Cyclic Meso-ionic Compounds. Part X.[1] Synthesis, Spectroscopic Properties, and Chemistry of 1,3,4-Thiadiazolium-2-aminides and their Rearrangement to 1,3,4-Triazolium-2-thiolates

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Representatives of a new class of meso-ionic heterocycles have been prepared which are derivatives (VIII) of 1,3,4-thiadiazolium-2-aminide. Their physical properties and chemical reactions are discussed, including their isomerisation to derivatives (VII) of 1,3,4-triazolium-2-thiolate.

In the preceding paper[1] we described the isomeric meso-ionic systems (IV) and (V) and their interconversion (IV) ⟶ (V) in ethanol, which we suggest takes place *via* the betaine (VI). This was the first example of constitutional isomerism exhibited by meso-ionic heterocycles of the general types (I) and (II). Our interest in meso-ionic compounds has led us to investigate the possibility of preparing other examples of constitutional isomers of the types (I) and (II).

The 1,3,4-triazolium-2-thiolates (VII) were first prepared by Busch and his co-workers[2] by the reaction of 1,3,4-thiadiazolium-2-thiolates (I; X = Y = S) with primary amines and also by the reaction of 1,4-diarylthiosemicarbazides with acid chlorides. Schönberg[3] in 1938 recognised the dipolar nature of Busch's compounds (VII)[2] and pointed out that two constitutions were possible, namely, the 1,3,4-triazolium-2-thiolate structure (VII) or, alternatively, the 1,3,4-thiadiazolium-2-aminide structure (VIII). Furthermore, Schönberg[3] interpreted the existence of two forms of some of these compounds [*e.g.* (VIIg), m.p.s 236 and 255—256°] in terms of an interconversion of the two isomeric structures (VII) and (VIII). However, it has been shown that the two forms are simply polymorphic modifications of the 1,3,4-triazolium-2-thiolates (VII).[4] Later, Baker, Ollis, and Poole[5] pointed out that the molecules [(VII) or (VIII)] belonged to the general class of meso-ionic compounds (I), but the decision between the two possible constitutional formulae (VII) and (VIII) was not made. Recently, several groups[6-8] have investigated the structure of Busch's compounds and have shown by a combination of physical and chemical methods that the correct constitution is (VII). The isomeric 1,3,4-thiadiazolium-2-aminides (VIII) have not been previously described. We now report the synthesis of the 1,3,4-thiadiazolium-2-aminides (VIII) and their isomerisation to the 1,3,4-triazolium-2-thiolates (VII).[9]

Our approach to the synthesis of the 1,3,4-thiadiazolium-2-aminides (VIII) was based on the understanding that the valence tautomer (IX) could cyclise spontaneously. The problem of synthesis was, therefore, reduced to that of discovering a route to carbodi-imides of the type (IX). Kühle[10] has described the synthesis of carbodi-imides by the reaction of primary amine hydrochlorides with isocyanide dichlorides (XI). We have therefore investigated the reaction between isocyanide dichlorides (XI) and *N*-thioacylhydrazines (XIII). A method for the preparation of *N*-thioacylhydrazines (XIII; R^1 = alkyl or aryl) from isosydnones (I; X = Y = O) has been described.[1] This method is more general than that of Jensen and his co-workers,[11] who have described a synthesis which is restricted to *N*-thioacyl-*N*-alkylhydrazines (XIII; R^1 = alkyl).

When *N*-thiobenzoyl-*N*-methylhydrazine (XIIIa) and phenyl isocyanide dichloride (XI; R^3 = Ph), in equivalent proportions, were dissolved in chloroform and heated under reflux, hydrogen chloride was evolved and the product was 2-anilino-4-methyl-5-phenyl-1,3,4-thiadiazolium chloride (Xc). By this method, the 1,3,4-thiadiazolium chlorides (Xc—f) were prepared in good yield as crystalline compounds. Their i.r. spectra show absorptions in the regions 2700—2900 and 1500—1540 cm^{-1} which can be attributed to the N–H stretching and N–H bending vibrations, respectively. An absorption in the region 1500—1600 cm^{-1} may be assigned to C=N stretching; this wavenumber is lower than that observed (1670—1700 cm^{-1}) for the salts of sydnone imines (III; X = O, Y = NH).[12] The n.m.r. spectra of the 1,3,4-thiadiazolium chlorides (X) show an NH signal at low field. In the n.m.r. spectrum of (Xf), the NH proton is coupled with the geminal *N*-methyl group giving an AX_3 system (τ_A −0·10, τ_X 7·03, J_{AX} 5 Hz).

Treatment of solutions of the pale yellow 1,3,4-thiadiazolium chlorides (X) in chloroform with ammonia gave the 1,3,4-thiadiazolium-2-aminides (VIII), obtained

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

[2] 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 E. Blume, *ibid.*, p. 257.

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

[4] K. A. Jensen and A. Friediger, *Kgl. danske Videnskab. Selskab., Mat.-fys. Medd.*, 1943, **20**, 1.

[5] W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1949, 307; W. Baker and W. D. Ollis, *Quart. Rev.*, 1957, **11**, 15.

[6] K. T. Potts, S. K. Roy, and D. P. Jones, *J. Heterocyclic Chem.*, 1965, **2**, 105; *J. Org. Chem.*, 1967, **32**, 2245.

[7] G. W. Evans and B. Milligan, *Austral. J. Chem.*, 1967, **20**, 1779.

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

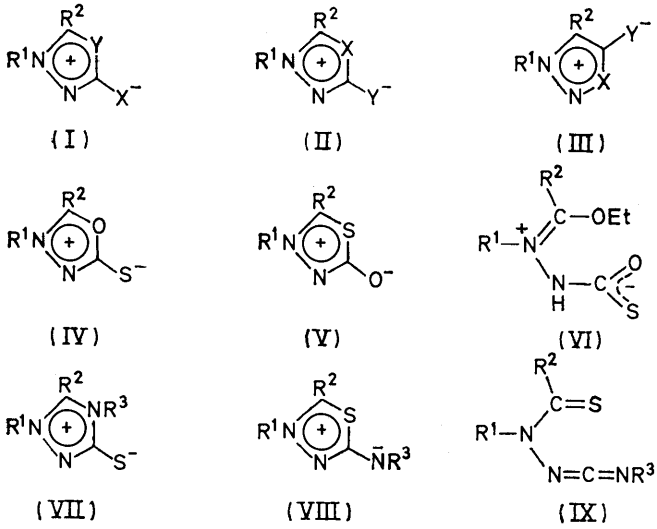
[9] W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1222.

[10] E. Kühle, G.P. 1,149,712/1961, Farbenfabriken Bayer AG.; E. Kühle, B. Anders, E. Klauke, H. Tarnow, and G. Zumach, *Angew. Chem. Internat. Edn.*, 1969, **8**, 20; E. Kühle, B. Anders, and G. Zumach, in 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic Press, New York, 1971, vol. 6, p. 127.

[11] K. A. Jensen, H. R. Baccaro, O. Buchardt, G. E. Olsen, C. Pedersen, and J. Toft, *Acta Chem. Scand.*, 1961, **15**, 1109.

[12] V. G. Yashunskii, E. M. Peresleni, and Y. N. Sheinker, *Izvest. Akad. Nauk S.S.R.*, 1962, **26**, 1295; V. G. Yashunskii and Y. N. Sheinker, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 1663.

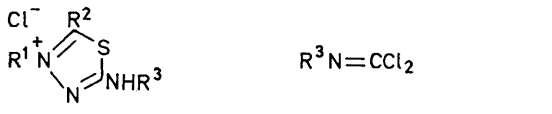
as deep red, viscous oils. The possibility that the treatment with ammonia had resulted in reactions additional to the liberation of the bases (VIII) from the hydrochlorides (X) was shown to be unlikely since the hydrochlorides (X) were regenerated by treatment of



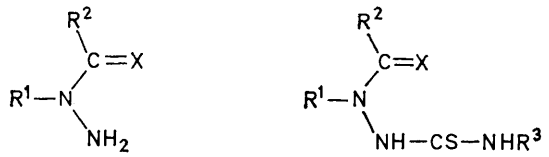
(I) (II) (III)

(IV) (V) (VI)

(VII) (VIII) (IX)



(X) (XI)



(XII) X = O (XV) X = O
(XIII) X = S (XVI) X = S
(XIV) X = NR^4 (XVII) X = NR^4

In formulae (IV)—(XVII)

a; R^1 = Me, R^2 = Ph
b; R^1 = R^2 = Ph
c; R^1 = Me, R^2 = R^3 = Ph
d; R^1 = Me, R^2 = Ph, R^3 = *p*-MeC_6H_4
e; R^1 = Me, R^2 = Ph, R^3 = *p*-ClC_6H_4
f; R^1 = R^3 = Me, R^2 = Ph
g; R^1 = R^2 = Ph, R^3 = CH_2Ph

the bases (VIII) with either hydrogen chloride in chloroform or dilute hydrochloric acid.

The spectroscopic properties of the 1,3,4-thiadiazolium-2-aminides (VIIIc—e), while not being conclusive, do support their formulation as meso-ionic compounds. Their i.r. spectra show absorption in the C=N stretching region (1550—1580 cm^{-1}) and valence tautomerism involving the structure (IX) is apparently excluded since absorption bands characteristic of NH and carbodiimide groupings ($\nu_{max.}$ 2130—2155 cm^{-1}) are absent. The n.m.r. spectra show *N*-methyl signals whose chemical shifts [(VIIIc) τ 6·14; (VIIId) τ 6·12; (VIIIe) τ 6·14] are very similar to those of similar meso-ionic compounds.[1] Their u.v. and visible spectral characteristics are exemplified by those of compound (VIIIc) [$\lambda_{max.}$ 254 (ε 11,300) and 408 nm (4100)]. The compounds (VIIIc—e) all show molecular ions in their mass spectra and a characteristic fragment ion (*m/e* 121) corresponding to $PhC\equiv\overset{+}{S}$. The dipole moment for compound (VIIIc) in benzene solution is 6·68 D $\pm$ 0·05,[13] in good accord with its meso-ionic structure.

The successful synthesis of compounds (VIII) encouraged their direct comparison with the 1,3,4-triazolium-2-thiolates (VII). The latter have been extensively studied, and methods for their synthesis are well documented.[2,6-8] A standard route for their preparation involves thermal cyclodehydration of thiosemicarbazides (XV), prepared[6,14] from *N*-acylhydrazines (XII) and aryl or alkyl isothiocyanates; this method was used for the synthesis of compounds (VIIc and f). During our present studies, two new routes to compounds of type (VII) have been discovered, and these were used to prepare compounds (VIId and e). *N*-Thioacylhydrazines (XIII) and aryl isothiocyanates give 1,3,4-triazolium-2-thiolates (VII) directly at room temperature. This transformation presumably involves the thiosemicarbazide (XVI) as a highly reactive intermediate which easily loses H_2S. This is in accord with expectation, but the other reaction is more surprising. *N*-Amino-*N*-methyl-*N'*-phenylbenzamidine (XIV; R^1 = Me, R^2 = R^4 = Ph) and aryl isothiocyanates also give 1,3,4-triazolium-2-thiolates (VII) directly at room temperature. This transformation also presumably involves a thiosemicarbazide (XVII) as intermediate, but surprisingly the formation of the product (VII) involves elimination of R^4NH_2 rather than H_2S.

These representative 1,3,4-triazolium-2-thiolates (VII) and 1,3,4-thiadiazolium-2-aminides (VIII) provide further examples of pairs of meso-ionic isomers structurally related by exchange of exocyclic and endocyclic heteroatoms or groupings. The two series exhibit some striking differences in physical and chemical properties.

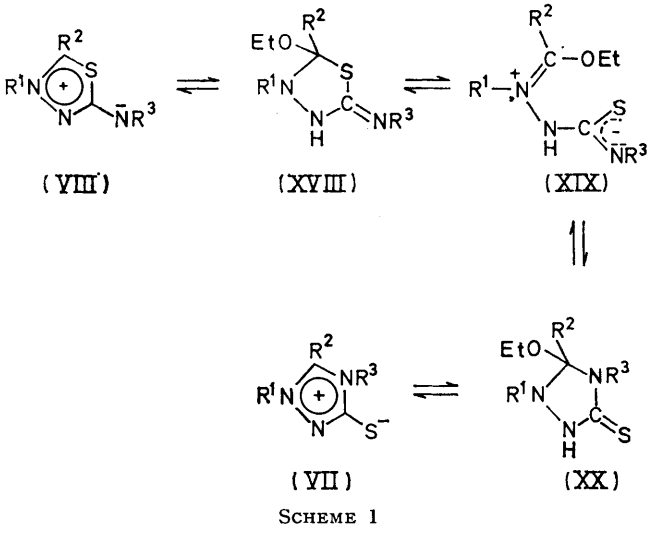
The 1,3,4-triazolium-2-thiolates (VII) are colourless, crystalline compounds with high melting points, whereas the 1,3,4-thiadiazolium-2-aminides (VIII) are red, viscous oils. The i.r. spectra of the compounds (VII) show absorption ($\nu_{max.}$ 1320—1330 cm^{-1}) attributable to C=S stretching and their u.v. spectra are exemplified by that of compound (VIIc) [$\lambda_{max.}$ 240 (ε 16,800) and 314 nm (3100)]. The mass spectra of corresponding isomers (VII) and (VIII) show some striking similarities as well as informative differences. They both show parent ions and a common fragment ion, $R^1\overset{+}{N}\equiv CR^2$. Compounds (VII) show the fragment ion $R^2C\equiv\overset{+}{N}R^3$, whereas compounds (VIII) show a different fragment ion, $R^2C\equiv\overset{+}{S}$.

[13] W. D. Ollis, C. A. Ramsden, and L. E. Sutton, forthcoming publication.

[14] R. L. Hinman and D. Fulton, *J. Amer. Chem. Soc.*, 1958, **80**, 1895.

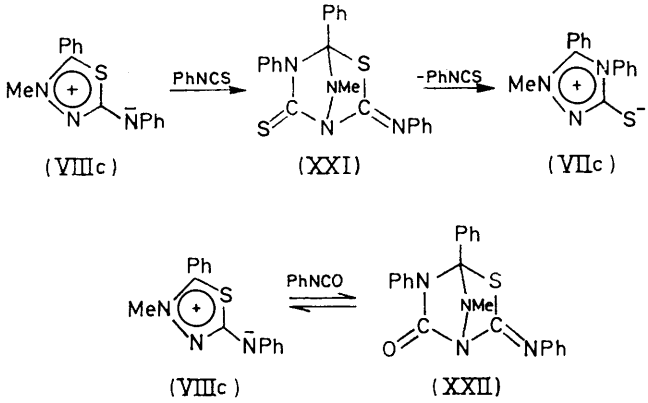
The isomerisation (VIII) ⟶ (VII) is achieved in almost quantitative yield by gentle heating in ethanol. This constitutes a further example of the interconversion (I) ⟶ (II) and the proposed mechanism (Scheme 1) again involves a betaine intermediate.[1] The alternative possibility was considered that the thiosemicarbazides (XV) were intermediates in the isomerisation (VIII) ⟶ (VII). This required the presence of a trace of water in the ethanol which was certainly a possibility. However, the thiosemicarbazides (XV) could be excluded as intermediates since they were not transformed in ethanolic solution at room temperature into compounds (VII), whereas even under these mild conditions the isomerisation (VIII) ⟶ (VII) still occurred. The ease of the isomerisation (VIIIf) ⟶ (VIIf) is such that we have been unable to isolate compound (VIIIf). Treatment of the 1,3,4-thiadiazolium chloride (Xf) with anhydrous ammonia in chloroform solution did not give the expected product (VIIIf), but yielded the isomer (VIIf) directly. The isomerisation (VIII) ⟶ (VII) may also be achieved using other basic reagents including warm aqueous 2N-sodium hydroxide or a warm solution of aniline in chloroform.

Two further methods of effecting the isomerisation (VIII) ⟶ (VII) have been discovered: they involve reaction mechanisms which are certainly different from those outlined in Scheme 1. When a solution of the



SCHEME 1

1,3,4-thiadiazolium-2-aminide (VIIIc) in benzene is treated with an excess of phenyl isothiocyanate at room temperature, the isomer (VIIc) is precipitated in high yield during a few minutes. In a control experiment, in the absence of phenyl isothiocyanate, no change was observed after 12 h. This isomerisation is novel in that it probably involves the bicyclic compound (XXI) (Scheme 2) as an intermediate, which by a 1,3-elimination of phenyl isothiocyanate then yields the thermodynamically more stable isomer (VIIc). The 1,3-dipolar cycloaddition between phenyl isothiocyanate and compound (VIIIc) leading to the intermediate (XXI) has ample precedent in the 1,3-dipolar cycloadditions exhibited by other meso-ionic compounds including the



SCHEME 2

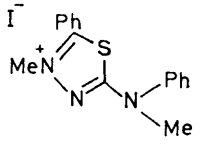
sydnones (III; X = Y = O)[15] and the isosydnones (I; X = Y = O).[16] Attempts to isolate the cycloadduct (XXI) have not been rewarded. However, opinion regarding the mechanism of this reaction (Scheme 2) was shown to be well-based because reaction between the 1,3,4-thiadiazolium-2-aminide (VIIIc) and phenyl isocyanate in benzene solution at room temperature rapidly yielded the crystalline cycloadduct (XXII). This substance was stable for several months at room temperature in the solid state, but it could not be recrystallised. When dissolved in chloroform, it rapidly reverted to the original 1,3,4-thiadiazolium-2-aminide (VIIIc) and phenyl isocyanate. No trace of compound (I; R^1 = Me, R^2 = Ph, Y = NPh, X = O) was detected in this reaction. The isolation of the cycloadduct (XXII) is excellent support for the mechanism proposed (Scheme 2) for the isomerisation (VIIIc) ⟶ (VIIc) promoted by phenyl isothiocyanate. This mechanism is also possibly relevant to a mechanistic interpretation of the following result. When the red liquid 1,3,4-thiadiazolium-2-aminide (VIIIc) is heated to 120°, it is almost immediately transformed into a colourless solid which is the isomer (VIIc).

The meso-ionic compounds (VII) and (VIII) show informative differences in their reactions towards methyl iodide. The 1,3,4-thiadiazolium-2-aminide (VIIIc) gives the methiodide (XXIII), m.p. 115° (τ_{NMe} 6·34). The isomer (VIIc) gives the methiodide (XXIV), m.p. 210° (τ_{SMe} 7·25). The compounds (VII) and (VIII) are basic towards mineral acid, and the transformation (VIII) ⟶ (X) has been mentioned earlier. Compound (VIIIc) gives a crystalline nitrate with dilute nitric acid; this recalls the use of 'nitron' (I; R^1 = Ph, R^2 = H, X = Y = NPh) as a specific precipitant for nitrates.[17]

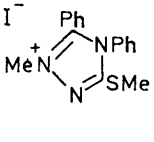
Compounds (VII) and (VIII) exhibit different reactions

[15] R. Huisgen, *Chem. Soc. Special Publ.*, No. 21, 1967, p. 51.
[16] Part VIII, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624.
[17] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis, Longmans, London, 3rd edn., 1962, p. 131.

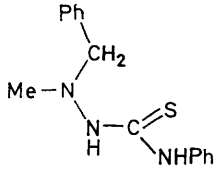
with lithium aluminium hydride in dioxan. The 1,3,4-thiadiazolium-2-aminide (VIIIc) is reduced to the known thiosemicarbazide [18] (XXV), whereas the isomeric 1,3,4-triazolium-2-thiolate (VIIc) yields the triazolidine (XXVI). The structural relation between the triazolidine (XXVI) produced by nucleophilic hydride and



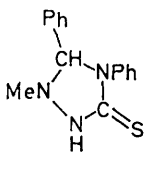
(XXIII)



(XXIV)



(XXV)



(XXVI)

the postulated intermediates (XVIII) and (XX) given in Scheme 1 provides some support for the proposals (Scheme 1) for the interconversion (VIII) ⟶ (VII).

A detailed survey of the mass spectra of 1,3,4-thiadiazolium-2-aminides (VIII) with other classes of meso-ionic compounds and the examination of the dipole moments of 1,3,4-triazolium-2-thiolates (VII) and 1,3,4-thiadiazolium-2-aminides (VIII) will be reported.[13]

EXPERIMENTAL

General experimental directions are given in Part VIII.[16]

2-Amino-1,3,4-thiadiazolium Chlorides (X).—A solution of *N*-thiobenzoyl-*N*-methylhydrazine [11] (XIIIa) (1·0 g) and phenyl isocyanide dichloride [19] (1·0 g) in chloroform (30 ml) was heated under reflux (45 min) with stirring. The solvent was evaporated off and the residual yellow oil washed with ether. The residue, which solidified, was crystallised from ethanol–ether. Recrystallisation gave *2-anilino-4-methyl-5-phenyl-1,3,4-thiadiazolium chloride* (Xc) (1·31 g, 72%), pale yellow rods, m.p. 195—196° (Found: C, 59·6; H, 4·6; Cl, 12·0; N, 13·6; S, 10·8. $C_{15}H_{14}ClN_3S$ requires C, 59·3; H, 4·6; Cl, 11·7; N, 13·8; S, 10·5%); $\lambda_{max.}$ 265 and 340 nm (ε 18,700 and 9200); $\nu_{max.}$ 1525 cm^{-1}; τ 2·1—3·0 (m, 10 aromatic H), τ 5·80 (s, NMe) and −2·67 (s, NH); *m/e* 267 ($M^{\cdot+}$ − HCl).

The following compounds were similarly prepared from *p*-tolyl isocyanide dichloride (XI; R^3 = *p*-tolyl),[20] *p*-chlorophenyl isocyanide dichloride (XI; R^3 = *p*-ClC_6H_4) [21] and methyl isocyanide dichloride (XI; R^3 = Me),[22] respectively: *4-methyl-5-phenyl-2-p-tolylamino-1,3,4-thiadiazolium chloride* (Xd) (1·15 g, 69%), yellow rods, m.p. 213° (Found: C, 61·0; H, 5·0; N, 13·0. $C_{16}H_{16}ClN_3S$ requires C, 60·5; H, 5·0; N, 13·2%); $\lambda_{max.}$ 268 and 346 nm (ε 21,000 and 8800); $\nu_{max.}$ 1510 and 1560 cm^{-1}; τ ($CDCl_3$–CF_3·CO_2H) 2·2—3·0 (m, 9 aromatic H), 5·83 (s, NMe), 7·67 (s, Me), and −4·37 (s, NH); *m/e* 281 ($M^{\cdot+}$ − HCl); *2-p-chloroanilino-4-methyl-5-phenyl-1,3,4-thiadiazolium chloride* (Xe) (1·33 g, 65%), bright yellow needles, m.p. 220° (Found: C, 53·2; H, 3·8; Cl, 20·8; N, 12·3; S, 9·6. $C_{15}H_{13}Cl_2N_3S$ requires C, 53·3; H, 3·85; Cl, 21·0; N, 12·4; S, 9·5%); $\nu_{max.}$ 1520 and 1555 cm^{-1}; τ ($CDCl_3$–CF_3·CO_2H) 2·29 (s, C_6H_5), 2·56 (m, 4 aromatic H), 5·80 (s, NMe), and −4·32br (s, NH); *m/e* 301 ($M^{\cdot+}$ − HCl) (^{35}Cl); *4-methyl-2-methylamino-5-phenyl-1,3,4-thiadiazolium chloride* (Xf) (0·83 g, 57%), needles, m.p. 201—202° (Found: C, 50·0; H, 4·9; Cl, 14·4; N, 17·5; S, 13·1. $C_{10}H_{12}ClN_3S$ requires C, 49·7; H, 5·0; Cl, 14·7; N, 17·4; S, 13·25%); $\lambda_{max.}$ 254 and 319 nm (ε 6700 and 8900); $\nu_{max.}$ 1600 cm^{-1}; τ 2·1—2·4 (m, C_6H_5), 5·80 (s, NMe), 7·03 (d, *J* 5 Hz, NMe), and −0·10 (q, *J* 5 Hz, NH); *m/e* 205 ($M^{\cdot+}$ − HCl).

1,3,4-Thiadiazolium-2-aminides (VIII).—Dry ammonia gas was passed over a suspension of 2-anilino-4-methyl-5-phenyl-1,3,4-thiadiazolium chloride (Xc) (1·0 g) in chloroform (20 ml). A bright red colour developed immediately and ammonium chloride was deposited. The solution was filtered and the filtrate was evaporated, giving a deep red oil. The oil, after drying under vacuum (P_2O_5), solidified to a bright red glass, *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-anilide* (VIIIc) (0·86 g, 98%) (Found: M^+, 267·0834. $C_{15}H_{13}N_3S$ requires *M*, 267·0830); $\lambda_{max.}$ 254 and 408 nm (ε 11,300 and 4100); $\nu_{max.}$ 1570 cm^{-1}; τ 2·4—3·1 (m, 10 aromatic H) and 6·14 (s, NMe).

The following compounds were similarly prepared: *4-methyl-5-phenyl-2-p-tolylamino-1,3,4-thiadiazolium-2-p-toluidide* (VIIId) (0·84 g, 95%), bright red oil (Found: M^+, 281·0990. $C_{16}H_{15}N_3S$ requires *M*, 281·0987); $\lambda_{max.}$ 253 and 410 nm (ε 13,300 and 4000); $\nu_{max.}$ 1575 cm^{-1}; τ 2·50 (s, C_6H_5), 2·88 (s, C_6H_4), 6·12 (s, NMe), and 7·70 (s, Me); *m/e* 281 ($M^{\cdot+}$) and 121 ($PhC{\equiv}\overset{+}{S}$); *4-methyl-5-phenyl-1,3,4-thiadiazolium-2-p-chloroanilide* (VIIIe) (0·85 g, 95%) (Found: M^+, 301·0438. $C_{15}H_{12}{}^{35}ClN_3S$ requires *M*, 301·0440); $\nu_{max.}$ 1565 cm^{-1}; τ 2·4—3·0 (m, 9 aromatic H) and 6·14 (s, NMe); *m/e* 301 ($M^{\cdot+}$) and 121 ($PhC{\equiv}\overset{+}{S}$).

Reaction of 4-Methyl-2-methylamino-5-phenyl-1,3,4-thiadiazolium Chloride (Xf) *with Ammonia.*—Dry ammonia was passed over a solution of compound (Xf) (1·0 g) in chloroform (20 ml). A yellow colouration immediately developed, suggesting that the 1,3,4-thiadiazolium-2-methylaminide (VIIIf) had been generated, but the colour faded within a few seconds. Ammonium chloride was removed and the mixture evaporated; the residue was crystallised from chloroform–ether to give 1,4-dimethyl-5-phenyl-1,3,4-triazolium-2-thiolate (VIIf) (0·71 g, 84%), leaflets, m.p. 280° (lit.,[6] 270—272°) (Found: C, 58·4; H, 5·2; N, 20·4; S, 15·6%; M^+, 205. Calc. for $C_{10}H_{11}N_3S$: C, 58·5; H, 5·4; N, 20·5; S, 15·6%; *M*, 205); $\nu_{max.}$ 1325 cm^{-1}; τ 2·29 (s, C_6H_5), 6·20 (s, NMe), and 6·40 (s, NMe).

1,3,4-Triazolium-2-thiolates (VII).—(*a*) *p*-Tolyl isothiocyanate (0·6 g) was added to a solution of *N*-amino-*N*-methyl-*N'*-phenylbenzamidine [6] (XIV; R^1 = Me, R^2 = R^4 = Ph) (0·9 g) in absolute alcohol (20 ml). After 12 h at room temperature, the crystals which had formed were collected. Recrystallisation from ethanol–ether gave *4-methyl-5-phenyl-1-p-tolyl-1,3,4-triazolium-2-thiolate* (VIId) (0·47 g, 42%), needles, m.p. 255—257° (Found: C, 68·1; H, 5·2; N, 14·8; S, 11·7%; M^+, 281. $C_{16}H_{15}N_3S$ requires

[18] R. L. Hinman, *J. Amer. Chem. Soc.*, 1956, **78**, 2463.
[19] R. S. Bly, G. A. Perkins, and W. L. Lewis, *J. Amer. Chem. Soc.*, 1922, **44**, 2896.
[20] G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 1940, 191.
[21] E. Kühle, B. Anders, and G. Zumach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 649.
[22] K. A. Petrov and A. A. Neĭmysheva, *Zhur. obshchei Khim.*, 1959, **29**, 2165.

C, 68·3; H, 5·4; N, 15·0; S, 11·4%; *M*, 281); $\lambda_{max.}$ 238 and 314 nm (ε 16,600 and 3100); $\nu_{max.}$ 1330 cm^{-1}; τ 2·50 (s, C_6H_5), 2·75 (s, C_6H_4), 6·16 (s, NMe), and 7·67 (s, Me).

(*b*) Compound (VIId) (0·60 g, 68%) was similarly prepared from *N*-thiobenzoyl-*N*-methylhydrazine (XIIIa) (0·5 g) and *p*-tolyl isothiocyanate (0·5 g).

1-p-*Chlorophenyl*-4-*methyl*-5-*phenyl*-1,3,4-*triazolium*-2-*thiolate* (VIIe).—(*a*) *p*-Chlorophenyl isothiocyanate (0·8 g) was added to *N*-amino-*N*-methyl-*N'*-phenylbenzamide [6] (XIV; R^1 = Me, R^2 = R^4 = Ph) (1·0 g) in ethanol (20 ml). The *product* (VIIe) was recrystallised from ethanol–ether; yield 0·63 g (59%), needles, m.p. 268° [Found: C, 60·2; H, 4·05; Cl, 12·1; N, 13·7; S, 11·0%; M^+, 301 (^{35}Cl). $C_{15}H_{12}ClN_3S$ requires C, 59·7; H, 4·0; Cl, 11·8; N, 13·9; S, 10·6%; *M*, 301 (^{35}Cl)]; $\lambda_{max.}$ 221, 239, and 318 nm (ε 20,850, 19,300, and 3300); $\nu_{max.}$ 1330 cm^{-1}; τ 2·3—2·8 (m, 9 aromatic H) and 6·28 (s, NMe).

(*b*) Compound (VIIe) (0·72 g, 80%) was similarly prepared from *N*-thiobenzoyl-*N*-methylhydrazine (XIIIa) (0·5 g) and *p*-chlorophenyl isothiocyanate (0·5 g).

Reaction of 1,3,4-*Thiadiazolium*-2-*aminides* (VIII) *with Ethanol*.—(*a*) 4-Methyl-5-phenyl-1,3,4-thiadiazolium-2-anilide (VIIIc) (1·0 g) was heated under reflux (2 h) with absolute ethanol (50 ml). The red colouration slowly faded. On cooling, colourless crystals were deposited and a second fraction was obtained by concentration. Recrystallisation from ethanol–ether gave 1,5-diphenyl-4-methyl-1,3,4-triazolium-2-thiolate (VIIc) (0·90 g, 90%), needles, m.p. 286—287° (lit.,[6] 277—278°) (Found: C, 67·25; H, 4·6; N, 16·0; S, 12·0%; M^+, 267. Calc. for $C_{15}H_{13}N_3S$: C, 67·4; H, 4·9; N, 15·7; S, 12·0%; *M*, 267); $\lambda_{max.}$ 240 and 314 nm (ε 16,800 and 3100); $\nu_{max.}$ 1330 cm^{-1}; τ 2·56 (s, C_6H_5), 2·62 (s, C_6H_5), and 6·17 (s, NMe), identical with an authentic sample.[6]

(*b*) A solution of compound (VIIIc) (1·0 g) in absolute ethanol (25 ml) was kept at room temperature (168 h). The red colour faded and the colourless needles which separated were collected and identified as the isomer (VIIc) (0·68 g, 68%), m.p. 286°.

The following compounds rearranged similarly in ethanol: 4-methyl-5-phenyl-1,3,4-thiadiazolium-2-*p*-toluidide (VIIId) gave 4-methyl-5-phenyl-1-*p*-tolyl-1,3,4-triazolium-2-thiolate (VIId) (0·87 g, 87%), m.p. 255—257°; $\nu_{max.}$ 1330 cm^{-1}, identical with an authentic sample (see above); 4-methyl-5-phenyl-1,3,4-thiadiazolium-2-*p*-chloroanilide (VIIIe) gave 1-*p*-chlorophenyl-4-methyl-5-phenyl-1,3,4-triazolium-2-thiolate (VIIe) (0·80 g, 80%), m.p. 268°; $\nu_{max.}$ 1330 cm^{-1}, identical with an authentic sample (see above).

Reactions of 4-*Methyl*-5-*phenyl*-1,3,4-*thiadiazolium*-2-*anilide* (VIIIc).—(a) *With aniline*. Compound (VIIIc) (0·5 g) in chloroform (20 ml) was heated under reflux (0·5 h) with aniline (1·0 g). The solution became colourless and on cooling and adding ether, 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-thiolate (VIIc) (0·30 g, 60%) was deposited, m.p. 286—287°, identical with an authentic sample.[6]

(b) *With sodium hydroxide*. Compound (VIIIc) (0·5 g) was stirred with 2N-sodium hydroxide (10 ml). The red oil was insoluble at first, but on heating under reflux a colourless solid formed. Extraction with chloroform, evaporation, and recrystallisation of the residue from chloroform–ether gave 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-thiolate (VIIc) (0·30 g, 60%), m.p. 285—287°, identical with an authentic sample.[6]

(c) *With phenyl isothiocyanate*. Compound (VIIIc) (0·4 g) was dissolved in sodium-dried benzene (10 ml) and phenyl isothiocyanate (0·5 g) was added. After several minutes at room temperature, a colourless solid began to separate. When the reaction was complete (30 min), the precipitate was collected and recrystallised from ethanol giving 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-thiolate (VIIc) (0·25 g, 62%), m.p. 287°, identical with an authentic sample.[6] An experiment in which the phenyl isothiocyanate had been omitted showed no change after 12 h.

(d) *With phenyl isocyanate*. Compound (VIIIc) (0·5 g) in benzene (10 ml) was stirred with phenyl isocyanate (2·0 g) at room temperature. A crystalline product immediately formed and the solution turned from deep red to pale yellow. The precipitate was collected, washed with ether, and dried giving 2,3,5,6-*tetrahydro*-2,3-*diphenyl*-6-*phenylimino*-2,5-*methylepimino*-1,3,5-*thiadiazin*-4-*one* (XXII) (0·52 g, 72%) as minute, pale yellow needles, m.p. 130—131° (Found: C, 68·1; H, 4·9; N, 14·2; S, 8·4. $C_{22}H_{18}N_4OS$ requires C, 68·4; H, 4·7; N, 14·5; S, 8·3%); $\nu_{max.}$ (KBr) 1340, 1490, 1550, and 1650 cm^{-1}.

(e) *Thermal rearrangement*. Compound (VIIIc) (0·5 g) was slowly heated in an oil-bath. At 120° the red oil rapidly formed a colourless solid which was recrystallised from ethanol–ether giving 4-methyl-1,5-diphenyl-1,3,4-triazolium-2-thiolate (VIIc) (0·40 g, 80%), m.p. 286—287°, identical with an authentic sample.[6]

(f) *With methyl iodide*. A solution of compound (VIIIc) (0·2 g) and methyl iodide (2·0 g) in benzene (20 ml) was heated under reflux (1 h) with stirring. After removal of the benzene, the product was recrystallised from chloroform–ether giving 4-*methyl*-2-N-*methylanilino*-5-*phenyl*-1,3,4-*thiadiazolium iodide* (XXIII) (0·16 g, 53%), pale yellow needles, m.p. 115° (Found: C, 46·9; H, 4·1; N, 10·1. $C_{16}H_{16}IN_3S$ requires C, 46·95; H, 3·9; N, 10·3%); $\nu_{max.}$ 1520—1560 cm^{-1}; τ 1·9—2·6 (m, 10 aromatic H), 5·75 (s, NMe), and 6·34 (s, NMe); *m/e* 267 ($M^{\cdot+}$ − MeI).

(g) *With hydrogen chloride*. Hydrogen chloride was passed through a solution of compound (VIIIc) (0·5 g) in chloroform (15 ml). The red colouration rapidly faded giving a pale yellow solution. Evaporation and recrystallisation from ethanol–ether gave 2-anilino-4-methyl-5-phenyl-1,3,4-thiadiazolium chloride (Xc) (0·51 g, 90%), pale yellow needles, m.p. 195°, identical with an authentic sample (see above).

(h) *With dilute nitric acid*. Compound (VIIIc) (0·5 g) was stirred with hot 2N-nitric acid (20 ml). A colourless solid which separated almost immediately was collected and recrystallised from ethanol–water giving 2-*anilino*-4-*methyl*-5-*phenyl*-1,3,4-*thiadiazolium nitrate* (0·40 g, 64%), pale yellow plates, m.p. 225—226° (Found: C, 54·9; H, 4·1; N, 17·2. $C_{15}H_{14}N_4O_3S$ requires C, 54·6; H, 4·2; N, 17·0%); $\lambda_{max.}$ 264 and 333 nm (ε 17,300 and 7850); $\nu_{max.}$ (KBr) 1520 and 1560 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·1—2·9 (m, 10 aromatic H), 5·83 (s, NMe), and 0·04br (s, NH); *m/e* 312 ($M^{\cdot+}$ − H_2O).

(i) *With lithium aluminium hydride*. Compound (VIIIc) (1·0 g) in dry dioxan (30 ml) was stirred with lithium aluminium hydride (100 mg) and the mixture was gently heated under reflux until the solution became colourless (10 min). After cooling, the excess of lithium hydride was destroyed by adding water (25 ml), dropwise at first, and inorganic residues were dissolved by adding a minimal volume of 2N-sodium hydroxide. The aqueous solution was extracted with chloroform and evaporated; crystallisation of the residue from ethanol gave 1-benzyl-1-methyl-4-phenylthiosemicarbazide (0·64 g, 63%), prisms, m.p.

143—144° (lit.,[18] 145—146·5°) (Found: C, 66·8; H, 5·9; N, 15·9. Calc. for $C_{15}H_{17}N_3S$: C, 66·4; H, 6·3; N, 15·5%); $\nu_{max.}$ 1520 cm^{-1}; τ 1·05 (s, NH), 1·77 (s, NH), 2·6—3·0 (m, 10 aromatic H), 6·12 (AA′, CH_2), and 7·31 (s, Me), identical with an authentic sample.[18]

Reaction of 4-*Methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-*thiolate* (VIIc) *with Methyl Iodide.*—A solution of compound (VIIc) (1·0 g) in ethanol (25 ml) was heated under reflux (6 h) with methyl iodide (2·0 g). The mixture was the evaporated and the residue was recrystallised from ethanol giving 4-*methyl*-2-*methylthio*-1,5-*diphenyl*-1,3,4-*triazolium iodide* (XXIV) (0·66 g, 43%), prisms, m.p. 210° (Found: C, 46·9; H, 3·7; I, 31·3; N, 10·0. $C_{16}H_{16}IN_3S$ requires C, 46·95; H, 3·9; I, 31·1; N, 10·3%); $\nu_{max.}$ 2900 cm^{-1}; τ 2·0—2·7 (m, 10 aromatic H), 5·90 (s, NMe), and 7·25 (s, SMe); *m/e* 267 ($M^{\cdot+}$ — MeI).

Reduction of 4-*Methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-*thiolate* (VIIc) *with Lithium Aluminium Hydride.*—Compound (VIIc) (0·5 g) was stirred under reflux with dioxan (10 ml) and lithium aluminium hydride (50 mg) was added. After 10 min, the solution was cooled to room temperature and the excess of lithium aluminium hydride was destroyed. Extraction with chloroform, evaporation, and crystallisation from chloroform–ether gave 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolidine*-2-*thione* (XXVI) (0·20 g, 40%) as prisms, m.p. 152—153° (Found: C, 66·7; H, 5·3; N, 15·5; S, 12·1%; M^+, 269. $C_{15}H_{15}N_3S$ requires C, 66·9; H, 5·6; N, 15·6; S, 11·9%; *M*, 269); $\lambda_{max.}$ 261 nm (ε 13,700); $\nu_{max.}$ (KBr) 1255 and 1275 cm^{-1}; τ 0·94br (s, NH), 2·72 (m, 10 aromatic H), 4·52 (s, CH), and τ 7·30 (s, Me).

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