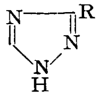
250. *Compounds related to Thiosemicarbazide. Part I. 3-Phenyl-1 : 2 : 4-triazole Derivatives.*

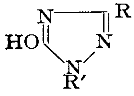
By Eric Hoggarth.

The preparation of 3-phenyl-1 : 2 : 4-triazole and two analogues by a novel route which involves the interaction of benzoyl *iso*thiocyanates with hydrazine is described. The constitutions of some of the products of side reactions have been elucidated.

3-Phenyl-1 : 2 : 4-triazole (I; R = Ph) was first prepared by Young and Oates (*J.*, 1901, **79**, 659) by heating 5-hydroxy-3-phenyl-1-methyl-1 : 2 : 4-triazole (II; R = Ph, R′ = Me) with phosphorus pentasulphide. The loss of a methyl group in similar reactions had been noted previously by Andreocci (*Atti R. Accad. Lincei*, 1890, **6**, 209). Later Young (*J.*, 1905, **87**, 625) obtained (I; R = Ph) from (II; R = Ph, R′ = H) with phosphorus pentasulphide, and the same compound has been prepared by Pellizzarri (*Gazzetta*, 1911, **41**, 20) by heating benzoylhydrazide (IV; R = Ph) with formamide or formylhydrazide with benzamide. All these reactions gave the product in very unsatisfactory yields. De and Roy Choudhury (*J. Indian Chem. Soc.*, 1928, **5**, 269) claimed that (I; R = Ph) was formed by oxidising benzylidenethiosemicarbazide with hydrogen peroxide, but the m. p. given by them (177°) is not in agreement with that given by Young and Oates (118·5—119°) and now confirmed.

Benzoyl *iso*thiocyanate has been shown to react with phenylhydrazine to give (mainly) 4-benzoyl-1-phenylthiosemicarbazide (Dixon, *J.*, 1889, **55**, 304; Johnson and Menge, *Amer. Chem. J.*, 1904, **32**, 358). We have found, however, that if the *iso*thiocyanate was dropped into an excess of hydrazine, a mixture of 3-*phenyl*-1 : 2 : 4-*triazole*-5-*thiol* (III; R = Ph) and benzoyl hydrazide (IV; R = Ph) was formed. It may be presumed that 4-benzoylthiosemicarbazide is formed first and then spontaneously cyclises with loss of water. If only one molecular proportion of hydrazine was used, side reactions took place and instead of the previously clear reaction liquid, a voluminous precipitate was formed. This precipitate consisted of 1 : 4-dibenzoylthiosemicarbazide (V; R = Ph), and the *salt* of this compound with hydrazine. The salt could be converted into (V; R = Ph) by treatment with mineral acid, and was prepared from an alcoholic solution of its constituent parts.


(I.)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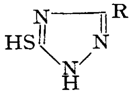
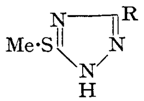

(III.)

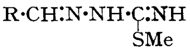
R·CO·NH·NH$_2$

(IV.)

R·CO·NH·NH·CS·NH·COR

(V.)


(VI.)


$\mathrm{R{\cdot}CH{:}N{\cdot}NH{\cdot}\underset{SMe}{C}{:}NH}$

(VII.)

p-*Methoxybenzoyl* and p-*chlorobenzoyl* iso*thiocyanates* were prepared by the method of Johnson and Chernoff (*J. Amer. Chem. Soc.*, 1912, **34**, 167). The *p*-methoxybenzoyl compound, a very low-melting solid, was added molten to excess of hydrazine hydrate in alcohol and gave the *thiol* (III; R = *p*-MeO·C_6H_4) and *p*-methoxybenzoylhydrazide (IV; R = *p*-MeO·C_6H_4). The yields of purified thiol in this case (averaging 37% in 3 runs) were always higher than in the reaction with benzoyl *iso*thiocyanate (23% in 3 runs). 1 : 4-*Di*-p-*methoxybenzoylthiosemicarbazide* (V; R = p-$\mathrm{MeO{\cdot}C_6H_4}$) was formed as a by-product when only 1 molecular proportion of hydrazine hydrate was taken, but a salt of the latter compound with hydrazine, though apparently formed, could not be crystallised. p-Chlorobenzoyl *iso*thiocyanate (dissolved in a little ether) reacted with excess of hydrazine to give the *thiol* (III; R = p-$\mathrm{ClC_6H_4}$) and p-chlorobenzoylhydrazide (IV; R = p-$\mathrm{ClC_6H_4}$). The yield of the thiol was again higher than with benzoyl *iso*thiocyanate (36% in 3 runs). When powdered p-chlorobenzoyl *iso*thiocyanate was used instead of an ethereal solution, a considerable amount of 1 : 4-*di*-p-*chlorobenzoylthiosemicarbazide* (V; R = p-$\mathrm{ClC_6H_4}$) was formed, even in the presence of an excess of hydrazine.

The thiols (III; R = Ph, p-$\mathrm{MeO{\cdot}C_6H_4}$, or p-$\mathrm{ClC_6H_4}$) were smoothly converted into the phenyltriazoles (I; R = Ph, p-$\mathrm{MeO{\cdot}C_6H_4}$, or p-$\mathrm{ClC_6H_4}$) by boiling in alcohol with Raney nickel catalyst. Compound (III; R = Ph) was also "desulphurised" by treatment with hydrogen peroxide. Confirmation of the assigned structures was obtained by methylation of two of the thiols to give the corresponding 5-methylthio-compounds (VI; R = Ph or p-$\mathrm{MeO{\cdot}C_6H_4}$) identical with those prepared by oxidation with ferric chloride of the corresponding 1-benzylidene-*S*-methyl*iso*thiosemicarbazides (VII; R = Ph or p-$\mathrm{MeO{\cdot}C_6H_4}$). 5-Methylthio-3-phenyl-1 : 2 : 4-triazole has been obtained by the latter route by De and Chakravarti (*J. Indian Chem. Soc.*, 1930, **7**, 875) using hydrogen peroxide as oxidising agent. Attempts have been made to prepare 5-amino-3-phenyl-1 : 2 : 4-triazole derivatives from the 5-methylthio-compounds on analogy with well-known reactions in the pyrimidine series, but no reaction could be detected between (VI; R = Ph) or the corresponding *sulphone* with ammonia or 2-diethylaminoethylamine.

EXPERIMENTAL.

3-*Phenyl*-1 : 2 : 4-*triazole*-5-*thiol* (III; R = Ph).—Hydrazine hydrate (70 c.c. containing 19·0 g. of hydrazine, by titration) and alcohol (130 c.c.) were stirred, with cooling by an ice-bath, whilst benzoyl *iso*thiocyanate (33 g.) was run in during 5 minutes. The temperature rose to 55°, and stirring at room temperature was continued overnight. The clear, pale yellow liquid was evaporated under reduced pressure, the residue diluted with water (200 c.c.), made strongly acid (hydrochloric acid), and the precipitate collected. This precipitate was ground in a mortar with N-hydrochloric acid (100 c.c.), and the solid again collected, washed well with water, and dried. The crude *thiol* (9·5 g., m. p. 240—245°) was crystallised from water (1 l.) with charcoal, giving colourless flat needles (8·1 g.), m. p. 256° (Found : C, 54·3; H, 4·0; N, 23·6; S, 17·7. $\mathrm{C_8H_7N_3S}$ requires C, 54·2; H, 4·0; N, 23·7; S, 18·1%). The acid extracts were exactly neutralised with sodium hydroxide solution and evaporated under reduced pressure, and the residue was extracted with chloroform. The solvent was evaporated from the dried extracts, leaving a colourless crystalline mass of benzoylhydrazide (18·5 g., m. p. 100—104°), which crystallised from benzene in large colourless prisms (12·6 g.), m. p. 112° not depressed by admixture with an authentic specimen, prepared as described by Curtius and Struve (*J. pr. Chem.*, 1894, **50**, 295) (Found : C, 62·2; H, 5·8; N, 20·8. Calc. for $\mathrm{C_7H_8ON_2}$: C, 61·8; H, 5·9; N, 20·6%).

When the above reaction was carried out with only 30 c.c. of the hydrazine hydrate solution, a precipitate was formed which was collected and washed with 50% aqueous alcohol. The filtrates were evaporated and separated into 3-phenyl-1 : 2 : 4-triazole-5-thiol (1·9 g., m. p. 254°) and benzoylhydrazide (5·5 g., m. p. 113°) as previously. The precipitate (7·5 g., m. p. 140—145°) was crystallised from alcohol (400 c.c.), giving the *hydrazine* salt of 1 : 4-dibenzoylthiosemicarbazide as colourless, flat, shining needles (1·1 g.), m. p. 157° (Found : C, 54·6, 54·5; H, 5·0, 4·75; N, 21·4; S, 9·6. $\mathrm{C_{15}H_{13}O_2N_3S,N_2H_4}$ requires C, 54·4; H, 5·1; N, 21·2; S, 9·7%). The mother-liquor was concentrated, filtered from flocculent material (charcoal), and allowed to crystallise, giving 1 : 4-dibenzoylthiosemicarbazide as colourless, square plates (0·75 g.), m. p. 174° (Found : C, 59·8; H, 4·0; N, 14·5; S, 10·7. Calc. for $\mathrm{C_{15}H_{13}O_2N_3S}$: C, 60·2; H, 4·35; N, 14·1; S, 10·7%). The hydrazine salt (0·5 g.) was dissolved in hot alcohol, treated with N-hydrochloric acid (10 c.c.), diluted with water, and the precipitated 1 : 4-dibenzoylthiosemicarbazide (0·35 g., m. p. 172°) crystallised from alcohol, giving colourless, square plates (0·25 g.), m. p. 173° (Found : C, 59·9; H, 3·9; N, 13·9%). A specimen of 1 : 4-dibenzoylthiosemicarbazide prepared by Fehrenbach and Stolle's method (*J. pr. Chem.*, 1929, **122**, 289) had m. p. 173° not depressed by admixture with the compound isolated in either of the above ways. The salt was formed by dissolving the dibenzoyl compound (0·5 g.) in alcohol, adding 50% hydrazine hydrate (1 c.c.) and allowing it to crystallise. Faintly yellow needles (0·25 g.), m. p. 156°, separated and were crystallised from alcohol, giving the salt, m. p. 157° not depressed by admixture with the compound isolated from the original reaction (Found : C, 54·3; H, 5·2; N, 21·2%). Care must be taken not to boil the alcoholic solutions of the salt or rapid decomposition with evolution of hydrogen sulphide takes place.

p-*Methoxybenzoyl* iso*Thiocyanate*.—p-Methoxybenzoyl chloride (51 g.) and lead thiocyanate (107 g.) were boiled with benzene (200 c.c.) (oil-bath) with good stirring for 1 hour, filtered, and the benzene removed under reduced pressure. The residue was distilled, giving a pale yellow oil, b. p. 133—135°/2·0 mm., which was redistilled (43 g.), b. p. 116—118°/0·3 mm., and then solidified to a crystalline mass of the iso*thiocyanate*, m. p. 28—30° (Found : N, 7·2; S, 16·3. $\mathrm{C_9H_7O_2NS}$ requires N, 7·25; S, 16·6%).

3-p-*Methoxyphenyl*-1 : 2 : 4-*triazole*-5-*thiol* (III; R = p-$\mathrm{MeO{\cdot}C_6H_4}$).—Hydrazine hydrate (35 c.c.) in alcohol (70 c.c.) was treated with p-methoxybenzoyl *iso*thiocyanate (19·3 g.), added molten from a warm tap-funnel during 5 minutes, and gave crude *thiol* (12·8 g., m. p. 240—242°) and p-methoxybenzoylhydrazide (6·0 g., m. p. 110°), separated as previously. The thiol was crystallised from alcohol (200 c.c.) and water (250 c.c.), giving large, faintly coloured needles (9·1 g.), m. p. 257° (Found : C, 51·7; H, 4·4; S, 15·4. $C_9H_9ON_3S$ requires C, 52·2; H, 4·35; S, 15·5%). The hydrazide was crystallised from xylene, giving colourless plates (2·4 g.), m. p. 133° not depressed by admixture with a sample of *p*-methoxybenzoylhydrazide prepared as described by Curtius and Melsbach (*J. pr. Chem.*, 1910, **81**, 501) (Found : C, 57·8; H, 5·8; N, 16·8. Calc. for $C_8H_{10}O_2N_2$: C, 57·8; H, 6·0; N, 16·9%). When only 15 c.c. of hydrazine hydrate were used in the above experiment, a precipitate separated; this was collected, and boiled with alcohol (200 c.c.) and concentrated hydrochloric acid (5 c.c.). Water was added, and the solid collected, and crystallised from 2-ethoxyethanol (much insoluble material), giving 1 : 4-*di*-p-*methoxybenzoylthiosemicarbazide* as colourless needles (0·25 g.), m. p. 210° not depressed by admixture with this compound prepared as below (Found : C, 56·5; H, 4·8; N, 12·0; S, 9·3. $C_{17}H_{17}O_4N_3S$ requires C, 56·8; H, 4·7; N, 11·7; S, 8·9%). The filtrate from the main part of the experiment gave the thiol (7·1 g.), m. p. 256°, and *p*-methoxybenzoylhydrazide (2·4 g.), m. p. 133°.

1 : 4-*Di*-p-*methoxybenzoylthiosemicarbazide* (V; R = *p*-MeO·C_6H_4).—*p*-Methoxybenzoylhydrazide (1·7 g.) was dissolved in warm alcohol (100 c.c.) and stirred whilst *p*-methoxybenzoyl *iso*thiocyanate (1·9 g.) was added during 5 minutes. The solid was collected after 1 hour, washed with water, and crystallised from 2-ethoxyethanol, giving colourless needles (2·8 g.), m. p. 210° (Found : C, 56·8; H, 4·6; S, 8·7%).

p-*Chlorophenyl* iso*Thiocyanate*.—This *compound* (prepared as described for the *p*-methoxybenzoyl analogue) was distilled, giving a pale yellow oil, b. p. 130—133°/2·0 mm., which solidified to a yellow crystalline mass, m. p. 48° (Found : N, 7·0; S, 15·9. C_8H_4ONClS requires N, 7·1; S, 16·2%).

3-p-*Chlorophenyl*-1 : 2 : 4-*triazole*-5-*thiol* (III; R = *p*-C_6H_4Cl).—Hydrazine hydrate (35 c.c.), alcohol (70 c.c.), and a solution of *p*-chlorobenzoyl *iso*thiocyanate (19·8 g.) in ether (60 c.c.) gave, as previously, the crude *thiol* (10 g.), m. p. 288°, and *p*-chlorobenzoylhydrazide (7·8 g.), m. p. 150°. The thiol was crystallised from aqueous alcohol, giving a white microcrystalline powder (8·5 g.), m. p. 296—297° (Found : C, 45·4; H, 2·4; N, 19·8; S, 14·8. $C_8H_6N_3ClS$ requires C, 45·4; H, 2·8; N, 19·9; S, 15·1%). The hydrazide crystallised from water in shining leaflets (6·2 g.), m. p. 164°, identical with the compound prepared by Kahl's method (*Centr.*, 1904, II, 1493) (Found : C, 49·6; H, 4·1; N, 16·6. Calc. for $C_7H_7ON_2Cl$: C, 49·3; H, 4·1; N, 16·4%). When the powdered *iso*thiocyanate (9·8 g.) was added to a rapidly stirred mixture of hydrazine hydrate (18 c.c.) and alcohol (35 c.c.), a thick precipitate was formed which after being stirred overnight, was collected, washed with alcohol, and crystallised from 2-ethoxyethanol, giving colourless needles of 1 : 4-*di*-p-*chlorobenzoylthiosemicarbazide* (0·85 g.), m. p. 235° (decomp.) (Found : C, 48·8; H, 3·0; S, 9·0. $C_{15}H_{11}O_2N_3Cl_2S$ requires C, 48·9; H, 3·0; S, 8·7%). The filtrates gave 3-*p*-chlorophenyl-1 : 2 : 4-triazole-5-thiol (1·1 g.), m. p. 292—293° (Found : S, 15·3%), and *p*-chlorophenylhydrazide (4·4 g.), m. p. 164° (Found : N, 16·7%).

1 : 4-*Di*-p-*chlorobenzoylthiosemicarbazide* (V; R = *p*-C_6H_4Cl).—*p*-Chlorobenzoyl *iso*thiocyanate (2·0 g.) and *p*-chlorobenzoylhydrazide (1·7 g.) gave the dibenzoyl compound (3·0 g.), m. p. 234° (decomp.), identical with this compound as isolated in the previous experiment (Found : C, 49·1; H, 2·9; S, 8·7%).

3-*Phenyl*-1 : 2 : 4-*triazole* (I; R = Ph).—(*a*) 3-Phenyl-1 : 2 : 4-triazole-5-thiol (1·8 g.) was boiled with Raney nickel catalyst (*ca.* 3·0 g.) in alcohol (20 c.c.) for 3 hours, filtered, and the filtrate evaporated, giving a colourless syrup which, on being scratched, solidified to a crystalline mass (1·4 g.), m. p. 110°. This crude material was free from sulphur and crystallised from light petroleum (b. p. 100—120°), giving 3-phenyl-1 : 2 : 4-triazole, which formed colourless needles (1·1 g.), m. p. 121° (Found : C, 66·1; H, 4·9; N, 28·6. Calc. for $C_8H_7N_3$: C, 66·2; H, 4·8; N, 29·0%).

(*b*) The same thiol (1·8 g.) was boiled in acetic acid (25 c.c.), and " perhydrol " (5 c.c.) added. When the vigorous reaction subsided, the acetic acid was evaporated under reduced pressure, the residue neutralised (sodium carbonate solution), the triazole extracted with ether, the extract dried (Na_2SO_4), and the solvent evaporated. The residue (1·3 g., m. p. 118°) was free from sulphur, and crystallised from light petroleum (b. p. 100—120°) in colourless needles (1·0 g.), m. p. 121° (Found : C, 65·9; H, 4·5%).

3-p-*Methoxyphenyl*-1 : 2 : 4-*triazole* (I; R = *p*-MeO·C_6H_4).—The thiol (2·1 g.) and Raney nickel catalyst (3·0 g.) in alcohol (25 c.c.) gave the *triazole*, which crystallised from methyl alcohol (small volume) giving large masses of colourless prisms (1·0 g.), m. p. 186° (Found : C, 61·5; H, 5·4; N, 23·7. $C_9H_9ON_3$ requires C, 61·7; H, 5·1; N, 24·0%).

3-p-*Chlorophenyl*-1 : 2 : 4-*triazole* (I; R = *p*-ClC_6H_4).—The thiol (1·05 g.) and Raney nickel catalyst gave the *triazole*, which crystallised from xylene in clumps of needles (0·5 g.), m. p. 182° (Found : C, 53·5; H, 3·2; N, 23·5. $C_8H_6N_3Cl$ requires C, 53·5; H, 3·3; N, 23·4%).

1-*Benzylidene*-S-*methyl*iso*thiosemicarbazide* (VII; R = Ph).—A mixture of the hydriodide of *S*-methyl*iso*thiosemicarbazide (11·5 g.) in water (5 c.c.) and benzaldehyde (5·5 g.) in alcohol (15 c.c.) was heated at 70—80° for 6 hours. Water (200 c.c.) was added, the alcohol removed under reduced pressure, and the hot solution filtered (charcoal) and allowed to crystallise. The resulting *hydriodide* (11·1 g., m. p. 78—82°) was crystallised from water, giving pale yellow needles (8·0 g.), m. p. 134° (after drying in a vacuum; sinters at 98°)(Found : C, 33·4; H, 3·7. $C_9H_{11}N_3S,HI$ requires C, 33·65; H, 3·7%). This salt (6·5 g.) was rubbed with warm 10% sodium carbonate solution until the liberated oil solidified, the solid collected, dissolved in boiling light petroleum (b. p. 60—80°, 250 c.c.), anhydrous potassium carbonate added, and the filtered solution allowed to crystallise, giving colourless prisms of the *base* (3·1 g.), m. p. 82° (Found : C, 55·7; H, 5·4; S, 16·8. $C_9H_{11}N_3S$ requires C, 55·95; H, 5·7; S, 16·6%). De and Chakravorty (*loc. cit.*) state that they were unable to crystallise this compound. No difficulty was experienced if the hydriodide was first purified.

1-p-*Methoxybenzylidene*-S-*methyl*iso*thiosemicarbazide* (VII; R = *p*-MeO·C_6H_4).—The hydriodide of *S*-methyl*iso*thiosemicarbazide (5·8 g.) and *p*-methoxybenzaldehyde (3·6 g.) gave a *hydriodide* (7·6 g.), m. p. 178° (sinters at 110°) (Found : C, 33·7; H, 3·6; N, 12·1. $C_{10}H_{13}ON_3S,HI$ requires C, 34·2; H, 4·0; N, 12·0%). The *thiosemicarbazide* (isolated as previously) crystallised from benzene–light petroleum (b. p. 60—80°), giving colourless needles (2·9 g.), m. p. 97° (Found : C, 53·9; H, 6·0; S, 14·0. $C_{10}H_{13}ON_3S$ requires C, 53·8; H, 5·8; S, 14·35%)

5-*Methylthio*-3-*phenyl*-1 : 2 : 4-*triazole* (VI; R = Ph).—(*a*) 3-Phenyl-1 : 2 : 4-triazole-5-thiol (1·8 g.) in alcohol (10 c.c.) was heated to 60°, treated with a solution of methyl iodide (1·5 g.) in alcohol (5 c.c.) in a closed vessel, set aside overnight, heated under reflux for 3 hours, and then evaporated under reduced pressure. The residue was rubbed with N-sodium hydroxide solution until it was almost all in solution, filtered (charcoal), and the filtrate exactly neutralised with N-hydrochloric acid. The precipitate (1·6 g., m. p. 160°) was crystallised from a small volume of 50% aqueous alcohol, giving the methylthio-compound as colourless leaflets (0·9 g.), m. p. 161° (Found: C, 56·5; H, 4·4; S, 16·8. Calc. for $C_9H_9N_3S$: C, 56·5; H, 4·7; S, 16·75%). De and Chakravorty (*loc. cit.*) give m. p. 164°. This compound was recovered unchanged after 6 hours' heating with 2-diethylaminoethylamine at 170—175°.

(*b*) 1-Benzylidene-*S*-methyl*iso*thiosemicarbazide (1·9 g.) in a mixture of acetic acid (25 c.c.) and water (25 c.c.) was stirred at 90° whilst a solution of ferric chloride (anhydrous, 3·5 g.) in water (10 c.c.) was added during 10 minutes. Stirring was continued at 90° until the reddish colour was discharged (0·5 hour), the solution evaporated under reduced pressure, and ether (100 c.c.) added, followed by an excess of 20% potassium hydrogen carbonate solution. After thorough shaking, the ether was poured off, the residue extracted with several small amounts of ether, and the solvent evaporated from the combined extracts. The residual solid (1·3 g., m. p. 156°) was crystallised first from aqueous alcohol and then from benzene, giving colourless flat needles (1·0 g.), m. p. 161° not depressed by the compound as prepared under (*a*) (Found: C, 57·0; H, 4·9; S, 16·6%).

5-*Methylthio*-3-p-*methoxyphenyl*-1 : 2 : 4-*triazole* (VI; R = *p*-MeO·C_6H_4).—(*a*) The thiol (1·1 g.) and methyl iodide (0·8 g.) in alcohol (50 c.c.) gave the *methylthio*-derivative, which crystallised from benzene containing a little light petroleum (b. p. 60—80°) in colourless leaflets or flat needles (0·8 g.), m. p. 126° (Found: C, 54·1; H, 4·7; N, 18·7; S, 14·9. $C_{10}H_{11}ON_3S$ requires C, 54·3; H, 5·0; N, 19·0; S, 14·5%).

(*b*) Oxidation of 1-*p*-methoxybenzylidene-*S*-methyl*iso*thiosemicarbazide (1·5 g.) in acetic acid (20 c.c.) and water (20 c.c.) by a solution of ferric chloride (anhydrous, 2·5 g.) in water (10 c.c.) as described for the benzylidene compound gave the methylthiotriazole (0·9 g., m. p. 120—122°), which crystallised from benzene–light petroleum (b. p. 60—80°) in colourless flat needles (0·75 g.), m. p. 126° not depressed by admixture with the compound prepared as in (*a*) (Found: C, 54·0; H, 4·8; S, 14·5%).

5-*Methylsulphonyl*-3-*phenyl*-1 : 2 : 4-*triazole*.—The methylthio-compound (1·9 g.) in acetic acid (30 c.c.) was treated at 25—30° with a solution of potassium permanganate (3·2 g.) in water (30 c.c.) added during 0·25 hour. The manganese dioxide was coagulated by warming on the steam-bath and filtered off, and the residue washed with 10% acetic acid. The filtrates were evaporated under reduced pressure, the residue made neutral with potassium hydrogen carbonate, and the precipitate extracted with chloroform. Evaporation of the solvent gave a colourless crystalline mass which crystallised from water or xylene in large colourless needles (1·0 g.), m. p. 160° (Found: C, 48·7; H, 4·1; S, 14·3. $C_9H_9O_2N_3S$ requires C, 48·5; H, 4·0; S, 14·4%). This *sulphone* was recovered unchanged after 15 hours' heating at 120° with alcoholic ammonia or after 6 hours at 160—170° with 2-diethylaminoethylamine.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
RESEARCH LABORATORIES, BLACKLEY, MANCHESTER, 9.

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