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CHEMISTRY OF BIUREAS—I

CYCLISATION OF ETHOXYCARBONYL DERIVATIVES OF THIOBIUREAS AND BITHIOUREAS

FREDERICK KURZER* and JANE L. SECKER
Royal Free Hospital School of Medicine (University of London), 8 Hunter Street, London WC1N 1BP, England

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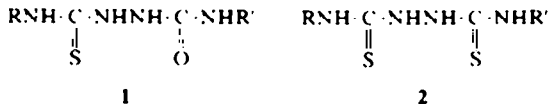
Abstract—The interaction of ethoxycarbonyl isothiocyanate with semicarbazides or thiosemicarbazides produces 1-ethoxycarbonyl-2-thiobiureas or bithioureas, respectively. The former are cyclisable to 2-ethoxycarbonamido-5-hydroxy-1,3,4-thiadiazole in acid, or to 2(H)-carbamoyl-3-hydroxy-5-alkylthio-1,2,4-triazoles, and thence to 3-hydroxy-5-mercapto-1,2,4-triazole in alkaline media. The ring-closure of the 1-ethoxycarbonylbithioureas proceeds similarly affording, under the influence of acids, 5-amino (or mercapto)-2-ethoxycarbonamido-1,3,4-thiadiazoles. The action of alkali produces compounds derived from 3-hydroxy-5-mercapto-1,2,4-triazole; the isolation, in a selected example, of the 2(H)-phenylthiocarbamoyl-derivative, elucidates the course of this reaction. Hydrazinolysis of 1-ethoxycarbonylbithiourea yields 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole.

Amongst the numerous syntheses of 1,3,4-thiadiazoles and 1,2,4-triazoles from linear precursors incorporating the thiosemicarbazide structure,[1-3] those based on the cyclisation of thiobiureas[4-6] **1** and bithioureas[7-9] **2** occupy a prominent position. We report, in this and the following paper, variants of these reactions involving novel ethoxycarbonyl derivatives of thiobiureas and bithioureas (**1**, **2**; R = COOEt, R' = H, Ph, NH_2, NHPh). The ethoxycarbonyl-group provides an additional reactive centre which may participate in the cyclisation process, the possible course of which is correspondingly diversified.



1 **2**

The immediate object of this work was the examination, in representative examples, of the influence of the ethoxycarbonyl-group on the direction of the cyclisation, and the correlation of the observations with comparable reactions. In a wider context, the work extends our study of linear adducts of hetero-cumulenes and urea-derivatives as precursors of heterocyclic compounds.[10]

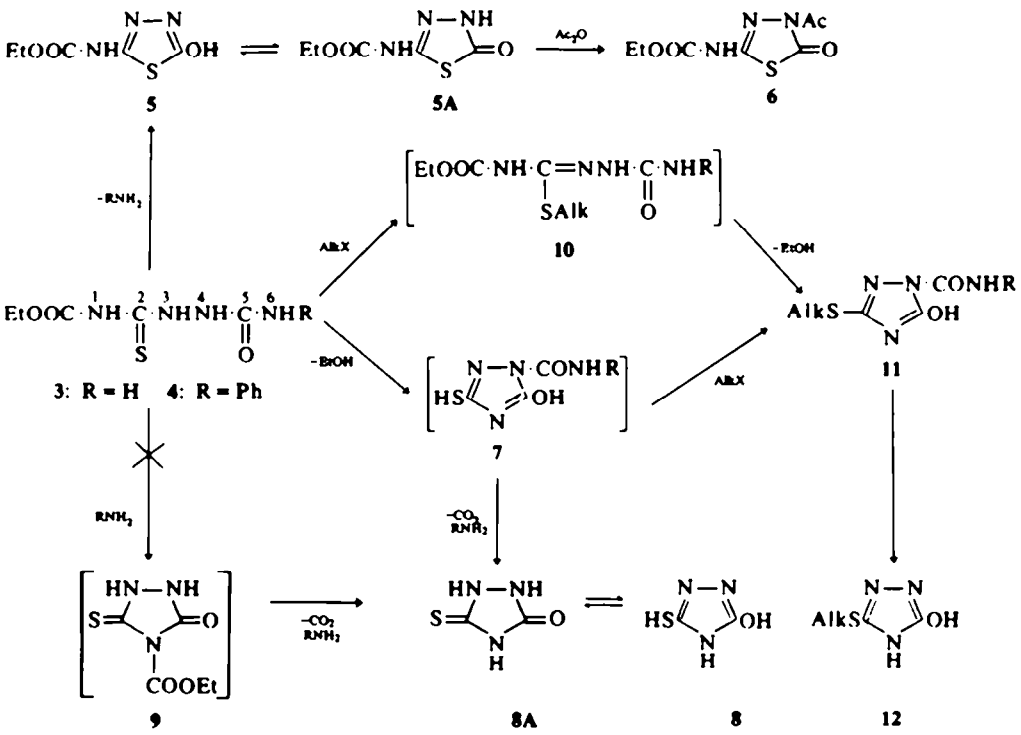
Thiobiurea derivatives. The interaction of equimolar quantities of ethoxycarbonyl isothiocyanate[11] and semicarbazides in dimethylformamide at room temperature afforded 1 - ethoxycarbonyl - 2 - thiobiureas **3**, **4** in good yield. The formulation of the adducts, based on the known[12] superior reactivity of hydrazido- over amido-groups towards heterocumulenes, agrees with their physical and chemical properties, especially their cyclisation. Their IR spectra include peaks characteristic of their individual structural features; these are discussed in conjunction with those of the corresponding bithioureas **13**, **14** (see below).

1-Ethoxycarbonyl-2-thiobiureas **3**, **4** and their bithiourea analogues **13**, **14** incorporate the NH·CS·NHNH·C(:NH) X-system in their structure, and are therefore expected[4,13,14] to cyclise to substituted 1,3,4-thiadiazoles in acidic, and to 1,2,4-triazoles in alkaline media. Their observed ring-closures do indeed conform to this general pattern, but present special features inherent in their particular structures.

1-Ethoxycarbonyl-6-phenyl-2-thiobiurea **4** was smoothly converted (90%) into 2 - ethoxycarbonamido - 5 - hydroxy - 1,3,4 - thiadiazole **5** by cold concentrated sulphuric acid, but resisted the action of hydrochloric acid even on boiling. The parent adduct **3** was recovered after treatment with *either* acid. The predominating thiadiazolinone-structure **5A** of the cyclisation product[15] is shown by its IR spectrum, which lacks hydroxyl-absorption, but includes an intense peak attributable to a ring-carbonyl group (1650 cm^{-1}). Its monoacetyl derivative, prepared for further characterisation, is formulated as an *N*-acyl-thiadiazolinone (probably **6**), in conformity with the retention of the ring-carbonyl peak in its spectrum (now at 1695 cm^{-1}). The carbethoxy-group (of **5**, **6**) gave rise to the usual high-intensity carbonyl-absorption at 1720–1740 cm^{-1}.

The action of alkali on 1-ethoxycarbonyl-2-thiobiureas **3**, **4** gave fair yields of 3 - hydroxy - 5 - mercapto - 1,2,4 - triazole **8**. The reaction may proceed by one of two routes, involving different initial cyclisation processes. Elimination of the elements of ethanol (originating from the 1-ethoxy-moiety and 4-imino-hydrogen of **3** or **4**) produces the intermediate 2(H)-carbamoyl-1,2,4-triazole **7**, which is converted into the observed product **8** on alkaline hydrolysis. Alternatively, initial loss of ammonia or amine (now involving the 1-imino-hydrogen of **3** or **4**), followed by hydrolysis, results in the same final product **8**, by way of the 4 - ethoxycarbonyl - 1,2,4 - triazolidine **9**. Evidence that the former mechanism is operative was obtained in the course of the attempted *S*-alkylation of the linear starting materials **3**, **4**.

These were unaffected by alkyl halides in neutral media (e.g. ethanol, acetone), a method effective for *S*-alkylating thioamides[16] and a wide range of thioureido-compounds.[17] *S*-Alkylation did occur in the presence of an equivalent of sodium ethoxide,[18,19] but was attended by ring-closure with loss of ethanol affording (by either sequence **3**→**7**→**11** or **3**→**10**→**11**) good yields of 2(H) - carbamoyl - 3 - hydroxy - 5 - alkylthio - 1,2,4 - triazoles (**11**; R = H, Ph; Alk = Me, CH_2Ph). Their structure was



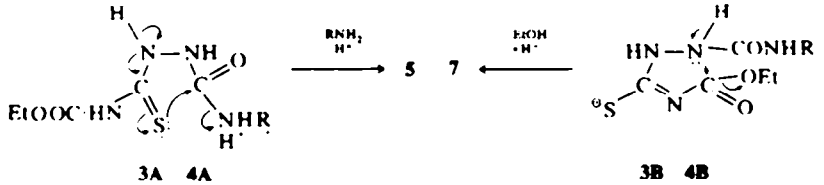
established by their spectral properties, and by the hydrolytic conversion by alkali of selected examples (**11**; R = H, Ph; Alk = CH_2Ph) into the known[20] 3 - benzylthio - 5 - hydroxy - 1,2,4 - triazole (**12**; Alk = CH_2Ph). The existence as stable isolable entities of the 2(H) - carbamoyl - 1,2,4 - triazoles **11** (which are a further[21] structural variant of the interesting 1(H)-acyl-1,2,4-triazoles[22]), provides experimental support for the postulated function of **7** as intermediates in the formation of **8**.

Theoretically, 1-ethoxycarbonyl-2-thiobiureas **3**, **4** are cyclisable to 5- or 7-membered hetero-rings, with elimination of hydrogen sulphide, water, ethanol, or amine, in at least 12 ways (not detailed here). The experiments show that two of these are favoured **3**, **4**→**5** or **8**/**11**. Mechanistically, the reactions may be interpreted in terms of familiar nucleophilic processes:[10,19] the observations imply that the centre of low electron density in **3**, **4**, at which intramolecular nucleophilic attack occurs, is the amide-carbon (C-5) in acid media **3A**, **4A**, and the carbethoxy-carbon in alkaline media **3B**, **4B**. The observed stability of **3** and **4** towards hydrochloric acid under conditions normally leading to 1,3,4-thiadiazole formation[10-14] is unexpected, especially since the very closely related 1 - imidoyl - 4 - ethoxycarbonyl - 3 - thiosemicarbazides (EtOOC·NH·CS·NHNH·C(:NH)R, derived from amidrazones) are cyclised to 1,3,4-thiadiazoles without difficulty.[9]

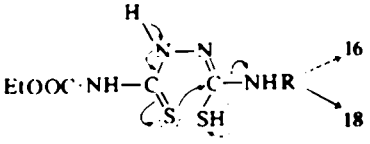
Bithiourea derivatives. Our study of ethoxycarbonylthiobiureas was supplemented by parallel work dealing with their bithiourea analogues. 1-Ethoxycarbonylbithiourea **13** and its 6-aryl-derivatives (**14**; Ar = Ph, *p*-Tol, *p*-BrC_6H_4) were readily accessible (75–85%) from ethoxycarbonyl isothiocyanate and the appropriate thiosemicarbazides. They precipitated lead sulphide from alkaline sodium plumbite, a reaction not given by their monothiobiurea analogues **3**, **4**; the eliminated sulphur is therefore likely to originate from their 5-thiocarbonyl-group.

The structural features of both the ethoxycarbonylthiobiureas **3**, **4** and bithioureas **13**, **14**, as well as those of their (thio)carbonohydrazide analogues (see Part II, subjoined), are clearly reflected in their IR spectra. The various modes of NH-vibration produce the usual bands between 3320 and 3150 cm^{-1}. The carbethoxy-group gives rise to strong ester-carbonyl peaks at 1715–20 cm^{-1}; prominent broad absorptions at 1220–40 cm^{-1} and at 1040–55 cm^{-1} are attributable to asymmetric and symmetrical ester C–O–C-vibration, but may possibly be also associated with contributions from the CS-group, and with N-C-S stretching vibration, respectively.[23] The considerable complexity of the 1200 cm^{-1}-bond favours such an interpretation. Strong peaks near 1550 cm^{-1} assignable to C–N–H vibration[24] are regarded as combination bands due to N–H-deformation and C–N-stretching vibration.[25] The thiobiureas **3**, **4** give rise to an intense amide carbonyl absorption at 1660–1675 cm^{-1}, which is absent in the bithioureas. The IR spectrum of authentic 1-ethoxycarbonylthiosemicarbazide,[26] determined for comparison, included all the relevant characteristic peaks (see Experimental).

The cyclisation of ethoxycarbonylbithioureas **13**, **14** gave substituted 1,3,4-thiadiazoles in acid, and 1,2,4-



triazoles in alkaline media. Of the eleven possible modes of ring closure, three were observed under the conditions employed. The action of ethanolic hydrochloric acid converted the linear parent-compound **13** into 2 - ethoxycarbonamido - 5 - mercapto - 1,3,4 - thiadiazole **18**, but acetic anhydride gave the corresponding 5-amino-compound (as its acetyl-derivative, **15**) involving loss of ammonia or hydrogen sulphide, respectively. Hydrochloric acid promoted the latter type of cyclisation of the 6-aryl-substituted bithioureas **14**, affording good yields of 2 - arylamino - 5 - ethoxycarbonamido - 1,3,4 - thiadiazoles **16**. The observations may be correlated by the usual intramolecular nucleophilic attack, by the 2-thiono-sulphur on the C-5-centre, and simultaneous detachment therefrom of the RNH- or HS-moiety: the relation between the acidic strength of the reagent, and the basic strength of the RNH-region (of **14**) appears to determine, which of the two residues is removed preferentially. An alternative nucleophilic cyclisation mechanism (attack by S-5 on C-2) is in accord with the cyclisation **14** → **16**, but not with **14** → **18**, and is therefore discounted.

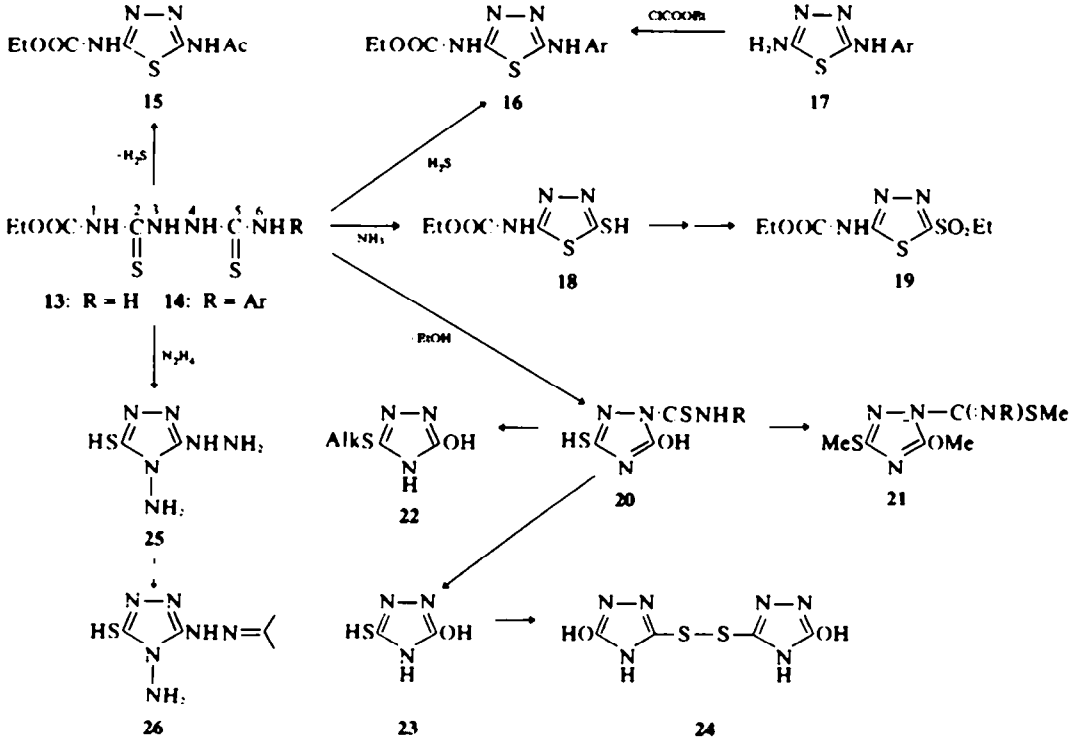


13, **14**

2 - Ethoxycarbonamido - 5 - mercapto - 1,3,4 - thiadiazole **18**[14] was characterised as the sulphone **19** by successive *S*-alkylation and oxidation. The structure of the 5 - amino - 2 - ethoxycarbonamido - 1,3,4 - thiadiazoles was confirmed by the synthesis of one example (**16**; Ar = Ph) from the preformed ring-system, by the action of ethyl chloroformate on authentic[26] 2 - amino - 5 - anilino - 1,3,4 - thiadiazole (**17**; Ar = Ph). In their behaviour on melting, the 2-amino-heterocyclics **16** were almost indistinguishable from their linear precursors **14**, corresponding pairs of compounds melting with decomposition in the same high temperature range: the bithioureas are evidently cyclised pyrolytically and then show the m.ps of **16**.

For the examination of the alkaline cyclisation of the bithiourea derivatives, the 6-phenyl-compound (**14**; R = Ph) proved particularly suitable, allowing the steps of the reaction to be established. As in the thiobiurea series **3**, **4**, the reaction proceeded with loss of ethanol, but was of additional interest in that the primary intermediate was isolable. Thus, brief treatment of 1 - ethoxycarbonyl - 6 - phenylbithiourea (**14**, R = Ph) with boiling 2N sodium hydroxide gave 3 - hydroxy - 5 - mercapto - 2(H) - phenylthiocarbamoyl - 1,2,4 - triazole (**20**; R = Ph) as main product (56–68%), together with smaller quantities (30–40%) of di(3 - hydroxy - 1,2,4 - triazol - 5 - yl) disulphide **24**. On more prolonged boiling, the proportion of the latter increased at the expense of the former. The hydrolytic removal from **20** (R = Ph) of the phenylthiocarbamoyl-group was apparent from the isolation of *N*,*N*'-diphenylthiourea, arising from phenyl isothiocyanate, when sodium carbonate was the cyclising agent. The disulphide **24** was the only product of the action of alkali on the parent bithiourea **13**. It arises undoubtedly by air oxidation of the primarily formed 3 - hydroxy - 5 - mercapto - 1,2,4 - triazole **23**, the alkaline hydrolysis product common to both the thiobiurea and bithiourea series.

The disulphide **24** was identical with authentic material.[13,20] The formulation of the 2(H)-phenylthiocarbamoyltriazole **20** was confirmed by the results of its more vigorous or prolonged alkaline hydrolysis, which gave 3 - hydroxy - 5 - mercapto - 1,2,4 - triazole **23**, or its 5-alkylthio-derivatives (**22**; Alk = $PhCH_2$, *p*-$O_2NC_6H_4CH_2$) in the presence of the appropriate benzyl halide. Its interaction with an excess of methyl iodide



and sodium methoxide (3 eqlts.) gave a trimethylated product formulated as **21**.

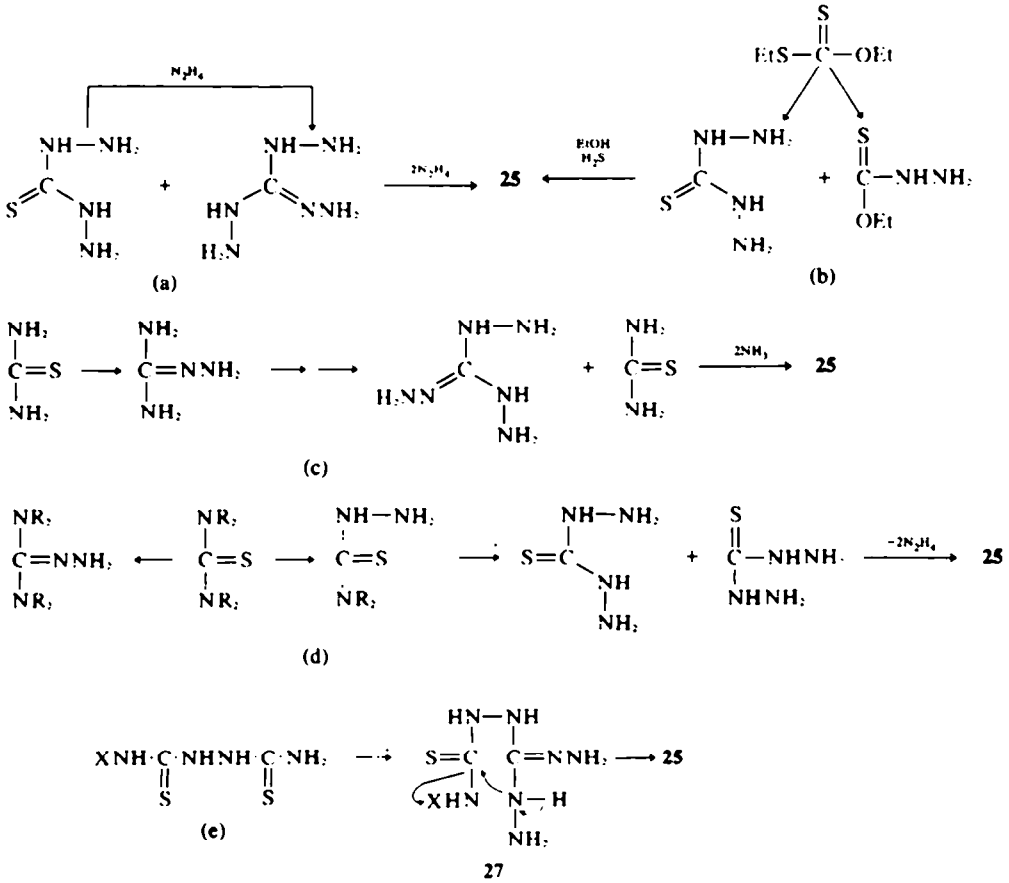
The action of boiling hydrazine on 1-ethoxycarbonylbithiourea **13** gave 4 - amino - 3 - hydrazino - 5 - mercapto - 1,2,4 - triazole **25** in fair yield. The product was identical with authentic material[27] and was convertible into a hexa-acetyl and a mono-isopropylidene derivative, formulated as **26**.

4 - Amino - 3 - hydrazino - 5 - mercapto - 1,2,4 - triazole **25** arises as a by-product in the hydrazinolysis of a variety of thioureido-[28-30] and dithiocarbonic acid-[31-34] derivatives, as well as 1,3,4-thiadiazoles[27,35] and other heterocyclic compounds;[36,37] under appropriate conditions, it may become the main product.[27,30,33,38,40] It is readily accessible by the action of hydrazine on thiourea,[40] but was thus first obtained from thiocarbonohydrazide.[27] Its formulation, originally[27] somewhat uncertain, was supported by degradation reactions,[28] and was firmly established by X-ray analysis,[41] the compound having assumed some importance as a sensitive colour reagent for aldehydes,[42,43] and as an indicator for the presence of thioureido-groups.[30]

The mechanism of the formation of **25** from its various linear precursors calls for brief comment in connection with the present work. The production of **25** by the hydrazinolysis of thiocarbonohydrazide[27,30,33] is suggested to involve the intermediate formation of triaminoguanidine, which would furnish **25** on condensation with unchanged reactant (see Scheme a). Dithiocarbonic acid derivatives (e.g. methyl dithiocarbazinate,[31] diethyl xanthate[32,33,38] may react similarly, having first been converted into thiocarbonohydrazide and thence triaminoguanidine. In these instances, the original dithiocarbonic acid derivative may, after partial hydrazinolysis, participate in the final condensation: Scheme (b) illustrates one example of the numerous possible sequences.

This mechanism can be extended to the formation of **25** from thiourea,[30,40] dithiourethanes,[34] or bithiourea,[28] if the replacement of imino- by hydrazino-groups[44] is taken into consideration. Thus, the production of **25** from thiourea is explicable by the stages outlined in Scheme (c). Although it has previously[30] been accounted for by the sequence shown in Scheme (d), we believe an interpretation involving triaminoguanidine to be more acceptable: it may reasonably be doubted that thiourea is converted into thiocarbonohydrazide by the action of hydrazine, without its thiocarbonyl-sulphur being replaced simultaneously or indeed preferentially. The fact that thiocarbonohydrazide yields the hydrazinotriazole **25** directly on treatment with alkali alone[30] does not invalidate the preferred mechanism (i.e. sequence c). The postulated role of triaminoguanidine in this and related reactions is supported by the known[39] efficient synthesis of **25** from triaminoguanidine and dimethyl trithiocarbonate.

In the present reaction **13**→**25**, the conversion of the ·$CSNH_2$ to the ·$C(:NNH_2)NHNH_2$-grouping would furnish the intermediate **27**, from which **25** can arise directly by cyclisation (Scheme e); the same overall effect would be achieved if one of the hydrazinolysis steps occurred at a later stage. The frequent production of **25**, even as a



Schemes (a)–(e).

minor product, in preference to the formation of more obvious triazoles is an observation of some interest, which suggests further experimental work for its complete elucidation.

EXPERIMENTAL

General. In this and the subsequent paper, compounds are named, for indexing purposes, as hydroxy- or mercapto-thiadiazoles and triazoles, although their true structures approach oxo- or thioxo-forms.

IR spectra were determined with a Unicam SP 200 instrument, using KBr discs. The following abbreviations are employed: vs, s, ms, m, w (for intensities); d, doublet; t, triplet; mult, multiplet; sh, shoulder; br, broad.

The "plumbite test" was performed by treating a solution or suspension of the compound in 3N sodium hydroxide with a few drops of 10% aqueous lead acetate containing a little acetic acid, and heating to boiling.

Light petroleum had b.p. 60–80°. Pyridine was the pure anhydrous grade.

Ethoxycarbonyl isothiocyanate was prepared in moderate yield by the interaction of potassium thiocyanate and ethyl chloroformate, using the procedure of Lamon.[45]

Thiobiurea derivatives

1-*Ethoxycarbonyl*-2-*thiobiurea* **3**. (a) *Preparation.* Finely powdered semicarbazide HCl (3.36 g, 0.03 mole) dissolved almost entirely on being stirred in dimethylformamide (90 ml) at room temp. Dropwise addition of ethoxycarbonyl isothiocyanate (3.95 g, 0.03 mole) gave a pale-yellow liquid, which was set aside at room temp. for 72 h, then added to ice-water (500 ml). The precipitate (*ca.* 5 g) which appeared slowly, gave on crystallisation from EtOH (250 ml), felted needles of **3** m.p. 186–188° (subl.) (3.45–4.2 g, 56–68%). (Found: C, 29.2; H, 4.9; N, 28.1; S, 15.4. $C_4H_{10}N_4O_2S$ requires: C, 29.1; H, 4.85; N, 27.2; S, 15.5%). IR: 3470s (NH_2); 3320s, 3220s, 3010m (NH); 1720s (ester CO); 1675s br (amide CO); 1555s, 1540s (NH/CN); 1255, 1245s (C–O–C, ?CS); 1050s (C–O–C, ?NCS); 1580s, 1345m, 1195s br, 775s, 660m cm^{-1} Plumbite test negative.

(b) *Stability to mineral acids.* A stirred soln of **3** in conc. sulphuric acid (0.003 mole in 8 ml), kept at room temp. for 4 h, then added to ice-water, gave the starting material (66%). **3** was also recovered (65%) after being refluxed in 50% ethanolic 1.5N HCl for 2 h.

(c) *Action of alkali.* A soln of **3** (1.03 g, 0.005 mole) in 3N NaOH (20 ml) was boiled under reflux for 30 min, then neutralised with 3N HCl (20 ml). The clear liquid was evaporated, and the residual crystalline solid extracted with boiling EtOH; the extracts slowly deposited a pale yellow granular solid (0.48 g). This dissolved on being stirred into 4N HCl (2 ml); the white solid, which appeared on storage was collected at 0°; it was 3 - hydroxy - 5 - mercapto - 1,2,4 - triazole **8** m.p. 203–205° (subl.) (0.28 g, 48%), identical (mixed m.p., IR spectrum) with authentic material prepared from 1-ethoxycarbonylthiosemicarbazide[20] by the method of Arndt, Milde and Tschenscher[4] (who give m.p. 206°).

Authentic specimens had the following IR spectra:

1-Ethoxycarbonylthiosemicarbazide:[20] 3450s (NH_2); 3320s, 3190vs (NH); 1720vs (ester CO); 1540s (NH/CN); 1245s br (C–O–C, ?CS); 1030m (C–O–C, ?NCS); 840m (?NCS); 2990m, 1615vs, 1500s, 1200m, 785w, 735w cm^{-1}.

3 - Hydroxy - 5 - mercapto - 1,2,4 - triazole:[4] 3200–2800s mult (NH); 1710vs vbr (CO); 1210s (?CS); 1025m (?NCS); 1540s br, 1430–1400m mult, 1120w, 785s, 745s cm^{-1}.

Sodium Salt Thereof[4] (Trihydrate): 3500–3100s mult, 1705vbr, 1635s, 1495s, 1430m, 1405m, 1210ms, 1065m, 990m, 770m, 750m, 690m cm^{-1}.

(d) *Attempted S-methylation.* Compound **3** (0.003 mole) was recovered (75%) after its soln in MeOH (40 ml)–MeI (8 ml) was kept at room temp. for 2 h, and then evaporated to small bulk in a vacuum.

2(H) - *Carbamoyl* - 3 - *hydroxy* - 5 - *methylthio* - 1,2,4 - *triazole* (**11**, Alk = Me; R = H). A suspension of **3** (1.03 g, 0.005 mole), in MeOH (30 ml) cleared on addition of a soln of sodium (0.115 g, 0.005 g atom) in MeOH (10 ml). The liquid was treated with MeI (7.1 g, 0.05 mole) at room temp., set aside for 3 h, vacuum-evaporated to quarter bulk, and added to H_2O. The needles (0.40 g, 46%) that separated slowly gave prisms of **11** (Alk = Me; R = H), m.p. 197–200° (from EtOH). (Found: C, 27.6; H, 4.0; N, 32.3; S, 18.2. $C_4H_6N_4O_2S$ requires: C, 27.6; H, 3.45; N, 32.2; S, 18.4%). IR: 3400s (NH_2); 3200vbr (NH); 1750s, 1730s d (amide CO); 1600, 1540s d (C=N); 1380m, 1307m, 1210m, 1140m, 990s, 975s, 745m, 700ms, 690m cm^{-1}.

5 - *Benzylthio* - 2(H) - *carbamoyl* - 3 - *hydroxy* - 1,2,4 - *triazole* (**11**; Alk = CH_2Ph; R = H). To a stirred suspension of **3** (2.06 g, 0.01 mole) in EtOH (40 ml)—benzyl chloride (1.90 g, 0.015 mole) at 50–60°, 3N NaOH (3.35 ml, 0.01 mole) was added dropwise, when the reactant dissolved, and sodium chloride began to deposit. Stirring at 60° was continued for 1 h, and the cooled liquid added to ice-water (150 ml). The resinous deposit which hardened on storage at 0°, gave, on crystallisation from EtOH–light petroleum (*ca.* 20 ml each), opaque minute prisms (1.55 g, 62%) of **11** (Alk = CH_2Ph; R = H), m.p. 155–157°. (Found: C, 47.8; H, 4.3; N, 22.1; S, 12.5. $C_{10}H_{10}N_4O_2S$ requires: C, 48.0; H, 4.0; N, 22.4; S, 12.8%). IR: 3400s (NH_2); 3350s, 3200sbr, 3080sbr (NH); 1765s, 1725sd (amide CO); 1595s (C=N); 745s, 700s (Ar); 1525ms, 1360s br, 1305s, 1175m, 1140m, 960vs, 710s cm^{-1}.

Alkaline hydrolysis. A soln of **11** (Alk = CH_2Ph; R = H) (0.50 g, 0.002 mole) in EtOH (10 ml)—3N NaOH (6 ml) was boiled under reflux for 1 h, the EtOH removed in a vacuum and the cooled cloudy liquid acidified with conc. HCl (effervescence). The resulting precipitate gave, on crystallisation from EtOH (5 ml), platelets (0.34 g, 82%) of 3 - benzylthio - 5 - hydroxy - 1,2,4 - triazole **12**; (Alk = $PhCH_2$), m.p. 182–184°, identical (mixed m.p., IR spectrum) with authentic material prepared by the action of benzyl chloride on 1 - ethoxycarbonyl - 3 - thiosemicarbazide by the method of Fromm and Nehring[20] (who give m.p. 182°). IR: 3150ms, 3050ms (NH); 2830m (Alk); 1750s (amide CO), 780m, 700s (Ar), 1680m, 1460m, 990m d, 765w cm^{-1}.

1-*Ethoxycarbonyl*-6-*phenyl*-2-*thiobiurea* **4**. (a) *Preparation.* This was obtained like the parent compound **3** by the use of 4-phenylsemicarbazide (4.53 g, 0.03 mole) (time of reaction, 2 h), and formed needles or prisms, m.p. 184–186° (from EtOH, *ca.* 250 ml) (6.35–7.2 g, 75–85%). (Found: C, 47.0; H, 5.0; N, 20.5; S, 10.8. $C_{11}H_{14}N_4O_2S$ requires: C, 46.8; H, 5.0; N, 19.9; S, 11.35%). IR: 3300s, 3230, 3200m d (NH); 3050w, 770s, 695s (Ar); 1720s (ester CO); 1660s (amide CO); 1555s, 1540s (NH/CN); 1250–1240s br (C–O–C, ?CS); 1055s (C–O–C, ?NCS); 1600m, 1450m, 1380–1300m (mult), 1190s, 740s cm^{-1}. Plumbite test negative.

(b) *Stability to mineral acids.* The product **4** was recovered (90%), after being refluxed in 1:1 aqueous ethanolic N HCl for 2 h.

(c) *Action of sulphuric acid.* The reactant **4** (0.56 g, 0.002 mole) dissolved slowly in conc. H_2SO_4 (5 ml), giving a colourless liquid, which was set aside at room temp. for 4 h, then stirred into ice-water. The gelatinous precipitate, and the (major) part separating from the filtrate on spontaneous partial evaporation (total, 0.34 g, 90%) was 2 - ethoxycarbonamido - 5 - hydroxy - 1,3,4 - thiadiazole **5**, m.p. and mixed m.p.[11] 262–264° (from EtOH). IR: 3320s, 3200m, 3100m (NH); 3000m (Et); 1720s (ester CO); 1645vs (NH/CN); 1605vs br (C=N); 1245vs br, 1065s (C–O–C); 1505m, 1320s, 790m, 710m, 670m cm^{-1}.

A soln of **5** (0.38 g, 0.002 mole) in acetic anhydride (4 g) was kept at 100° for 2 h, then added to ice-water. The solidified oil gave 2 - *ethoxycarbonamido* - 4 - *acetyl* - 1,3,4 - *thiadiazolin* - 5 - *one* (**6**), m.p. 175–176° (64%, from EtOH). (Found: C, 36.3; H, 3.9; N, 18.4; S, 14.0. $C_7H_9N_3O_4S$ requires: C, 36.4; H, 3.9; N, 18.2; S, 13.85%). IR: 3300vs (NH); 2960, 2820m d (Alk); 1740s, 1700vs (CO); 1615vs (C=N); 1230s br (mult), 1065s (C–O–C); 1500vs, 1375ms; 1020s, 975s, 770s, 755vs, 670m cm^{-1}.

(d) *Action of alkali* (as described for **3**) gave **8** (36%), identified as before.

5 - *Benzylthio* - 3 - *hydroxy* - 2(H) - *phenylcarbamoyl* - 1,2,4 - *triazole* (**11**; Alk = CH_2Ph; R = Ph) was obtained from **4** like the 2(H)-carbamoyl-analogue (R = H), forming felted needles (56%), m.p. 216–218° (from 2-ethoxyethanol, *ca.* 60 ml per g, recovery 80%). (Found: C, 58.7; H, 4.25; N, 17.2; S, 9.4. $C_{16}H_{14}N_4O_2S$

requires: C, 58.9; H, 4.3; N, 17.2; S, 9.8%). IR: 3120vs br (NH); 2830w (Alk); 1760–1740vs vbr (amide CO); 1605s (C=N); 755s, 695s (Ar); 1565s, 1530s, 1495m, 1455m, 1315s, 1245s, 1200s, 1140m, 975s, 725s cm $^{-1}$.

Alkaline hydrolysis of **11** (Alk = CH_2Ph; R = Ph) gave (82%) **12** (Alk = CH_2Ph), m.p. 182–184° (from EtOH) identified as before.[20]

Bithiourea derivatives

1-*Ethoxycarbonylbithiourea* **13**. (a) *Preparation.* A stirred soln of thiosemicarbazide (2.73 g, 0.03 mole) in dimethylformamide (50 ml) was treated during 5 min at room temp. with ethoxycarbonyl isothiocyanate (3.9 g, 0.03 mole), the yellow liquid set aside for 12 h, then stirred into ice-water. Crystallisation of the pale-yellow precipitate from EtOH (*ca.* 500 ml) gave lustrous felted needles (5–5.65 g, 75–85%) of **13** m.p. 179–181°. (Found: C, 26.7; H, 4.6; N, 25.6; S, 28.2. Calc. for $C_4H_{10}N_4O_2S_2$: C, 27.0; H, 4.5; N, 25.2; S, 28.8%). IR: 3450m (NH_2); 3300m, 3180s, 3010m (NH); 1735s (ester CO); 1540s br (NH/CN); 1250, 1245s d; 1220s (C–O–C; ?CS); 1050ms (C–O–C, ?NCS); 1615s, 1500–1485s (mult), 1175s, 760m, 740m, 670m cm $^{-1}$ Plumbite test positive. Lit.[4] m.p. 180–182°.

(b) *Action of acetic anhydride.* A soln of **13** (1.11 g, 0.005 mole) in acetic anhydride (12 ml) was boiled under reflux for 2 h (initial evolution of H_2S). The pale yellow solid was collected at room temp. (filtrate F), giving silky needles (0.75 g, 65%) of 2 - *acetamido* - 5 - *ethoxycarbonamido* - 1,3,4 - *thiadiazole* (**15**), m.p. indefinite (darkens from 260°, shrinks at 340°, melted by *ca.* 360°) (from EtOH). (Found: C, 36.5; H, 4.4; N, 24.6; S, 14.1. $C_7H_{10}N_4O_3S$ requires: C, 36.5; H, 4.35; N, 24.35; S, 13.9%). IR: 3450ms, 3230ms (NH); 2940ms (Alk); 1720s (ester CO); 1670ms (CO); 1595–1590s br (C=N); 1240s, 1060ms (C–O–C); 2700w, 1540s br, 1375ms, 1320s br, 975w, 770w, 660w cm $^{-1}$.

Filtrate F was stirred into H_2O (60 ml). The solid that separated slowly was the *diacetyl-derivative*, forming prisms (0.27 g, 20%), m.p. 194–196° (from EtOH). (Found: C, 40.1; H, 4.6; N, 20.45; S, 11.8. $C_6H_{12}N_4O_4S$ requires: C, 39.7; H, 4.4; N, 20.6; S, 11.8%). IR: 3180ms (NH); 2980–2900ms mult (Alk); 1755s, 1715, 1710s d (ester CO); 1565s br (C=N); 1260–1240s br, 1095s (C–O–C), 2780ms, 1380m, 1370m, 1320m, 995ms, 770ms, 675w cm $^{-1}$.

(c) *Action of hydrochloric acid.* The reactant **13** (1.11 g, 0.005 mole) dissolved gradually in boiling 3N HCl (20 ml)–EtOH (35 ml). After 1 h, most of the EtOH was removed from the colourless liquid, which deposited 2 - ethoxycarbonamido - 5 - mercapto - 1,3,4 - thiadiazole **18** (0.87 g, 85%), forming opaque prisms, m.p. 205–207° (from H_2O). Lit m.p.[15] 204–205°. (Found: C, 29.6; H, 3.4; N, 20.9. Calc. for $C_5H_7N_3O_2S_2$: C, 29.3; H, 3.4; N, 20.5%). IR: 3270ms, 3050ms (NH); 2860ms (Et); 1690s (ester CO); 1585s (C=N); 1245–1240s (C–O–C, ?CS); 1075s (C–O–C); 1505m, 1480m, 1465m, 1320s, 1010m, 775, 760s d, 680m cm $^{-1}$.

On more prolonged refluxing (2 h) in 2N HCl–EtOH (1:1), **18** was isolated in 52% yield. The filtrate therefrom deposited more crystalline material (m.p. 130–135°; 0.21–0.29 g, 18–25%) which gave, on crystallisation from light petroleum, opaque needles of 2 - ethoxycarbonamido - 5 - ethylthio - 1,3,4 - thiadiazole, m.p. 133–135°. (Found: C, 36.2; H, 4.7; N, 17.8; S, 26.4. $C_7H_{11}N_3O_2S_2$ requires: C, 36.05; H, 4.7; N, 18.0; S, 27.5%), identified by its IR spectrum (see immediately below).

2 - *Ethoxycarbonamide* - 5 - *ethylthio* - 1,3,4 - *thiadiazole.* Compound **18** (0.51 g, 0.0025 mole), was dissolved in a soln of sodium (0.058 g, 0.0025 g atom) in EtOH (25 ml) treated with EtBr (1.65 g, 0.015 mole) and boiled under reflux for 1 h. The solvent was removed in a vacuum, and the residue extracted with boiling light petroleum. The extracts deposited the 5-*ethylthio*-compound (0.35 g, 60%), m.p. 133–135°. IR: 3250ms (NH); 2980m, 2930–2880m (mult) (Et); 1720s (ester CO); 1580ms br (C=N); 1250s br d, 1070w (C–O–C); 2700m, 1325s, 1045w, 800w, 770, 760w d, 690w cm $^{-1}$.

Compound **18** was recovered (80%) after being refluxed in 66% ethanolic 2N HCl for 6 h.

Ethyl(5 - *ethoxycarbonamido* - 1,3,4 - *thiadiazol* - 2 - *yl*)*Sulphone* **19**. A stirred soln of the foregoing 5-ethylthiol (0.46 g, 0.002 mole) in glacial acetic acid (6 ml) was treated dropwise at 40–45° with 30% hydrogen peroxide (1.36 ml, 0.012 mole). The soln was kept at 80° for 1.5 h, evaporated to half bulk in a vacuum, and added to H_2O. The white precipitate gave **19** as needles (0.32 g, 60%), m.p. 138–140° (from EtOH–H_2O, 2:1) (Found: C, 31.6; H, 4.1; N, 15.8. $C_7H_{11}N_3O_4S_2$ requires: C, 31.7; H, 4.15; N, 15.85%). IR: 3450ms, 3160m (NH); 2920ms (Et); 1725s (ester CO); 1560s (C=N); 1325s br, 1315s sh, 1150s (SO_2); 1235s br, 1075m (C–O–C); 2770m, 1265m, 1120ms, 1045m, 1005m, 770, 765, 760m t, 720ms, 695w cm $^{-1}$.

(d) *Action of alkali.* A soln of **13** (1.11 g, 0.005 mole) in 2N NaOH (20 ml) was refluxed for 10 min, neutralised with conc. HCl (evolution of H_2S) and vacuum-evaporated to dryness. The residue was extracted with EtOH (3 × 10 ml) and the combined extracts evaporated. The residue, crystallised from acidified H_2O, gave faintly yellow needles of di(3 - hydroxy - 1,2,4 - triazol - 5 - yl)disulphide **24** m.p. 232–236° (0.37 g, 64%), identified by its IR spectrum (see immediately below).

Di(3 - *hydroxy* - 1,2,4 - *triazol* - 5 - *yl*)*disulphide* **24**. To a suspension of **23**[4,20] (1.17 g, 0.01 mole) in EtOH (30 ml) at 70° was added in *one* portion 6% hydrogen peroxide (6.2 ml, 0.011 mole) acidified with 3N HCl (6 drops). The yellow liquid was boiled for 5 min, then reduced in volume under reduced pressure. The resulting crystalline precipitate, collected at 0° (0.93 g, 80%) gave faintly yellow needles of **24**, m.p. 234–236° (decomp.) (from acidified boiling H_2O, 80% recovery). Lit. m.p. 246°,[13] 245°.[20] (Found: C, 20.7; H, 1.95; N, 36.7; S, 26.9. Calc. for $C_4H_4N_6O_2S_2$: C, 20.7; H, 1.7; N, 36.2; S, 27.6%). IR: 3160m, 3030m (NH); 1708vs, 1695vs d (amide CO); 1045ms (?NCS); 2820m, 2750m, 1508w, 1435ms, 1335w, 1205w, 1080w, 985s, 825ms br, 780ms, 745ms, 720m, 665w cm $^{-1}$.

(e) *Action of Hydrazine.* A soln of **13** (2.22 g, 0.01 mole) in hydrazine hydrate (15 ml) was boiled under reflux for 2 h, distilled to small bulk (*ca.* 6 ml), added to ice-water (20 ml) and neutralised with glacial acetic acid (10 ml) (evolution of H_2S). The grey precipitate (m.p. 214–216°, 0.66 g, 45%) was 4 - amino - 3 - hydrazino - 5 - mercapto - 1,2,4 - triazole **25**. (Found: C, 16.9; H, 4.2; N, 56.8; S, 21.4. Calc. for $C_2H_6N_6S$: C, 16.4; H, 4.1; N, 57.5; S, 21.9%). IR: 3270–3210s br, 2920m (NH); 1645s, 1600s (C=N); 1510s, 1420m, 1335m d, 1155s, 1090s, 980, 960s d, 850w br, 810w br, 705m, 655m cm $^{-1}$. It was identical with authentic **25** prepared (75%) by the method of Stollé and Bowles[27] (who give m.p. 228° decomp.).

Isopropylidene-derivative **26**. On being boiled (3 h) under reflux in acetone (500 ml)–EtOH (10 ml)–3N acetic acid (2 drops), **25** (0.15 g, 0.001 mole) dissolved slowly. The liquid was evaporated to small bulk: the separated solid gave prisms (0.15 g, 80%) of **26**, m.p. 204–206° (from acetone–EtOH). (Found: C, 32.7; H, 4.9; N, 45.3. $C_5H_{10}N_6S$ requires: C, 32.3; H, 5.4; N, 45.2%). IR: 3140ms, 2950m (NH); 1640s, 1610m sh (C=N); 1490s, 1310m, 1085m, 1050m, 955w br, 875w, 715w br, 690w cm $^{-1}$.

Hexaacetyl-derivative. A soln of **25** (0.15 g, 0.001 mole) in acetic anhydride (5 ml) was boiled under reflux for 1 h, then stirred into H_2O (25 ml). The white solid (m.p. 140–145°, 0.15 g, 38%) gave prisms of the *derivative*, m.p. 147–149° (from EtOH). (Found: C, 42.2; H, 4.6; N, 21.0; S, 8.0. $C_{14}H_{16}N_6O_6S$ requires: C, 42.2; H, 4.5; N, 21.1; S, 8.0%). IR: 3000w (NH); 2990w (Me); 1755vs, 1720s br (acyl CO); 1610ms (C=N); 1440–1425m br, 1375–1365ms br, 1350ms, 1280–1260s, 1200s, 1035m, 710m, 695m, 650m cm $^{-1}$. Authentic **25**[27] gave the same derivative (28%).

3 - *Benzylthio* - 5 - *hydroxy* - 1(H) - (S - *benzyl*)*isothiocarbamoyl* - 1,2,4 - *triazole*

A stirred suspension of **13** (1.11 g, 0.005 mole) in EtOH (30 ml)–benzyl chloride (0.76 g, 0.006 mole) was treated dropwise with 3N NaOH (4 ml, 0.012 mole) and kept at 60° for 1 h. The soln was stirred into ice-water and set aside at 0°, when the resinous turbidity solidified. Crystallisation from EtOH–light petroleum gave the *substituted* 1,2,4-*triazole* as a microcrystalline opaque powder (1.16 g, 65%), m.p. 128–130°. (Found: C, 57.0; H, 4.4; N, 15.75; S, 18.0. $C_{17}H_{16}N_4OS_2$ requires: C, 57.3; H, 4.5; N, 15.7; S, 18.0%). IR: 3250m, 3050m (NH); 2950m d (Alk); 1740–1730s br, 1720–1710ms sh (CO/C=N); 740m, 695s (Ar); 1540m, 1380s, 965ms, 845m, 790m, 715m cm $^{-1}$.

1 - *Ethoxycarbonyl* - 6 - *phenylbithiourea* (**14**; R = Ph) was obtained like **13** from 4-phenyl-3-thiosemicarbazide (5.0 g, 0.03

mole) (time of reaction, 2 h), forming prismatic needles (6.75–7.6 g, 75–85%), m.p. 210–212° (slight sintering at 190–200°) (from EtOH). (Found: C, 44.1; H, 4.9; N, 19.0; S, 21.0. $C_{11}H_{14}N_4O_2S_2$ requires: C, 44.3; H, 4.7; N, 18.8; S, 21.5%). IR: 3240s (NH); 3050–3000ms, 770s, 700s (Ar); 1720s (ester CO); 1530, 1520s d (NH/CN); 1225–1215s br, 1250sh (C–O–C, ?CS); 1040s (C–O–C, ?NCS); 1600m, 1475s br, 1380m, 1325m, 1180s, 1165s, 855m cm $^{-1}$. Plumbite test positive.

The following were obtained by the same procedure:

1 - *Ethoxycarbonyl* - 6 - p - *tolylbithiourea* (**14**; R - *p*-Tol) lustrous platelets, m.p. 258–260° (decomp., after turning yellow at 205°), (from acetone–ethanol, 3:2) (82%). (Found: C, 46.35; H, 5.4; N, 18.1. $C_{12}H_{16}N_4O_2S_2$ requires: C, 46.15; H, 5.1; N, 17.95%). IR: 3220s, 3150ms (NH); 3000s (Ar); 1720s (ester CO); 1520s (NH/CN); 1220s (C–O–C, ?CS); 1040s (C–O–C, ?NCS); 820ms (*p*-disub. Ar); 1465s br, 1180s, 1165s, 855ms, 730m cm $^{-1}$.

1 - p - *Bromophenyl* - 6 - *ethoxycarbonylbithiourea* (**14**; R = *p*-BrC_6H_4), pale yellow prisms, m.p. 264–266° (decomp., after turning yellow at 200°) (from acetone–ethanol) (80%). (Found: C, 35.2; H, 3.4; N, 14.9. $C_{11}H_{13}BrN_4O_2S_2$ requires: C, 35.0; H, 3.45; N, 14.95%). IR: 3200s (NH); 3000s, 765s, 705m (Ar); 1715s (ester CO); 1550–1520s mult (NH/CN); 1245–1210s mult (C–O–C, ?CS); 1055ms (C–O–C, ?NCS), 820ms (*p*-disub. Ar); 1495–1450s mult, 870ms, 735ms cm $^{-1}$.

1 - *Ethoxycarbonyl* - 6 - *phenylbithiourea*. *Reactions*: (a) *Action of Hydrochloric Acid*. A soln of **14** (R = Ph) (1.49 g, 0.005 mole) in 1:1 aqueous-ethanolic N HCl (75 ml) was refluxed for 1 h (loss of H_2S), then vacuum-evaporated to *ca.* half volume. The white solid gave, on crystallisation from EtOH (25 ml), platelets (0.63 g, 48%) of 2 - *anilino* - 5 - *ethoxycarbonamido* - 1,3,4 - *thiadiazole*, identical with authentic material (see below).

The following were obtained by the same procedure:

2 - *Ethoxycarbonamido* - 5 - p - *toluidino* - 1,3,4 - *thiadiazole*, pale yellow needles, m.p. 257–259° (decomp.) (from EtOH–H_2O, 3:1) (72%). (Found: C, 52.2; H, 5.2; N, 19.95. $C_{12}H_{14}N_4O_2S$ requires: C, 51.8; H, 5.0; N, 20.1%). IR: 3370s, 3200w (NH); 2900–2700m mult (Et); 1690s (ester CO); 1600–1580s br (C=N); 1265s br, 1240ms sh, 1065s (C–O–C); 810ms (*p*-disub. Ar); 770, 760m d, 695m (Ar); 1550m, 1525ms, 1370ms, 1320s br, 1120m cm $^{-1}$.

2 - p - *Bromoanilino* - 5 - *ethoxycarbonamido* - 1,3,4 - *thiadiazole*, faintly yellow minute prisms, m.p. 265–267° (decomp., after turning yellow at 210°), (65%). (Found: C, 38.8; H, 3.9; N, 16.3. $C_{11}H_{11}BrN_4O_2S$ requires: C, 38.5; H, 3.2; N, 16.3). IR: 3380ms, 3150w (NH); 2990w, 2920w, 2820–2700w (Et); 1695s (ester CO); 1605s br (C=N); 1265s–1240w (sh), 1065s (C–O–C); 825m (*p*-disub. Ar); 765m, 695w (Ar); 1525, 1520s d, 1495m, 1375m, 1325s, 790m cm $^{-1}$.

2 - *Anilino* - 5 - *ethoxycarbonamido* - 1,3,4 - *thiadiazole* (**16**; R = Ph). A soln of **17** (R = Ph) (0.38 g, 0.002 mole)[4a] in pyridine (8 ml)-triethylamine (0.5 ml) was treated with ethyl chloroformate (0.24 g, 0.0022 mole), kept at 100° for 30 min, then stirred into conc. HCl (8 ml)-ice. The faintly yellow precipitate gave platelets (75%) of **16** (R - Ph) m.p. 226–228° (from EtOH). (Found: C, 50.5; H, 4.7; N, 21.4; S, 12.0. $C_{11}H_{12}N_4O_2S$ requires: C, 50.0; H, 4.5; N, 21.2; S, 12.1%). IR: 3400w d, 3280m, 3200m (NH); 2990m (Alk); 1725s (ester CO); 1230s, 1050s (C–O–C); 745s, 695m (Ar); 1570m, 1535s, 1525–1510s br, 1450m, 1325–1315s d cm $^{-1}$.

(b) *Action of sodium carbonate*. The reactant **14** (R – Ph) (1.5 g, 0.005 mole) dissolved in 3N Na_2CO_3 (25 ml) on heating. The pale yellow soln, which deposited a temporary cloudiness (odour of phenyl isothiocyanate), was boiled under reflux for 30 min. The crystalline solid which separated on cooling was *N,N'*-diphenylthiourea, m.p. 152–153° (0.40 g, 70%). Careful evaporation of the neutralised filtrate (concentrated HCl) gave 3 - hydroxy - 5 - mercapto - 1,2,4 - triazole (as the sodium salt trihydrate[4]), forming thin needles, m.p. 329–331° (0.58 g, 60%), identified by its IR spectrum (see above).

3 - *Hydroxy* - 5 - *mercapto* - 2(H) - *phenylthiocarbamoyl* - 1,2,4 - *triazole* **20** (R = Ph). (a) *Preparation*. A soln of **14** (R = Ph) (3.0 g, 0.01 mole) in 2N NaOH (45 ml) was refluxed for 10 min. The resulting turbid liquid was quickly cooled by the addition of a little ice, and acidified with conc. HCl (*ca.* 10 ml) (loss of H_2S). The white precipitate (filtrate F) gave, on crystallisation from EtOH (75 ml per g, recovery *ca.* 70%), pale-yellow prismatic needles of **20** (R = Ph), m.p. 198–200° (subl.) (1.4–1.7 g, 56–68%). (Found: C, 43.1; H, 3.5; N, 22.1; S, 24.7. $C_9H_8N_4OS_2$ requires: C, 42.9; H, 3.2; N, 22.2; S, 25.4%). IR: 3450m br, 3050m br (NH); 1720s (amide CO); 1600m (C=N); 1265–1250s d (?CS); 760m, 700s (Ar); 1540m, 1510s br, 1425m, 1380m br, 1165m br, 980s cm $^{-1}$.

Filtrate F gave, on spontaneous partial evaporation, pale yellow needles (0.35–0.46 g, 30–40%) of di(3 - hydroxy - 1,2,4 - triazol - 5 - yl)disulphide, identical with authentic material (IR, see above). More prolonged refluxing (0.5 h) using 3N NaOH lowered the yield of the main product (to 35%), giving a correspondingly larger proportion (60%) of the disulphide.

Hydrolysis of **20** (R = Ph) by 3N NaOH gave **23** (as the sodium salt trihydrate[4]) (80%).

(b) *Methylation*. **20** (R = Ph) (1.01 g, 0.004 mole), suspended in MeOH (30 ml), dissolved on addition of sodium (0.28 g, 0.012 g atom) in MeOH (10 ml). The yellow liquid, treated with MeI (8.5 g, 0.06 mole), was boiled under reflux for 1 h, then reduced to small volume in a vacuum, and diluted with H_2O. The resinous material solidifying on storage gave microprisms of the *trimethyl-derivative* **21**, m.p. 149–151° (0.56 g, 48%) (from EtOH–H_2O). (Found: C, 48.2; H, 5.1; N, 18.9. $C_{12}H_{14}N_4OS_2$ requires: C, 49.0; H, 4.8; N, 19.05%). IR: 3450m br, 3050m (NH); 2920w, 2850w (Alk); 1625s (C=N); 780ms, 760m, 700s (Ar); 1700vs, 1535s, 1455, 1440m d, 1360s, 1210ms, 1125m, 990m, 975m, 955ms cm $^{-1}$.

(c) *S-Benzylation*. The reactant **20** (R = Ph) (0.50 g, 0.002 mole) dissolved when its stirred suspension in EtOH (30 ml)–benzyl chloride (0.56 g, 0.0044 mole) was treated with 3N NaOH (1.35 ml, 0.004 mole) at 60°. Addition of the partly evaporated liquid to ice water, neutralisation with ammonia, and storage at 0°, gave a white resin, which formed microcrystalline (0.19 g, 46%) **22** (Alk = CH_2Ph) m.p. 179–181° (from $CHCl_3$–light petroleum), identical with authentic material.[20]

The use of *p*-nitrobenzyl chloride (0.69 g, 0.004 mole) in the foregoing procedure gave (0.21 g, 42%) pale-yellow microcrystalline 3 - hydroxy - 5 - *p* - nitrobenzylthio - 1,2,4 - triazole, (from $CHCl_3$–light petroleum), identical (mixed m.p. 210–212°, IR spectrum) with authentic material described in Part II (sub-joined).

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