 \longrightarrow AcNH{\cdot}C_6H_4{\cdot}SO_2N{:} + N_2$
(I) (II)

This is similar to the first step in the Curtius rearrangement. For the azide (I), this preliminary decomposition appears to require a fairly high temperature; subsequently the electrophilic radical (II) attacks an electron-rich centre in the added compound. This mechanism for the decomposition of sulphonyl azides has been well established,[6] and in

Some reactions of N-acetylsulphanilyl azide (I)




Reagents: 1, $Ph{\cdot}NMe_2$; 2, NaOH; 3, $NH_3$; 4, $C_5H_5N$; 5, $o\text{-}C_6H_4Me_2$; 6, $p\text{-}Me_2C_6H_4$; 7, $C_5H_{11}N$.

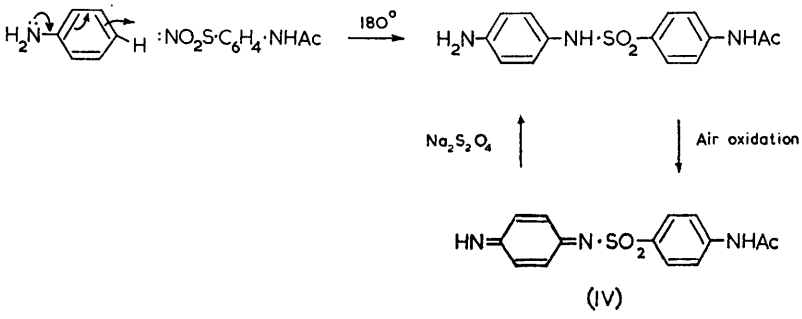
particular it accounts for products obtained with *o*- and *p*-xylene (cf. ref. 7); pyridine;[8] and with *NN*-dimethylaniline. In the latter case, the product was first thought to be the sulphonamide, *p*-(*N*⁴-acetylsulphanilyl amido)-*NN*-dimethylaniline; but it is now considered to be *N*-(*p*-acetamidobenzenesulphonimido)dimethylaniline (III) (cf. ref. 8).

(ii) The other mechanism involves direct attack by a nucleophile on the electrophilic sulphur atom of the intact azide molecule and loss of hydrazoic acid:

$p\text{-}AcNH{\cdot}C_6H_4{\cdot}SO_2N_3 + NaOH \longrightarrow p\text{-}NH_2{\cdot}C_6H_4{\cdot}SO_3H + HN_3$
(after acidification)

Such a scheme accounts for the products obtained with sodium hydroxide, ammonia, and piperidine, and apparently operates at rather lower temperatures than (i).

With boiling aniline the azide (I) gives a violet gum, whose colour is discharged by reduction, possibly indicating formation of an indamine type of structure (IV):




(IV)

[6] Heacock and Edmison, *J. Amer. Chem. Soc.*, 1960, **82**, 3460; Dermer and Edmison, *ibid.*, 1955, **77**, 70.
[7] Curtius and Rissom, *Z. angew. Chem.*, 1913, **26**, 134; *J. prakt. Chem.*, 1930, **125**, 303.
[8] Ashley, Buchanan, and Easson, *J.*, 1947, 60; Buchanan and Levine, *J.*, 1950, 2248; Datta, *J. Indian Chem. Soc.*, 1947, **24**, 109.

TABLE 1.

$N^4$-Acetylsulphanilylhydrazones.

*p*-Ac·NH·$C_6H_4$·$SO_2$NH·N=CHR

| R | M. p. | Formula | Found (%) C | H | N | S | Required (%) C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|
| (*a*) *From aldehydes* | | | | | | | | | | |
| n-$C_7H_{15}$ | Amorphous | $C_{16}H_{25}N_3O_3S$ | 56·2 | 7·3 | 11·9 | 9·6 | 56·6 | 7·4 | 12·4 | 9·4 |
| n-$C_8H_{17}$ | ,, | $C_{17}H_{27}N_3O_3S$ | 57·4 | 7·4 | 11·6 | 9·4 | 57·8 | 7·65 | 11·9 | 9·1 |
| 2-HO·$C_{10}H_6$ | 224° | $C_{19}H_{17}N_3O_4S$ | 60·2 | 4·6 | — | 8·0 | 59·5 | 4·4 | — | 8·35 |
| 2-Pyridyl | 140 | $C_{14}H_{14}N_4O_3S$ | 52·5 | 4·85 | — | 9·8 | 52·8 | 4·4 | — | 10·1 |
| 2-Pyrrolyl | 166—170 | $C_{13}H_{14}N_4O_3S$ | 50·8 | 4·8 | — | 10·2 | 51·0 | 4·6 | — | 10·5 |
| $Me_2CH·CH_2·CHMe·[CH_2]_2$– | 141 | $C_{18}H_{29}N_3O_3S$ | 58·3 | 7·5 | — | 9·0 | 58·9 | 7·9 | — | 8·7 |
| (*b*) *From sugars* | | | | | | | | | | |
| Glucose | 140 | $C_{14}H_{21}N_3O_8S$ | 42·7 | 5·6 | — | 7·8 | 43·0 | 5·4 | — | 8·2 |
| Galactose | 150 | $C_{14}H_{21}N_3O_8S$ | 42·4 | 5·7 | — | 7·9 | 43·0 | 5·4 | — | 8·2 |
| Arabinose | 162—163 | $C_{13}H_{19}N_3O_7S$ | 43·7 | 5·5 | — | 9·4 | 43·2 | 5·3 | — | 8·9 |
| Mannose | 142 | $C_{14}H_{21}N_3O_8S$ | 43·5 | 5·7 | — | 7·2 | 43·0 | 5·4 | — | 8·2 |
| Rhamnose | 126—128 | $C_{14}H_{21}N_3O_8S$ | 43·6 | 5·8 | — | 7·7 | 43·0 | 5·4 | — | 8·2 |
| Xylose | 146—148 | $C_{13}H_{19}N_3O_7S$ | 43·8 | 5·2 | — | 9·2 | 43·2 | 5·3 | — | 8·9 |
| (*c*) *From ketones* | | *p*-AcNH·$C_6H_4$·$SO_2$NH·N=CRR′ | | | | | | | | |
| R R′ | | | | | | | | | | |
| Me $HO_2C$ | 184—186 | $C_{11}H_{13}N_3O_5S$ | 43·7 | 4·8 | — | 10·3 | 44·15 | 4·35 | — | 10·7 |
| $EtO_2C·CH_2$ $EtO_2C·CH_2$ | 86—90 | $C_{17}H_{23}N_3O_7S$ | 49·8 | 5·8 | — | 7·7 | 49·4 | 5·6 | — | 7·75 |
| Me n-$C_5H_{11}$ | 172—173 | $C_{15}H_{23}N_3O_3S$ | 55·4 | 6·7 | — | 9·5 | 55·4 | 7·1 | — | 9·8 |
| Me $Ph·CH_2$ | 200 | $C_{17}H_{19}N_3O_3S$ | 58·8 | 5·2 | — | 9·3 | 59·1 | 5·5 | — | 9·3 |
| –$CH_2·CMe_2·CH_2·CHMe·CH_2$– | 179—180 | $C_{17}H_{25}N_3O_3S$ | 58·1 | 7·4 | — | 8·1 | 58·1 | 7·1 | — | 9·1 |
| 3-Cholestanylidene | 192 | $C_{35}H_{55}N_3O_3S$ | 69·9 | 8·7 | — | 5·5 | 70·3 | 9·2 | — | 5·35 |
| Me 4-Cl·$C_6H_4$ | 219·5 | $C_{16}H_{16}ClN_3O_3S$ | 52·3 | 4·35 | — | 8·9 | 52·5 | 4·4 | — | 8·75 |
| –$C_6H_4$·NH·CO– | 202 | $C_{16}H_{14}N_4O_4S$ | 53·6 | 3·9 | 15·5 | 8·9 | 53·2 | 4·2 | 15·0 | 8·8 |
| –$C_6H_4$·$C_6H_4$– | 218—220 | $C_{21}H_{17}N_3O_3S$ | 64·8 | 4·4 | — | 8·0 | 64·45 | 4·35 | — | 8·2 |

TABLE 2.

| Dicarbonyl compound | M. p. | Formula | Found (%) C | H | N | S | Required (%) C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|
| Diacetyl: di-deriv. | 215° | $C_{20}H_{24}N_6O_6S_2$ | 46·7 | 4·8 | — | 11·9 | 47·2 | 4·8 | — | 12·6 |
| Acetylacetone: mono-deriv. | 165—166 | $C_{13}H_{17}N_3O_4S$ | 50·7 | 4·1 | — | 10·5 | 50·2 | 5·5 | — | 10·3 |
| di-deriv. | 170—172 | $C_{21}H_{25}N_6O_6S_2$ | 47·6 | 5·0 | — | 11·4 | 48·4 | 4·8 | — | 12·3 |
| Acetonylacetone: mono-deriv. | No m. p. | $C_{14}H_{19}N_3O_4S$ | 52·1 | 5·6 | — | 10·4 | 51·7 | 5·8 | — | 9·8 |
| di-deriv. | 174 | $C_{22}H_{28}N_6O_6S_2$ | 48·9 | 5·1 | — | 11·6 | 49·25 | 5·3 | — | 11·9 |
| Cyclohexane-1,3-dione: mono-deriv. | 220 | $C_{14}H_{17}N_3O_4S$ | 51·6 | 5·5 | — | 9·6 | 52·0 | 5·3 | — | 9·9 |
| di-deriv. | 170 | $C_{22}H_{28}N_6O_6S_2$ | 49·8 | 4·8 | — | 11·7 | 49·4 | 4·9 | — | 12·0 |
| Dimedone: mono-deriv. | 175—176 | $C_{16}H_{21}N_3O_4S$ | 54·3 | 6·25 | — | 8·9 | 54·7 | 6·0 | — | 9·1 |
| di-deriv. | 158—160 | $C_{24}H_{30}N_6O_6S_2$ | 49·9 | 5·7 | — | 11·5 | 51·2 | 5·3 | — | 11·4 |
| Benzil di-deriv. | 200—202 | $C_{30}H_{28}N_6O_6S_2$ | 56·8 | 4·6 | — | 10·5 | 57·0 | 4·4 | — | 10·1 |
| Terephthaldehyde di-deriv. | 235—238 | $C_{24}H_{22}N_6O_6S_2$ | 51·4 | 4·6 | — | 11·2 | 51·8 | 4·35 | — | 11·5 |

## Experimental

Melting points were determined by using sealed tubes (to minimise decomposition). $N^4$-Acetylsulphanilohydrazide was prepared as described by Curtius and Stoll.[9]

*Table* 1. The hydrazones were made as described by Cremlyn;[10] the sugar derivatives generally required acetonitrile as solvent (cf. ref. 11).

*Table* 2. By using one or two molecular proportions of acetylsulphanilohydrazide, it was generally possible to obtain both the mono- and di-hydrazones. They were purified by several recrystallisations from ethanol. The dihydrazones were generally darker than the mono-hydrazones, and did not give a yellow precipitate with 2,4-dinitrophenylhydrazine.

*Table* 3. The *N'*-acyl derivatives were obtained by treatment of acetylsulphanilohydrazide with the appropriate acyl or sulphonyl chloride in a mixture of pyridine and dioxan at room temperature.

Table 3.

*N'*-Acyl derivatives *p*-Ac·NH·$C_6H_4$·$SO_2$·NHNHR'.

| | | | Found (%) | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| R' | M. p. | Formula | C | H | N | S | C | H | N | S |
| 4-Me·$C_6H_4$,$SO_2$ ..... | 220° | $C_{15}H_{17}N_3O_5S_2$ | 47·3 | 4·7 | — | 16·8 | 47·0 | 4·4 | — | 16·7 |
| Me·$SO_2$ ..... | 226—228 | $C_9H_{13}N_3O_5S_2$ | 35·6 | 4·1 | — | 20·2 | 35·2 | 4·2 | — | 20·8 |
| Ph·$SO_2$ ..... | 202 | $C_{14}H_{15}N_3O_5S_2$ | 45·9 | 4·3 | — | 16·9 | 45·5 | 4·1 | — | 17·35 |
| 4-Ac·NH·$C_6H_4$,$SO_2$ ... | 240—242 | $C_{16}H_{18}N_4O_6S_2$ | 44·7 | 4·6 | — | 14·6 | 45·1 | 4·3 | — | 15·0 |
| Ph·CO ..... | 220—222 | $C_{15}H_{15}N_3O_4S$ | 53·7 | 4·3 | 13·1 | 10·2 | 54·05 | 4·5 | 12·6 | 9·6 |
| Ph·NH·CO ..... | 210—211 | $C_{15}H_{16}N_4O_4S$ | 51·7 | 4·8 | 16·5 | 9·0 | 51·7 | 4·6 | 16·1 | 9·2 |
| (1,4)-Ac·NH·$C_{10}H_6$·$SO_2$ | 230—232 | $C_{20}H_{20}N_4O_6S_2$ | 49·9 | 4·3 | 12·1 | 13·8 | 50·4 | 4·2 | 11·7 | 13·4 |

*Bromination of N-Acetylsulphanilohydrazide.*—(a) *With excess of bromine.* The hydrazide (5 g.) dissolved in boiling water (300 c.c.) was gradually treated with bromine (11 g.; 3 mol.), and after a few minutes' heating a pink solid began to separate. A little more bromine was added to give a permanent red colour and heating was continued for 1 hr. On cooling, the precipitated solid was collected and recrystallised from boiling ethanol with a little decolourising charcoal, yielding a white solid (3·1 g.), m. p. 119—121° (Found: C, 21·5; H, 1·35; Br, 72·4; N, 4·3. Calc. for $C_6H_4Br_3N$: C, 21·8; H, 1·2; Br, 72·7; N, 4·2%). This compound was unchanged after alkaline hydrolysis, and gave no m. p. depression on mixing with a genuine sample of 2,4,6-tribromoaniline (m. p. 120°).

(*b*) *With 2 mol. of bromine.* The hydrazide (1 g.) in boiling water (200 c.c.) was treated with bromine (1·5 g.; 2 mol.), and after ¼ hr. the precipitate was collected and recrystallised from aqueous methanol. The product was a white solid (0·7 g.), m. p. 146—148° (Found: Br, 57·2; N, 4·8. Calc. for $C_7H_7Br_2NO$: Br, 56·9; N, 4·5%) and gave no depression of m. p. on admixture with 2,4-dibromoacetanilide (m. p. 146°).

*Attempted Nitration of* N-*Acetylsulphanilohydrazide.*—The hydrazide (2 g.) in glacial acetic acid (6 c.c.) was cooled to 0° while concentrated sulphuric acid (5 c.c.) was added; then nitrating mixture [concentrated nitric acid (2·5 c.c.) and concentrated sulphuric acid (2 c.c.)] was slowly introduced so that the temperature was kept below 5°. After addition, the mixture was allowed to warm up to 40° (15 min.), then cooled (10 min.) and poured on to crushed ice. The pale yellow solid was collected and recrystallised twice from aqueous ethanol giving white needles (0·7 g.), m. p. 112—114° (decomp.) (Found: C, 39·9; H, 3·3; N, 23·1; S, 13·4. Calc. for $C_8H_8N_4O_3S$: C, 40·0; H, 3·3; N, 23·3; S, 13·3%). There was no depression of m. p. on mixing with authentic *N*-acetylsulphanilyl azide (m. p. 112—114°), and the infrared spectrum showed a peak at 4·7 μ characteristic of the azide group. Attempted nitration of *p*-toluenesulphonyl hydrazide, under similar conditions, also yielded the corresponding sulphonyl azide, m. p. 24—26° (lit.,[12] m. p. 22°).

$N^4$-*Acetylsulphanyl Azide* (by nitrosation).—$N^4$-Acetylsulphanilohydrazide (2·3 g.) suspended in concentrated hydrochloric acid (10 c.c.) at 0° was gradually treated with a solution of sodium nitrite (7·0 g.; 1 mol.) in water (10 c.c.), keeping the temperature below 5° (after addition the mixture gave a positive reaction with starch–iodide paper). It was left 1 hr. at 0°,

[9] Curtius and Stoll, *J. prakt. Chem.*, 1926, **112**, 117.
[10] Cremlyn, *J.*, 1962, 2133.
[11] Westphal, Feier, Lüderitz, and Fromme, *Biochem. Z.*, 1954, **326**, 139.
[12] Curtius and Klavehn, *J. prakt. Chem.*, 1926, **112**, 65.

and the precipitated solid was filtered, washed with ice–water, and recrystallised from chloroform–ether mixture, yielding $N^4$-acetylsulphanilyl azide (1·5 g.), m. p. 112—114° (decomp.) (lit.,[8] m. p. 113—114°) (Found: C, 39·7; H, 3·6; N, 22·8. Calc. for $C_8H_8N_4O_3S$: C, 40·0; H, 3·3; N, 23·3%). The compound has also been prepared,[8,9,13] by condensation of *N*-acetylsulphanilyl chloride with sodium azide; however the nitrosation method appeared to give a cleaner product. Other *sulphonyl azides* obtained by the latter procedure were: *N*-acetamidonaphthalene-1,4-, m. p. 154—156° (Found: C, 49·2; H, 3·2; S, 11·3. $C_{12}H_{10}N_4O_3S$ requires: C, 49·7; H, 3·5; S, 11·0%); *p*-tolyl, m. p. 25—26° (lit.,[12] m. p. 22°) (Found: C, 42·6; H, 3·9; S, 15·8. Calc. for $C_7H_7N_3O_2S$: C, 42·6; H, 3·6; S, 16·2%).

*Hydrolysis of* $N^4$-*Acetylsulphanilyl Azide.*—The azide (2 g.) was heated with concentrated hydrochloric acid (10 c.c.) at 70—80° for 1 hr., cooled, and treated with solid sodium hydrogen carbonate until just alkaline. The precipitate was collected washed with water, and crystallised from aqueous ethanol, giving sulphanilyl azide (1·8 g.), m. p. 38—40° (lit.,[9] m. p. 36°) (Found: C, 36·6; H, 3·4; N, 27·7. Calc. for $C_6H_6N_4O_2S$: C, 36·3; H, 3·0; N, 28·3%).

*Reactions of* $N^4$-*Acetylsulphanilyl Azide.*—*Ammonolysis.* The azide (1 g.) was dissolved in dioxan (20 c.c.) and concentrated ammonia ((*d* 0·88; 10 c.c.) added. The solution was heated at 100° for 3 hr., the solvent was distilled off, and the solid residue washed with water. Crystallisation from methanol gave $N^4$-acetylsulphanilamide (0·7 g.), m. p. 218—219° (undepressed on mixing with an authentic specimen).

*Alkaline hydrolysis.* The azide (1 g.) was boiled under reflux with 5N-sodium hydroxide solution (20 c.c.) for 5 hr. The solution was cooled, and acidified with conc. hydrochloric acid, when colourless needles separated; these were collected, washed with a little ice–water, and dried. The yield was 0·8 g. decomp. pt. 300—340°. The compound was identified as sulphanilic acid by conversion into the *S*-benzylisothiuronium salt, m. p. 188° (lit., 187°).

*Pyrolysis.* The azide (1 g.) was melted and the temperature gradually raised; gas was evolved, and the liquid became reddish-brown, until at 150° a vigorous decomposition occurred, producing clouds of finely divided carbon. On heating it at 130° for ½ hr., 70% of the azide was recovered unchanged.

Other experiments illustrating the relative stability of the azide are:

*Attempted alcoholysis.* After boiling with ethanol for 5 hr., 80% of the azide was recovered. With boiling n-butanol (6 hr.) there was 60% recovery; but with boiling n-pentyl alcohol (8 hr.) no crystalline material could be isolated.

*Reaction with aniline.* By boiling the azide with an alcoholic solution of aniline for 4 hr., 80% of unchanged material was obtained. However, when the azide was boiled with excess of aniline, the mixture became violet after 10 min. It was allowed to cool to room temperature, and was extracted with ether (to remove excess of base), leaving a dark violet uncrystallisable gum. This was insoluble in ether, but readily dissolved in ethanol forming a deep violet solution; the colour was rapidly discharged by shaking with an alkaline solution of sodium dithionite. On standing in air, the reduced solution gradually regained its original colour.

*With* NN-*dimethylaniline.* The azide (3 g.) was heated at 130—140° with excess of dimethylaniline (20 c.c.) for 6 hr. On cooling the dark blue solution deposited a gum soluble in ethanol forming a purple solution which, after charcoal treatment and concentration, gave *N*-(*p*-acetamidobenzenesulphonimido)dimethylaniline (300 mg.), m. p. 215—217° (Found: C, 57·5; H, 5·6; N, 12·3. $C_{16}H_{19}N_3O_3S$ requires: C, 57·7; H, 5·7; N, 12·6%). [The sulphonamide, *p*-($N^4$-acetylsulphanilyl amido)-*NN*-dimethylaniline has m. p. 196° [14]].

*With piperidine.* The azide (3 g.) was boiled under reflux with piperidine (20 c.c.) for 6 hr. After evaporation *in vacuo* the residue was recrystallised from ethanol (in the presence of decolourising charcoal), yielding *N*-($N^4$-acetylsulphanilyl)piperidine, a white solid (1 g.), m. p. 158—160° (lit.,[15] m. p. 156°) (Found: C, 54·9; H, 6·2; N, 9·7. Calc. for $C_{13}H_{18}N_2O_3S$: C, 55·3; H, 6·4; N, 9·9%).

*With xylenes.* The azide (3 g.) was boiled under reflux with *o*-, *m*-, or *p*-xylene (200 c.c.) for 8 hr. After cooling, the brownish residue was crystallised from aqueous ethanol–dioxan mixture in the presence of activated charcoal. *o*-Xylene afforded the 4-(*N*-acetylsulphanilyl) derivative (1 g.), m. p. 210° (Found: C, 59·9; H, 5·6; N, 8·5; S, 10·4. $C_{16}H_{18}N_2O_3S$ requires

[13] Doering and DePuy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.
[14] Ganapati, *J. Indian Chem. Soc.*, 1938, **15**, 525.
[15] Goldyrev and Postovskii, *J. Appl. Chem.* (*U.S.S.R.*), 1938, **11**, 316.

C, 60·4; H, 5·7; N, 8·8; S, 10·0%). *p*-Xylene gave the 2-(*N*-acetylsulphanilyl) derivative (2 g.), m. p. 242—244° (Found: C, 59·8; H, 5·8; N, 8·4; S, 10·1%). *m*-Xylene yielded no solid product.

*With pyridine.* The azide (8·2 g.) was boiled with pyridine, as described by Ashley *et al.*,[8] yielding *N*-(*p*-acetamidobenzenesulphinamido)pyridine (1·5 g.), m. p. 296—298° (lit.,[8] m. p. 298—300°) from aqueous ethanol (Found: C, 53·3; H, 5·1; S, 11·4. Calc. for $C_{13}H_{13}N_3O_3S$: C, 53·6; H, 4·5; S, 11·0%). A similar reaction with quinoline gave only an uncrystallisable brown oil.

*Condensation with trichloromethanesulphenyl chloride.* The hydroxysulphonylhydrazone reacted with an excess of the sulphenyl chloride, as described previously,[16] and the products were recrystallised from ethanol. This reaction was performed with the sulphonylhydrazones from the following carbonyl compounds, giving products with the cited m. p.s and anaytical data: isatin, 145—148° (Found: C, 45·5; H, 2·8; S, 15·0. $C_{17}H_{13}Cl_3N_4O_4S_2$ requires: C, 46·0; H, 2·9; S, 14·4%); 4-hydroxybenzaldehyde, 185—190° (Found: C, 40·2; H, 2·6; S, 13·2. $C_{16}H_{14}Cl_3N_3O_4S_2$ requires: C, 39·8; H, 2·9; S, 13·3%); 2-hydroxybenzaldehyde, 162—163° (Found: C, 39·9; H, 3·1; S, 13·0%); 4-hydroxyacetophenone, 157° (Found: C, 40·6; H, 2·7; S, 12·2. $C_{17}H_{16}Cl_3N_3O_4S_2$ requires: C, 41·1; H, 3·2; S, 12·9%).

The author thanks Mr. E. Sherlock, of Imperial Chemical Industries Limited (Agricultural Division), for arranging the microanalysis and biological testing of these compounds.

Hatfield College of Technology,
Roe Green, Hatfield, Herts. [*Received, March* 31*st*, 1964.]

[16] Cremlyn, *J.*, 1963, 1329.