# **326.** *Compounds related to Thiosemicarbazide. Part VI. Further Routes to* 4 : 5-*Diamino*-3-*phenyl*-4 : 1 : 2-*triazole and Related Compounds.*

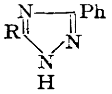
By Eric Hoggarth.

Alternative routes to 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole (Part V) have been examined. The compound was found among the products of the reaction of hydrazine with 1 : 4-dibenzoyl-*S*-methyl*iso*thiosemicarbazide and with 1-benzoylthiosemicarbazide and its *S*-methyl ether. Reaction with the last compound was most satisfactory from a preparative point of view, and several compounds substituted in the phenyl nucleus and in the 5-amino-group were prepared in this manner. 1-Benzoyl-*S*-methyl*iso*thiosemicarbazide reacted with methylhydrazine to give a compound, $C_9H_{11}N_5$, whose properties indicated that it was 5-α-methylhydrazino-3-phenyl-1 : 2 : 4-triazole.

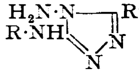
In Part V (*J.*, 1950, 614) it was reported that 1 : 4-dibenzoylthiosemicarbazide (I) reacted with hydrazine to give 3-phenyl-1 : 2 : 4-triazole-5-thiol (II; R = SH), benzhydrazide, and 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole (III; R = H, R′ = Ph). The yield of the last compound was small and alternative routes to it have been sought. On treatment with methyl iodide and sodium hydroxide, 1 : 4-dibenzoylthiosemicarbazide (I) gave the *S-methyl*iso*thiosemicarbazide* which when heated behaved like an *S*-methyl ether of a 1-benzoylthiosemicarbazide (Part III, *J.*, 1949, 1918) in readily losing methanethiol to give 2-benzamido-5-phenyl-1 : 3 : 4-oxadiazole (IV; R = Bz) (also prepared by benzoylating the parent amine). With hydrazine, 1 : 4-dibenzoyl-*S*-methyl*iso*thiosemicarbazide gave some of the diamino-triazole (III; R = H, R′ = Ph) together with benzhydrazide and a *compound* $C_{15}H_{13}ON_5$. The last was not identical with the monobenzoyl derivative of (III; R = H, R′ = Ph) mentioned in Part V (*loc. cit.*) and unlike that benzoyl derivative was not hydrolysed to (III; R = H, R′ = Ph) by acid. The constitution of this compound has not yet been established.

Ph·CO·NH·NH·CS·NH·CO·Ph

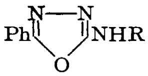
(I.)



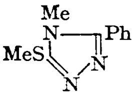
(II.)



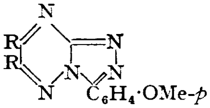
(III.)



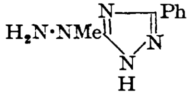
(IV.)



(V.)



(VI.)



(VII.)

1-Benzoylthiosemicarbazide was heated with an alcoholic solution of hydrazine in a stream of nitrogen, and the effluent gas washed with acidified lead acetate solution. Only 10—15% of the expected lead sulphide (on the basis of complete elimination) was formed, and the reaction products were separated, giving a small amount of 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole, the remainder consisting of the triazole-thiol (II; R = SH). By this method, 4 : 5-*diamino*-3-p-*methoxyphenyl*- (III; R = H, R′ = *p*-MeO·$C_6H_4$) and 4-*amino*-5-*anilino*-3-*phenyl*-4 : 1 : 2-*triazole* (III; R = R′ = Ph) were prepared, the yield in the last case being much higher than with other 1-benzoylthiosemicarbazides examined. Both 1-*p*-chlorobenzoylthiosemicarbazide and 1-benzoyl-4-methylthiosemicarbazide gave a very small amount of hydrogen sulphide and none of the corresponding diamine was isolated. However, all the preceding diamino-triazoles and 4 : 5-*diamino*-3-p-*chlorophenyl*- (III; R = H, R′ = *p*-$C_6H_4Cl$) and 4-*amino*-5-*methylamino*-3-*phenyl*-4 : 1 : 2-*triazole* (III; R = Me, R′ = Ph) were prepared by reaction of the corresponding benzoyl-*S*-methyl*iso*thiosemicarbazides with hydrazine, and this is the best preparative method although it is necessary to separate the triazole from two other reaction products, namely, the corresponding benzhydrazides and 2-amino-5-phenyl-1 : 3 : 4-oxadiazoles. The reaction with 1-benzoyl-4 : *S*-dimethyl*iso*thiosemicarbazide was further complicated by the formation of 5-methylthio-3-phenyl-4-methyl-4 : 1 : 2-triazole (V) in addition to the other products. The occurrence of this compound amongst the products of cyclisation of this *S*-methyl*iso*thiosemicarbazide with acids has been reported (Part III, *loc. cit.*). Two new 3-p-*methoxyphenyl*-1 : 2 : 4 : 7 : 9-*penta-azaindenes* (VI; R = Me or Ph) were formed by condensation of (III; R = H, R′ = *p*-MeO·$C_6H_4$) with diacetyl and benzil respectively, as described in Part V.

Reaction between 1-benzoyl-*S*-methyl*iso*thiosemicarbazide and methylhydrazine gave the amino-oxadiazole (IV; R = H) and a *compound* $C_9H_{11}N_5$. However, this compound cannot be the expected 5-amino-4-methylamino-3-phenyl-4 : 1 : 2-triazole, since it was freely soluble in dilute alkalis, indicating the presence of a hydrogen atom on one of the nitrogen atoms of the triazole ring. It was therefore a 5-methylhydrazino-1 : 2 : 4-triazole and since it formed a *benzylidene* and a p-*methoxybenzylidene* derivative was probably 5-α-methylhydrazino-3-phenyl-1 : 2 : 4-triazole (VII). In a similar experiment using *NN*-dimethylhydrazine, the major product, apart from amino-oxadiazole (IV; R = H) was 5-methylthio-3-phenyl-1 : 2 : 4-triazole (II; R = SMe), the dimethylhydrazine having induced cyclisation of the *S*-methyl*iso*thiosemicarbazide in the manner previously noted with other organic bases (Part IV, *J.*, 1950, 612). Only a small amount of the methylthio-triazole was formed in the reaction with methylhydrazine (which resembles, in this, piperidine and, as mentioned below, dimethylamine) and, except for the reaction with 1-benzoyl-4 : *S*-dimethyl*iso*thiosemicarbazide noted above, such cyclisations have not been detected with hydrazine. A very small amount of a compound $C_{10}H_{12}N_4$ was isolated from the reaction between 1-benzoyl-*S*-methyl*iso*thiosemicarbazide and *NN*-dimethylhydrazine and this proved to be 5-*dimethylamino*-3-*phenyl*-1 : 2 : 4-*triazole* (II; R = $NMe_2$) identical with a specimen prepared by treating the thiosemicarbazide with dimethylamine. It is probable that the dimethylhydrazine prepared by reduction of nitrosodimethylamine (*Org. Synth. Coll.*, Vol. II, 211) contained a trace of dimethylamine, which would account for the occurrence of the dimethylamino-triazole.

## EXPERIMENTAL.

The compounds mentioned below, which are not new, have been prepared in work described in earlier papers in this series and in each case (though this is not specifically mentioned in the text) mixed melting-point determinations have been made to confirm identity.

1 : 4-*Dibenzoyl*-S-*methyl*iso*thiosemicarbazide*.—The dibenzoylthiosemicarbazide (12·0 g.) in N-sodium hydroxide (40 c.c.) was ground finely to give a dispersion of the yellow sodium salt and shaken vigorously with methyl iodide (4·0 c.c.) and alcohol (20 c.c.) until the yellow colour was completely discharged, a little more methyl iodide being added as necessary. The solid was collected, dried in a vacuum, and crystallised from alcohol–ethyl acetate (50 : 50), care being taken to avoid overheating, giving large, colourless, refractive prisms (7·5 g.), m. p. 171° (Found : C, 61·8; H, 5·0; S, 10·5. $C_{16}H_{15}O_2N_3S$ requires C, 61·4; H, 4·8; S, 10·2%).

2-*Benzamido*-5-*phenyl*-1 : 3 : 4-*oxadiazole* (IV; R = Bz).—The above *S*-methyl*iso*thiosemicarbazide (1·0 g.) was heated in an oil-bath at 150° for 30 minutes and then cooled and the residue crystallised from alcohol, giving colourless needles (0·5 g.), m. p. 201° not depressed by a specimen prepared by benzoylation of the amino-oxadiazole (Fehrenbach and Stolle, *J. pr. Chem.*, 1929, **122**, 289) (Found : C, 68·2; H, 4·4. Calc. for $C_{15}H_{11}O_2N_3$ : C, 67·9; H, 4·2%).

*Reaction of* 1 : 4-*Dibenzoyl*-S-*methyl*iso*thiosemicarbazide with Hydrazine*.—The *S*-methyl*iso*thiosemicarbazide (5·2 g.), alcohol (20 c.c.), and 50% hydrazine hydrate (5·0 c.c.) were refluxed for 12 hours and the solvent was removed under reduced pressure. Water (50 c.c.) was added, followed by concentrated hydrochloric acid, and the insoluble hydrochloride was collected and sucked dry. The filtrates were evaporated to half bulk and then cooled and a further crop of hydrochloride was collected. The united solid (1·7 g.) was rubbed with 10% potassium hydrogen carbonate solution, and the solid *product* collected (1·5 g.; m. p. 180—186°) and crystallised from ethyl acetate, giving small colourless needles (0·75 g.), m. p. 196° (Found: C, 64·3; H, 4·7; N, 24·9. $C_{15}H_{13}ON_5$ requires C, 64·5; H, 4·7; N, 25·1%). The original acid filtrates were concentrated to half bulk, and (with good cooling) treated with 40% potassium hydroxide solution (20 c.c.). The solid was collected (1·2 g.) and crystallised from water, giving colourless plates (0·7 g.) of 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole, m. p. 223° (Found : C, 55·3; H, 5·4. Calc. for $C_8H_9N_5$ : C, 54·9; H, 5·1%). The original alkaline filtrates were made just acid with acetic acid and evaporated under reduced pressure and the dry residue was extracted with chloroform. Evaporation of the dried extracts gave benzhydrazide (1·5 g.) which crystallised from benzene in colourless plates (1·0 g.), m. p. 112° (Found : C, 62·0; H, 6·1. Calc. for $C_7H_8ON_2$ : C, 61·8; H, 5·9%).

*Reaction of* 1-*Benzoylthiosemicarbazide with Hydrazine*.—1-Benzoylthiosemicarbazide (3·9 g.), alcohol (50 c.c.), and 50% hydrazine hydrate (8·0 c.c.) were refluxed in a stream of nitrogen and the effluent gas was washed in acidified lead acetate solution. When evolution of hydrogen sulphide ceased (6 hours) the precipitated lead sulphide was collected in a Gooch crucible, well washed, and dried at 110° (0·71 g.). The reaction liquid was evaporated under reduced pressure, water (100 c.c.) added, and the resultant solution made strongly acid with hydrochloric acid. The precipitate was collected (1·8 g.; m. p. 230—238°) and crystallised from water with a little alcohol (it was necessary to cool the solution slowly and to filter it from a small flocculent precipitate which separated first and appeared to hinder crystallisation), giving colourles needles (0·8 g.) of 3-phenyl-1 : 2 : 4-triazole-5-thiol, m. p. 256—257° (Found : C, 54·1; H, 4·2. Calc. for $C_8H_7N_3S$ : C, 54·2; H, 4·0%). The flocculent precipitate afforded on crystallisation a little more of the thiol (0·1 g.; m. p. 256°). The original acid filtrate was evaporated and treated with 10N-sodium hydroxide (10 c.c.), and the solid collected (0·5 g.; m. p. 220°) and crystallised from water, giving colourless plates (0·3 g.) of 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole, m. p. 223° (Found : C, 55·0; H, 5·2%).

The following were obtained in analogous experiments : 4 : 5-*diamino*-3-p-*methoxyphenyl*- (III; R = H, R′ = *p*-MeO·$C_6H_4$), colourless glistening plates, m. p. 242°, from water (Found : C, 52·5;

H, 5·5; N, 34·6. $C_9H_{11}ON_5$ requires C, 52·7; H, 5·4; N, 34·1%) [3-*p*-methoxyphenyl-1 : 2 : 4-triazole-5-thiol, colourless needles, m. p. 255°, from aqueous alcohol, was also isolated (Found: C, 51·9; H, 4·4. Calc. for $C_9H_9ON_3S$: C, 52·2; H, 4·35%)], and *4-amino-5-anilino-3-phenyl-4 : 1 : 2-triazole* (III; R = R′ = Ph), colourless leaflets, m. p. 286°, from 2-ethoxyethanol (Found: C, 67·0; H, 5·5; N, 27·9. $C_{14}H_{13}N_5$ requires C, 66·9; H, 5·2; N, 27·9%) [3 : 4-diphenyl-4 : 1 : 2-triazole-5-thiol, colourless needles, m. p. 280°, from alcohol was also isolated (Found: C, 66·0; H, 4·6. Calc. for $C_{14}H_{11}N_3S$: C, 66·4; H, 4·3%)]. Under the same conditions, 1-benzoyl-4-methylthiosemicarbazide gave only 3-phenyl-4-methyl-4 : 1 : 2-triazole-5-thiol, colourless needles, m. p. 166°, from aqueous alcohol (Found: C, 56·5; H, 4·8. Calc. for $C_9H_9N_3S$: C, 56·5; H, 4·7%), and 1-*p*-chlorobenzoylthiosemicarbazide gave only 3-*p*-chlorophenyl-1 : 2 : 4-triazole-5-thiol, colourless small needles, m. p. 298°, from aqueous alcohol (Found: S, 15·3. Calc. for $C_8H_6N_3ClS$: S, 15·1%). Very little lead sulphide was formed in the second pair of experiments but the amounts of it formed in the first pair were 0·9 g. and 2·6 g. respectively in experiments on the same scale as that with 1-benzoylthiosemicarbazide (0·02 g.-mol.).

*Reaction of 1-Benzoyl-S-methyl*iso*thiosemicarbazide with Hydrazine.*—The *S*-methyl*iso*thiosemicarbazide (5·1 g.), 50% hydrazine hydrate (9 c.c.), and alcohol (25 c.c.) were set aside for 12 hours and then refluxed for 1 hour. The solvents were evaporated under reduced pressure, the residue was dissolved in water (25 c.c.), and 40% potassium hydroxide solution (15 c.c.) added slowly with good cooling. The solid was collected and washed with a little ice-water. The filtrates were made just acid with acetic acid and benzhydrazide was isolated as previously and crystallised from benzene, giving colourless plates (0·9 g.), m. p. 112° (Found: C, 61·5; H, 5·5%). The solid precipitated by potassium hydroxide was dissolved in water (50 c.c.) and N-hydrochloric acid (20 c.c.), filtered (charcoal), and carefully neutralised with potassium hydrogen carbonate. The precipitate was collected and crystallised from alcohol, giving colourless prisms (0·7 g.) of 2-amino-5-phenyl-1 : 3 : 4-oxadiazole (IV; R = H), m. p. 242—244° (Found: C, 59·7; H, 4·3. Calc. for $C_8H_7ON_3$: C, 59·6; H, 4·3%). The original neutralised solution was concentrated under reduced pressure, and, with strong cooling, 40% potassium hydroxide solution was added. The precipitated 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole (1·2 g.) was crystallised from water or alcohol, giving large colourless plates (0·9 g.), m. p. 226° (Found: C, 55·1; H, 5·1; N, 40·3%).

*4 : 5-Diamino-3-*p*-methoxyphenyl-4 : 1 : 2-triazole* (III; R = H, R′ = *p*-MeO·$C_6H_4$).—*p*-Methoxybenzoyl-*S*-methyl*iso*thiosemicarbazide (4·8 g.) reacted as above, giving *p*-methoxybenzhydrazide, colourless prisms (1·5 g.), m. p. 136° from xylene (Found: C, 57·5; H, 6·0. Calc. for $C_8H_{10}O_2N_2$: C, 57·8; H, 6·0%), 2-amino-5-*p*-methoxyphenyl-1 : 3 : 4-oxadiazole, colourless needles (0·8 g.), m. p. 248—249°, from alcohol (Found: C, 56·9; H, 4·8. Calc. for $C_9H_9O_2N_3$: C, 56·6; H, 4·7%), and the diamine, colourless plates (0·7 g.), m. p. 242°, from water (Found: C, 52·5; H, 5·5; N, 34·5%).

This diamine, by reaction with diacetyl and benzil as described for 4 : 5-diamino-3-phenyl-4 : 1 : 2-triazole (Part V, *loc. cit.*), gave *3-*p*-methoxyphenyl-5 : 6-dimethyl-1 : 2 : 4 : 7 : 9-penta-azaindene* (VI; R = Me), yellow needles, m. p. 215°, from alcohol (Found: C, 60·9; H, 5·1. $C_{13}H_{13}ON_5$ requires C, 61·2; H, 5·1%), and the corresponding *5 : 6-diphenyl* compound (VI; R = Ph), deep yellow needles, m. p. 247°, from alcohol (Found: C, 72·6; H, 4·4. $C_{23}H_{17}ON_5$ requires C, 72·8; H, 4·5%).

*4 : 5-Diamino-3-*p*-chlorophenyl-4 : 1 : 2-triazole* (III; R = H, R′ = *p*-$C_6H_4Cl$).—1-*p*-Chlorobenzoyl-*S*-methyl*iso*thiosemicarbazide (12·1 g.), treated as for the benzoyl compound, gave *p*-chlorobenzhydrazide, colourless plates (3·9 g.), m. p. 164° from water (Found: C, 49·1; H, 3·7. Calc. for $C_7H_7ON_2Cl$: C, 49·3; H, 4·1%). The separation using bicarbonate was unsatisfactory in this case and the solid product insoluble in sodium hydroxide was repeatedly extracted with small amounts of hot water, the united filtrates were concentrated, filtered (charcoal), and allowed to crystallise, giving the *diamine* as colourless leaflets (1·4 g.), m. p. 236° (Found: C, 46·0; H, 3·7; N, 33·7. $C_8H_8N_5Cl$ requires C, 45·8; H, 3·8; N, 33·4%). The residue left after extraction with water crystallised from alcohol, giving long yellow needles (0·7 g.) of 2-amino-5-*p*-chlorophenyl-1 : 3 : 4-oxadiazole, m. p. 273—274° (Found: C, 49·1; H, 3·2. Calc. for $C_8H_6ON_3Cl$: C, 49·1; H, 3·1%).

*4-Amino-5-methylamino-3-phenyl-4 : 1 : 2-triazole* (III; R = Me, R′ = Ph).—1-Benzoyl-4 : *S*-dimethyl*iso*thiosemicarbazide (4·6 g.), alcohol (25 c.c.), and 50% hydrazine hydrate (8·0 c.c.) were refluxed together for 6 hours and the solvent was removed under reduced pressure. The residue was treated with water (50 c.c.) and 40% potassium hydroxide solution (10 c.c.), and the solid collected and dried (3·6 g.) (Found: S, 8·1%). The solid was refluxed with benzene (50 c.c.) and light petroleum (b. p. 60—80°; 50 c.c.) and filtered hot from an insoluble residue. This residue was crystallised twice from ethyl acetate, giving colourless glistening leaflets (0·2 g.) of the *diamine*, m. p. 222° (Found: C, 56·3; H, 6·0; N, 37·3. $C_9H_{11}N_5$ requires C, 57·2; H, 5·8; N, 37·0%). The benzene–light petroleum extracts were re-heated, filtered (charcoal), and allowed to crystallise slowly, giving a mixture of large plates and clumps of small needles. The plates were removed as fully as possible by hand (0·5 g.; m. p. 125—128°) and recrystallised from the same solvents, giving large colourless plates (0·3 g.) of 5-methylthio-3-phenyl-4-methyl-4 : 1 : 2-triazole, m. p. 137° (Found: C, 58·2; H, 5·4; S, 15·5. Calc. for $C_{10}H_{11}N_3S$: C, 58·5; H, 5·4; S, 15·6%); the residual crystals were dissolved in the mother-liquor, filtered (charcoal), and allowed to crystallise slowly; the liquor was decanted from the clumps of small needles (0·8 g.; m. p. 150—152°) which were recrystallised from the same solvents, giving colourless needles (0·5 g.) of 2-methylamino-5-phenyl-1 : 3 : 4-oxadiazole, m. p. 153° (Found: C, 61·5; H, 5·0. Calc. for $C_9H_9ON_3$: C, 61·8; H, 5·1%).

*4-Amino-5-anilino-3-phenyl-4 : 1 : 2-triazole* (III; R = R′ = Ph).—1-Benzoyl-4-phenyl-*S*-methyl*iso*thiosemicarbazide (3·2 g.) gave the diamine which crystallised from 2-ethoxyethanol in colourless leaflets (0·25 g.), m. p. 288° (Found: C, 66·6; H, 5·4%), and 2-anilino-5-phenyl-1 : 3 : 4-oxadiazole which crystallised from alcohol in colourless needles (1·7 g.), m. p. 212° (Found: C, 70·5; H, 5·0. Calc. for $C_{14}H_{11}ON_3$: C, 70·8; H, 4·6%). These compounds were separated by extracting the more soluble oxadiazole with alcohol.

*Reaction of 1-Benzoyl-S-methyl*iso*thiosemicarbazide with Methylhydrazine.*—The *S*-methyl*iso*thiosemicarbazide (8·4 g.), alcohol (25 c.c.), and methylhydrazine (5·0 c.c.) were refluxed together for 12 hours and evaporated under reduced pressure. Water (15 c.c.) was added, and, with strong cooling, 10N-sodium hydroxide (15 c.c.) added with shaking. The solid was collected, washed with a little N-NaOH, and dried in a vacuum (1·5 g.; m. p. 222—228°). None of the procedures used above for separating a 4 : 5-diamino-4 : 1 : 2-triazole gave an analogous substance and by crystallisation of this material from alcohol, colourless prisms (1·2 g.) of 3-amino-5-phenyl-1 : 3 : 4-oxadiazole, m. p. 242°, were obtained. The original alkaline liquor was made just acid with acetic acid, and the precipitate allowed to harden, collected, washed with water (5·5 g.; m. p. 168—170°) (Found : S, 1·7%), ground with N-hydrochloric acid (20 c.c.) for 2 minutes, and quickly filtered. The extraction was repeated on the residue (0·8 g.) using acid (5 c.c.) and giving an ultimate residue (0·05 g.), which crystallised from aqueous alcohol in colourless plates, m. p. 161—162° (5-methylthio-3-phenyl-1 : 2 : 4-triazole). The acid extracts were neutralised with potassium hydrogen carbonate, giving precipitates (3·0 g., m. p. 178—180°; and 0·5 g., m. p. 180—181°) which were crystallised from aqueous alcohol, giving colourless glistening plates (2·8 g. in all), m. p. 184—185°, of 5-*a-methylhydrazino*-3-*phenyl*-1 : 2 : 4-*triazole* (Found : C, 57·1, 57·2; H, 5·5, 5·6; N, 36·4. $C_9H_{11}N_5$ requires C, 57·1; H, 5·8; N, 37·0%). When this compound (0·5 g.) was refluxed with alcohol (10 c.c.) and benzaldehyde (1·0 c.c.) for 12 hours and evaporated under reduced pressure, crystallisation from aqueous alcohol gave colourless needles (0·5 g.) of the *benzylidene* compound, m. p. 191—192° (Found : C, 69·5; H, 5·6; N, 25·4. $C_{16}H_{15}N_5$ requires C, 69·3; H, 5·4; N, 25·3%). By use of *p*-anisaldehyde (1·0 c.c.) in place of benzaldehyde, the corresponding p-*methoxybenzylidene* compound was obtained as colourless prisms (0·7 g.), m. p. 192—193° (Found : C, 66·3; H, 5·7. $C_{17}H_{17}ON_5$ requires C, 66·45; H, 5·5%).

*Reaction of* 1-*Benzoyl*-S-*methyl*iso*thiosemicarbazide with* NN-*Dimethylhydrazine*.—The above experiment was repeated using *NN*-dimethylhydrazine (12 c.c.) and gave 2-amino-5-phenyl-1 : 3 : 4-oxadiazole (5·5 g.), m. p. 241—242°. No 4 : 5-diamino-4 : 1 : 2-triazole could be detected. The precipitate (0·8 g.; m. p. 154—156°) (Found : S, 16·4%) obtained from the alkaline mother-liquors by making them just acid with acetic acid was almost pure 5-methylthio-3-phenyl-1 : 2 : 4-triazole and crystallised from aqueous alcohol in colourless shining leaflets (0·6 g.), m. p. 162—163° (Found : S, 16·7. Calc. for $C_9H_9N_3S$ : S, 16·75%). The faintly acid mother-liquors were extracted with ether in an automatic apparatus, the solvent was removed, and the residue crystallised twice from benzene–light petroleum (b. p. 60—80°) giving hard, refractive, faintly yellow prisms (0·1 g.), m. p. 203—204° not depressed by admixture with 5-*dimethylamino*-3-*phenyl*-1 : 2 : 4-*triazole* (see below) (Found : C, 64·3; H, 6·3; N, 30·0. $C_{10}H_{12}N_4$ requires C, 63·8; H, 6·4; N, 29·8%).

5-*Dimethylamino*-3-*phenyl*-1 : 2 : 4-*triazole* (II; R = $NMe_2$).—A mixture of 1-benzoyl-*S*-methyl*iso*thiosemicarbazide (4·2 g.), alcohol (25 c.c.), and dry dimethylamine (6·0 g.) was heated in a sealed tube at 100° for 12 hours. After the solvent had been removed and the residue made alkaline with N-sodium hydroxide (50 c.c.), 2-amino-5-phenyl-1 : 3 : 4-oxadiazole (0·5 g.), m. p. 241—242°, was isolated in the usual way. The precipitate obtained from the alkaline liquor by neutralising it with acetic acid (3·0 g.; m. p. 185—190°) (Found : S, 2·3%) was rubbed with N-hydrochloric acid (30 c.c.). An almost clear solution was obtained, and then a very sparingly soluble hydrochloride rapidly separated. This was collected, ground once with N-hydrochloric acid, again collected, and washed with a little N-hydrochloric acid. Neutralisation of the filtrates with potassium hydrogen carbonate gave the methylthio-triazole, colourless plates (0·25 g.), m. p. 162—163° from aqueous alcohol (Found : S, 17·1%). The insoluble hydrochloride was dissolved in hot water (80 c.c.), filtered hot, and made just alkaline with potassium hydrogen carbonate, giving the dimethylamino-triazole which crystallised from aqueous alcohol in large, colourless, hard, refractive prisms (2·0 g.), m. p. 207—208° (Found : C, 63·7; H, 6·2%).

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