Addition-Cyclisations of Ethoxycarbonyl Isothiocyanate with Hydrazine Derivatives as a Source of Thiadiazoles and Triazoles

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Ethoxycarbonyl isothiocyanate reacts additively with hydrazine, ethoxycarbonylhydrazine, as well as amino- and 1,2-diaminoguanidine. Simultaneous or subsequent cyclisation of the resulting 1:1- or 2:1-adducts in acidic or alkaline media yields substituted 1,3,4-thiadiazoles or 1,2,4-triazoles, respectively.

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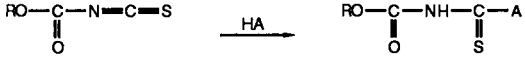
Alkoxycarbonyl isothiocyanates **A** are bifunctional reagents capable of participating in a wide range of addition-cyclisations [1]. The strong electron-attracting power of their alkoxycarbonyl-group enhances the reactivity of the adjacent isothiocyanato-function and promotes nucleophilic addition at this centre **A** → **B** [2]. Simultaneous or subsequent cyclisation of the adducts gives access to a variety of 5- or 6-membered heterocyclic structures, including bicyclic condensed ring-systems [1]. In our previous study [3-5] of this group of reactions, the use of reactants incorporating free hydrazino-groups, including amidrazones [3], (thio)semicarbazides [4], and (thio)-carbonohydrazides [5] has provided a versatile route to substituted 1,3,4-thiadiazoles and 1,2,4-triazoles. We now report further variants of this synthetic approach, employing the prototype hydrazine itself and some of its simple congeners.

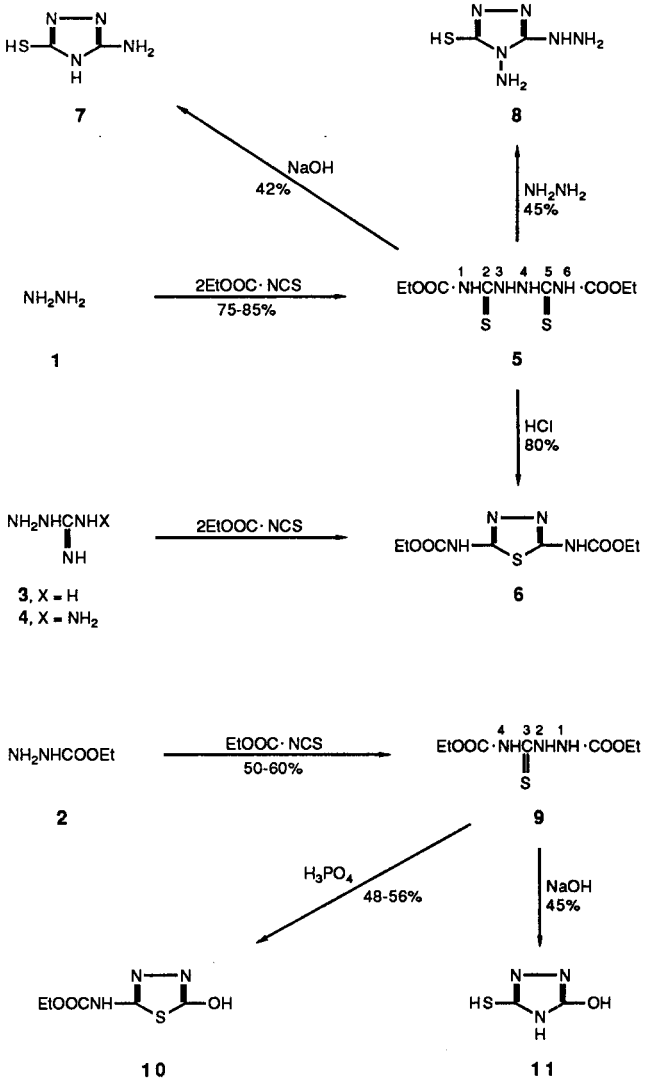


A **B**

Hydrazine reacted additively with 2 moles of ethoxycarbonyl isothiocyanate in dimethylformamide at room temperature, producing 1,6-bis(ethoxycarbonyl)bithiourea (**5**) in excellent yield. Interaction of equimolar quantities of the reactants did not terminate at the monoaddition stage, but gave again the diadduct **5**, albeit in reduced yield. In this respect, the reaction resembles that of carbono- and thiocarbonohydrazide, where rapid addition at the two symmetrically placed hydrazino groups precludes the formation of the monoadducts [5]. The structure **5** assigned to the linear bithiourea is consistent with its spectral (see below) and chemical properties.

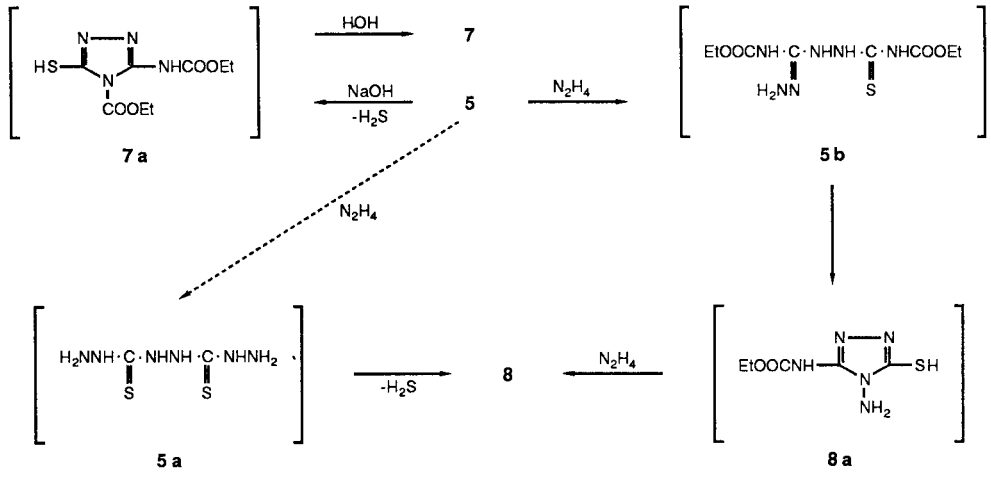
It was cyclised by ethanolic hydrochloric acid to 2,5-bis-(ethoxycarbonamido)-1,3,4-thiadiazole (**6**) almost quantitatively. This was also the product of the attempted *S*-alkylation of **5** by iodomethane-methanol, emphasising the readiness with which this ring-closure occurs. The evolution of methanethiol indicates that the intermediate formation and cyclisation of the monomethylthio-ester of **5** is at least partly involved in this reaction.

Scheme 1



The action of alkali or hydrazine on **5** produced

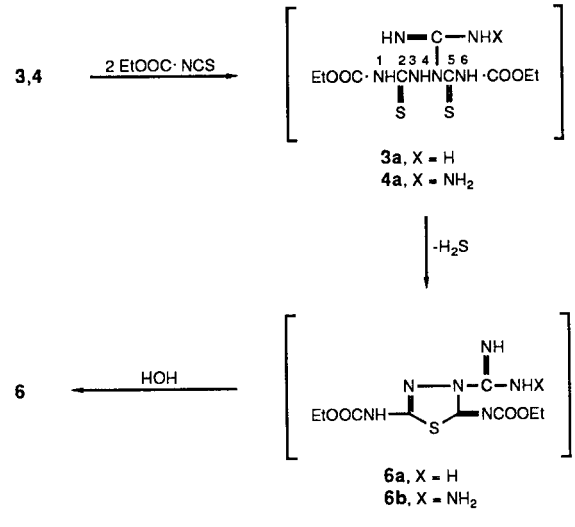
Scheme 2



moderate yields of 3-amino-5-mercapto- (**7**) or 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (**8**), respectively. The former is thought to arise from the primarily formed bis-ethoxycarbonyl-derivative **7a** by hydrolysis. The origin of the latter **8** is less decided: although 1,6-diaminobithiourea (**5a**) would be an obvious precursor of **8**, its generation from **5** by hydrazinolysis affecting ethoxycarbonamido (.NHCOOEt) - rather than thiono-groups is regarded with reservation, and alternative pathways need to be considered. The sequence **5** → **5b** → **8a** → **8** (Scheme 2) has the merit of being directly comparable with our previous interpretation of the analogous hydrazinolysis of 1-ethoxycarbonylbithiourea [4]. The overall results are in accord with the established cyclisation patterns of structures incorporating the .(HS)C=N-N=C(NHR).-moiety, which are cyclised to substituted 1,3,4-thiadiazoles and 1,2,4-triazoles in acidic and alkaline media, respectively [6].

No appreciable interaction occurred between aminoguanidine (**3**) and ethoxycarbonyl isothiocyanate under the mild conditions applicable to the hydrazine addition. Reaction did set in when catalysed by triethylamine, preferably at 100°, but then proceeded beyond the adduct-stage to yield 2,5-bis(ethoxycarbonamido)-1,3,4-thiadiazole (**6**). The reaction is explicable in terms of an initial addition of one mole of isothiocyanate at each of the adjacent nitrogens of the hydrazino-moiety of **3**, followed by cyclisation and hydrolysis of the resulting diadduct (Scheme 3: **3** → **3a** → **6a** → **6**). The second molecule of isothiocyanate enters the penultimate NH-group (*i.e.* N^4 in **3a**) so rapidly that its employment in equimolar proportions results in the same product **6**, though in proportionally diminished yields. The reaction between 1,2-diaminoguanidine (**4**) and ethoxycarbonyl isothiocyanate took the same course and is

Scheme 3



correlated with that of **3** by an identical mechanism (Scheme 3: **4** → **4a** → **6b** → **6**). The cause of the consistently lower yields of **6** obtainable from **3** and **4** (compared with those from hydrazine) is ascribed to the increased intervention of side-reactions in the multistage process.

Rapid diaddition of heterocumulenes at adjacent hydrazino-nitrogens in amino- and 1,2-diaminoguanidines (**3** and **4**) and their oxo- and thiono-analogues (NH_2NH-CXNHY; X = O, S; Y = H, NH_2), often to the exclusion of potential sites elsewhere, is known to occur when carbodiimides are the added species [7]. In contrast, iso(thio)-cyanates tend to react preferentially at all available terminal hydrazino-nitrogens [7], but evidence for limited vicinal diaddition has been obtained in the case of aroyl

isothiocyanates [8]. The present observations suggest that this latter mode of action may by favoured by acyl iso-(thio)cyanates generally, but the available information does not as yet provide guidelines for predicting the prevailing course of the addition.

The interaction of equimolar quantities of ethoxycarbonylhydrazine (**2**) and ethoxycarbonyl isothiocyanate gave good yields of the linear 1:1 adduct **9**. Previous attempts to synthesise this compound by the action of ethyl chloroformate on thiosemicarbazide had failed, resulting by partial desulphurisation in inseparable mixtures [9]. 1,4-Bis(ethoxycarbonyl)-3-thiosemicarbazide (**9**) proved less prone to cyclisation than its analogues derived from other heterocumulenes, including iso(thio)cyanates [10], aroyl isothiocyanates [11], and carbodiimides [11,12]; it was stable to mineral acids and gave an *S*-methylisothio-derivative. Polyphosphoric acid at 120° effected ring-closure with elimination of the elements of ethanol rather than water, to afford the 1,3,4-thiadiazole **10** in moderate yield. Alkali cleaved much of the reactant **9** into smaller fragments, including hydrazine, so that only little of the expected 3-hydroxy-5-mercapto-1,2,4-triazole (**11**) was isolated.

The spectral properties of the new products agree with their proposed structures. The ir spectra of the linear adducts resemble in their main features those of comparable precedents [4,5] including authentic 1-ethoxycarbonyl-3-thiosemicarbazide [4,9]. Their multiple NH-groups give rise to bands near 3400 and 3000 cm^{-1}, the former being ascribed to amide-NH vibration [13a]. Intense broad peaks at *ca* 1560 cm^{-1}, indicative of C-N-H vibration [14], are regarded as combination bands due to NH-deformation and C-N - stretching [14,15]. The ethoxycarbonyl-group produces the expected carbonyl absorption at *ca* 1750 cm^{-1}; bands at *ca* 1200 and 1000 cm^{-1}, originating from asymmetrical and symmetrical ester -C-O-C- vibration [13b] may, in the present structures, receive contributions from effects of the N-C-S - grouping [16,17]. The ir spectra of the heterocyclic products are similarly interpreted (see Experimental) and conform on their part to those of their prototypes [4,5,16].

Table 1

Proton NMR Spectra

Compound [a]	CH_3 of Et	CH_2 of Et	CH_3 of SMe	NH
5	1.26 3H t	4.22 2H q	-	11.73 1H s 13.10 1H s
9 [b]	1.17 3H t 1.13 3H t	4.28 2H q 4.12 2H q	-	12.1 s [c]
9a [b]	1.14 3H t 1.04 3H t	4.25 2H q 4.05 2H q	2.53 3H s	10.9 s [c]
6	1.23 3H t	4.29 2H q	-	-
10	1.19 3H t	4.23 2H q	-	13.0 s [c]
13 [d]	1.21 3H t	4.25 2H q	-	13.25 s [c]

9a = *S*-Methyl derivative of **9**.

[a] Chemical shifts are in ppm downfield from tetramethylsilane (δ = 0). The solvent was pyridine-d_5, except for **5**, where dimethyl sulphoxide-d_6 was used. [b] The signals of the two ethoxycarbonyl-groups are not separately assignable. [c] Broad shallow signal, integration indistinct. [d] Additional aromatic proton signals at 8.01 d, 7.98 d, 7.49 t, 7.48 t and 7.45 t ppm (total 5H).

The ^1H and ^{13}C nmr spectra of representative compounds are displayed in Tables 1 and 2 in accordance with their proposed assignments. The signals of the methyl-and methylene-protons of the carbethoxy-group are readily identified by their multiplicities and integration, as well as their appropriate chemical shifts [18]; those of the NH-groups consist, except in the case of **5**, of very broad and shallow bands, with ill-defined integrations. In the carbon nmr spectra, the carbethoxy-groups give rise to three signals of the expected [19] resonances. An additional low-

Table 2

Carbon NMR Spectra

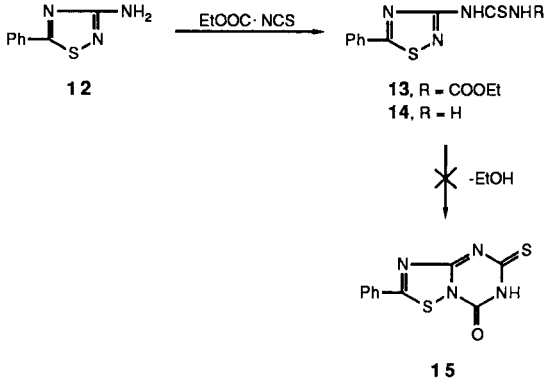
Compound [a]	CS, C-SMe	C=O	>C= (Het)	CH_2	CH_3	C-Ar
5	170.8 s	153.4 s	-	62.4 t	14.0 q	-
9 [b]	182.8 s	156.7 s 154.1 s	-	62.5 t 61.7 t	14.7 q 14.3 q	-
9a [b]	141.2 s	154.9 s 153.8 s	-	62.0 t 61.1 t	14.7 q [c] 14.3 q	-
6	-	*154.9 s	*158.1 s	62.3 t	14.6 q	-
10	-	154.6 s	171.6 s [d] 147.4 s [d]	62.15 t	14.5 q	-
13	188.0 s	154.1 s	179.3 s [d] 163.4 s [d]	62.7 t	14.3 q	130.3 s 132.7 d 129.7 d [e] 127.6 d [e]

9a = *S*-Methyl derivative of **9**. *Signals are interchangeable horizontally.

[a], [b] as for Table 1. [c] Signal of double intensity due to two methyl carbons. [d] The singlets of the two heteroaromatic carbons are not separately assignable (see text). [e] Signals of double intensity.

field singlet is produced by the thiocarbonyl-carbon [20] of **9** and **13** and is displaced significantly to higher field upon *S*-methylation (*i.e.* **9** → **9a**, from 182 to 141 ppm), resembling in this respect the corresponding signals of thioaroylsemicarbazides (ArCSNHNHCONHR) [20]. The singlets of the two heteroaromatic carbons of **10** and **13** cannot be individually identified, chiefly because the shielding of the comparable carbon atom of the symmetrical compound (*i.e.* C2 = C5 of **6**) is not sufficiently close to either to permit a valid differentiation.

In conclusion, attention is drawn to the usefulness of ethoxycarbonyl isothiocyanate as a reagent for expanding amino- to thioureido-groupings [1] when the low basicity or unfavourable solubility of the amine precludes the direct addition of the elements of thiocyanic acid by the conventional procedures [21]. The method is now exemplified by the synthesis of authentic 3-thioureido-5-phenyl-1,2,4-thiadiazole (**14**), which was required for confirming the structure of its 3-ureido-analogue obtained by another synthetic route [22]. The 3-amine reacted additively with 1 mole of ethoxycarbonyl isothiocyanate to yield the ω-(ethoxycarbonyl)thiourea **13**, which, though stable towards acids, was smoothly decarboxylated by alkalis to the free thiourea **14**. Unlike comparable adducts derived from other α-aminoazoles [1,23-25], **13** was not cyclisable by intramolecular condensation: it was either unaffected or totally decomposed in several of the established cyclisation procedures [23,25], so that the 1,2,4-thiadiazolo-[2,3-*a*]-*s*-triazine **15** was not obtainable by this route.



12 **13**, R = COOEt; **14**, R = H **15**

EXPERIMENTAL

Melting points are uncorrected. Light petroleum had bp 60-80°. Infrared spectra were recorded on a Unicam SP 1000 instrument, using potassium bromide discs. In the ir spectral data the abbreviations have the following meaning: s strong, m medium, w weak, br broad, sh shoulder, d doublet, mult multiplet. Unassigned ir peaks are not listed expect for compounds **5** and **9**. Proton and carbon nmr spectra were obtained on a Bruker WM 250 Fourier transform instrument operating at 250 and 62.9 MHz respectively, tetramethylsilane being the internal standard.

1,6-Bis(ethoxycarbonyl)bithiourea (**5**).

To a stirred solution of hydrazine hydrate (1.0 g, 20 mmoles) in dimethylformamide (40 ml), ethoxycarbonyl isothiocyanate (5.75 g, 44 mmoles) was added dropwise at room temperature, when a white precipitate appeared in the warm liquid after a few minutes. Stirring at room temperature was continued for 3 hours, the mixture set aside over night, then added to ice-water (600 ml). The pale-yellow precipitate gave minute opaque prisms (from chloroform-light petroleum) or needles (from ethanol, 80 ml per g) of **5**, mp indefinite (turning yellow at 260°, darkening at 300°, not melted by 360°), (yield, 4.4-5.0 g, 75-85%); ir: ν 3450 mw (NH amide), 3190 vs, 3020 mw (NH), 2990 mw sh, 1480 vs br (CH_3, CH_2), 1725 vs (C=O ester), 1540 vs (NH/CN), 1250 s, 1210 vs (C-O ester, ? CS), 1040 vs (C-O-C, ? NCS), 1295 m, 1180 s, 1095 m, 770 m, 710 m br cm^{-1}.

Anal. Calcd. for $C_8H_{14}N_4O_4S_2$: C, 32.65; H, 4.8; N, 19.05; S, 21.8. Found: C, 32.85; H, 4.6; N, 19.0; S, 21.6.

2,5-Bis(ethoxycarbonamido)-1,3,4-thiadiazole (**6**).

A suspension of **5** (0.59 g, 2 mmoles) in ethanol (40 ml)-3*M* hydrochloric acid (10 ml)-water (5 ml) was refluxed for 2 hours, when the reactant dissolved gradually and hydrogen sulphide was evolved. The solution was vacuum-evaporated to a small volume and the separated solid crystallised from a large volume of ethanol (200 ml per g), yielding pale-ivory microprisms of **6** (0.42 g, 80%), mp indefinite (darkens from 260°, shrinks at 340°, not melted by 360°); ir: ν 3450 mw (NH amide), 3160 vs (NH), 2950 s br, 1490, 1460 m (CH_3, CH_2), 1725, 1710 vs d (C=O ester), 1590 s (NH/CN), 1240 vs br (C-O ester), 1070, 1050 s d (C-O-C, ? NCS) cm^{-1}.

Anal. Calcd. for $C_6H_{10}N_4O_4S$: C, 36.9; H, 4.6; N, 21.5; S, 12.3. Found: C, 36.7; H, 4.8; N, 21.9; S, 12.6.

1,6-Bis(ethoxycarbonyl)bithiourea (**5**). Reactions:

(a) Action of Alkali.

A solution of **5** (1.47 g, 5 mmoles) in ethanol (15 ml)-3*M* sodium hydroxide (10 ml) was refluxed for 1 hour, vacuum-distilled to *ca* half-volume and acidified with 3 *M* acetic acid. The precipitate, collected at 0° and crystallised from water, gave microprisms of 3-amino-5-mercapto-1,2,4-triazole (**7**) (0.24 g, 42%), identical (mixed mp, ir) with authentic material prepared from bithiourea [26], lit mp 303° [26], 298° dec [27].

(b) Action of Hydrazine.

A solution of **5** (1.47 g, 5 mmoles) in hydrazine hydrate (15 ml) was refluxed for 2 hours, distilled to half-bulk, diluted with water, and neutralised with glacial acetic acid (evolution of hydrogen sulphide). The resulting crystalline precipitate was 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (**8**) (0.33 g, 45%), identical (mixed mp 220-222° dec, ir) with authentic material [4,28], lit mp [28] 228° dec.

(c) Attempted *S*-Methylation.

When refluxed in methanol (150 ml), iodomethane (35.5 g, 250 mmoles), **5** (1.47 g, 5 mmoles) dissolved gradually. The solution was refluxed for 5 hours (evolution of methanethiol), then evaporated to small volume. The separated white solid, rinsed with methanol, gave **6** (0.73 g, 56%), identified by ir (see above).

Aminoguanidine (**3**): Action of Ethoxycarbonyl Isothiocyanate.

Finely powdered **3**-hydrochloride (1.22 g, 11 mmoles), nearly dissolved in stirred dimethylformamide (25 ml)-triethylamine (2 ml), was treated dropwise with ethoxycarbonyl isothiocyanate (3.30 g, 25 mmoles). The yellow solution was kept at 100° for 1 hour, then added to ice-water. The resulting pale-yellow solid, collected at 0°, formed microprisms of **6** (from ethanol) (1.37 g, 48%), identified by ir (see above). The use of 10 mmoles of ethoxycarbonyl isothiocyanate (12 hours at room temperature) gave the same product **6** in diminished yields (18-22%), showing that a monoadduct is not obtainable by this route.

1,2-Diaminoguanidine (**4**): Action of Ethoxycarbonyl Isothiocyanate.

The use of **4**-hydriodide [29] (2.39 g, 11 mmoles) in the foregoing procedure (3 hours at 100°) gave **6** (1.1 g, 38%), identified by ir.

1,4-Bis(ethoxycarbonyl)-3-thiosemicarbazide (**9**).

A solution of ethoxycarbonylhydrazine (**2**, 4.6 g, 44 mmoles) in dimethylformamide (80 ml)-triethylamine (2 ml), treated with ethoxycarbonyl isothiocyanate (5.2 g, 40 mmoles), was kept at 100° for 30 minutes, vacuum-distilled to small bulk (12-15 ml), then stirred into ice-water (100 ml). The precipitated oil solidified rapidly and gave, on crystallisation from chloroform-light petroleum, platelets of **9** (4.7-5.6 g, 50-60%), mp 111-113°; ir: ν 3350-3300 vs t (NH amide), 3000 s (NH), 1730 vs, 1705 vs d (C=O ester), 1555-1515 vs mult (NH/CN), 1285-1275 vs, 1235 ms (C-O ester), 1040 s (C-O-C, ? NCS), 1380 m, 1355 m, 1200-1180 vs, 890 ms, 775 vs cm^{-1}.

Anal. Calcd. for $C_7H_{13}N_3O_4S$: C, 35.7; H, 5.5; N, 17.9; S, 13.6. Found: C, 35.85; H, 5.4; N, 18.2; S, 13.7.

Stability to acids.

The reactant **9** (1.17 g, 5 mmoles) was recovered (72%) after its solution in 3 *M* hydrochloric acid (25 ml)-ethanol (5 ml) was refluxed for 1 hour, or (76%) after its solution in concentrated sulphuric acid (12 ml) was kept at room temperature for 6 hours.

S-Methyl-1,4-bis(ethoxycarbonyl)-3-isothiosemicarbazide (**9a**).

The solution obtained by dissolving **9** (1.17 g, 5 mmoles) in one of sodium (0.115 g, 5 mmoles) in methanol (15 ml), was treated with iodomethane (14.2 g, 100 mmoles), boiled under reflux for 30 minutes, distilled to small volume and added to water. The white precipitate which appeared slowly gave, on crystallisation from ethanol, the *S*-methyl thioether **9a** as opaque microneedles (0.58 g, 46%), mp 114-115°; ir: ν 3450 ms, 3300 s, 3250 s (NH amide), 3110 ms (NH), 3000 ms, 2950 m (CH_3, CH_2), 1750 vs (C=O ester), 1565 vs, 1535 s (NH/CN), 1225 vs br (C-O ester), 1085 vs (C-O-C, ? NCS) cm^{-1}.

Anal. Calcd. for $C_8H_{15}N_3O_4S$: C, 38.55; H, 6.0; N, 16.9; S, 12.85. Found: C, 38.6; H, 5.8; N, 16.4; S, 12.95.

1,4-Bis(ethoxycarbonyl)-3-thiosemicarbazide (**9**). Reactions:

(a) Action of Polyphosphoric Acid.

Finely powdered **9** (2.35 g, 10 mmoles) was added to melted polyphosphoric acid (50 g), kept at 120-130° for 30 minutes and the colourless viscous (cooled) liquid stirred into ice-water (150 ml). The white precipitate (0.91-1.06 g, 48-56%, pure by ir) gave, on crystallisation from ethanol, microprisms of 2-ethoxycarbonamido-5-hydroxy-1,3,4-thiadiazole (**10**), mp 258-260°, identical (mixed mp, ir) with authentic material (obtained [30] from 2-ethoxycarbonamido-1,3,4-thiadiazole-5-sulphonamide) lit mp [30] 263-265°.

Anal. Calcd. for $C_5H_7N_3O_3S$: C, 31.75; H, 3.7; N, 22.2; S, 16.9. Found: C, 31.3; H, 3.9; N, 22.6; S, 16.9.

(b) Action of Alkali.

A solution of **9** (2.35 g, 10 mmoles) in 3 *M* sodium hydroxide (50 ml) was refluxed for 1 hour, evaporated to half volume, just acidified with concentrated hydrochloric acid (effervescence of carbon dioxide, some hydrogen sulphide) and vacuum-evaporated to dryness. Extraction of the residue with boiling ethanol and partial evaporation gave needles (0.53 g, 45%) of 3-hydroxy-5-mercapto-1,2,4-triazole (**11**) mp 200-202° dec, lit mp 206° [31]; 202° dec [9].

Anal. Calcd. for $C_2H_3N_3OS$: C, 20.5; H, 2.6; N, 35.9. Found: C, 20.1; H, 2.8; N, 35.6.

Alternatively, the alkaline hydrolysate was acidified with 3 *M* hydrochloric acid (50 ml) and treated with 0.05 *M* aqueous picric acid (10 mmoles), when hydrazine picrate hemihydrate, mp 196-197° (from 80% ethanol) was slowly deposited (yield, 0.85 g, 32%) lit mp 201° [32].

Anal. Calcd. for $N_2H_4 \cdot C_6H_3N_3O_7 \cdot \frac{1}{2}H_2O$: C, 26.7; H, 3.0; N, 25.9. Found: C, 26.9; H, 3.2; N, 26.2.

1-Ethoxycarbonyl-3-(5'-phenyl-1',2',4'-thiadiazol-3'-yl)thiourea (**13**).

A stirred suspension of finely powdered 3-amino-5-phenyl-1,2,4-thiadiazole [33] (**12**, 3.55 g, 20 mmoles) in anhydrous ether (40 ml) was treated dropwise with ethoxycarbonyl isothiocyanate (2.62 g, 20 mmoles), and stirring at room temperature continued for 12 hours. The resulting pale-yellow powder gave, on crystallisation from ethanol (*ca* 40 ml per g), opaque microprisms of **13**, (3.2-4.0 g, 52-65%), mp 178-180°. The use of pyridine as solvent (room temperature, 3 hours) gave the same product in diminished yield; ir: ν 3200 s (NH amide), 3060, 3000 s d (NH), 1780 s (C=O ester), 1590-1570 vs br (NH/CN), 1230 s br (C-O ester), 1080 s (C-O-C, ? NCS), 775 s, 690 ms (Ar) cm^{-1}.

Anal. Calcd. for $C_{12}H_{13}N_4O_2S_2$: C, 46.75; H, 3.9; N, 18.2; S, 20.8. Found: C, 46.7; H, 3.95; N, 18.2; S, 20.7.

Stability to Acids.

The material was recovered nearly quantitatively after its solution in concentrated sulphuric acid (1 mmole in 5 ml) had been kept at room temperature for 3 hours, then stirred into ice-water. It was also substantially unaffected by boiling *M* ethanolic (80%) hydrochloric acid (1.5 hours). Cyclisation to **15** did not occur under the following conditions: Pyrolysis at 190-200° for 20 minutes [23] gave an uncrystallisable red oil. After being refluxed in dimethylformamide for 2 hours, **13** gave only a trace of solid, but was recovered (64%) after being refluxed in pyridine for 1 hour [25].

5-Phenyl-3-thioureido-1,2,4-thiadiazole (**14**).

To a boiling suspension of **13** (1.54 g, 5 mmoles) in ethanol (60 ml), 3 *M* sodium hydroxide (6.7 ml, 20 mmoles) was added, the resulting solution refluxed for 1 hour, then vacuum-evaporated to one third of its bulk, and a small amount of separated pale-yellow solid removed by filtration. Acidification with 3 *M* hydrochloric acid produced a white precipitate (some evolution of hydrogen sulphide), giving, on crystallisation from dimethylformamide (*ca* 15 ml per g), opaque white microprisms of **14**, (0.85 g, 72%), identical (mixed mp 246-248°, ir) with material obtained from 1-benzoyl-3-(5'-phenyl-1',2',4'-thiadiazol-3'-yl)thiourea [22].

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