Cyclic Meso-ionic Compounds. Part IX.[1] Synthesis, Spectroscopic Properties, and Chemistry of 1,3,4-Thiadiazolium-2-olates and 1,3,4-Oxadiazolium-2-thiolates [2]

By **Allan R. McCarthy, W. David Ollis,*** and **Christopher A. Ramsden,** Department of Chemistry, The University, Sheffield S3 7HF

The synthesis, spectroscopic properties, and reactions of 1,3,4-thiadiazolium-2-olates (III) and 1,3,4-oxadiazolium-2-thiolates (IV) are reported. The results establish the existence of corresponding pairs of isomeric meso-ionic compounds whose isomerisation [(IV) ⟶ (III)] involves exchange between endocyclic and exocyclic heteroatoms.

THE meso-ionic 1,3,4-thiadiazolium-2-thiolates (I), often referred to as '*endo*-thiodihydrothiodiazoles', are a well-characterised meso-ionic system [3,4] first prepared by Busch and his co-workers.[5] Hoegerle,[6] in 1958, reported the synthesis of the oxygen analogues of Busch's '*endo*-thiodihydrothiodiazoles' and these meso-ionic compounds are referred to as isosydnones (II). The synthesis of a number of isosydnones (II) has been reported [7-10] and their physical [10] and chemical properties [1,7] have been investigated. Although the synthesis and chemistry of the meso-ionic systems (I) and (II) has been of great interest, the synthesis of the monosulphur analogues (III) and (IV) has been reported only recently.[2,11] In continuation of our research on meso-ionic systems, we have prepared derivatives of the meso-ionic 1,3,4-thiadiazolium-2-olates (III) and 1,3,4-oxadiazolium-2-thiolates (IV). The possible existence of meso-ionic isomers of the general type (XI) and (XII) was first recognised by Schönberg [12] as early as 1938.

[1] Part VIII, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, preceding paper.

[2] Preliminary account, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *Chem. Comm.*, 1968, 499.

[3] W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.

[4] M. Ohta and H. Kato, in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, pp. 117—248.

[5] M. Busch, *Ber.*, 1895, **28**, 2635; M. Busch and H. Münker, *J. prakt. Chem.*, 1899, **60**, 212; M. Busch and F. Best, *ibid.*, p. 225; M. Busch, *ibid.*, 1903, **67**, 201; M. Busch, W. Kamphausen, and S. Schneider, *ibid.*, p. 216; M. Busch and S. Schneider, *ibid.*, p. 246; M. Busch and G. Blume, *ibid.*, p. 257.

[6] K. Hoegerle, *Helv. Chim. Acta*, 1958, **41**, 548.

[7] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan*, 1961, **34**, 668.

[8] E. B. Roche and L. B. Kier, *J. Pharm. Sci.*, 1965, **54**, 1700.

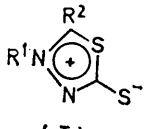
[9] C. Ainsworth, *Canad. J. Chem.*, 1965, **43**, 1607.

[10] A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc.* (*B*), 1969, 1185.

[11] A. Y. Lazaris, *J. Org. Chem.* (*U.S.S.R.*), 1967, **3**, 1856; 1968, **4**, 1786.

[12] A. Schönberg, *J. Chem. Soc.*, 1938, 824.

Later, Baker, Ollis, and Poole [13] described the general class of meso-ionic heterocycles and predicted that new members of this class, including isomers of the general types (XI) and (XII), might be prepared. Although meso-ionic systems of the general type (XI) are well known, pairs of isomers of the general types (XI) and (XII) have only recently been described.[2] Details of our study [2] of the synthesis and properties of the meso-ionic isomers (III) and (IV) are now reported.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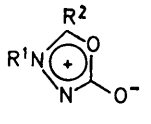
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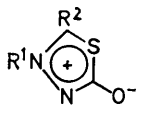
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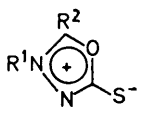
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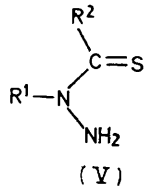
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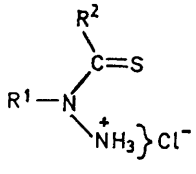
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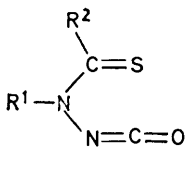
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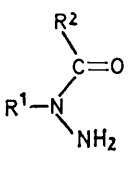
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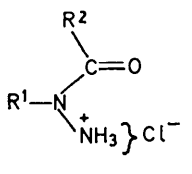
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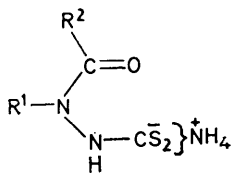
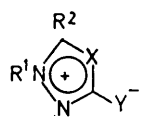

(X)

In formulae (I)—(X)
a; $R^1 = R^2 = Ph$. b; $R^1 = Me$, $R^2 = Ph$. c; $R^1 = Ph$, $R^2 = Me$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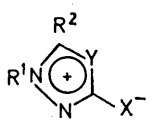
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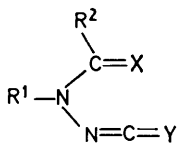
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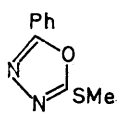
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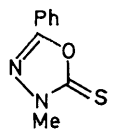
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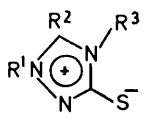

(XVI)

The synthesis of the 1,3,4-thiadiazolium-2-olates (III) is based on the synthesis of the isosydnones (II) from *N*-acylhydrazine hydrochlorides (IX) and phosgene.[10] It was expected that treatment of the *N*-thioacylhydrazine hydrochlorides (VI) with phosgene would yield the 1,3,4-thiadiazolium-2-olates (III), a synthesis which can be regarded as proceeding *via* the tautomeric isocyanate intermediate (VII). The preparation of *N*-thioacylhydrazines (V; R^1 = alkyl) from carboxymethyl dithiobenzoates and monosubstituted hydrazines has been extensively studied by Jensen and his co-workers,[14] but this approach cannot be used for the synthesis of *N*-aryl-*N*-thioacylhydrazines (V; R^1 = aryl). A study [10] of isosydnones (II) has led to a novel synthesis of *N*-thioacylhydrazines (V) which can be used to prepare both *N*-alkyl and *N*-aryl derivatives (V; R^1 = alkyl or aryl). Treatment of 4,5-diphenylisosydnone (IIa) [10] with hydrogen sulphide in chloroform solution in the presence of pyridine at room temperature afforded *N*-thiobenzoyl-*N*-phenylhydrazine (Va) in good yield; no reaction was observed when pyridine was omitted. When 4-methyl-5-phenylisosydnone (IIb) [10] was treated with hydrogen sulphide in the presence of triethylamine, *N*-thiobenzoyl-*N*-methylhydrazine (Vb) (42%) was isolated together with *N*-benzoyl-*N*-methylhydrazine (VIIIb) (13%). The mechanisms shown in Scheme 1 are proposed for these reactions.

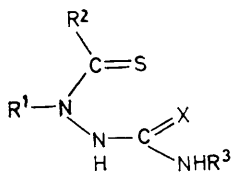
Treatment of the *N*-thioacylhydrazine hydrochlorides (VIa and b) with phosgene by boiling ethyl acetate gave good yields of the 1,3,4-thiadiazolium-2-olates (IIIa and b), obtained as crystalline compounds with sharp melting points, soluble in chloroform or ethanol, but only sparingly soluble in benzene. Since our preliminary publication [2] and that of Lazaris [11] on the synthesis of the meso-ionic 1,3,4-thiadiazoles (III), similar synthetic routes to these compounds have been described.[15,16]

Two routes to the 1,3,4-oxadiazolium-2-thiolates (IV) have been reported. Sandström and Wennerbeck [17] treated the 1,3,4-oxadiazole (XIV) with methyl iodide to form a mixture of two methiodides which on treatment with hot pyridine gave the 1,3,4-oxadiazole (XV) together with the meso-ionic 2-thiolate (IVb). This synthesis is not a general route to the meso-ionic system (IV), a general synthesis of which has been described by Lazaris.[11] Treatment of the ammonium dithiocarbamate (Xa) with phosphoryl chloride–triethylamine gives the 1,3,4-oxadiazolium-2-thiolate (IVa). By this method, we prepared the 1,3,4-oxadiazolium-2-thiolates (IVa and b) for direct comparison with the isomeric 1,3,4-thiadiazolium-2-olates (IIIa and b). Furthermore, we have shown that compound (IVb) prepared by this method is identical with a sample prepared by the

[13] W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1949, 307.
[14] K. A. Jensen, H. R. Baccaro, O. Buchardt, G. E. Olsen, C. Pedersen, and J. Toft, *Acta Chem. Scand.*, 1961, **15**, 1109.
[15] K. T. Potts and C. Sapino, jun., *Chem. Comm.*, 1968, 672.
[16] R. Grashey, M. Baumann, and W. D. Lubos, *Tetrahedron Letters*, 1968, 5877.

method of Sandström and Wennerbeck.[17] A third method for the synthesis of 1,3,4-oxadiazolium-2-thiolates (IV) involves the reaction between *N*-acylhydrazines (VIII) and thiophosgene.[18] The 1,3,4-oxadiazolium-2-thiolates (IV) are pale yellow, crystalline compounds with sharp melting points, almost insoluble in benzene, but fairly soluble in ethanol and chloroform.

The pairs of meso-ionic isomers (IIIa and IVa) and (IIIb and IVb) show distinct physical and chemical properties. The i.r. spectra of the 1,3,4-thiadiazolium-2-olates (IIIa and b) show a strong i.r. absorption in the 1650 cm^{-1} region which can be attributed to carbonyl stretching. This wavenumber is lower than that of the carbonyl absorption in the isosydnones (II) (1758—1770 cm^{-1}) [10] or the sydnones (1718—1770 cm^{-1}).[19] The i.r.



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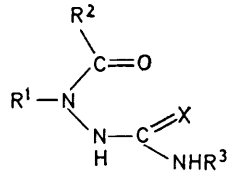
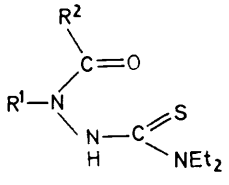


(XVIII)



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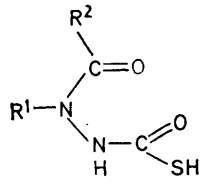

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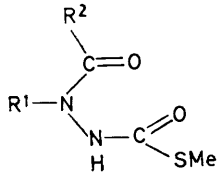
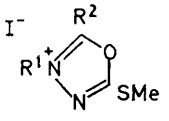


(XXI)



(XXII)

spectra of the 1,3,4-oxadiazolium-2-thiolates (IVa and b) show an absorption in the 1420 cm^{-1} region which can be attributed to thione stretching. The corresponding absorption in the 1,3,4-thiadiazolium-2-thiolates (I) occurs at 1350 cm^{-1}. The absence of NH, isocyanate, and isothiocyanate bands in the i.r. spectra of (III) and (IV) provide support for their formulation as cyclic meso-ionic structures rather than as the alternative valence tautomeric isocyanates (XIII; X or Y = O or S).

The n.m.r. spectra of compounds (III) and (IV) are consistent with their formulation as aromatic meso-ionic systems. Thus, the chemical shifts of the *N*-methyl singlets in the 4-methyl derivatives (IIIb) (τ 6·10) and (IVb) (τ 5·83) are very similar to those of the isosydnone (IIb) (τ 5·83) [10] and the 1,3,4-thiadiazolium-2-thiolate (Ib) (τ 5·96);[20] these compounds show a downfield shift (*ca.* 0·6 Hz) with respect to the *N*-methyl singlet of the *N*-acylhydrazines (Vb) (τ 6·68) and (VIIIb) (τ 6·82). This relative deshielding of the *N*-methyl substituent may be attributed to a combination of the partial positive charge associated with the heterocyclic ring and a ring current characterising the aromaticity of the meso-ionic system.

The u.v. spectra of the isomeric systems (III) and (IV) are similar to the u.v. spectra of related isosydnones (II)[10] and are consistent with a meso-ionic structure.

Mass spectrometry has been a useful tool in this study, and provides a decisive method for distinguishing between the isomeric systems (III) and (IV). Thus, the mass spectrum of (IIIb), in addition to a parent ion at *m/e* 192, shows a fragment ion at *m/e* 121 corresponding to $PhC{\equiv}\overset{+}{S}$. The mass spectrum of the isomer (IVb) also shows a parent ion at *m/e* 192, but a strong fragment ion occurs at *m/e* 105 corresponding to $PhC{\equiv}\overset{+}{O}$. Clearly the fragmentation patterns of these two molecules, (IIIb) and (IVb), are very similar, but the differences between the fragment ions are characteristic. A more detailed analysis of the fragmentation pathway of the meso-ionic systems (III) and (IV), together with a comparative examination of the mass spectra of meso-ionic compounds of the general types (XI) and (XII) will be reported.[21]

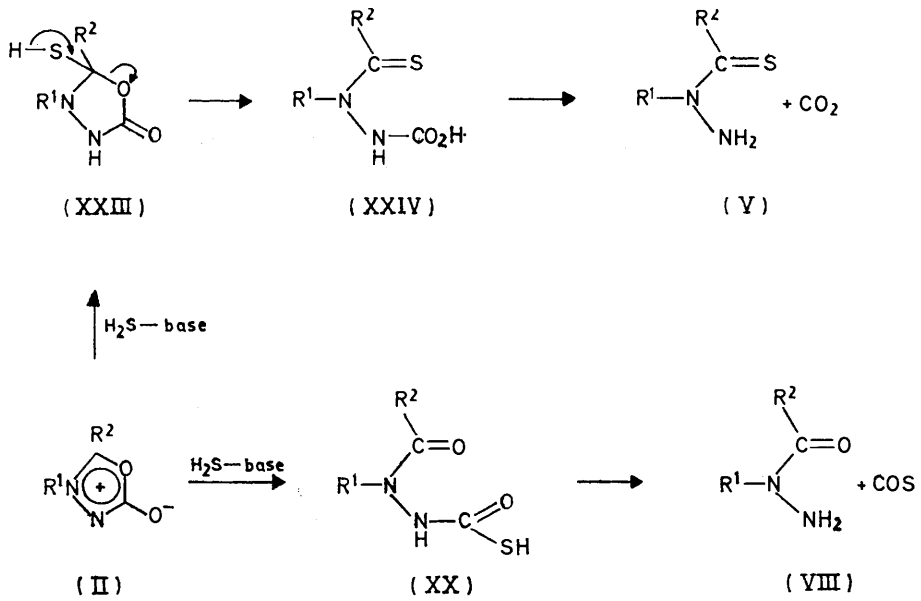
The dipole moments of derivatives of the systems (III) and (IV) in benzene solution have been measured and the results [22] are consistent with their meso-ionic formulation. Thus, spectral properties and dipole moments fully support the isomeric meso-ionic structures (III) and (IV).

The isosydnones (II) react with alcohols and amines to give urethanes and semicarbazides, respectively.[6,7] When the meso-ionic 1,3,4-thiadiazolium-2-olate (IIIa) was heated under reflux with ethanol no reaction took place; (IIIa) was also recovered unchanged after being heated with aniline at 100° for 1 h. Mild acidic hydrolysis of the isosydnone (IIa) [7] generates the *N*-acylhydrazine (VIIIa). In contrast, the 1,3,4-thiadiazolium-2-olate (IIIa) was recovered unchanged after being heated with dilute hydrochloric acid for 4 h. It appears that the 1,3,4-thiadiazolium-2-olates (III) are more stable than the isosydnones (II), and in this aspect they resemble the 1,3,4-thiadiazolium-2-thiolates (I). Some other chemical reactions of the 1,3,4-thiadiazolium-2-olates (III) have recently been reported.[16]

The 1,3,4-oxadiazolium-2-thiolates (IVa and b) have been found to react with aniline to give the 1,3,4-triazolium-2-thiolates (XVI; R^1 = Me, Ph; $R^2 = R^3$ = Ph). In this respect they resemble the 1,3,4-thiadiazolium-2-thiolates (I), which react with aniline to give the

[17] J. Sandström and I. Wennerbeck, *Acta Chem. Scand.*, 1966, **20**, 57.
[18] R. Grashey, N. Keramaris, and M. Baumann, *Tetrahedron Letters*, 1970, 5087.
[19] F. H. C. Stewart, *Chem. Rev.*, 1964, **64**, 129.
[20] W. D. Ollis and C. A. Ramsden, unpublished result.
[21] Part XIII, W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 645.
[22] C. W. Atkin, A. N. M. Barnes, P. G. Edgerley, and L. E. Sutton, *J. Chem. Soc.* (*B*), 1969, 1194.

same product (XVI).[23] The isosydnone (IIa) [7] and the 1,3,4-thiadiazolium-2-olate (IIIb) [16] have been reported to react with aniline to give the semicarbazides (XVIII; $R^1 = R^2 = R^3 = Ph$, X = O) and (XVII; $R^1 = Me$, $R^2 = R^3 = Ph$, X = O), respectively. It is reasonable to suppose that the 1,3,4-oxadiazolium-2-thiolates (IVa and b) and the 1,3,4-thiadiazolium-2-thiolates (I) react with aniline to give initially the thiosemicarbazides (XVIII; R^1 = Me or Ph, $R^2 = R^3 = Ph$, X = S) and (XVII; $R^3 = Ph$, X = S), respectively, which then undergo a rapid thermal cyclisation giving the 1,3,4-triazolium-2-thiolates (XVI). The semicarbazides (XVII and XVIII; X = O) only undergo cyclisation in the presence of a basic catalyst.[16] In the reactions (I) ⟶ (XVI) and (IV) ⟶ (XVI) involving aniline, the postulate that the thiosemicarbazides (XVII and XVIII; X = S) are intermediates is supported by the result of the reaction with diethylamine of the 1,3,4-oxadiazolium-2-thiolates (IVa and b), which yielded the thiosemicarbazides (XIX; $R^1 = R^2 = Ph$) and (XIX; $R^1 = Me$, $R^2 = Ph$), respectively.

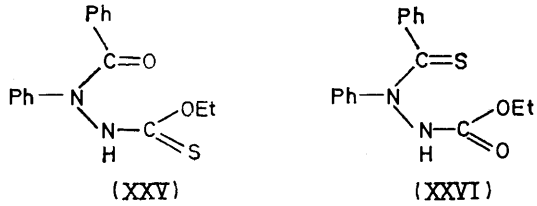


SCHEME 1

The 1,3,4-oxadiazolium-2-thiolate (IVb) when heated under reflux with water gave *N*-benzoyl-*N*-methylhydrazine (VIIIb). This reaction probably proceeds by initial hydrolytic cleavage to the thiocarbamic acid (XX; $R^1 = Me$, $R^2 = Ph$) followed by dethiocarboxylation to the hydrazine (VIIIb); this is analogous to the acid-catalysed hydrolysis of 4,5-diphenylisosydnone (IIa) to *N*-benzoyl-*N*-phenylhydrazine (VIIIa).[7]

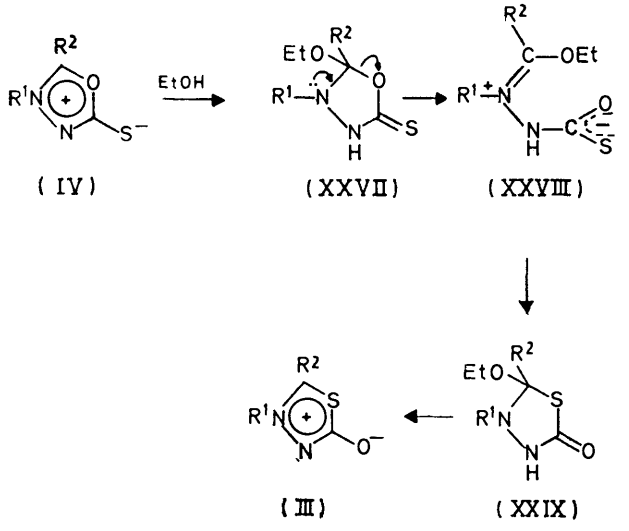
It has been found that, like the 1,3,4-thiadiazolium-2-thiolates (I), the 1,3,4-oxadiazolium-2-thiolates (IVa and b) react with methyl iodide to form methiodides (XXII). Under similar conditions, the isomeric meso-ionic compounds (III) do not form methiodides. The methiodides (XXII; $R^1 = Me$, $R^2 = Ph$ and $R^1 = R^2 = Ph$) were obtained as golden needles, but were extremely unstable and could not be recrystallised. The crystals, even at room temperature, decompose over a period of weeks giving dark, amorphous residues. The methiodide (XXII; $R^1 = Me$, $R^2 = Ph$) was identical with a sample prepared [17] from the 1,3,4-oxadiazole (XIV). The methiodides (XXII) were readily hydrolysed by water or aqueous ethanol (95%) giving the *N*-substituted *N*′-aroyl-*N*′-(methylthio)carbonylhydrazines (XXI; $R^1 = Me$, $R^2 = Ph$ and $R^1 = R^2 = Ph$). The 1,3,4-oxadiazolium-2-thiolate (IVb) did not form a hydrochloride when a solution in chloroform was treated with hydrogen chloride under various conditions.

The 1,3,4-oxadiazolium-2-thiolate (IVb) in boiling ethanol was transformed into the isomeric 1,3,4-thiadiazolium-2-olate (IIIb). This reaction was also found to proceed, but more slowly and not to completion, in t-butyl alcohol. However, no isomerisation was observed when the 1,3,4-oxadiazolium-2-thiolate (IVb) was heated in aprotic solvents such as benzene, tetrahydrofuran, or acetone, whereas the isomerisation (IVb) ⟶ (IIIb) took place smoothly in benzene–ethanethiol. When the 1,3,4-oxadiazolium-2-thiolate (IVa) was heated under reflux with ethanol, the isomeric 1,3,4-thiadiazole (IIIa) was not isolated; instead a mixture of the two acyclic ethanolysis products (XXV) and (XXVI) was formed. The mass spectrum of this mixture [(XXV) + (XXVI)]



[23] M. Ohta, H. Kato, and T. Kaneko, *Bull. Chem. Soc. Japan*, 1967, **40**, 579.

shows fragment ions at *m/e* 105 and 121 corresponding to the ions $PhC{\equiv}\overset{+}{O}$ and $PhC{\equiv}\overset{+}{S}$, respectively. This requires that the rearrangement reaction (IV) ⟶ (IIIa) takes place as well as ring cleavage by ethanol. The rearrangement (IV) ⟶ (III) probably proceeds *via* the betaine intermediate (XXVIII) [2] as shown in Scheme 2.



SCHEME 2

EXPERIMENTAL

General experimental directions are given in Part VIII.[1]

N-Thiobenzoyl-N-phenylhydrazine (Va).—Dry hydrogen sulphide was passed (2 h) into a solution of 4,5-diphenylisosydnone (IIa) (2·0 g) [10] in pyridine (5 ml) and chloroform (50 ml) at room temperature. Evaporation afforded a residual yellow oil which crystallised from ethanol and was identified as *N-thiobenzoyl-N-phenylhydrazine* (1·35 g, 71%), pale yellow needles, m.p. 116—117° (Found: M^+, 228·0725. $C_{13}H_{12}N_2S$ requires *M*, 228·0721); $\nu_{max.}$ 3350 cm^{-1}; τ 2·82 (m, 10 aromatic H) and 4·05br (s, NH_2).

N-Thiobenzoyl-N-methylhydrazine (Vb).—Dry hydrogen sulphide was passed (4 h) into a solution of 4-methyl-5-phenylisosydnone (IIb) (1·0 g) [10] and triethylamine (5 ml) in chloroform (25 ml). Concentration afforded a yellow oil which slowly crystallised. The crystals (an unidentified triethylamine derivative) were collected (0·22 g). Evaporation of the filtrate gave a residual yellow oil which was sublimed at 100° at 0·05 mmHg. The yellow solid obtained was chromatographed on 1 mm silica plates with chloroform as eluant to give *N*-benzoyl-*N*-methylhydrazide (VIIIb) (0·11 g, 13%) and *N*-thiobenzoyl-*N*-methylhydrazine (Vb) (0·4 g, 42%), needles, m.p. 90—91° (from ethanol) (lit.,[14] 91—92°) (Found: N, 16·4%; M^+, 166. Calc. for $C_8H_{10}N_2S$: N, 16·8%; *M*, 166); $\nu_{max.}$ 3220 (NH) and 1220 (C=S) cm^{-1}; τ 2·66 (m, C_6H_5), 4·00br (s, NH_2), and 6·68 (s, NMe).

4,5-Diphenyl-1,3,4-thiadiazolium-2-olate (IIIa).—Hydrogen chloride was passed (2 h) through a well-cooled solution of *N*-thiobenzoyl-*N*-phenylhydrazine (Va) (1·9 g) in chloroform (100 ml). The chloroform was evaporated off giving *N*-thiobenzoyl-*N*-phenylhydrazine hydrochloride (VIa) (2·2 g) as a bright yellow solid, m.p. 102—112°; $\nu_{max.}$ 3700—2200 cm^{-1}. *N*-Thiobenzoyl-*N*-phenylhydrazine hydrochloride (VIa) (2·1 g) and a solution of phosgene (3·5 g) in ethyl acetate (100 ml) were heated under reflux (30 min). The hydrazine hydrochloride (VIa) slowly dissolved and hydrogen chloride was evolved giving a yellow solution which afforded a yellow solid upon concentration. Recrystallisation from dioxan–ether gave the *product* (IIIa) (1·2 g, 60%), yellow prisms, m.p. 176—178° (Found: C, 66·1; H, 3·9; N, 11·3; S, 12·7%; M^+, 254. $C_{14}H_{10}N_2OS$ requires C, 66·1; H, 4·0; N, 11·0; S, 12·6%; *M*, 254); $\lambda_{max.}$ 234 and 335 nm (ε 13,300 and 6800); $\nu_{max.}$ 1653 cm^{-1}; τ 2·5—2·9 (m, aromatic H).

4-Methyl-5-phenyl-1,3,4-thiadiazolium-2-olate (IIIb).—Hydrogen chloride was passed (1 h) through a solution of *N*-thiobenzoyl-*N*-methylhydrazine (Vb) (1·35 g) in chloroform at 0°. Evaporation gave *N*-thiobenzoyl-*N*-methylhydrazine hydrochloride (VIb), which was then heated under reflux with a solution of phosgene (4·0 g) in ethyl acetate (100 ml). Vigorous evolution of hydrogen chloride took place and the solid dissolved (15 min). The solution was concentrated and the residue was collected and washed with ethyl acetate. Recrystallisation from dioxan–ether yielded the *product* (IIIb) (0·9 g, 56%), prisms, m.p. 168—170° (Found: C, 56·2; H, 4·2; N, 14·8; S, 16·65%; M^+, 192. $C_9H_{18}N_2S$ requires C, 56·2; H, 4·2; N, 14·6; S, 16·7%; *M*, 192); $\lambda_{max.}$ 232 and 317 nm (ε 7450 and 6950); $\nu_{max.}$ 1652 cm^{-1}; τ 2·42 (s, C_6H_5) and 6·10 (s, NMe).

N-Benzoyl-N-methylhydrazine (VIIIb).—*N*-Benzoyl-*N*-methylhydrazine hydrochloride (IXb) (10·0 g) [10] was stirred with water (50 ml) at room temperature and 2N-sodium hydroxide (*ca.* 25 ml) was added slowly (to pH 9). The solution was extracted with chloroform, giving *N*-benzoyl-*N*-methylhydrazine (VIIIb) (6·9 g, 86%) as crystals, m.p. 45—47° (lit.,[9] b.p. 130° at 1 mmHg) after sublimation (40—45° at 0·1 mmHg) (Found: C, 63·8; H, 6·5; N, 18·6%; M^+, 150. Calc. for $C_8H_{10}N_2O$: C, 64·0; H, 6·7; N, 18·7%; *M*, 150); $\nu_{max.}$ 1630 cm^{-1}; τ 2·60 (s, C_6H_5), 5·54br (s, NH_2), and 6·82 (s, NMe).

4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb).—*N*-Benzoyl-*N*-methylhydrazine (10·0 g) in ethanol (30 ml) was cautiously shaken with carbon disulphide (5·0 g) and aqueous ammonia (4·0 g; *d* 0·88). The mixture was kept at room temperature overnight, then the pale yellow crystals (Xb) were collected and dried under vacuum. Without further purification, the ammonium dithiocarbamate (Xb) (10·5 g) was suspended in ether (180 ml) and stirred at −5° with triethylamine (9·6 g). A solution of phosphoryl chloride (7·2 g) in ether (36 ml) was added dropwise (1 h) and the mixture allowed to come to room temperature overnight. The solid residue was collected and shaken with water (4 h). A solution of the residual solid in chloroform was then dried ($MgSO_4$) and evaporated under reduced pressure, and the product (IVb) was recrystallised twice from chloroform–ether to give pale yellow needles (2·3 g, 18%), m.p. 227—229° (lit.,[17] 227—229°), identical with a sample prepared by the method of Sandström and Wennerbeck [17] (Found: C, 56·2; H, 4·2; N, 14·65; S, 16·5. Calc. for $C_9H_8N_2OS$: C, 56·2; H, 4·2; N, 14·6; S, 16·7%); $\lambda_{max.}$ 252 and 340 nm (ε 11,900 and 6000); $\nu_{max.}$ (KBr) 1420 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—2·4 (m, C_6H_5) and 5·83 (s, NMe); $M^{\cdot+}$, 192.

4,5-Diphenyl-1,3,4-oxadiazolium-2-thiolate (IVa).—By the same procedure as in the preceding experiment, *N*-benzoyl-*N*-phenylhydrazine (VIIIa) (10·0 g) yielded compound (IVa), yellow needles (6·0 g, 50%), m.p. 175—176° [lit.,[11] 170—171° (decomp.)] (Found: C, 65·8; H, 3·9; N, 11·1; S, 13·0%; M^+, 254. Calc. for $C_{14}H_{10}N_2OS$: C, 66·1; H, 4·0; N, 11·0; S, 12·6%; *M*, 254); $\lambda_{max.}$ 255 and 363 nm

(ε 21,000 and 4800); $\nu_{max.}$ (KBr) 1420 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·1—2·6 (aromatic H).

Reaction of 4,5-Diphenyl-1,3,4-oxadiazolium-2-thiolate (IVa) *with Aniline.*—Compound (IVa) (0·2 g) and aniline (0·1 g) were heated under reflux (20 h) in toluene (10 ml) and then stirred at room temperature (36 h). The solid product was collected and recrystallised twice from ethanol–ether to give 1,4,5-triphenyl-1,3,4-triazolium-2-thiolate (XVI; $R^1 = R^2 = R^3 =$ Ph) (0·12 g, 45%), pale yellow needles, m.p. 332—333° (decomp.) (lit.,[24] 325°) (Found: S, 9·5%; M^+, 329. Calc. for $C_{20}H_{15}N_3S$: S, 9·7%; *M*, 329); $\nu_{max.}$ 1330, 1355, 1450 and 1490 cm^{-1}.

Reaction of 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb) *with Aniline.*—Compound (IVb) (0·2 g) and aniline (0·2 g) were heated under reflux (18 h) in toluene (10 ml) and then stirred at room temperature (36 h). The solid product was collected and recrystallised from ethanol–ether to give 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-thiolate (XVI; R^1 = Me, $R^2 = R^3$ = Ph) (0·4 g, 55%), m.p. 278—279° (lit.,[25] 277—278°); $\nu_{max.}$ (KBr) 1330 cm^{-1}, identical with an authentic sample.[25]

Reaction of 4,5-diphenyl-1,3,4-oxadiazolium-2-thiolate (IVa) *with Diethylamine.*—Compound (IVa) (0·5 g) was heated under reflux (3 h) with diethylamine (2·0 g) in dry benzene (50 ml). After cooling, the solution was concentrated and the crystalline product collected and recrystallised from benzene, giving *1-benzoyl-4,4-diethyl-1-phenylthiosemicarbazide* (XIX; $R^1 = R^2$ = Ph) (0·49 g, 75%), needles, m.p. 147—148° (Found: C, 66·0; H, 6·4; N, 12·7; S, 9·8%; M^+, 327. $C_{18}H_{21}N_3OS$ requires C, 66·1; H, 6·4; N, 12·8; S, 9·8%; *M*, 327); $\nu_{max.}$ 1650 cm^{-1}; τ 1·33 (s, NH), 2·3—3·0 (m, 10 aromatic H), 6·24 [q, *J* 7 Hz, $(CH_2{\cdot}CH_3)_2$], and 8·74 [t, *J* 7 Hz, $(CH_3{\cdot}CH_2)_2$].

Reaction of 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb) *with Diethylamine.*—Compound (IVb) (0·1 g) was heated under reflux (3 h) with diethylamine (1·9 g) in dry benzene (15 ml). After cooling, the crystalline product was collected and recrystallised from benzene giving *1-benzoyl-4,4-diethyl-1-methylthiosemicarbazide* (XIX; R^1 = Me, R^2 = Ph) (0·1 g, 60%), needles, m.p. 177° (Found: C, 58·65; H, 7·3; N, 16·1; S, 12·4%; M^+, 327. $C_{13}H_{19}N_3OS$ requires C, 58·9; H, 7·2; N, 15·85; S, 12·1%; *M*, 327); $\nu_{max.}$ (KBr) 1650 cm^{-1}.

Hydrolysis of 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb).—Compound (IVb) and water (25 ml) were heated under reflux (48 h); the mixture was evaporated and the residual oil was fractionated by thick-layer chromatography giving *N*-benzoyl-*N*-methylhydrazine (VIIIb), m.p. 42°; $\nu_{max.}$ 1630 cm^{-1}, identical with an authentic sample.

Reaction of 4,5-Diphenyl-1,3,4-oxadiazolium-2-thiolate (IVa) *with Methyl Iodide.*—Compound (IVa) (0·2 g) was heated under reflux (2 h) with benzene (25 ml) and methyl iodide (2·0 g). The mixture was then evaporated and the residual crystalline product was washed with methyl iodide and collected. The yellow crystals, too unstable for further purification, were identified as *2-methylthio-4,5-diphenyl-1,3,4-oxadiazolium iodide* (XXII; $R^1 = R^2$ = Ph) (0·25 g, 78%), m.p. 143—145°; $\nu_{max.}$ (KBr) 1510, 1555, and 1600 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—2·7 (m, 10 aromatic H) and 7·11 (s, SMe); *m/e* 254 ($M^{+\cdot}$ – MeI).

Reaction of 2-Methylthio-4,5-diphenyl-1,3,4-oxadiazolium Iodide (XXII; $R^1 = R^2$ = Ph) *with Water.*—Compound (XXII; $R^1 = R^2$ = Ph) (0·5 g) was dissolved in the minimum volume of boiling water and set aside for 24 h. The crystals which formed were collected and recrystallised from water to give *N-benzoyl-N'-(methylthio)carbonyl-N-phenylhydrazine* (XXI; $R^1 = R^2$ = Ph) (0·4 g, 69%), m.p. 126—127° (Found: C, 63·2; H, 5·0; N, 9·9; S, 11·4%; M^+, 286. $C_{15}H_{14}N_2O_2S$ requires C, 62·95; H, 4·9; N, 9·8; S, 11·2%; *M*, 286); $\nu_{max.}$ 1670 cm^{-1}; τ 1·65 (s, NH), 2·2—2·8 (m, 10 aromatic H), and 7·60 (s, SMe).

Reaction of 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb) *with Methyl Iodide.*—Compound (IVb) (0·2 g) was heated under reflux (2 h) with benzene (25 ml) and methyl iodide (2·0 g). The mixture was evaporated and the residue was washed with methyl iodide; the yellow crystals, too unstable for further purification, were identified as 2-methylthio-4-methyl-5-phenyl-1,3,4-oxadiazolium iodide (XXII; R^1 = Me, R^2 = Ph) (0·3 g, 86%), m.p. 165°; $\nu_{max.}$ (KBr) 1500 and 1600 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1·8—2·4 (m, 5 aromatic H), 5·67 (s, NMe), and 7·16 (s, SMe); *m/e* 192 ($M^{+\cdot}$ – MeI), identical with a sample prepared by the method of Sandström and Wennerbeck.[17]

Reaction of 2-Methylthio-4-methyl-5-phenyl-1,3,4-oxadiazolium Iodide (XXII; R^1 = Me, R^2 = Ph) *with Water.*—Compound (XXII; R^1 = Me, R^2 = Ph) (0·5 g) was dissolved in the minimum volume of hot 95% ethanol, and after cooling the solution was kept at 0° (12 h). The crystalline precipitate was collected and recrystallised from ethanol giving *N-benzoyl-N-methyl-N'-(methylthio)carbonylhydrazine* (XXI; R^1 = Me, R^2 = Ph) (0·2 g, 61%), needles, m.p. 108—110° (Found: C, 53·3; H, 5·1; N, 12·35; S, 14·4. $C_{10}H_{12}N_2O_2S$ requires C, 53·6; H, 5·4; N, 12·5; S, 14·3%); $\nu_{max.}$ (KBr) 1635 and 1700 cm^{-1}; τ 1·70 (s, NH), 2·3—2·8 (m, 5 aromatic H), 6·70 (s, NMe), and 7·70 (s, SMe); *m/e* 177 ($M^{+\cdot}$ – SMe).

Isomerisation of 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-thiolate (IVb).—(*a*) Compound (IVb) (0·4 g) was heated under reflux (3 h) in absolute ethanol (25 ml). After cooling, the solution was concentrated and kept at 0° (24 h). The crystalline product was collected, giving 4-methyl-5-phenyl-1,3,4-thiadiazolium-2-olate (IIIb) (0·33 g, 82%), identical with an authentic sample.

(*b*) Compound (IVb) (0·1 g) in dry benzene (15 ml) was heated under reflux (48 h) with ethanethiol (4·0 g). Evaporation gave a pale yellow solid which was recrystallised from ethanol yielding the thiadiazole (IIIb) (0·05 g, 50%), identical with an authentic sample.

Reaction of 4,5-Diphenyl-1,3,4-oxadiazolium-2-thiolate (IVa) *with Ethanol.*—Compound (IVa) (0·3 g) in absolute ethanol (25 ml) was gently heated under reflux (4 h). After concentration, ether was added, the mixture was set aside at 0° for 24 h, and the crystalline product was collected. This was a mixture (0·06 g, 17%), m.p. 165—172°, of *N*-benzoyl-*N'*-ethoxy(thiocarbonyl)-*N*-phenylhydrazine (XXV) and *N*-thiobenzoyl-*N'*-ethoxycarbonyl-*N*-phenylhydrazine (XXVI); $\nu_{max.}$ 1490 and 1640 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·3—3·0 (m, 10 aromatic H), 5·44 (q, *J* 7 Hz, CH_2), and 8·67 (t, *J* 7 Hz, CH_3); *m/e* 300 ($M^{+\cdot}$), 105 ($PhC{\equiv}\overset{+}{O}$), and 121 ($PhC{\equiv}\overset{+}{S}$).

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