

Sulphonohydrazides and Related Compounds. Part XIII.† Some Sulphanilohydrazides

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N-Carbamoylsulphanilyl chloride has been condensed with hydrazine and the hydrazide converted into hydrazones. Similarly *NN'*-diphenylurea has been converted into the 4,4'-bis-sulphonyl azide. Attempted chlorosulphonation of *NN'*-di-*o*-, *-m*-, and *-p*-tolylureas gave the corresponding bis-sulphonic acids. Reaction of *p*-succinimido-benzenesulphonyl chloride with hydrazine gave *N*-(4-hydrazino-4-oxobutyl)sulphanilohydrazide.

ALTHOUGH phenylurea (I) on treatment with an excess of hot chlorosulphonic acid is known¹ to give the sulphanilyl chloride (II), use of a molar equivalent of acid at 60° gave a water-soluble product. This we thought to be either the sulphonic acid (III) or (IV);

† Part XII, R. J. W. Cremlyn and J. L. Turner, *J. Chem. Soc. (C)*, 1970, 2629.

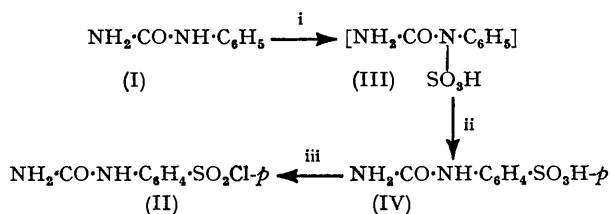
¹ G. Travagli, *Ann. Chim. farm.*, 1940, 148 (*Chem. Abs.*, 1943, **37**, 1998).

compound (IV) was thought more likely since sulphonic acid groups have been reported to undergo acid-catalysed migration^{2a} (*e.g.* phenylsulphamic acid rearranges to sulphanilic acid^{2b}). Evidence for a similar chlorosulphonation mechanism was observed³ with

² (a) H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, p. 124; (b) p. 257.

³ R. J. W. Cremlyn and R. Hornby, *J. Chem. Soc. (C)*, 1969, 1341.

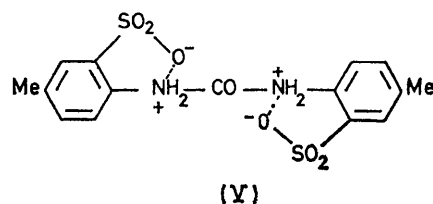
phenylacetic acid; treatment with an excess of chloro-sulphuric acid at 0° gave a water-soluble product and the sulphonyl chloride was only formed on heating.⁴



Reagents: i, ClSO₃H; ii, Heat; iii, hot excess of ClSO₃H

Although *NN'*-diphenylurea with an excess of chloro-sulphuric acid gave the 4,4'-bis-sulphonyl chloride,⁵

by the action of phosphorus pentachloride on the disodium salt of (V) which cannot exist as a zwitterion.



The i.r. spectra of the *N*-carbamoylsulphanilylhydrazones (Table 1) showed absorption in the regions 3500—3440 (NH₂), 3360—3320, and 3260—3200 (NH) (see ref. 7a). The 4,4'-Ureylenebisbenzenesulphonylhydra-

TABLE 1
N-Carbamoylsulphanilylhydrazones, *p*-NH₂·CONH·C₆H₄·SO₂NH=N=CRR'

R	R'	M.p.	Formula	Found (%)				Required (%)			
				C	H	N	S	C	H	N	S
H	H	164—165 ^a	C ₈ H ₁₀ N ₄ O ₃ S	39.4	4.5	22.7	12.9	39.7	4.2	23.1	13.2
Me	Me	181 ^b	C ₁₀ H ₁₄ N ₄ O ₃ S	44.7	5.5	20.3	11.5	44.4	5.2	20.7	11.8
Me	Et	168—169	C ₁₁ H ₁₆ N ₄ O ₃ S	46.3	5.3	19.3	11.1	46.5	5.7	19.7	11.3
Et	Et	173—175	C ₁₂ H ₁₈ N ₄ O ₃ S	47.9	5.8	19.2	10.4	48.3	6.1	18.8	10.7
	-[CH ₂] ₄ -	148—150 ^c	C ₁₂ H ₁₆ N ₄ O ₃ S	48.3	5.7	18.6	10.5	48.6	5.4	18.9	10.8
	-[CH ₂] ₅ -	165—167 ^d	C ₁₃ H ₁₈ N ₄ O ₃ S	49.9	5.6	17.8	10.0	50.3	5.85	18.1	10.3
Me	C ₆ H ₅	209—211	C ₁₅ H ₁₆ N ₄ O ₃ S	54.2	4.9	17.1		54.2	4.85	16.9	
H	4-ClC ₆ H ₄	211—213	C ₁₄ H ₁₃ ClN ₄ O ₃ S	47.7	3.8	15.7		47.7	3.7	15.9	
H	4-HO·C ₆ H ₄	210—212 ^e	C ₁₄ H ₁₄ N ₄ O ₄ S	50.1	3.9	16.6	9.4	50.3	4.2	16.8	9.6
H	4-O ₂ N·C ₆ H ₄	180—182	C ₁₄ H ₁₃ N ₄ O ₅ S	46.3	3.8	18.9		46.0	4.1	19.2	
H	2-O ₂ N·C ₆ H ₄	184	C ₁₄ H ₁₃ N ₄ O ₅ S	46.4	3.9	19.0		46.0	4.1	19.2	
H	3,4-Cl ₂ C ₆ H ₃	195	C ₁₄ H ₁₂ Cl ₂ N ₄ O ₃ S	43.05	3.1	14.3		43.1	3.1	14.4	

^a ν_{max} . 3460, 3360, 3200 (NH), 1690 (CO), 1320, 1160 (SO₂) cm⁻¹. ^b ν_{max} . 3460, 3360, 3220 (NH), 1680 (CO), 1330, 1160 (SO₂).
^c ν_{max} . 3440, 3340, 3240, 3220 (NH), 1685 (CO), 1330, 1150 (SO₂). ^d ν_{max} . 3440, 3320, 3225 (NH), 1710 (CO), 1320, 1160 (SO₂).
^e ν_{max} . 3500 (OH), 3400, 3260 (NH), 1680 (CO), 1150 (SO₂).

TABLE 2
4,4'-Ureylenebisbenzenesulphonylhydrazones (RR'C=N·NH·SO₂·C₆H₄·NH-)₂CO

R	R'	M.p.	Formula	Found (%)			Required (%)		
				C	H	N	C	H	N
Me	Me	183 ^a	C ₁₆ H ₂₄ N ₆ O ₅ S ₂	47.2	4.7	17.7	47.4	5.0	17.5
Et	Et	189	C ₂₃ H ₃₂ N ₆ O ₅ S ₂	51.8	6.2	15.3	51.4	6.0	15.6
	-[CH ₂] ₅ -	200—204	C ₂₅ H ₃₀ N ₆ O ₅ S ₂	53.4	5.6	14.8	53.5	5.7	15.0
H	4-ClC ₆ H ₄	248—250	C ₂₇ H ₂₂ Cl ₂ N ₆ O ₅ S ₂	50.4	3.2	12.9	50.2	3.4	13.0
Me	Ph	230—232	C ₂₅ H ₂₂ N ₆ O ₅ S ₂	58.0	4.7	13.7	57.6	4.6	13.9
H	H	225 ^b	C ₁₇ H ₁₆ N ₆ O ₅ S ₂	42.8	3.5	19.6	42.5	3.8	19.8
Me	H	210 ^c	C ₁₇ H ₂₀ N ₆ O ₅ S ₂	45.2	4.5	18.7	45.1	4.4	18.6
H	3,4-Cl ₂ C ₆ H ₃	230—233 ^d	C ₂₇ H ₂₀ Cl ₄ N ₆ O ₅ S ₂	45.3	3.0	12.1	45.4	2.8	11.8

^a ν_{max} . 3370br (NH), 1680 (CO), 1330, 1180 (SO₂) cm⁻¹. ^b ν_{max} . 3380br (NH), 1690br (CO), 1330, 1170 (SO₂). ^c ν_{max} . 3380br (NH), 1710 (CO), 1330, 1150 (SO₂). ^d ν_{max} . 3360br (NH), 1680 (CO), 1320, 1150 (SO₂).

NN'-di-*o*-tolyl-, *m*-tolyl-, and *p*-tolyl-urea, gave only the corresponding bis-sulphonic acids; this was probably due to steric effects which prevented the conversion of the sulphonic acid into sulphonyl chloride.⁶ 4,4'-Ureylene-di-3-methyl- and -2-methyl-benzenesulphonic acids gave the corresponding bis-sulphonyl chlorides upon treatment with phosphorus pentachloride but 2,2'-ureylenebis-5-methylbenzenesulphonic acid was unaffected probably because it exists as the zwitterionic structure (V). The bis-sulphonyl chloride was obtained

⁴ J. Stewart, *J. Chem. Soc.*, 1922, 2555.

⁵ G. J. Braz, M. V. Lizgunova, and A. A. Chemeriskaya, *J. Appl. Chem. (U.S.S.R.)*, 1946, **19**, 379 (*Chem. Abs.*, 1947, **41**, 1215).

⁶ R. J. W. Cremllyn, *J. Chem. Soc. (C)*, 1967, 77.

zones (Table 2) showed a broad band at 3380—3360 (NH). The amide I carbonyl band appeared in the range 1710—1680 (ref. 7b) and the S-O antisymmetric and symmetric stretching vibrations were at 1330—1320 and 1180—1150 cm⁻¹ respectively (ref. 7c)

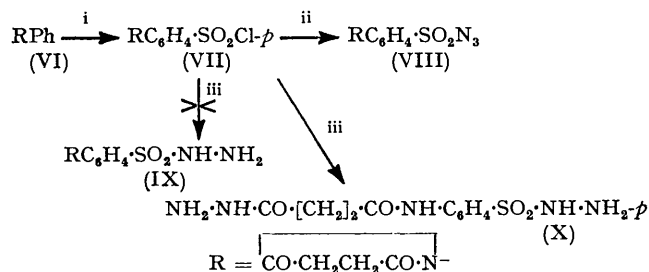
In view of the general biological activity of imides⁸ and the known fungicidal action of sulphanilohydrazides,⁹ it was considered that compounds like *p*-succinimidobenzenesulphonohydrazide (IX) might have fungicidal properties. *N*-Phenylsuccinimide (VI) with

⁷ (a) K. Nakanishi, 'Infrared Spectroscopy,' Holden-Day Inc., San Francisco, 1962, p. 45; (b) p. 47; (c) p. 54.

⁸ M. K. Hargreaves, J. G. Pritchard, and H. R. Dave, *Chem. Rev.*, 1970, **70**, (4), 466.

⁹ R. J. W. Cremllyn, *J. Chem. Soc.*, 1962, 2133.

chlorosulphuric acid gave the sulphonyl chloride (VII) which with sodium azide afforded the sulphonyl azide (VIII); treatment of (VII) however, with an excess of hydrazine hydrate at 0°, gave not the expected sulphonylhydrazide (IX), but the bis-hydrazide (X):



Reagents: i, ClSO₃H; ii, NaN₃; iii, N₂H₄·H₂O

The bis-hydrazide arises from cleavage of the carbon-nitrogen bond which, although generally requiring drastic reaction conditions, is not unknown to occur under mild conditions with activated amides.^{10,11}

N-Phenylphthalimide has been converted into the *p*-sulphonyl chloride which, with sodium azide, gave the corresponding sulphonyl azide.

EXPERIMENTAL

I.r. spectra were measured as Nujol mulls with an Infra-red 237 spectrometer and m.p.s were determined in open capillary tubes.

N-Carbamoylsulphanilyl Chloride (II).—Phenylurea (I) (22.4 g) was heated with chlorosulphuric acid (40 ml, 3 mol) at 60° for 2 h. The solution was poured on crushed ice, to give the sulphanilyl chloride (II) (20 g), m.p. 139—141° (from benzene) (lit.,¹ 144°), v_{max} 3480, 3400 (NH₂), 3260, 3220 (NH), 1720 (CO), 1365, and 1160 (SO₂) cm⁻¹.

N-Carbamoylsulphanilohydrazide.—*N*-Carbamoylsulphanilyl chloride (20 g) was condensed with hydrazine hydrate (16 ml; 98%) in ethanol (20 ml) at room temperature for 5 h, to give the *sulphanilohydrazide* as white flakes (14 g) (from ethanol), m.p. 168—170° (decomp.) (Found: C, 36.4; H, 4.4; N, 24.6; S, 13.6. C₇H₁₀N₄O₃S requires: C, 36.5; H, 4.4; N, 24.35; S, 13.9%), v_{max} 3500, 3400, 3240 (NH), 1690 (CO), 1330, and 1160 (SO₂) cm⁻¹.

N-Carbamoylsulphanilylhydrazones (Table 1).—The derivatives from aliphatic ketones were obtained by boiling the hydrazide with an ethanolic solution of the ketone for 1—2 h and leaving the mixture at room temperature for 3 h. The reactions were more rapid for aldehydes.

N-Phenyl-*N*-carbamoylsulphanilohydrazide.—*N*-Carbamoylsulphanilyl chloride (2 g) with phenylhydrazine (1 ml) and pyridine (4 ml) in ethanol (10 ml) was left overnight at room temperature; it gave the *N*-phenyl derivative (1.4 g) (from aq. ethanol), m.p. 166—168° (decomp.) (Found: C, 51.3; H, 4.6; N, 18.0. C₁₃H₁₄N₄O₃S requires: C, 51.0; H, 4.6; N, 18.3%).

N-Dimethylcarbamoyl-*N*-carbamoylsulphanilohydrazide.—Similarly *N*-carbamoylsulphanilohydrazide (1.2 g) with *NN'*-dimethylcarbamoyl chloride (0.6 ml) in pyridine (20 ml) gave the *NN'*-dimethylcarbamoyl-hydrazide as needles (200 mg) (from ethanol), m.p. 210—212° (decomp.)

* After drying at 120—130°/0.1 mmHg for 12 h.

¹⁰ H. Paulsen and D. Stoye, in 'The Chemistry of Amides,' ed. J. Zabicky, Interscience, London, 1970, p. 527.

(Found: C, 39.7; H, 4.8; N, 23.1; S, 10.4. C₁₀H₁₅N₅O₄S requires: C, 39.9; H, 5.0; N, 23.25; S, 10.6%).

4,4'-Ureylenebisbenzenesulphonyl Chloride.—*NN'*-Diphenylurea (28 g) was heated with chlorosulphuric acid (60 ml) at 80° for 1½ h to give the bis-sulphonyl chloride (20 g) (from acetone), m.p. 210—212° (lit.,⁵ 207—211°) (Found: C, 38.1; H, 2.7. Calc. for C₁₃H₁₀Cl₂N₂O₆S₂: C, 38.2; H, 2.4%), v_{max} 3340, 3300 (NH), 1680 (CO) 1330, and 1180 (SO₂) cm⁻¹.

4,4'-Ureylenebisbenzenesulphonylhydrazide.—*4,4'*-Ureylenebisbenzenesulphonyl chloride (10 g) was condensed with hydrazine hydrate (8 ml of 98%) for 12 h at room temperature, to give the *bis-sulphonylhydrazide* (4.3 g) (from ethanol), m.p. 225° (decomp.) (Found: C, 38.7; H, 3.8; N, 21.3; S, 16.1. C₁₃H₁₆N₆O₆S₂ requires: C, 39.0; H, 4.0; N, 21.0; S, 16.0), v_{max} 3450 (NH₂), 3300 (broad, NH), 1680 (CO), 1390, and 1170 (SO₂) cm⁻¹.

4,4'-Ureylenebisbenzenesulphonylhydrazones (Table 2).—For the derivatives of aliphatic ketones, the bis-hydrazide was boiled with the carbonyl compound in ethanol for 2 h and left overnight. With aromatic carbonyl compounds, the reaction was boiled for ½ h and then allowed to cool to room temperature.

4,4'-Ureylenebisbenzenesulphonyl Azide.—*4,4'*-Ureylenebisbenzenesulphonyl chloride (4.0 g) dissolved in acetone (20 ml) was treated with a concentrated aqueous sodium azide (2.6 g) at 0° for 3 h. To give the *bis-sulphonyl azide* (from ethanol) (0.5 g), m.p. 176—178° (Found: C, 37.1; H, 2.4; N, 26.3. C₁₃H₁₀N₆O₆S₂ requires: C, 36.9; H, 2.4; N, 26.5%), v_{max} 3200 (broad, NH), and 2100 (N₃) cm⁻¹.

4,4'-Ureylenebisbenzenesulphonamide.—The bis-sulphonyl chloride (5 g) with ammonium hydroxide solution (*d* 0.88)—ethanol gave the bis-sulphonamide (1.7 g), m.p. 288—290° (lit.,¹ 272—274°) (Found: C, 41.9; H, 4.0; N, 14.8; S, 17.1. C₁₃H₁₄N₄O₆S₂ requires: C, 42.2; H, 3.8; N, 15.1; S, 17.3%).

Investigation of the Reaction of Phenylurea (I) with Chlorosulphuric Acid.—Phenylurea (5 g) and chlorosulphuric acid (3 ml, 1 mol equiv.) in chloroform (10 ml) at 0°C for 1.5 h gave starting material on work-up.

A similar reaction at 60° for 2 h gave a water-soluble product; this when heated with an excess of chlorosulphuric acid (3 mol equiv.), gave the sulphanilyl chloride (II), m.p. 138—141°.

*Chlorosulphonation of Di-*o*-Tolylurea.*—*Di-*o*-Tolylurea* (18.2 g) was heated with chlorosulphuric acid (30 ml) at 80—85° for 4½ h. The mixture was poured onto ice and the mixture concentrated (reduced pressure) to give a white crystalline solid (12.3 g),* m.p. 200° (Found: C, 44.6; H, 4.4; N, 6.8; S, 15.0. The *bis-sulphonic acid*, C₁₅H₁₆N₂O₇S₂ requires: C, 45.0; H, 4.0; N, 7.0; S, 15.0%). The bis-sulphonic acid (20 g) and phosphorus pentachloride (40 g) were heated at 100° for 4½ h; the mixture was poured onto ice to give *4,4'*-ureylenebis-3-methylbenzenesulphonyl chloride, as prisms (11.3 g), m.p. 158—160° (from acetone) (Found: C, 41.0; H, 3.0; N, 6.6. C₁₅H₁₄Cl₂N₂O₆S₂ requires: C, 41.2; H, 3.2; N, 6.4%).

4,4'-Ureylenebis-3-methylbenzenesulphonamide.—The bis-sulphonyl chloride (2 g) with ammonium hydroxide (*d*, 0.88; 10 ml) in warm acetone (10 ml) gave the *bis-sulphonamide* (1 g), m.p. 220° (Found: C, 45.1; H, 4.6; N, 14.2. C₁₅H₁₈N₄O₆S₂ requires: C, 45.2; H, 4.55; N, 14.1%).

¹¹ I. B. Hannout, E. A. Hassan, A. M. Islam, and I. M. Ismail, *U.A.R. J. Chem.*, 1970, **13** (2), 199.

Chlorosulphonation of Di-m-tolylurea.—Di-m-tolylurea (16.2 g) was similarly heated with chlorosulphuric acid (27 ml) to give the 4,4'-bis-sulphonic acid (12.5 g), m.p. 200° † (Found: C, 44.6; H, 4.4; N, 7.0; S, 15.0. $C_{15}H_{16}N_2O_7S_2$ requires C, 45.0; H, 4.0; N, 7.0; S, 15.0%). The disulphonic acid and phosphorus pentachloride gave the bis-sulphonyl chloride (9.2 g), m.p. 150–152° (Found: C, 41.5; H, 3.3; N, 6.3. $C_{15}H_{14}Cl_2N_2O_5S_2$ requires C, 41.2; H, 3.2; N, 6.4%).

4,4'-Ureylenebis-2-methylbenzenesulphonamide.—The bis-sulphonyl chloride (2 g), with ammonium hydroxide-acetone, gave the bis-sulphonamide (1 g), m.p. 210° (Found: C, 45.4; H, 4.7; N, 14.2. $C_{15}H_{18}N_4O_5S_2$ requires C, 45.2; H, 4.55; N, 14.1%).

Chlorosulphonation of Di-p-tolylurea.—Di-p-tolylurea (24 g) was heated with chlorosulphuric acid to give the bis-sulphonic acid (V) (26 g), m.p. 200° † (Found: C, 44.7; H, 4.2; N, 7.3. $C_{15}H_{16}N_2O_7S_2$ requires C, 45.0; H, 4.0; N, 7.0%). The disodium salt (7 g) with phosphorus pentachloride gave the bis-sulphonyl chloride (3.6 g), m.p. 130–132° (Found: C, 40.8; H, 3.5; N, 6.8. $C_{15}H_{14}Cl_2N_2O_5S_2$ requires C, 41.2; H, 3.2; N, 6.4%).

4,4'-Ureylene-bis-3-methylbenzenesulphonohydrazide.—4,4'-Ureylene-3-methylbenzenesulphonyl chloride (6.3 g) with hydrazine hydrate (5 ml) in ethanol (10 ml) gave the bis-sulphonohydrazide (5.8 g) (from ethanol), m.p. 146–148° (Found: C, 41.8; H, 5.0; N, 19.4; S, 15.1. $C_{15}H_{20}N_6O_5S_2$ requires: C, 42.1; H, 4.7; N, 19.6; S, 14.9%).

p-Succinimidobenzenesulphonyl Chloride (VII).—N-Phenylsuccinimide (VI) (15 g) with chlorosulphuric acid (25 ml, 4 mol) at 70–80° for 2 h gave the sulphonyl chloride (VII) (12.5 g), m.p. 195–198° (lit.,¹² 197.5–198.5°). [Treatment with ammonia-acetone gave the sulphonamide, m.p. 233° (lit.,¹³ 234–238°).]

p-Succinimidobenzenesulphonyl Azide (VIII).—p-Succinimidobenzenesulphonyl chloride (VII) (2 g) dissolved in acetone, was shaken with a concentrated aqueous solution of sodium azide (1.3 g) for 2 h at 0°, to give the sulphonyl azide (VIII) as plates (2 g) (from aq. acetone), m.p. 142° (Found: C, 42.6; H, 2.7; N, 19.7; S, 11.8. $C_{10}H_8N_4O_4S$ requires C, 42.9; H, 2.9; N, 20.0; S, 11.4%).

Methyl p-Succinimidobenzenesulphonate.—The sulphonyl chloride (1 g) was boiled under reflux with methanol (20 ml) for 1 h, to give the methyl benzenesulphonate as needles

(0.8 g), m.p. 154° (Found: C, 48.7; H, 4.1; N, 5.0; S, 11.8. $C_{11}H_{11}NO_5S$ requires C, 49.1; H, 4.1; N, 5.2; S, 11.9%).

Reaction of p-Succinimidobenzenesulphonyl Chloride (VII) with Hydrazine.—The sulphonyl chloride (VII) (9 g) was gradually added to a stirred solution of hydrazine hydrate (5 ml; 98%) in ethanol (10 ml) at 0°. After 3 h at room temperature, recrystallisation from methanol gave the sulphanilohydrazide (X) (6.5 g), m.p. 169° (decomp.) (Found: C, 40.35; H, 4.8; N, 22.9; S, 10.4. $C_{10}H_{15}N_5O_4S$ requires C, 39.9; H, 5.0; N, 23.25; S, 10.6%). Boiling the bishydrazide (X) (1.5 g) with acetone for 45 min gave the corresponding bis-acetone hydrazone (1.2 g), m.p. 192–195° (Found: C, 50.2; H, 6.1; N, 18.1; S, 8.3. $C_{16}H_{23}N_5O_5S$ requires C, 50.4; H, 6.0; N, 18.4; S, 8.4%).

Treatment with boiling ethanolic o-nitrobenzaldehyde (2 mol equiv.) for 1 h, gave the bis-O-nitrobenzaldehyde hydrazone as pale yellow prisms (from ethanol), m.p. 200° (Found: C, 50.6; H, 3.9; N, 17.0; S, 5.7. $C_{24}H_{21}N_7O_8S$ requires C, 50.8; H, 3.7; N, 17.3; S, 5.6%). The following bis-hydrazones were similarly prepared: acetophenone, m.p. 208–209° (Found: C, 61.8; H, 5.2; N, 14.1; S, 6.1. $C_{28}H_{27}N_5O_4S$ requires C, 61.9; H, 5.3; N, 13.9; S, 6.3%), 3,4-dichlorobenzaldehyde, m.p. 218–220° (Found: C, 46.7; H, 2.9; N, 11.7; S, 5.0. $C_{24}H_{19}Cl_4N_5O_4S$ requires C, 46.8; H, 3.1; N, 11.4; S, 5.2%).

p-Phthalimidobenzenesulphonyl Azide.—p-Phthalimidobenzenesulphonyl chloride (3.2 g; m.p. 242°, lit.,¹⁴ 239–240°) with sodium azide (1.3 g) in aqueous acetone gave the sulphonyl azide as plates (from acetone) (2 g), m.p. 158–159° (decomp.) (Found: C, 51.3; H, 2.7; N, 16.8. $C_{14}H_8N_4O_4S$ requires C, 51.2; H, 2.5; N, 17.1%), ν_{max} . 3270 (NH), 2120 (N₃), 1710 (CO), 1350, 1180 (SO₂) cm⁻¹.

p-Phthalimidobenzenesulphonamide.—The sulphonyl chloride (1.5 g) with ammonia-ethanol gave the sulphonamide as plates (from aq. ethanol) (1.0 g), m.p. 330–332° (lit.,¹⁵ 334°).

[1/2295 Received, 3rd December, 1971]

¹² C. W. Picard, E. Reid, and D. E. Seymour, *J. Chem. Soc.*, 1946, 751.

¹³ R. Adams, P. H. Long, and A. Johanson, *J. Amer. Chem. Soc.*, 1939, **61**, 2342.

¹⁴ J.P. 176,976/1948 (*Chem. Abs.*, 1951, **45**, 6659a).

¹⁵ C. W. Picard, E. Reid, J. Reynolds, and D. E. Seymour, *J. Chem. Soc.*, 1948, 821.