938. 2-*Benzoyldithiocarbazinic Acid and Related Compounds.*

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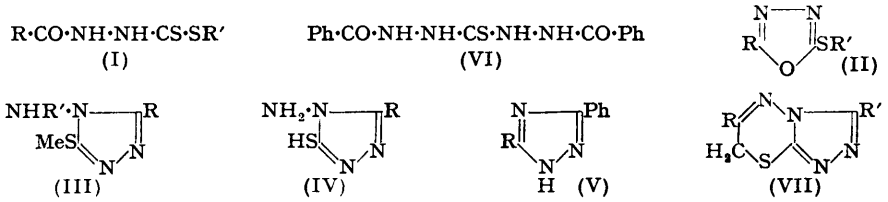
Heating of an appropriate hydrazide, carbon disulphide and alcoholic potassium hydroxide gave various substituted 2-benzoyldithiocarbazinic acids and 2-acetylthiocarbazinic acid. In absence of alkali reaction took a different course. Benzhydrazide and carbon disulphide in alcohol gave 1 : 2-dibenzoylhydrazine and 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole; in pyridine there was formed, in addition, 4-benzamido-5-mercapto-3-phenyl-4 : 1 : 2-triazole (isolated as its methylthio-derivative). Methyl 2-benzoyldithiocarbazinate and hydrazine formed 4-amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole and this was converted into the above benzamido-derivative. The cyclisation reactions of 2-benzoyldithiocarbazinic acids and their methyl esters have been examined.

Busch and Starke (*J. pr. Chem.*, 1916, **93**, 49), by treating benzhydrazide with carbon disulphide and potassium hydroxide in alcohol, obtained 2-benzoyldithiocarbazinic acid (I; R = Ph, R′ = H) as a crystalline potassium salt, which was easily alkylated to give esters of the type (I; R = Ph, R′ = alkyl). In the same way we have prepared (I; R = *p*-C_6H_4Cl, *p*-MeO·C_6H_4 or Me, R′ = H or Me). However, in absence of potassium hydroxide, benzhydrazide and carbon disulphide in alcohol gave 1 : 2-dibenzoylhydrazine and 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole (II; R = Ph, R′ = H), the constitution of which followed from identity of its methylation product with 2-methylthio-5-phenyl-1 : 3 : 4-oxadiazole (II; R = Ph, R′ = Me) (*J.*, 1949, 1918). An attempt to remove the sulphur atom from the mercapto-oxadiazole with Raney nickel gave, unexpectedly, benzamide. When benzhydrazide and carbon disulphide reacted in pyridine, the dibenzoylhydrazine fraction contained a considerable quantity of a sulphur-containing compound which was eventually isolated as its *S*-methyl derivative, $C_{16}H_{14}ON_4S$, and was shown by synthesis to be 4-benzamido-5-methylthio-3-phenyl-4 : 1 : 2-triazole (III; R = Ph, R′ = Bz). The parent thiol presumably arises by cyclisation of an intermediate formed from two molecules of benzhydrazide and one of carbon disulphide, *e.g.*, 1 : 5-dibenzoylthiocarbazide (VI). An attempt to prepare (VI) from benzhydrazide by thiocarbonyl chloride gave only the mercapto-oxadiazole (II; R = Ph, R′ = H) and unchanged benzhydrazide. Recently, Dornov and Brunken (*Chem. Ber.*, 1949, **82**, 121) and Lieser and Nischk (*ibid.*, p. 527) reported that benzhydrazide and carbonyl chloride gave 2-hydroxy-5-phenyl-1 : 3 : 4-oxadiazole.

Methyl 2-benzoyldithiocarbazinate (I; R = Ph, R′ = Me) reacted with hydrazine,

to give 4-amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (IV; R = Ph), the constitution being established as follows. Methylation gave a methylthio-derivative, whose nature was confirmed by oxidation to a sulphone. By mild oxidation, the thiol gave a



disulphide which, like related compounds (cf., Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1510), on dissolution in alkali regenerated the thiol. Treatment of the methylthio-derivative with nitrous acid eliminated an amino-group in a reaction characteristic of 4-amino-triazoles (Curtius, Darapsky, and Müller, *Ber.*, 1907, **40**, 836), giving 5-methylthio-3-phenyl-1 : 2 : 4-triazole (V; R = SMe) (*J.*, 1949, 1160). Furthermore, treatment of (IV; R = Ph) with Raney nickel removed the sulphur atom, giving 4-amino-3-phenyl-4 : 1 : 2-triazole, converted by nitrous acid into 3-phenyl-1 : 2 : 4-triazole (V; R = H) (*loc. cit.*). The compound $C_{16}H_{14}ON_4S$ resisted acid or alkaline hydrolysis, but it was obtained by benzoylation of 4-amino-5-methylthio-3-phenyl-4 : 1 : 2-triazole. Both 4-amino-3-phenyl- and 4-amino-5-methylthio-3-phenyl-4 : 1 : 2-triazole with *p*-dimethylaminobenzaldehyde gave well-defined benzylidene derivatives. The analogous compounds (IV; R = *p*-MeO·C_6H_4 or Me) were prepared from the corresponding methyl dithiocarbazinates and characterised as their methylthio-derivatives. A by-product $C_2H_6N_6S$, formed in the reaction with methyl 2-acetyldithiocarbazinate, proved to be 4-amino-3-hydrazino-5-mercapto-4 : 1 : 2-triazole (IV; R = NH·NH_2) (following paper).

The structures of the amino-thiols were confirmed on treating them with phenacyl bromide. Bose and his co-workers (*J. Indian Chem. Soc.*, 1924, **1**, 51; 1925, **2**, 95; 1927, **4**, 257) have shown that, in general, phenacyl bromide and compounds containing the system $NH_2{\cdot}\overset{|}{N}{=}\overset{/}{C}{\cdot}SH$ give derivatives of 5-phenyl-1 : 3 : 4-thiadiazine. 4-Amino-5-mercapto-3-phenyl- and -3-methyl-4 : 1 : 2-triazole gave what, by analogy, were regarded as 6 : 7-dihydro-3 : 5-diphenyl-7-thia-1 : 2 : 4 : 9-tetra-azaindene (VII; R = R′ = Ph) and the corresponding compound (VII; R = Ph, R′ = Me). The compound (VII; R = H, R′ = Ph) was obtained with bromoacetal under slightly different conditions. Unlike the cases studied by Bose and Nandi (*J. Indian Chem. Soc.*, 1930, **7**, 961) cyclisation did not occur when 4-amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole reacted with ethyl chloroacetate, the intermediate ethyl 4-amino-3-phenyl-4 : 1 : 2-triazol-5-yl thioacetate alone being isolated. This with alkali gave the corresponding thioglycollic acid, also obtained from the mercaptotriazole and chloroacetic acid.

The reactions between potassium or methyl 2-benzoyldithiocarbazinate and acidic or basic reagents similar to those which cause cyclisation of 1-benzoylthiosemicarbazides and their *S*-methyl derivatives (*J.*, 1949, 1163, 1918) were not so diverse as with the latter. Treatment of the potassium salt with dilute mineral acid precipitated the free acid which gradually dissolved with formation of carbon disulphide and benzhydrazide. With hot syrupy phosphoric acid, the principal product was benzoic acid with smaller amounts of 1 : 2-dibenzoylhydrazine and 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole. Both potassium and methyl dithiocarbazinate were converted in very good yield into the mercapto-oxadiazole by boiling pyridine. This was a convenient preparative method and the thiols (II; R = *p*-C_6H_4Cl, *p*-MeO·C_6H_4, or Me, R′ = H) were prepared from the corresponding potassium dithiocarbazinate and characterised as their methyl derivatives (II; R = *p*-C_6H_4Cl, *p*-MeO·C_6H_4, or Me, R′ = Me).

Experimental

The following salts were obtained in high yields as described by Busch and Starke (*loc. cit.*), by stirring together the corresponding hydrazides (1 mol.), carbon disulphide (1·5 mols.), and a solution of potassium hydroxide (1·5 mols.) in absolute alcohol, for 2—3 hours at 35—40° and

then for 12—18 hours at room temperature. The pale yellow crystals which slowly formed were collected and crystallised from alcohol containing very little water. The esters were prepared by shaking aqueous solutions of the potassium salts with a slight excess of methyl iodide in a pressure bottle for 2—3 hours. The precipitate was crystallised from aqueous alcohol, or in the case of methyl 2-acetyldithiocarbazinate from benzene containing a small amount of ethyl acetate. In the case of the latter compound, which was appreciably soluble in water, the precipitate was usually oily and was isolated by ether-extraction.

Potassium, colourless leaflets or needles, m. p. 292—296° (decomp.) (Found : C, 38·2; H, 2·7; S, 25·4. Calc. for $C_8H_7ON_2S_2K$: C, 38·4; H, 2·8; S, 25·6%), and methyl 2-benzoyldithiocarbazinate, colourless needles, m. p. 172° (Busch and Starke give m. p. 170° for the ester but do not record a m. p. for the salt) ; *potassium*, pale yellow needles, m. p. 265—266° (decomp.) (Found : C, 38·5; H, 3·3; S, 22·6. $C_9H_9O_2N_2S_2K$ requires C, 38·6; H, 3·2; S, 22·9%), and *methyl* 2-p-*methoxybenzoyldithiocarbazinate*, colourless needles, m. p. 155—157° (Found : C, 46·8; H, 4·7; S, 24·6. $C_{10}H_{12}O_2N_2S_2$ requires C, 46·9; H, 4·7; S, 25·0%) ; *potassium*, pale yellow needles, m. p. 308—310° (decomp.) (Found : C, 33·8; H, 2·5; S, 22·8. $C_8H_6ON_2ClS_2K$ requires C, 33·7; H, 2·1; S, 22·5%), and *methyl* 2-p-*chlorobenzoyldithiocarbazinate*, colourless, flat needles, m. p. 183—184° (Found : C, 41·3; H, 3·5. $C_9H_9ON_2ClS_2$ requires C, 41·5; H, 3·5%) ; *potassium*, pale yellow prisms, m. p. 180—182° (decomp.; sinters at 165°) (Found : C, 19·0; H, 2·7; S, 33·9. $C_3H_5ON_2S_2K$ requires C, 19·1; H, 2·7; S, 34·0%), and *methyl* 2-*acetyldithiocarbazinate*, colourless plates, m. p. 122—123° (Found : C, 29·5; H, 4·9; S, 38·6. $C_4H_8ON_2S_2$ requires C, 29·3; H, 4·9; S, 39·0%).

2-*Mercapto*-5-*phenyl*-1 : 3 : 4-*oxadiazole* (II; R = Ph, R′ = H).—(*a*) A mixture of benzhydrazide (27·2 g.), alcohol (100 c.c.) and carbon disulphide (18·0 c.c.) was refluxed, with stirring, overnight, the solvent removed under reduced pressure, and the residue rubbed with water until it crystallised. The solid (10·9 g.) crystallised from 50% aqueous alcohol (300 c.c.) on cooling slowly to 30°. At this temperature the colourless glistening plates were filtered off quickly on a large warm Buchner funnel and washed with a little cold alcohol. A mass of fibrous crystals immediately separated from the mother-liquor. The first crop (5·0 g.) recrystallised from alcohol, giving 2-*mercapto*-5-*phenyl*-1 : 3 : 4-*oxadiazole*, colourless plates or flat needles, m. p. 218—220° (Found : C, 53·9; H, 3·3. $C_8H_6ON_2S$ requires C, 53·9; H, 3·4%). The original mother-liquor was heated to dissolve the crystals, somewhat concentrated, filtered (charcoal), and allowed to cool slowly. The mixture of crystals (3·5 g.) was separated (partly) by hand-picking into 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole, m. p. and mixed m. p. 216—218°, and 1 : 2-dibenzoylhydrazine, m. p. and mixed m. p. 236—237°. The mixture was shaken with N-sodium hydroxide (20 c.c.), alcohol (2·0 c.c.), and methyl iodide (2·0 c.c.) for 0·5 hour and then extracted with ether; the ethereal extracts were evaporated and the residue distilled, giving 2-methylthio-5-phenyl-1 : 3 : 4-oxadiazole (1·2 g.), b. p. 218—220°/60 mm., m. p. 32—33° not depressed by an authentic specimen (*J.*, 1949, 1918). The alkaline residue after extraction was made acid, and the precipitate crystallised from aqueous alcohol, giving 1 : 2-dibenzoylhydrazine (1·6 g.), fibrous needles, m. p. 236—238° not depressed by an authentic sample (Autenrieth and Spiess, *Ber.*, 1901, **34**, 187).

(*b*) Benzhydrazide (13·6 g.), dry pyridine (25 c.c.), and carbon disulphide (9·0 c.c.) were refluxed gently for 12 hours. Water (200 c.c.) was added, then concentrated hydrochloric acid (good cooling) until strongly acid, and the precipitate was collected, dissolved in 0·5N-sodium hydroxide (300 c.c.), filtered, and reprecipitated with acid. The solid was collected (16·0 g.) and crystallised from 50% aqueous alcohol (400 c.c.), with slow cooling and collection at 30°. Colourless plates separated first, as described in (*a*). Recrystallisation gave 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole (7·5 g.), m. p. 219—220° (Found : C, 53·9; H, 3·3; S, 18·1. $C_8H_6ON_2S$ requires C, 53·9; H, 3·4; S, 18·0%). The original mother-liquor was evaporated to half its bulk, and the solid collected (5·7 g.) and methylated with methyl iodide (3·0 c.c.) in N-sodium hydroxide (30 c.c.) and alcohol (5·0 c.c.) as in (*a*). By ether extraction, 2-methylthio-5-phenyl-1 : 3 : 4-oxadiazole (1·3 g.), b. p. 190—192°/30 mm., m. p. 30—32°, was obtained. The aqueous residue was filtered and treated with acid, and the precipitate was crystallised from alcohol (15 c.c.), giving 1 : 2-dibenzoylhydrazine (0·5 g.), m. p. 234—236°. The mother-liquors slowly deposited very large yellow prisms (1·3 g.), which from a small volume of alcohol gave colourless prisms (1·0 g.) of 4-*benzamido*-5-*methylthio*-3-*phenyl*-4 : 1 : 2-*triazole*, m. p. 193° not depressed by this compound as prepared below (Found : C, 61·6; H, 4·8; N, 17·8; S, 10·4. $C_{16}H_{14}ON_4S$ requires C, 61·9; H, 4·5; N, 18·1; S, 10·3%). This compound (1·5 g.) was refluxed for 12 hours with N-sodium hydroxide (15 c.c.), and the liquid was cooled and made acid, and the precipitate crystallised from alcohol, giving unchanged starting material (1·2 g.),

m. p. 192—193°. A similar experiment in which concentrated hydrochloric acid (5 c.c.) and alcohol (10 c.c.) were used gave a similar result.

2-Mercapto-5-phenyl-1 : 3 : 4-oxadiazole (3·6 g.) in N-sodium hydroxide (20 c.c.) was shaken with methyl iodide (2·0 c.c.) and alcohol (2·0 c.c.) for 0·5 hour, and the oil separated with ether, dried, and distilled, giving a colourless oil, b. p. 180—183°/20 mm., which solidified to a mass of colourless prisms, m. p. 36—37° alone or mixed with 2-methylthio-5-phenyl-1 : 3 : 4-oxadiazole (Found : C, 56·4; H, 3·9. Calc. for $C_9H_8ON_2S$: C, 56·25; H, 4·2%). The mercapto-oxadiazole (1·8 g.) was refluxed in alcohol (50 c.c.) with Raney nickel (*ca.* 10·0 g.) for 1·5 hours, the filtered solution evaporated, and the residue crystallised from benzene–light petroleum (b. p. 60—80°), giving flattened needles (0·5 g.) of benzamide, m. p. and mixed m. p. 130° (Found : C, 69·0; H, 6·0. Calc. for C_7H_7ON : C, 69·4; H, 5·8%).

Reaction of Benzhydrazide with Thiocarbonyl Chloride.—Benzhydrazide (13·6 g.) was dissolved in water (100 c.c.) by heating, the solution cooled quickly to 20° with stirring, and thiocarbonyl chloride (5·8 g.) in ether (20 c.c.) was added during 10 minutes. The temperature rose to 30°. After 2 hours the solid was collected, ground with N-hydrochloric acid, and collected. The acid filtrate was united with the original filtrates, made just alkaline with ammonia, and evaporated under reduced pressure, giving a residue which on extraction with hot benzene gave unchanged benzhydrazide (5·2 g.), m. p. 112—113°. The solid insoluble in acid dissolved almost completely in N-sodium hydroxide (100 c.c.) and after filtration (charcoal) was precipitated with acid; the solid (9·5 g.) crystallised from aqueous alcohol, giving colourless glistening plates, m. p. 218—220°, of 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole.

4-Amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (IV; R = Ph).—Methyl 2-benzoyldithiocarbazinate (9·0 g.) was refluxed with alcohol (30 c.c.) and 75% hydrazine hydrate (9·0 c.c.) for 4 hours. Water (100 c.c.) was added, the alcohol removed under reduced pressure, the residue cooled and made strongly acid with strong hydrochloric acid, and the precipitate collected and washed with water. This *thiol* (6·2 g.) crystallised from 50% aqueous alcohol (200 c.c.) as colourless flat needles (4·5 g.), m. p. 204—205° (Found : C, 50·3; H, 4·3; N, 28·8; S, 16·5. $C_8H_8N_4S$ requires C, 50·0; H, 4·1; N, 29·2; S, 16·7%).

4-Amino-5-methylthio-3-phenyl-4 : 1 : 2-triazole (III; R = Ph, R′ = H).—The thiol (10·0 g.) in N-sodium hydroxide (100 c.c.) was shaken with methyl iodide (8·5 c.c.) and alcohol (10 c.c.) for 0·5 hour, yielding the *methyl* derivative, colourless needles (6·5 g.), m. p. 154—155° (from aqueous alcohol) (Found : C, 52·2; H, 5·0; S, 15·5. $C_9H_{10}N_4S$ requires C, 52·4; H, 4·9; S, 15·5%), soluble in N-hydrochloric acid although an insoluble hydrochloride gradually separated. The triazole (1·0 g.) and *p*-dimethylaminobenzaldehyde (0·8 g.) were refluxed in alcohol (20 c.c.) with potassium hydroxide (0·1 g.) for 3 hours, water was added, and the *p-dimethylaminobenzylidene* compound (1·5 g.) collected and crystallised from methyl alcohol as large yellow needles, m. p. 183—184° (Found : C, 64·0; H, 5·7; S, 9·6. $C_{18}H_{19}N_5S$ requires C, 64·1; H, 5·6; S, 9·5%).

4-Amino-5-methanesulphonyl-3-phenyl-4 : 1 : 2-triazole.—The methylthiotriazole (10·3 g.) was stirred in acetic acid (150 c.c.) at 20° whilst a solution of potassium permanganate (16·0 g.) in water (150 c.c.) was added during 0·5 hour, at $\not>25°$. After 0·5 hour, the whole was cooled and sulphur dioxide passed in at 10—15°, until the colour was discharged. Ammonia was added to alkalinity and the solid collected and crystallised from aqueous alcohol, giving the *sulphone* as colourless needles (5·0 g.), m. p. 198° (Found : C, 45·5; H, 4·3; S, 13·4. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2; S, 13·5%).

Di-(4-amino-3-phenyl-4 : 1 : 2-ditriaz-5-yl) Disulphide.—The mercaptotriazole (9·6 g.) in N-sodium hydroxide (55 c.c.) was titrated with N-potassium ferricyanide (50·1 c.c. required). The precipitated *disulphide* crystallised from a large volume of aqueous alcohol as colourless needles (5·4 g.), m. p. 174—176° (Found : C, 49·9, 50·1; H, 4·1, 3·9; S, 16·4. $C_{16}H_{14}N_8S_2$ requires C, 50·2; H, 3·7; S, 16·8%). A solution of this compound (0·5 g.) in N-sodium hydroxide was treated with acetic acid, and the precipitated thiol crystallised from aqueous alcohol as colourless flat needles, m. p. 200—201°.

4-Amino-5-mercapto-3-p-methoxyphenyl- (IV; R = *p*-MeO·C_6H_4), colourless needles, m. p. 205—206° (from alcohol) (Found : C, 49·0; H, 4·9; S, 14·2. $C_9H_{10}ON_4S$ requires C, 48·6; H, 4·5; S, 14·4%), and *4-amino-3-p-methoxyphenyl-5-methylthio-4 : 1 : 2-triazole* (III; R = *p*-MeO·C_6H_4, R′ = H), colourless, glistening needles, m. p. 201—202° (from alcohol) (Found : C, 51·1; H, 5·4; S, 13·8. $C_{10}H_{12}ON_4S$ requires C, 50·85; H, 5·1; S, 13·6%), were obtained analogously.

4-Amino-5-mercapto-3-methyl-4 : 1 : 2-triazole (IV; R = Me).—(*a*) Methyl 2-acetyldithiocarbazinate (51·0 g.), alcohol (150 c.c.) and hydrazine hydrate (75 c.c. of 75%) were refluxed

for 5 hours, then evaporated, and the residue dissolved in N-sodium hydroxide (500 c.c.). The filtered solution was made acid with acetic acid, and the precipitate collected and washed with hot water (300 c.c.) [residue A; 11·5 g.; m. p. 220—222° (decomp.)]. The united filtrates were concentrated and extracted with ether, and the residual *thiol* left on evaporation of the solvent crystallised from water as colourless plates (6·1 g.), m. p. 205—206° (decomp.) (Found : C, 27·8; H, 4·8; N, 42·6; S, 23·9. $C_4H_6N_4S$ requires C, 27·7; H, 4·6; N, 43·1; S, 24·6%).

(*b*) Repetition of the above experiment with 10% hydrazine hydrate (450 c.c.) (no alcohol) gave 4-amino-5-mercapto-3-methyl-4 : 1 : 2-triazole (25·2 g.), m. p. 204—205°, and only traces of the insoluble residue A. An example of a difference in the proportions of certain triazoles formed by aqueous or alcoholic hydrazine is reported by Arndt and Bielich (*Ber.*, 1923, **56**, 809). 4-*Amino*-3-*methyl*-5-*methylthio*-4 : 1 : 2-*triazole*, colourless plates, m. p. 160° (from alcohol–ethyl acetate), was very soluble in water and was extracted from the methylation liquid by ether (Found : C, 33·4; H, 5·3; N, 38·9; S, 22·0. $C_4H_8N_4S$ requires C, 33·3; H, 5·5; N, 38·9; S, 22·2%). 4-Amino-5-mercapto-3-methyl-4 : 1 : 2-triazole reacted immediately with benzaldehyde in cold N-hydrochloric acid, giving the 4-*benzylideneamino*-compound, colourless needles, m. p. 204—205° (from alcohol) (Found : C, 54·5; H, 4·7; S, 14·3. $C_{10}H_{10}N_4S$ requires C, 55·0; H, 4·6; S, 14·7%).

The residue (A) (above) was insoluble in ordinary organic solvents but soluble in N-sodium hydroxide or N-hydrochloric acid. From water, in which it was very sparingly soluble, were obtained colourless needles, m. p. 232—233° (decomp.), identical with a specimen of 4-amino-3-hydrazino-5-mercapto-4 : 1 : 2-triazole (following paper) (Found : C, 16·7; H, 4·2; N, 57·3; S, 21·6. Calc. for $C_2H_6N_6S$: C, 16·4; H, 4·1; N, 57·5; S, 21·9%). This compound (1·0 g.) in hot N-hydrochloric acid (50 c.c.) was shaken with benzaldehyde (2·0 c.c.) in alcohol (5·0 c.c.); the dibenzylidene compound crystallised from *n*-propyl alcohol as pale yellow plates (0·7 g.), m. p. 246° not depressed by an authentic specimen (*loc. cit.*) (Found : C, 59·6; H, 4·3; N, 26·0; S, 9·8. Calc. for $C_{16}H_{14}N_6S$: C, 59·6; H, 4·4; N, 26·1; S, 9·9%).

5-*Methylthio*-3-*phenyl*-1 : 2 : 4-*triazole* (V; R = SMe).—4-Amino-5-methylthio-3-phenyl-4 : 1 : 2-triazole (2·1 g.) was dissolved in a hot mixture of N-hydrochloric acid (20 c.c.) and water (50 c.c.), then cooled quickly, and the fine suspension stirred whilst 0·5N-sodium nitrite (20 c.c.) was added during 5 minutes. There was some foaming and a thick precipitate was formed. This was dissolved by the cautious addition of 40% potassium hydroxide solution. The liquid was filtered and made just acid with acetic acid, and the sticky precipitate allowed to harden. From aqueous alcohol, colourless clumps of plates (1·7 g.), m. p. 162°, not depressed by an authentic specimen of 5-methylthio-3-phenyl-1 : 2 : 4-triazole, were formed (Found : S, 16·9. Calc. for $C_9H_9N_3S$: S, 16·75%).

3-p-*Methoxyphenyl*-5-*methylthio*-1 : 2 : 4-*triazole*.—In an experiment, similar to the above, 4-amino-3-*p*-methoxyphenyl-5-methylthio-4 : 1 : 2-triazole (2·4 g.) gave 3-*p*-methoxyphenyl-5-methylthio-1 : 2 : 4-triazole, colourless plates (1·9 g.), m. p. and mixed m. p. 125—126°, from benzene (Found : S, 14·2. Calc. for $C_{10}H_{11}ON_3S$: S, 14·5%).

4-*Amino*-3-*phenyl*-4 : 1 : 2-*triazole*.—4-Amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (5·0 g.), alcohol (100 c.c.), and Raney nickel (*ca.* 20 g.) were refluxed with stirring for 1·5 hours, then filtered through filter paper pulp from greenish colloidal material, and the residue was washed with boiling alcohol. The filtrates were evaporated under reduced pressure, and the residue was dissolved in boiling ethyl acetate (100 c.c.) and, after concentration, filtered and allowed to crystallise. Colourless plates (1·7 g.) of the *product*, m. p. 85—87°, separated and, recrystallised from benzene, had m. p. 89—90° (Found : C, 59·8; H, 5·1; N, 34·9. $C_8H_8N_4$ requires C, 60·0; H, 5·0; N, 35·0%). This compound (0·5 g.) and *p*-dimethylaminobenzaldehyde (0·5 g.) were refluxed with alcohol (10 c.c.) and potassium hydroxide (0·1 g.), water was added, and the precipitate crystallised from aqueous alcohol, giving 4-p-*dimethylaminobenzylideneamino*-3-*phenyl*-4 : 1 : 2-*triazole hemihydrate* as yellowish-green needles (0·6 g.), m. p. 154—155° (slow heating; melted instantly in a bath at 135°) (Found : C, 68·2, 68·1; H, 5·8, 6·0. $C_{17}H_{17}N_5,0·5H_2O$ requires C, 68·0; H, 6·0%).

3-*Phenyl*-1 : 2 : 4-*triazole* (V; R = H).—4-Amino-3-phenyl-4 : 1 : 2-triazole (0·8 g.), treated with nitrous acid as described for the corresponding 5-methylthio-compound, gave 3-phenyl-1 : 2 : 4-triazole, colourless needles (0·35 g.), m. p. and mixed m. p. 120° [from light petroleum (b. p. 100—120°)] (Found : C, 65·8; H, 4·8. Calc. for $C_8H_7N_3$: C, 66·2; H, 4·8%).

4-*Benzamido*-5-*methylthio*-3-*phenyl*-4 : 1 : 2-*triazole* (III; R = Ph, R′ = Bz).—4-Amino-5-methylthio-3-phenyl-4 : 1 : 2-triazole (2·1 g.), dry pyridine (10·0 c.c.), and freshly distilled benzoyl chloride (1·5 g.) were refluxed for 0·5 hour and poured on ice and water. After acidification with hydrochloric acid, the sticky precipitate was collected and ground with N-sodium

hydroxide (100 c.c.). The turbid solution was clarified (charcoal) and acidified; the precipitate, when crystallised first from xylene and then from a small volume of alcohol, gave colourless prisms (1·6 g.) (Found: C, 61·9; H, 4·7; S, 10·4%), m. p. 192—193°, not depressed by the benzamido-derivative obtained as above.

6 : 7-*Dihydro*-3 : 5-*diphenyl*-7-*thia*-1 : 2 : 4 : 9-*tetra-azaindene* (VI; R = R′ = Ph).—4-Amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (2·0 g.) and phenacyl bromide (2·0 g.) were refluxed in absolute alcohol (50 c.c.) for 2 hours. The solvent was evaporated under reduced pressure, the residue ground with 2N-hydrochloric acid (100 c.c.) at 40°, and the insoluble material ground with 2N-sodium hydroxide. The final insoluble residue (2·7 g.; m. p. 205—206°) crystallised from 50% aqueous alcohol, giving the *thiatetra-azaindene* as colourless leaflets (2·0 g.), m. p. 214—215° (Found: C, 65·4; H, 4·0; N, 19·4; S, 10·9. $C_{16}H_{12}N_4S$ requires C, 65·7; H, 4·1; N, 19·2; S, 11·0%).

6 : 7-*Dihydro*-3-*methyl*-5-*phenyl*-7-*thia*-1 : 2 : 4 : 9-*tetra-azaindene* (VI; R = Ph, R′ = Me).—This *compound*, obtained similarly, crystallised from alcohol in colourless needles, m. p. 186—187° (Found: C, 57·4; H, 4·6; S, 13·8. $C_{11}H_{10}N_4S$ requires C, 57·4; H, 4·4; S, 13·9%).

6 : 7-*Dihydro*-3-*phenyl*-7-*thia*-1 : 2 : 4 : 9-*tetra-azaindene* (VI; R = H, R′ = Me).—4-Amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (2·0 g.) was unaffected by bromoacetal (3·0 g.) in boiling alcohol (50 c.c.) during 6 hours. When the same quantities of amino-thiol and bromoacetal were ground together and heated on the water-bath, a vigorous reaction took place and, after extraction of the solid residue with acid and alkali, crystallisation from aqueous alcohol gave the *indene* derivative as colourless prisms (1·5 g.), m. p. 144° (Found: C, 55·7; H, 3·8; S, 14·3. $C_{10}H_8N_4S$ requires C, 55·6; H, 3·7; S, 14·8%).

Ethyl (4-*Amino*-3-*phenyl*-4 : 1 : 2-*triazol*-5-*ylthio*)*acetate*.—4-Amino-5-mercapto-3-phenyl-4 : 1 : 2-triazole (2·0 g.) and ethyl chloroacetate (3·0 g.) were heated under reflux in alcohol (50 c.c.) for 6 hours. The solvent was evaporated off under reduced pressure, the residue ground with water (50 c.c.) and N-sodium hydroxide (20 c.c.), and the insoluble *ester* (2·3 g.) crystallised from alcohol, giving colourless needles (1·5 g.), m. p. 172—173° (Found: C, 51·6; H, 5·0; S, 11·7. $C_{12}H_{14}O_2N_4S$ requires C, 51·8; H, 5·0; S, 11·5%). This (0·25 g.) was refluxed with N-sodium hydroxide (20 c.c.) for 1 hour. Cooling and acidification with hydrochloric acid gave the *acid* (0·2 g.), which crystallised from alcohol as colourless plates, m. p. 183—184° (decomp.), soluble in dilute hydrochloric acid or potassium hydrogen carbonate solution (Found: C, 48·0; H, 4·1; S, 13·1. $C_{10}H_{10}O_2N_4S$ requires C, 48·0; H, 4·0; S, 12·8%). The same compound, m. p. 185° (decomp.), was obtained from the amino-thiol and chloroacetic acid.

Cyclisations of 2-Benzoyldithiocarbazinic acid.—(*a*) The potassium salt (5·0 g.) in water (50 c.c.) was cautiously acidified with concentrated hydrochloric acid. A thick precipitate formed, which slowly effervesced with evolution of carbon disulphide and dissolution. After some hours, a small residue was collected and crystallised from aqueous alcohol, giving 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole, colourless needles, m. p. 216—217° (0·05 g.). The original filtrate was made just alkaline with ammonia and evaporated under reduced pressure, the residue extracted with chloroform, the solvent evaporated, and the residue crystallised from water, giving benzhydrazide (1·5 g.), m. p. 113°.

(*b*) The potassium salt (10·0 g.) was added during 0·5 hour to a mixture of syrupy phosphoric acid (25 c.c.) and phosphoric oxide (*ca.* 10 g.) with stirring at 120°, and stirring and heating were continued for 0·5 hour. Benzoic acid sublimed. Ice and water were added, and the solid was methylated as above. Ether-extraction afforded 2-methylthio-5-phenyl-1 : 3 : 4-oxadiazole, b. p. 183—184°/28 mm., prisms (0·5 g.), m. p. 36—37°. The aqueous residue from the ether-extraction gave, on acidification, benzoic acid (0·9 g.), m. p. 121°. The original acid filtrates were made just alkaline with ammonia, evaporated under reduced pressure, and extracted with chloroform, and the residue left on evaporation of the solvent crystallised from water (*ca.* 100 c.c.) giving colourless felted needles (0·3 g.) of 1 : 2-dibenzoylhydrazine, m. p. 234—236°. The mother-liquor was concentrated to about one quarter of its bulk, filtered hot (charcoal), and allowed to crystallise, giving benzhydrazide, colourless plates (2·0 g.), m. p. 112°.

(*c*) The potassium salt (5·0 g.) was heated to the b. p. in dry pyridine (30 c.c.). A thick precipitate suddenly formed. Water (50 c.c.) was added, and the solution filtered (charcoal) and made acid with hydrochloric acid. The precipitate was washed with water (2·9 g.), and crystallised from aqueous alcohol, giving 2-mercapto-5-phenyl-1 : 3 : 4-oxadiazole (2·3 g.), m. p. and mixed m. p. 218—220°.

(*d*) When methyl 2-benzoyldithiocarbazinate (4·5 g.) was used in place of the potassium salt in (*c*), reaction was much slower, but after 20 hours' refluxing the same mercapto-oxadiazole (2·9 g.), m. p. 218—220°, was obtained.

2-*Mercapto*-5-p-*methoxyphenyl*- (II; R = *p*-MeO·C_6H_4, R' = H), needles, m. p. 204—206° (from alcohol) (Found: C, 51·9; H, 3·9; S, 15·2. $C_9H_8O_2N_2S$ requires C, 51·9; H, 3·8; S, 15·4%) [methylthio-derivative, needles, m. p. 101° (from light petroleum), identical with the compound as prepared previously (*J.*, 1949, 1918)], and 2-*mercapto*-5-p-*chlorophenyl*-1 : 3 : 4-*oxadiazole* (II; R = *p*-C_6H_4Cl, R' = H), felted needles, m. p. 175—176° (from aqueous alcohol) (Found: C, 45·6; H, 2·5; S, 15·2. $C_8H_5ON_2ClS$ requires C, 45·2; H, 2·4; S, 15·1%), were obtained analogously (method *c*).

2-*Mercapto*-5-*methyl*-1 : 3 : 4-*oxadiazole* (II; R = Me, R' = H).—Cyclisation of potassium 2-acetyldithiocarbazinate was much slower than that of the foregoing benzoyl derivatives. The salt (19·0 g.) and dry pyridine (50 c.c.) were refluxed for 18 hours, water (150 c.c.) was added, and the solution made acid with hydrochloric acid. A small brown precipitate was removed and after crystallisation from xylene proved to be sulphur, large yellow prisms (0·25 g.), m. p. 118—119°. The filtrate was extracted with ether in an automatic apparatus and the residue left on evaporation of the solvent crystallised from benzene–light petroleum (b. p. 60—80°) in colourless plates, m. p. 78° (Found: C, 31·3; H, 3·5; S, 27·7. $C_3H_4ON_2S$ requires C, 31·0; H, 3·4; S, 27·6%). This *thiol* (1·2 g.), when methylated as above, gave 5-*methyl*-2-*methylthio*-1 : 3 : 4-*oxadiazole* (II; R = R' = Me), plates [from light petroleum (b. p. 80—100°)] (0·9 g.), m. p. 72—73° (depressed below room temperature by the parent thiol) (Found: C, 37·1; H, 4·8; S, 24·4. $C_4H_6ON_2S$ requires C, 36·9; H, 4·6; S, 24·6%).

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