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The Action of Hydrazine Hydrate on Isodithiobiurets

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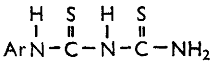
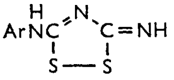
Hydrazine hydrate reacts with warm ethanolic solutions of 1-aryl-4-methyl-4-isodithiobiurets to yield 3-amino-5-anilino-1,2,4-triazoles, but 2-ethyl-1-phenyl-2-isodithiobiuret afforded 3-anilino-5-mercapto-1,2,4-triazole.

THE action of hydrazine hydrate in dilute alcoholic[1] solution on 1-phenyldithiobiuret (I; Ar = Ph), and in aqueous solution on 1-aryldithiobiurets (I)[2,3] and thiurets (II)[2,3] has been shown to yield the triazoles (III) and (IV). Presumably (III) is formed by elimination of ammonia from the unstable intermediate (V), and (IV) by elimination of hydrogen sulphide from (VI). It is known that 2,4-di-isodithiobiurets react readily to form triazoles by elimination of two molecules of thiol.[4,5] It was decided to study the action of hydrazine hydrate on some 1-aryl-4-methyl-4-isodithiobiurets (VII). It was expected[6] that methanethiol would be liberated with formation of (VI), followed by ring closure to yield a 3-amino-5-anilino-1,2,4-triazole (IV); this was so, but some 3-amino-5-mercapto-1,2,4-triazole (VIII)[7] was also formed. When, however, 2-ethyl-1-phenyl-2-isodithiobiuret was treated with hydrazine hydrate 3-anilino-5-mercapto-1,2,4-triazole (III; Ar = Ph) was obtained. In view of the use of 3-amino-1,2,4-triazole as a plant-growth regulator[8] the aminoanilinotriazoles (IV) are being studied in this Department by Mr. John Roberts.


(I)

$\mathrm{Ar\overset{H}{N}-\overset{S}{\overset{\|}{C}}-\overset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2}$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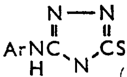
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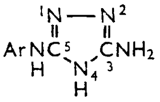
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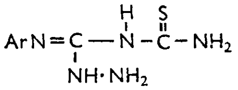
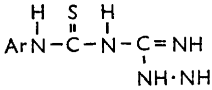
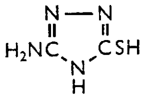
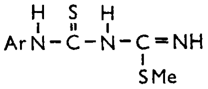

(V)

$\mathrm{ArN=\underset{NH\cdot NH_2}{\underset{|}{C}}-\overset{H}{N}-\overset{S}{\overset{\|}{C}}-NH_2}$


(VI)

$\mathrm{Ar\overset{H}{N}-\overset{S}{\overset{\|}{C}}-\overset{H}{N}-\underset{NH\cdot NH_2}{\underset{|}{C}}=NH}$


(VIII)


(VII)

$\mathrm{Ar\overset{H}{N}-\overset{S}{\overset{\|}{C}}-\overset{H}{N}-\underset{SMe}{\underset{|}{C}}=NH}$

The 1-aryl-4-methyl-4-isodithiobiurets were prepared from aryl isothiocyanates and *S*-methylisothiourea in aqueous ethanol as described by Underwood and Dains.[4] Unfortunately the yields of isodithiobiurets are disappointing, especially when electron-withdrawing groups are substituted in the ring, whereupon thiourethanes[9] are formed in considerable amounts.

EXPERIMENTAL

Isothiocyanates were prepared from the corresponding anilines as follows: trichloromethanesulphenyl chloride (31 ml.) was added slowly to a well-stirred mixture of the aniline (0·25 mole), chloroform (100 ml.), 2N-hydrochloric acid (250 ml.), and stannous chloride (84 g.), the mixture stirred for 4 hr. (more hydrochloric acid and chloroform was added if needed to keep the mixture mobile), filtered, the chloroform layer separated, dried (Na_2SO_4), the chloroform distilled off, and the isothiocyanate purified by vacuum distillation. *p*-Nitrophenyl isothiocyanate was recrystallised from acetic acid.

1-*Aryl*-4-*methyl*-4-*isodithiobiurets from Aryl Isothiocyanates and* S-*Methyl-isothiourea*.—*S*-Methylisothiourea sulphate (14 g.) was dissolved in water (100 ml.); ethanol (100 ml.)

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[3] E. Fromm, *et. al.*, *Annalen*, 1924, **437**, 106.

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[5] F. H. S. Curd, D. G. Davey, D. N. Richardson, and R. B. Ashworth, *J. Chem. Soc.*, 1949, 1739.

[6] E. S. Scott and L. F. Audrieth, *J. Org. Chem.*, 1954, **19**, 1231.

[7] L. E. A. Godfrey and F. Kurzer, *J. Chem. Soc.*, 1960, 3437.

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was added, followed by 10% sodium carbonate solution (53 ml.). The mixture was warmed almost to boiling, the arylisothiocyanate (0·1 mole) added, the mixture shaken for a few minutes, and allowed to cool. Next day the product was filtered off (filtrate A) washed with aqueous ethanol, then water, and recrystallised from ethanol. The following 4-methyl-4-isodithiobiurets were obtained (yields of recrystallised product in parentheses): 1-phenyl-(65%), prisms, m. p. 124°; 1-o-*tolyl*-, (23%), prisms, m. p. 113—114° (Found: N, 17·75. $C_{10}H_{13}N_3S_2$ requires N, 17·6%); 1-p-*tolyl*- (21%), prisms, m. p. 116—117° (Found: N, 17·8%); 1-*p*-chlorophenyl-[10] (40%), m. p. 135—136°; 1-(2,5-*dichlorophenyl*)- (36%), felted needles, m. p. 126—127° (Found: N, 14·75. $C_9H_9Cl_2N_3S_2$ requires N, 14·3%); 1-(2,4-*dichlorophenyl*)- (34%), prisms, m. p. 102° (Found: N, 14·8%); 1-(2,4-*dibromophenyl*)-, prisms, m. p. 113—115° (Found: N, 11·0. $C_9H_9Br_2N_3S_2$ requires N, 11·0%); 1-p-*cyanophenyl*- (43%), felted needles, m. p. 152—153° (Found: N, 22·3. $C_{10}H_{10}N_4S_2$ requires N, 22·4%); 1-p-*methoxyphenyl*- (39%), plates, m. p. 129—130° (Found: N, 16·6. $C_{10}H_{13}N_3OS_2$ requires N, 16·5%), 1-p-*nitrophenyl*- (8%), felted needles, m. p. 177—178° (Found: N, 20·75. $C_9H_{10}N_4O_2S_2$ requires N, 20·75%); 1-m-*trifluoromethylphenyl*- (47%), bunched needles, m. p. 133—134° (Found: N, 14·1. $C_{10}H_{10}F_3N_3S_2$ requires N, 14·3%).

The filtrate (filtrate A) from the preparation of 1-(2,5-dichlorophenyl)-4-methyl-4-isodithiobiuret, was diluted with several volumes of water, and the precipitate obtained (14·8 g.) dissolved in a mixture of ethanol (100 ml.) and water (20 ml.). Sodium sulphide (10 g.) was added, and the mixture refluxed in a stream of hydrogen sulphide for 1½ hr., poured into water (500 ml.), and filtered (filtrate B). The residue (9 g.) on recrystallisation from ethanol afforded *N*-(2,5-dichlorophenyl)-thiourethane (5·8 g., 23%), plates, m. p. 79—80° (Found: C, 42·6; H, 3·4; N, 5·75; S, 13·0. Calc. for $C_9H_9Cl_2NOS$: C, 43·2; H, 3·6; N, 5·6; S, 12·8%) (Brown and Dyson [9] give m. p. 80°). Acidification of filtrate B with acetic acid yielded 1-(2,5-*dichlorophenyl)dithiobiuret* (0·6 g.), m. p. 174—175° (Found: C, 34·5; H, 2·5; N, 15·2. $C_8H_7Cl_2N_3S_2$ requires C, 34·3; H, 2·5; N, 15·0%).

Similarly filtrate A, from the preparation of 1-*m*-trifluoromethylphenyl-4-methyl-4-isodithiobiuret, yielded N-m-*trifluoromethylphenylthiourethane* (10%), needles, m. p. 98—99° (Found: C, 48·1; H, 4·3. $C_{10}H_{10}F_3NOS$ requires C, 48·2; H, 4·0%) (the same compound was obtained by refluxing *m*-trifluoromethylphenyl isothiocyanate with absolute ethanol), and 1-m-*trifluoromethylphenyldithiobiuret*, m. p. 138—139° (Found: C, 38·3; H, 2·85; N, 14·95. $C_9H_8F_3N_3S_2$ requires C, 38·7; H, 2·85; N, 15·05%).

Thiohydrolysis of 1-*p*-cyanophenyl-4-methyl-4-isodithiobiuret afforded 1-p-*cyanophenyldithiobiuret*, m. p. 180—181° (Found: C, 45·2; H, 3·15; N, 23·7. $C_9H_8N_4S_2$ requires C, 45·75; H, 3·4; N, 23·75%).

3-*Amino*-5-*anilino*-1,2,4-*triazoles from* 1-*Aryl*-4-*methyl*-4-*isodithiobiurets and Hydrazine Hydrate*.—3-*Amino*-5-*anilino*-1,2,4-*triazole*. Hydrazine hydrate (8·5 ml. 60%, 0·1 mole) was added to 1-phenyl-4-methyl-4-isodithiobiuret (11·25 g., 0·5 mole) in ethanol (60 ml.) and the mixture refluxed for 30 min. Water (120 ml.) was added, the mixture cooled, and 3-amino-5-anilino-1,2,4-triazole (4·72 g., 54%), plates, m. p. 163—165°, filtered off. On acidification with acetic acid the filtrate deposited 3-amino-5-mercapto-1,2,4-triazole (1·14 g., 20%), m. p. 301—302°.

The following 3-amino-1,2,4-triazoles were obtained similarly: 5-*o*-toluidino- (65%, after ethanol boiled off from the reaction mixture), m. p. 166°; 5-*p*-toluidino- (56%), needles from water, m. p. 183°; 5-p-*chloroanilino*- (71%), needles from ethanol, m. p. 246—248° (Found: C, 46·15; H, 4·0; Cl, 16·6; N, 33·5. $C_8H_8ClN_5$ requires C, 45·8; H, 3·8; Cl, 16·95; N, 33·4%); 5-(2,4-*dichloroanilino*)- (90%), needles from ethanol, m. p. 196—198° (Found: C, 39·2; H, 2·9. $C_8H_7Cl_2N_5$ requires C, 39·3; H, 2·9%); 5-(2,4-*dibromoanilino*)- (89%), bunched needles from ethanol, m. p. 211—212° (Found: C, 29·2; H, 2·3; N, 20·6. $C_8H_7Br_2N_5$ requires C, 28·8; H, 2·1; N, 21·0%); 5-m-*trifluoromethylanilino*- (78%), fine needles from aqueous ethanol, m. p. 238—240° (Found: C, 45·15; H, 3·4; N, 28·6. $C_9H_8F_3N_5$ requires C, 44·5; H, 3·3; N, 28·8%); 5-*p*-*anisidino*- (42%), needles from ethanol, m. p. 205—206° (Found: C, 53·25; H, 5·6. $C_9H_{11}N_5O$ requires C, 52·6; H, 5·4; N, 34·2%).

On refluxing 1-(2,5-dichlorophenyl)-4-methyl-4-isodithiobiuret (5·88 g., 0·02 mole) in ethanol (30 ml.) with 60% hydrazine hydrate (3·4 ml.), solid separated after 10 min. On cooling 3-*amino*-5-(2,5-*dichloroanilino*)-1,2,4-*triazole* (3·75 g., 82%), felted needles, m. p. 264—265°, was obtained (Found: C, 39·55; H, 2·4; N, 28·9. $C_8H_7Cl_2N_5$ requires C, 39·3; H, 2·9; N, 28·7%). Similarly 1-*p*-cyanophenyl-4-methyl-4-isodithiobiuret afforded 3-*amino*-5-p-*cyanoanilino*-1,2,4-*triazole* (91%), needles, m. p. 316—318° (Found: C, 53·65; H, 4·0; N, 41·5. $C_9H_8N_6$ requires C, 54·0; H, 4·0; N, 42·0%).

3-*Amino*-5-p-*anisidino*-1,2,4-*triazole*.—A mixture of *N*-cyano-*N'*-*p*-methoxyphenyl-*S*-methylisothiourea (0·4 g.),[11] ethanol (5 ml.), water (10 ml.), and 60% hydrazine hydrate (0·8 ml.) was refluxed for 2 hr. On cooling 3-amino-5-*p*-anisidino-1,2,4-triazole (0·355 g., 96%), needles, m. p. 205—206° was obtained (Found: C, 52·15; H, 5·6, N, 34·2%).

3-*Anilino*-5-*mercapto*-1,2,4-*triazole from* 2-*Ethyl*-1-*phenyl*-2-*isodithiobiuret*.—A solution of 2-ethyl-1-phenyl-2-isodithiobiuret [12] (2·4 g., 0·01 mole) in ethanol (18 ml.) was refluxed with 60% hydrazine hydrate (2·4 ml.) for 30 min., and cooled. Water was added, the solution acidified with hydrochloric acid, and the product filtered off and washed with water, (1·3 g., 68%), m. p. 281—282° (Found: C, 50·35; H, 4·25. Calc. for $C_8H_8N_4S$: C, 50·0; H, 4·15%).

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