

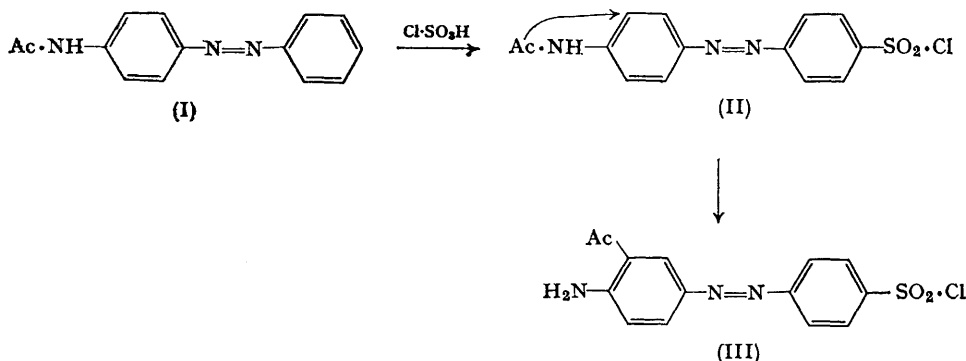
1189. Derivatives of Azobenzenesulphonyl Hydrazide.

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In a search for new pest-control agents a number of derivatives of azobenzenesulphonyl hydrazide have been prepared, including hydrazones from aliphatic and aromatic aldehydes and ketones, *N*-acyl derivatives, and several azobenzenesulphonyl azides. The compounds were characterised by their ultraviolet and infrared spectra, and these are briefly discussed.

AZOBENZENESULPHONYL HYDRAZIDE has been obtained¹ by treatment of the sulphonyl chloride with hydrazine hydrate in benzene; however, this procedure was found unsatisfactory and has been modified, as indicated in the Experimental section. The hydrazide has been converted into a large number of derivatives (Tables 1—5) by standard methods. These compounds were synthesised primarily as potential protectant fungicides,² in view of the activity of sulphonamides towards several plant diseases,³ and the effectiveness of certain derivatives of *p*-aminoazobenzene as seed dressings particularly against *Pythium ultimum* on peas.⁴ Azobenzene is converted into the *p*-sulphonic acid by 20% oleum at 130°,⁵ and into the *p*-sulphonyl chloride by excess of chlorosulphonic acid at 125°. These conditions are drastic compared with those required for the analogous reactions with aromatic hydrocarbons, *e.g.*, chlorosulphonation at -5° to 30° for ½ hr. in carbon tetrachloride as diluent;⁷ and the resistance of azobenzene towards chlorosulphonation is probably due to initial protonation by the chlorosulphonic acid.

Attempts were made to extend this method to the preparation of 1-acetamidoazobenzene-4-sulphonyl chloride (II); however, with chlorosulphonic acid at 125° only a dark oily product, containing none of the required sulphonyl chloride, was obtained. Analogously, it has been found that, while chlorosulphonation of acetanilide proceeds excellently at 60°,⁸ when the temperature is raised to 100° only a black oily product results. These reactions may involve the migration of the acetyl group into the nucleus, followed by attack of the reagent on the free amino-group and simultaneous oxidative decomposition of the intermediate (III):



It is known⁹ that a number of *N*-substituted aromatic amines undergo acid-catalysed rearrangements to the *o/p*-substituted amines. In contrast, when chlorosulphonation of

¹ O. Westphal, H. Feier, O. Lüderitz, and I. Fromme, *Biochem. Z.*, 1954, **326**, 139.

² R. J. W. Cremlyn, *Internat. Pest Control*, 1963, **5**, 10.

³ D. Rudd-Jones, *Outlook on Agric.*, 1956, **1**, 111.

⁴ M. J. A. Geoghegan and J. A. Silk, G.P. 1,115,982/1961.

⁵ A. Chrzaszczewska and C. Dobrowolski, *Roczniki Chem.*, 1937, **17**, 411.

⁶ I. A. Pearl, *J. Org. Chem.*, 1945, **10**, 205.

⁷ R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," Wiley, New York, 1953, p. 822.

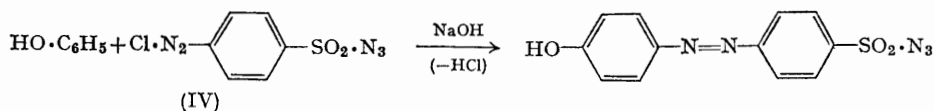
⁸ S. Smiles and J. Stewart, *Org. Synth.*, Coll. Vol. I, p. 8.

⁹ M. J. S. Dewar, "Molecular Rearrangements," Interscience, New York, 1963, Part I, p. 308.

p-acetamidoazobenzene (I) was attempted at 60°, the starting material was substantially unchanged; but it has been found that at 80° a low yield of the desired sulphonyl chloride (II) could be isolated, and this was converted into the corresponding sulphonyl hydrazide. Analogous reactions using *p*-(*NN*-dimethylamino)azobenzene did not give pure products.

Reduction of azobenzenesulphonyl hydrazide by tin and hydrochloric acid gave a mixture of aniline and sulphanilohydrazide,¹⁰ whereas alkaline sodium hydrosulphite afforded azobenzenesulphonyl hydrazide (cf. ref. 6).

Several azobenzenesulphonyl azides have been obtained by coupling diazotised sulphanilohydrazide (IV) with an alkaline solution of a phenol; for example:



The ultraviolet spectrum of azobenzenesulphonyl hydrazide showed three main absorption bands, at 227, 321, and 445 $\text{m}\mu$ (ϵ 11,500, 19,700, 650). The first arises from the substituted benzenoid groups¹¹ and the rest are due to the azobenzene group (cf. ref. 12). In the aliphatic azobenzenesulphonylhydrazones, the corresponding bands are 228—230 (ϵ 15,000—28,000), 323—325 (ϵ 25,000—45,000), and 445—450 $\text{m}\mu$ (ϵ 650—660). With the aromatic analogues there is further increase in the intensity of the first two bands: 225—230 (ϵ 38,000—50,000) and 320—325 $\text{m}\mu$ (ϵ 54,000—61,000).

In the infrared spectra of azobenzenesulphonyl hydrazide and hydrazones, the bands in the region 3390—3225 cm^{-1} are probably associated with the N—H bond.¹³ Thus, the hydrazide has three intense bands, at 3390, 3311, and 3225 cm^{-1} (3 N—H bonds); the sulphonamide has two bands, at 3334 and 3225 cm^{-1} (2 N—H bonds); and the hydrazones have a single band at 3225 cm^{-1} (1 N—H bond). The bands found at 1320—1330 cm^{-1} and at 1180 cm^{-1} are known¹⁴ to be due to the two stretching vibrations of the S—O linkage. Also, all the compounds examined exhibited three strong bands, at 925, 770, and 690 cm^{-1} , which it is concluded are due to the azo-group (cf. ref. 15). In the azobenzenesulphonyl azides (Table 5) there was an additional very intense band at 2140 cm^{-1} indicative of the azide group.¹³

EXPERIMENTAL

Melting points were determined by using sealed tubes (to minimise decomposition). The infrared spectra were obtained with a Grubb-Parsons GS3 instrument with samples in the form of pressed discs in potassium bromide.

Azobenzenesulphonyl Chloride.—This was prepared by the method of Pearl⁶ (cf. ref. 16), except that the product was recrystallised from acetone.

4-Azobenzenesulphonimido-4'-azobenzene.—Azobenzene-*p*-sulphonyl chloride (1.4 g.), dissolved in warm dioxan (30 c.c.), was treated with pyridine (1 c.c.) and *p*-aminoazobenzene (0.9 g.). The mixture was left at room temperature for 4 days, the solvent was removed *in vacuo*, and the residue recrystallised from ethanol (after charcoal treatment), giving the *sulphonamide* as red needles (1 g.), m. p. 184—187° (Found: C, 64.9; H, 4.1; N, 15.3; S, 7.3. $\text{C}_{24}\text{H}_{19}\text{N}_5\text{O}_2\text{S}$ requires C, 65.3; H, 4.3; N, 15.9; S, 7.3%).

Azobenzene-p-sulphonyl hydrazide (cf. ref. 1).—Azobenzene-*p*-sulphonyl chloride (35 g.) was added gradually to a stirred mixture of hydrazine hydrate (30 c.c. of 98%), pyridine (20 c.c.), and

¹⁰ R. J. W. Cremlyn, *J.*, 1962, 2133.

¹¹ A. Gillam and E. S. Stern, "Electronic Absorption Spectra," Edward Arnold Ltd., London, 1954, p. 175.

¹² A. H. Cook, D. G. Jones, and J. B. Polya, *J.*, 1939, 1315.

¹³ R. J. W. Cremlyn and D. N. Waters, unpublished work.

¹⁴ R. Adams and J. J. Tjepkema, *J. Amer. Chem. Soc.*, 1948, 70, 4204.

¹⁵ K. S. Tetlow, *Research*, 1950, 3, 187.

¹⁶ H. M. Flowers and W. S. Reith, *Biochem. J.*, 1953, 53, 657.

dioxan (60 c.c.). This caused heating and the mixture was occasionally cooled; after addition had been completed, stirring was continued for 4 hr. and then the mixture was set aside overnight. The precipitate was filtered with suction, and well washed with water and methanol, yielding the pure hydrazide (32 g.) as glistening plates, m. p. 140—142° (decomp.) [lit.,¹ 154° (decomp.)] (m. p. depends on the rate of heating, cf. ref. 10) (Found: C, 52.1; H, 4.7; N, 20.2; S, 11.6. Calc. for C₁₂H₁₂N₄O₂S: C, 52.2; H, 4.4; N, 20.3; S, 11.6%). From the mother liquor a by-product (1 g.) was obtained as lustrous orange plates, m. p. 202—203° (decomp.) (after two recrystallisations from ethanol-dioxan) (Found: C, 51.9; H, 5.5; N, 20.0; S, 11.4%). The nature of this compound is obscure, since the bisazobenzenesulphonyl derivative melts at 246—248° (Table 4).

Azobenzene-p-sulphonylhydrazones.—These compounds (Tables 1 and 2) were prepared by heating the hydrazide and the aldehyde or ketone in ethanol. The products were purified by rapid recrystallisation from boiling ethanol, but those from the higher aliphatic aldehydes gave unsatisfactory analyses (cf. ref. 10). The sugar derivatives generally required acetonitrile as solvent (cf. ref. 1), and that from benzophenone boiling dioxan.

TABLE I.

Aldehyde azobenzenesulphonylhydrazones, C₆H₅·N=N·C₆H₄·SO₂NH-N=CH·R.

R	M. p.	Formula	Found (%)			Required (%)		
			C	H	S	C	H	S
<i>From aliphatic aldehydes</i>								
Me	198—200°	C ₁₄ H ₁₄ N ₄ O ₂ S	55.9	5.0	10.8	55.6	4.7	10.6
Et.	195—196	C ₁₅ H ₁₆ N ₄ O ₂ S	57.3	5.4	10.0	57.0	5.1	10.1
Pr ⁿ	190	C ₁₆ H ₁₈ N ₄ O ₂ S	58.5	5.7	9.7	58.2	5.5	9.7
Pr ^t	196	C ₁₆ H ₁₈ N ₄ O ₂ S	58.6	5.9	9.9	58.2	5.5	9.7
n-C ₆ H ₁₃	136—140	C ₁₉ H ₂₄ N ₄ O ₂ S	63.7	7.75	7.2	61.3	6.45	8.6
Glucose	200—202*	C ₁₈ H ₂₂ N ₄ O ₇ S	49.4	5.1	7.5	49.3	5.1	7.3
Rhamnose	153—156†	C ₁₈ H ₂₂ N ₄ O ₆ S	50.6	5.7	7.5	51.2	5.25	7.6
Xylose	200—204	C ₁₇ H ₂₀ N ₄ O ₆ S	50.5	5.1	7.9	50.0	4.9	7.8
Mannose	146	C ₁₈ H ₂₂ N ₄ O ₇ S	48.6	5.2	7.4	49.3	5.1	7.3
Ribose	194—196	C ₁₇ H ₂₀ N ₄ O ₆ S	50.6	5.2	7.9	50.0	4.9	7.8
Arabinose	176—178	C ₁₇ H ₂₀ N ₄ O ₆ S	50.3	5.1	7.9	50.0	4.9	7.8
Galactose.....	—	C ₁₈ H ₂₂ N ₄ O ₇ S	50.0	5.1	7.9	49.3	5.1	7.3
<i>From aromatic aldehydes</i>								
Ph.	176—178°	C ₁₉ H ₁₆ N ₄ O ₂ S	63.0	4.8	8.8	62.6	4.4	8.8
o-Cl·C ₆ H ₄	178—180	C ₁₉ H ₁₅ ClN ₄ O ₂ S	57.6	4.0	7.6	57.2	3.8	8.0
p-Cl·C ₆ H ₄	180—181	C ₁₉ H ₁₅ ClN ₄ O ₂ S	56.9	4.0	8.0	57.2	3.8	8.0
o-HO·C ₆ H ₄	202—204	C ₁₉ H ₁₆ N ₄ O ₃ S	60.5	4.9	7.5	60.0	4.2	8.4
p-HO·C ₆ H ₄	198—200	C ₁₉ H ₁₆ N ₄ O ₃ S	59.7	4.4	8.5	60.0	4.2	8.4
2-HO·C ₁₀ H ₆	214—216	C ₂₂ H ₁₇ N ₄ O ₃ S	64.8	4.5	7.0	64.4	4.2	7.4
o-NO ₂ ·C ₆ H ₄	193—199	C ₁₉ H ₁₅ N ₅ O ₄ S	55.6	3.8	7.7	55.75	3.7	7.8
m-NO ₂ ·C ₆ H ₄	190—192	C ₁₉ H ₁₅ N ₅ O ₄ S	55.5	4.0	7.8	55.75	3.7	7.8
p-NO ₂ ·C ₆ H ₄	182—184	C ₁₉ H ₁₅ N ₅ O ₄ S	55.9	4.2	7.55	55.75	3.7	7.8
p-MeO·C ₆ H ₄	176—178	C ₂₀ H ₁₈ N ₄ O ₃ S	61.1	4.6	7.8	60.9	4.6	8.1
Ph·CH=CH.....	188—190	C ₂₁ H ₁₈ N ₄ O ₂ S	64.9	5.1	8.1	64.6	4.6	8.2
p-NMe ₂ ·C ₆ H ₄	162—164	C ₂₁ H ₂₁ N ₅ O ₂ S	61.3	5.8	7.8	61.9	5.2	7.85
3-MeO, 4-HO, C ₆ H ₃ ...	160—163	C ₂₀ H ₁₈ N ₄ O ₄ S	59.0	5.1	7.35	58.5	4.4	7.8
2-Pyrrolyl	188—190	C ₁₇ H ₁₅ N ₅ O ₂ S	58.1	4.6	8.8	57.8	4.25	9.1
2-Pyridyl.....	190	C ₁₈ H ₁₅ N ₅ O ₂ S	59.7	4.2	9.2	59.2	4.1	8.8
3,5-Cl ₂ C ₆ H ₃	159—161	C ₁₉ H ₁₄ Cl ₂ N ₄ O ₂ S	52.5	3.3	7.1	52.65	3.2	7.4

* Lit.,¹ m. p. 191°. † Lit.,¹ m. p. 164°.

Mono- and Bis-hydrazones from Dicarboxyl Compounds.—By using one or two molecular proportions of the hydrazide it was generally possible to obtain both the mono- and bis-hydrazones. The products (Table 3) were purified by several recrystallisations from boiling ethanol. The bishydrazones were red, as compared with the orange colour of the monohydrazones, and did not form a precipitate with 2,4-dinitrophenylhydrazine (cf. ref. 17).

N-Substituted Azobenzene-p-sulphonyl Hydrazides.—The hydrazide was treated with the appropriate acyl or sulphonyl chloride (1.5 mols.) in a mixture of pyridine and dioxan at room

TABLE 2.

Ketone azobenzenesulphonylhydrazones, $C_6H_5 \cdot N \cdot N \cdot C_6H_4 \cdot SO_2NH \cdot N \cdot CRR$.

R	R'	M. p.	Formula	Found (%)			Required (%)		
				C	H	S	C	H	S
<i>From aliphatic ketones.</i>									
Me	Me	198—200°	$C_{15}H_{16}N_4O_2S$	56.9	5.0	10.0	57.0	5.1	10.1
Me	Et	194—195	$C_{16}H_{18}N_4O_2S$	57.6	5.4	9.7	58.2	5.5	9.7
Me	Pr ⁿ	140	$C_{17}H_{20}N_4O_2S$	58.5	6.1	10.0	59.3	5.8	9.3
Me	Bu ¹	134	$C_{18}H_{22}N_4O_2S$	60.0	6.4	9.0	60.3	6.1	8.9
Me	Pr ¹	160	$C_{17}H_{20}N_4O_2S$	58.8	6.0	9.3	59.3	5.8	9.3
Me	n-C ₅ H ₁₁	136—138	$C_{19}H_{24}N_4O_2S$	61.5	6.8	8.6	61.3	6.45	8.6
Me	EtO ₂ C·CH ₂	120—122	$C_{18}H_{20}N_4O_4S$	55.9	5.6	8.4	55.7	5.2	8.2
	-[CH ₂] ₄ -	192—194	$C_{17}H_{18}N_4O_2S$	59.8	5.55	9.6	59.65	5.2	9.3
	-[CH ₂] ₅ -	176—178	$C_{18}H_{20}N_4O_2S$	60.5	5.7	9.0	60.7	5.7	9.0
	-CH(CO ₂ Et)·[CH ₂] ₃ -	180—182	$C_{20}H_{22}N_4O_4S$	57.6	4.8	8.1	58.0	5.35	7.7
	-CH ₂ -CH[Me] ₂ ·CH ₂ ·CHMe·CH ₂ -	154	$C_{21}H_{26}N_4O_2S$	63.2	6.5	8.2	63.3	6.5	8.0
Me	CO ₂ H	155—156	$C_{15}H_{14}N_4O_4S$	52.2	4.4	8.6	52.0	4.1	9.2
Me	CH(OH)·Me	124—126	$C_{16}H_{18}N_4O_3S$	55.8	5.3	8.5	55.5	5.2	9.2
<i>From aromatic ketones.</i>									
Me	Ph	202—204°	$C_{20}H_{18}N_4O_2S$	63.7	4.5	8.5	63.5	4.8	8.5
Me	Ph·CH ₂	132—134	$C_{21}H_{20}N_4O_2S$	64.6	5.35	8.4	64.3	5.1	8.2
Me	<i>p</i> -HO·C ₆ H ₄	224—226	$C_{20}H_{18}N_4O_3S$	61.4	4.8	8.5	60.9	4.6	8.1
Me	<i>p</i> -Br·C ₆ H ₄	196—198	$C_{20}H_{17}BrN_4O_2S$	52.9	3.9	7.5	52.5	3.7	7.0
Me	<i>p</i> -Me·C ₆ H ₄	200	$C_{21}H_{20}N_4O_2S$	63.8	5.3	8.3	64.3	5.1	8.2
Me	<i>p</i> -Cl·C ₆ H ₄	195	$C_{20}H_{17}ClN_4O_2S$	58.2	4.4	7.8	58.2	4.1	7.75
Ph	Ph·CH·OH	203—206	$C_{26}H_{22}N_4O_3S$	66.8	4.5	7.2	66.4	4.7	6.8
Ph	Ph	165—168	$C_{25}H_{20}N_4O_2S$	67.8	4.7	7.7	68.2	4.6	7.3
	-C ₆ H ₄ -NH·CO-	210	$C_{20}H_{15}N_5O_3S$	59.3	4.1	8.1	59.3	3.7	7.9
	-C ₆ H ₄ ·C ₆ H ₄ -	203—205	$C_{25}H_{18}N_4O_2S$	69.1	4.1	7.0	68.5	4.1	7.3

TABLE 3.

Mono- and bis-hydrazones from dicarbonyl compounds.

Compound	M. p.	Formula	Found (%)			Required (%)		
			C	H	S	C	H	S
Me·CO·CO·Me								
Monohydrazone	155—156°	$C_{16}H_{16}N_4O_3S$	56.2	4.9	9.2	55.8	4.7	9.6
Bishydrazone	213	$C_{28}H_{26}N_8O_4S_2$	55.3	4.6	10.4	55.8	4.35	10.6
Me·CO·CH ₂ ·CO·Me								
Monohydrazone	177—178	$C_{17}H_{18}N_4O_3S$	57.3	5.0	9.3	57.0	5.1	8.9
Me·CO·[CH ₂] ₂ ·CO·Me								
Monohydrazone	180—182	$C_{18}H_{20}N_4O_3S$	58.6	5.5	9.0	58.1	5.4	8.6
Cyclohexane-1,3-dione								
Monohydrazone	173—175	$C_{18}H_{18}N_4O_3S$	57.8	4.8	8.6	58.4	4.9	8.6
Bishydrazone	215—216	$C_{30}H_{28}N_8O_4S_2$	57.9	4.9	10.0	57.3	4.5	10.2
5,5-Dimethylcyclohexane-1,3-dione								
Monohydrazone	190—192	$C_{20}H_{22}N_4O_3S$	60.2	5.7	8.4	60.3	5.6	8.0
<i>p</i> -OHC·C ₆ H ₄ ·CHO	232—233	$C_{32}H_{26}N_8O_4S_2$	59.3	4.5	9.4	59.1	4.0	9.8
Ph·CO·CO·Ph								
Bishydrazone	187	$C_{38}H_{30}N_8O_4S_2$	63.4	4.25	9.9	63.0	4.1	9.75

temperature. The other derivatives (Table 4) were obtained by condensation of azobenzene-*p*-sulphonyl chloride with a substituted hydrazide under similar conditions.

Azobenzenesulphonyl Azides.—The parent compound was made by the action of nitrous acid on the sulphonyl hydrazide at 0°. The other compounds (Table 5) were obtained by diazotisation of sulphanilohydrazide¹⁰ with excess (> 2 mols.) of nitrous acid; this suspension was dropped into a stirred alkaline solution of the phenol at 0°. After ½ hr. at 0° the precipitate was filtered off, washed with water, and recrystallised from ethanol.

Attempted Chlorosulphonation of p-(NN-Dimethylamino)azobenzene.—*p*-(NN-Dimethylamino)-azobenzene (10 g.) was gradually added to chlorosulphonic acid (35 c.c., 10 mols.); the dark solution was heated at 80° for 1½ hr., allowed to cool to room temperature, and poured on to crushed ice. The mixture was stirred for 2 hr. at 0°, and filtration gave a dark-purple solid (12 g.). This

TABLE 4.

Derivatives, Ph·N=N·C₆H₄·SO₂·NH-NH·R.

R	M. p.	Formula	Found (%)			Required (%)		
			C	H	S	C	H	S
Ph.....	160°	C ₁₈ H ₁₆ N ₄ O ₂ S	60·8	4·7	9·4	61·4	4·5	9·1
			(N, 15·8)			(N, 15·9)		
<i>p</i> -NO ₂ ·C ₆ H ₄	195	C ₁₈ H ₁₅ N ₅ O ₄ S	55·0	4·2	7·7	54·4	3·8	8·1
2,4-(NO ₂) ₂ C ₆ H ₃	225—227	C ₁₈ H ₁₄ N ₆ O ₆ ·S	47·4	3·4	7·4	48·8	3·4	7·7
			(N, 19·6)			(N, 19·1)		
Me·SO ₂	210—212	C ₁₃ H ₁₄ N ₄ O ₄ S ₂	44·0	4·5	17·4	44·1	4·0	18·1
Ph·SO ₂	229—230	C ₁₈ H ₁₆ N ₄ O ₄ S ₂	51·6	4·5	15·2	51·9	3·9	15·4
<i>p</i> -Me·C ₆ H ₄ ·SO ₂	229—231	C ₁₉ H ₁₈ N ₄ O ₄ S ₂	52·9	5·0	14·6	53·0	4·2	14·9
<i>p</i> -Ac·NH·C ₆ H ₄ ·SO ₂	228	C ₂₀ H ₁₉ N ₅ O ₅ S ₂	49·5	4·0	13·15	49·1	3·9	13·4
(1,4)-Ac·NH·C ₁₀ H ₆ ·SO ₂	198—201	C ₂₄ H ₂₁ N ₅ O ₅ S ₂	54·0	4·0	12·2	53·4	4·2	12·6
Ph·N ₂ ·C ₆ H ₄ ·SO ₂	246—248	C ₂₄ H ₂₀ N ₆ O ₄ S ₂	55·8	4·1	12·1	55·4	3·8	12·3
Me·CO.....	183—185	C ₁₄ H ₁₄ N ₄ O ₃ S	53·2	4·5	9·6	52·8	4·4	10·1
Ph·CO.....	202—203	C ₁₉ H ₁₆ N ₄ O ₃ S	60·6	4·2	7·9	60·0	4·2	8·4
NH ₂ ·CO.....	246—248	C ₁₃ H ₁₃ N ₅ O ₃ S	48·9	4·4	9·8	48·9	4·1	10·0
NH ₂ ·CS.....	214—215	C ₁₃ H ₁₃ N ₅ O ₂ S ₂	47·0	4·0	18·7	46·6	3·9	19·1
Ph·NH·CO.....	198—200	C ₁₉ H ₁₇ N ₅ O ₃ S	57·3	4·8	7·7	57·7	4·3	8·1
			(N, 17·2)			(N, 17·7)		

TABLE 5.

Azobenzenesulphonyl azides, Ar·N=N·C₆H₄·SO₂·N₃.

Ar	M. p.	Formula	Found (%)				Required (%)			
			C	H	N	S	C	H	N	S
Ph.....	117—118°	C ₁₂ H ₉ N ₅ O ₂ S	50·4	3·5	—	10·7	50·2	3·2	—	11·1
<i>p</i> -HO·C ₆ H ₄	135—137	C ₁₂ H ₉ N ₅ O ₃ S	—	—	23·25	10·3	—	—	23·1	10·55
2-HO·C ₁₀ H ₆	173—175	C ₁₆ H ₁₁ N ₅ O ₃ S	—	—	19·8	8·4	—	—	19·8	9·1
2-HO,5-Cl,C ₆ H ₃	135—137	C ₁₂ H ₈ ClN ₅ O ₃ S	—	—	21·4	9·5	—	—	20·7	9·5
4-HO·C ₁₀ H ₆	185—187	C ₁₆ H ₁₁ N ₅ O ₃ S	54·8	3·4	19·4	—	54·4	3·1	19·8	—
3-Me,4-HO,C ₆ H ₃	140	C ₁₃ H ₁₁ N ₅ O ₃ S	49·7	3·8	21·85	—	49·2	3·5	22·1	—

was precipitated twice from boiling acetone giving an amorphous purple solid (5 g.), m. p. > 300° (Found: C, 47·2; H, 4·6; S, 11·2. Calc. for C₁₄H₁₄ClN₃O₂S: C, 51·6; H, 4·3; S, 9·8%).

Condensation with Hydrazine.—The crude sulphonyl chloride (5 g.) was shaken with an excess of hydrazine hydrate in dioxan giving a sticky brown solid, m. p. 140—150° (decomp.), which could not be purified. It was, therefore, boiled with acetone yielding a scarlet powder (1 g.), m. p. 190—192° (decomp.) (Found: C, 55·3; H, 6·2. C₁₄H₁₇N₅O₂S requires C, 52·7; H, 5·4%).

1-Acetamidoazobenzene-4-sulphonyl Hydrazide.—*p*-Acetamidoazobenzene (20 g.) was heated with chlorosulphonic acid (freshly distilled; 60 c.c.) at 80° for 1 hr., and poured on to ice. After the mixture had been stirred at 0° for ½ hr., the rather oily precipitate was filtered off, washed with ice-water, then with methanol, and dried by suction. The crude sulphonyl chloride (16 g.) was gradually added to a stirred mixture of hydrazine hydrate (20 c.c. of 98%), sodium carbonate (8 g.), and water (60 c.c.); the mixture was stirred at room temperature for 24 hr. The solid product was filtered off, washed with water, and recrystallised from boiling ethanol-dioxan yielding the *hydrazide* as an orange solid (8 g.), m. p. 166—168° (decomp.) (Found: C, 50·0; H, 5·1; S, 9·3. C₁₄H₁₅N₅O₃S requires C, 50·5; H, 4·5; S, 9·6%). The hydrazide was converted, by standard methods, into the following derivatives: *acetone hydrazone*, m. p. 199—200° (Found: C, 54·2; H, 5·3; S, 8·1. C₁₇H₁₉N₅O₃S requires C, 54·7; H, 5·1; S, 8·6%); *cyclohexanone hydrazone*, m. p. 190—191° (Found: C, 57·7; H, 5·9; S, 7·9. C₂₀H₂₃N₅O₃S requires C, 58·1; H, 5·6; S, 7·75%); *benzaldehyde hydrazone*, m. p. 221—222° (Found: C, 59·7; H, 4·7; S, 7·5. C₂₁H₁₉N₅O₃S requires C, 59·85; H, 4·5; S, 7·6%); *ethyl methyl ketone hydrazone*, m. p. 206—208° (Found: C, 55·4; H, 5·8; S, 7·8. C₁₈H₂₁N₅O₃S requires C, 55·8; H, 5·4; S, 8·3%).

Reduction of p-Azobenzenesulphonyl Hydrazide.—(a) *By tin and hydrochloric acid.* The hydrazide (2 g.) was suspended in dilute hydrochloric acid and granulated tin (5 g.) was gradually added. The mixture was boiled under reflux until colourless, and was then cooled, made alkaline, and extracted with ether. The extract was washed with water, dried (Na₂SO₄), and evaporated to yield aniline, identified as the *N*-benzoyl derivative (0·7 g.), m. p. 160—161°. The aqueous layer was

centrifuged (to remove inorganic material) and the solution carefully neutralised with dilute hydrochloric acid; the resultant white precipitate was filtered, washed with cold water, and recrystallised from ethanol giving sulphanilohydrazide (0.8 g.), m. p. 130—131° (lit.,¹⁸ 131°) undepressed on admixture with a genuine sample.

(b) *By sodium hydrosulphite.* The hydrazide (2 g.) was added to an alkaline solution of sodium dithionite (4 g.) and the suspension warmed on a water-bath until it became colourless (approx. 1 hr.). The mixture was cooled and the white solid product filtered off, washed with water, and recrystallised from ethanol, yielding *p-hydrazobenzenesulphonyl hydrazide* as small needles (1 g.), m. p. 153—155° (decomp.) (Found: C, 52.0; H, 5.4; S, 11.0. $C_{12}H_{14}N_4O_2S$ requires C, 51.8; H, 5.1; S, 11.5%). When a suspension of this material was shaken in air it gradually became orange showing that the azo-bond has not been broken in this reduction [cf. method (a)].

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¹⁸ W. Stoll and T. Curtius, *J. prakt. Chem.*, 1926, **112**, 117.
