Cyclic Meso-ionic Compounds. Part 16.[1a] Synthesis, Spectroscopic Properties, and Chemistry of 1,2,3,4-Oxatriazolium-5-thiolates, 1,2,3,4-Thiatriazolium-5-olates, and 1,2,3,4-Thiatriazolium-5-thiolates [1b]

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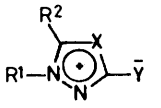
Three new classes of meso-ionic heterocycle, 1,2,3,4-oxatriazolium-5-thiolates (9), 1,2,3,4-thiatriazolium-5-olates (10), and 1,2,3,4-thiatriazolium-5-thiolates (11), have been prepared and their physical and chemical properties examined.

When the term meso-ionic was first introduced,[2] a general type of meso-ionic heterocycle with the structure (1; X or Y = NR, O, S) was recognised. The meso-ionic 1,3,4-thiadiazolium-2-thiolates (1; X = Y = S) [3]



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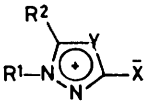


(2)

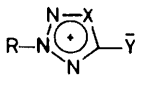
a; X = O, Y = S
b; X = S, Y = NR^3
c; X = NR^3, Y = NR^4

and 1,2,4-triazolium-3-aminides (1; X = NR^1, Y = NR^2) [4] belonged to this class and the possible existence of new types was predicted. Subsequently, the preparation and properties of all nine of the possible meso-ionic systems (I; X or Y = NR, O, or S) have been reported and several examples of the interconversion (1 ⟶ 2) have been discovered.[4-9] Our interest in meso-ionic systems has now led us to investigate another class of meso-ionic molecule which has the general structure (3) and to examine the possibility of isomerism of structures of the type (3) and (4). We now report the preparation of new meso-ionic systems belonging to the general class (3) and their interconversion (3 ⟶ 4).

A route to the meso-ionic 3-aryl-1,2,3,4-oxatriazolium-5-olates (5; R = aryl), although not recognised as such, was encountered as early as 1896 by von Pechmann, who treated potassium phenylhydrazonomethanedisulphonate [PhNH·N=C($SO_3^-K^+$)$_2$] with nitrous acid.[10] The 3-aryl derivatives (5; R = aryl) have also been prepared by the reaction of diazonium salts with nitroform [$HC(NO_2)_3$] or the potassium salt of dinitromethane [$K^+\{HC(NO_2)_2\}$].[11] The 3-alkyl compounds (5; R = alkyl) can be prepared by the condensation of *N*-nitroso-*N*-alkyl hydrazines (6) with phosgene [12] or by treatment of 1-alkylsemicarbazides (7) with nitrous acid. In the latter preparation, the intermediate *N*-nitroso-*N*-alkylsemicarbazides (8) have been isolated at low temperature.[13]

In spite of the variety of preparative routes to the oxatriazolium olates (5), no preparation of the closely related monothio-(9) and (10) or dithio-compounds (11) have been reported. We now report the successful synthesis of 3-aryl derivatives of the 1,2,3,4-oxatriazolium-5-thiolates (9), 1,2,3,4-thiatriazolium-5-olates (10), and 1,2,3,4-thiatriazolium-5-thiolates (11).

In analogy to the preparation of the oxatriazolium-olates (5) from 1-alkylsemicarbazides (7) and nitrous acid,[13] the thiolates (9) are prepared by nitrosation of arylhydrazinium salts of the 3-aryldithiocarbazates (12). The salts (12), formed by treatment of arylhydrazines with carbon disulphide, were suspended in chloroform and addition of hydrochloric acid and sodium nitrite gave the meso-ionic oxatriazoliumthiolates (9a—e). This reaction may well proceed *via* the nitrosoaryldithiocarbazates (13) which cyclise with elimination of



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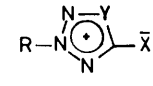

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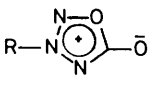

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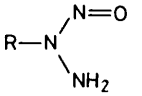

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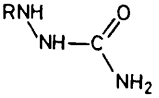

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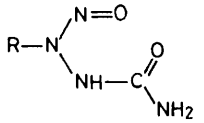

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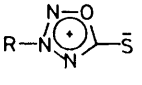

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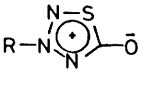

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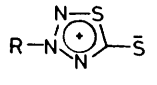

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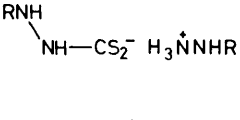

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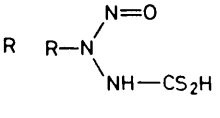

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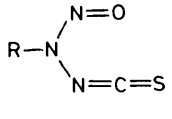

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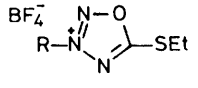

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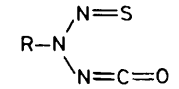

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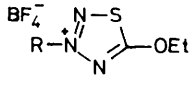

(17)

a; R = Ph, b; R = *p*-MeC_6H_4, c; R = *p*-ClC_6H_4, d; R = *p*-$MeO{\cdot}C_6H_4$, e; R = *p*-$EtO{\cdot}C_6H_4$

hydrogen sulphide, but attempts to isolate these intermediates (13) were not successful.

The spectroscopic properties of the oxatriazolium-thiolates (9a—e) support their formulation as meso-

ionic compounds. Their i.r. spectra show a strong absorption in the C=S stretching region (1 365—1 375 cm^{-1}) and valence tautomerism involving the structure (14) can be excluded since absorption bands characteristic of the isothiocyanate group (*ca.* 2 060 cm^{-1}) are absent. The n.m.r. spectra are of little diagnostic value, but are entirely consistent with the meso-ionic structures (9a—e). Their u.v. and visible spectra are exemplified by compound (9a) [$\lambda_{max.}$ 259 and 394 nm (ε 21 650 and 2 605)] and they show the same features as other meso-ionic systems. The compounds (9a—e) all show molecular ions in their mass spectra. A detailed analysis of the mass spectra of these compounds (9a—e) and a comparison with the mass spectra of similar meso-ionic systems is given in Part 20.[14] The dipole moments of the oxatriazoliumthiolates (9) in benzene solution have been reported elsewhere and these fully support the meso-ionic structure (9).[15] The dipole moment of the compound (9a) was found to be 6.83 D.

The meso-ionic oxatriazoliumthiolates (9a—e) are yellow, crystalline compounds with sharp melting points (*ca.* 100—150°). Treatment of (9a) with hot aqueous alkali gives phenyl azide and with hot dilute sulphuric acid gives phenol in low yield. Attempts to carry out 1,3-dipolar cycloadditions of compounds (9) with alkenes, alkynes, or heterocumulenes were unrewarding. The meso-ionic heterocycles (9) could not be alkylated with methyl iodide, but treatment of their solutions in dichloromethane at room temperature with triethyloxonium tetrafluoroborate gave the crystalline tetrafluoroborates (15).

We have previously described several examples of the isomerisation (1 ⟶ 2) in ethanol solution,[1,4,6,7] but these transformations were all restricted to meso-ionic systems of the general type (1). We now report an isomerisation of the general type (3 ⟶ 4). When heated under reflux in aqueous ethanolic ammonia, the meso-ionic oxatriazoliumthiolates (9a—e) were transformed to the meso-ionic 1,2,3,4-thiatriazolium-5-olates (10a—e). These compounds (10a—e) represent a new class of meso-ionic heterocycle and the pairs of isomers (9a—e and 10a—e) represent a new example of the isomerism of meso-ionic compounds of the general type (3) and (4). This isomerisation (9 ⟶ 10) may well proceed *via* a betaine intermediate similar to those considered for similar transformations of meso-ionic isomers.[4,6,7]

The meso-ionic thiatriazoliumolates (10a—e) are quite distinct from the isomeric oxatriazoliumthiolates (9a—e) in their physical and chemical properties. The compounds (10a—e) are colourless or pale yellow and crystalline. Their i.r. spectra show a strong absorption in the C=O stretching region (1 675—1 680 cm^{-1}) and the absence of isocyanate absorption bands (*ca.* 2 260 cm^{-1}) excludes the possibility of valence tautomerism to the structure (16). Their n.m.r. spectra are consistent with the proposed structures (10). Their u.v. and visible spectra are similar to, but distinct from, those of the isomeric oxatriazoliumthiolates (9a—e), and are exemplified by compound (10a) [$\lambda_{max.}$ 215sh, 280, and 330 nm (ε 9 850, 11 000, and 4 250)]. Compounds (10a—e) all show molecular ions in their mass spectra, but whereas the oxatriazoliumthiolates (9a—e) lose NO· from the molecular ion, the thiatriazoliumolates (10a—e) lose NS·. Dipole moments of the thiatriazoliumolates (10a—e) in benzene solution have been reported[15] and these support the meso-ionic structure; the dipole moment of (10a) was found to be 4.39 D.

The 3-phenyl compound (10a) was hydrolysed to phenyl azide by aqueous sodium hydroxide, but was recovered unchanged from hot 80% sulphuric acid. Like the meso-ionic oxatriazoliumthiolates (9a—e), the meso-ionic thiatriazoliumolates (10a—e) are unreactive towards 1,3-dipolarophiles such as alkenes, alkynes, and heterocumulenes, and they do not form salts with methyl iodide. Also, like the oxatriazoliumthiolates (9), they react with triethyloxonium tetrafluoroborate at room temperature, the products being the tetrafluoroborates (17).

The tetrafluoroborates (17a—c) are stable, colourless, crystalline compounds whose spectral properties completely support the structure (17). When the tetrafluoroborates (17a—c) in aqueous dimethylformamide solution were treated with aqueous sodium sulphide at room temperature, the meso-ionic 1,2,3,4-thiatriazolium-5-thiolates (11a—c) were formed. These orange, crystalline compounds (11) represent another new class of meso-ionic heterocycle and their proposed structure is fully supported by their spectral properties. The i.r. spectra show a strong absorption in the C=S stretching region (1 265—1 270 cm^{-1}) although at lower frequency than the C=S absorption in the closely related oxatriazoliumthiolates (9) (1 365—1 375 cm^{-1}).

The n.m.r. spectra are entirely consistent with the structures (11a—c). The u.v. and visible spectra show the same features as the spectra of the oxatriazoliumthiolates (9) and the thiatriazoliumolates (10) and are exemplified by compound (11a) [$\lambda_{max.}$ 233, 292, and 450 nm (ε 3 940, 20 200, and 1 715)]. The mass spectra show a strong molecular ion which loses a thionitroxyl radical (NS·).

EXPERIMENTAL

General experimental details are given in Part 8.[16]

Arylhydrazinium Salts of 3-Aryldithiocarbazates (12).—Phenylhydrazine (32.0 g) was dissolved in ethanol (350 ml) and carbon disulphide (24.0 g) was immediately added to the vigorously stirred solution. The dense, crystalline precipitate which formed was collected, washed with ether, and dried in air. The salt (12a) (36.3 g, 84%) was used without further purification.

The following salts were similarly prepared: (12b) (28.5 g, 68%) from *p*-tolylhydrazine (12c) (29.2 g, 62%) from *p*-chlorophenylhydrazine, (12d) (27.8 g, 56%) from *p*-methoxyphenylhydrazine, and (12e) (29.1 g, 52%) from *p*-ethoxyphenylhydrazine.

3-Aryl-1,2,3,4-oxatriazolium-5-thiolates (9).—Phenylhydrazinium salt 3-phenyldithiocarbazate (12a) (2.92 g) was suspended in chloroform (300 ml), and ice (20 g) and 3M-hydrochloric acid (10 ml) were added with vigorous stirring.

Dropwise addition of 3M-sodium nitrite (10 ml) to the rapidly stirred solution gave an intense yellow-green colouration. The chloroform layer was quickly separated, washed with water and dilute sodium hydrogen carbonate solution, and then dried ($MgSO_4$). Evaporation gave a crystalline product which after recrystallisations from ethanol–water and carbon tetrachloride gave 3-*phenyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9a) (0.79 g, 44%) as yellow needles, m.p. 100° (Found: C, 47.1; H, 3.0; N, 24.3%; $M^{\cdot+}$, 179. $C_7H_5N_3OS$ requires C, 46.9; H, 2.8; N, 23.45%; *M*, 179); $\lambda_{max.}$ 259 and 394 nm (ε 21 650 and 2 605); $\nu_{max.}$ 1 365 cm^{-1}; τ 1.7—2.7 (m, ArH).

The following compounds were similarly prepared: 3-p-*tolyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9b) (0.78 g, 40%), yellow needles, m.p. 103° (Found: C, 49.5; H, 3.7; N, 21.9%; $M^{\cdot+}$, 193. $C_8H_7N_3OS$ requires C, 49.8; H, 3.6; N, 21.75%; *M*, 193); $\lambda_{max.}$ 256, 285, and 395 nm (ε 16 900, 13 950, and 2 665); $\nu_{max.}$ 1 370 cm^{-1}; τ 1.90 and 2.45 (A_2B_2 system, J_{AB} 9 Hz, *p*-MeC_6H_4), and 7.43 (s, Me); 3-p-*chlorophenyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9c) (0.82 g, 38%), deep yellow needles, m.p. 106° [Found: C, 39.6; H, 2.0; N, 19.9%; $M^{\cdot+}(^{35}Cl)$, 213. $C_7H_4ClN_3OS$ requires C, 39.4; H, 1.9; N, 19.7%; $M(^{35}Cl)$, 213]; $\lambda_{max.}$ 232sh, 261, 274infl., and 388 nm (ε 6 510 18 000, 15 640, and 3 445); $\nu_{max.}$ 1 375 cm^{-1}; τ 1.80 and 2.28 (A_2B_2 system, J_{AB} 9 Hz, *p*-ClC_6H_4); 3-p-*methoxyphenyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9d) (0.9 g, 43%), lustrous yellow needles, m.p. 133° (Found: C, 46.0; H, 3.4; N, 20.2%; $M^{\cdot+}$, 209. $C_8H_7N_3O_2S$ requires C, 45.9; H, 3.35; N, 20.1%; *M*, 209); $\lambda_{max.}$ 251 and 323 nm (ε 13 150 and 12 800); $\nu_{max.}$ 1 370 cm^{-1}; τ 1.87 and 2.83 (A_2B_2, J_{AB} 9 Hz, *p*-$MeOC_6H_4$), and 6.16 (s, OMe); 3-p-*ethoxyphenyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9e) (1.0 g, 45%), lustrous yellow needles, m.p. 140° (Found: C, 48.4; H, 4.1; N, 18.9%; $M^{\cdot+}$, 223. $C_9H_9N_3O_2S$ requires C, 48.45; H, 4.1; N, 18.8%; *M*, 223); $\lambda_{max.}$ 252 and 325 nm (ε 15 450 and 13 530); $\nu_{max.}$ 1 365 cm^{-1}; τ 1.86 and 2.85 (A_2B_2, J_{AB} 9 Hz, *p*-$EtOC_6H_4$), 5.78 (q, *J* 7 Hz, OCH_2Me), and 8.50 (t, *J* 7 Hz, OCH_2Me).

Reactions of 3-*Phenyl*-1,2,3,4-*oxatriazolium*-5-*thiolate* (9a).—(a) *With dilute sulphuric acid.* Compound (9a) (2.0 g) was heated under reflux with 10% sulphuric acid (50 ml). When the evolution of dinitrogen tetraoxide had ceased (1.5 h), the mixture was extracted with ether and evaporation of the ethereal solution gave a pale yellow oil (0.5 g). This product was identified as phenol by treatment with tosyl chloride which gave phenyl tosyiate, m.p. 94—95° (lit.,[17] 93°), identical with an authentic sample.

(b) *With sodium hydroxide.* Compound (9a) (2.0 g) was heated under reflux with 10% sodium hydroxide solution (50 ml) until ammonia was no longer evolved (1 h). Steam distillation of the oily mixture gave phenyl azide (0.2 g, 15%) as a pale yellow oil, identical with an authentic sample.

(c) *With triethyloxonium tetrafluoroborate.* Compound (9a) (0.8 g) was added to a solution of triethyloxonium tetrafluoroborate (1.0 g) [18] in dry dichloromethane (20 ml) and the mixture was set aside at room temperature (24 h). Addition of ether to the chilled solution gave a brown, crystalline precipitate (1.2 g). Recrystallisation from acetone–ether afforded 3-*phenyl*-5-*ethylthio*-1,2,3,4-*oxatriazolium tetrafluoroborate* (15a) (1.1 g, 84%) as prisms, m.p. 90° (Found: C, 36.4; H, 3.3; N, 14.3. $C_9H_{10}BF_4N_3OS$ requires C, 36.6; H, 3.4; N, 14.2%); $\nu_{max.}$ (KBr) 1 020—1 130br and 1 440 cm^{-1}; τ($CDCl_3$–$CF_3{\cdot}CO_2H$), 1.5—2.2 (m, 5 ArH), 6.23 (q, *J* 7 Hz, OCH_2Me), and 8.87 (t, *J* 7 Hz, OCH_2Me); *m/e* 179 ($M^{\cdot+}$ − $EtBF_4$).

3-*Aryl*-1,2,3,4-*thiatriazolium*-5-*olates* (10).—3 Phenyl-1,2,-3,4 oxatriazolium-5-thiolate (9a) (0.5 g) was dissolved in warm ethanol (20 ml) and ammonia solution (5 ml, sp.gr. 0.88) was added. The solution was heated under reflux with stirring (0.5 h) and then cooled and refrigerated (12 h). The solid precipitate was recrystallised from carbon tetrachloride and identified as 3-*phenyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10a) (0.2 g, 40%), needles, m.p. 99° (Found: C, 47.2; H, 2.9; N, 23.4%; $M^{\cdot+}$, 179. $C_7H_5N_3OS$ requires C, 46.9; H, 2.8; N, 23.45%; *M*, 179); $\lambda_{max.}$ 215sh, 280, and 330infl. nm (ε 9 850, 11 000, and 4 250); $\nu_{max.}$ 1 680 $cm.^{-1}$; τ 1.2—2.5 (m, ArH).

The following compounds were similarly prepared: 3-p-*tolyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10b) (0.2 g, 40%), pale yellow needles, m.p. 144° (Found: C, 50.0; H, 3.8; N, 21.7%; $M^{\cdot+}$, 193. $C_8H_7N_3OS$ requires C, 49.8; H, 3.8; N, 21.75%; *M*, 193); $\lambda_{max.}$ 217sh, 294, and 333infl. nm (ε 8 120, 9 750, and 5 080); $\nu_{max.}$ 1 675 cm^{-1}; τ 1.82 and 2.57 (A_2B_2, J_{AB} 9 Hz, *p*-MeC_6H_4), and 7.50 (s, Me); 3-p-*chlorophenyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10c) (0.3 g, 60%), lustrous plates, m.p. 201° [Found: C, 39.7; H, 1.9; N, 19.5%; $M^{\cdot+}(^{35}Cl)$, 213. $C_7H_4ClN_3OS$ requires C, 39.4; H, 1.9; N, 19.7%; $M(^{35}Cl)$, 213]; $\lambda_{max.}$ 223, 288, and 338infl. nm (ε 9 150, 10 080, and 4 510); $\nu_{max.}$ 1 680 cm^{-1}; τ 1.74 and 2.40 (A_2B_2, J_{AB} 9 Hz, *p*-ClC_6H_4); 3-p-*methoxyphenyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10d) (0.2 g, 40%), pale yellow needles, m.p. 179° (Found: C, 46.2; H, 3.6; N, 20.3%; $M^{\cdot+}$, 209. $C_8H_7N_3O_2S$ requires C, 45 9; H, 3.35; N, 20.1%; *M*, 209); $\lambda_{max.}$ 216sh, 235infl., and 326 nm (ε 9 860, 7 650, and 12 950); $\nu_{max.}$ 1 675 cm^{-1}; τ 1.77 and 2.93 (A_2B_2, J_{AB} 9 Hz, *p*-$MeOC_6H_4$), and 6.05 (s, OMe); 3-p-*ethoxyphenyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10e) (0.2 g, 40%), pale yellow needles, m.p. 183° (Found: C, 48.6; H, 4.0; N, 19.0%; $M^{\cdot+}$, 223. $C_9H_9N_3O_2S$ requires C, 48.45; H, 4.1; N, 18.8%; *M*, 223); $\lambda_{max.}$ 222sh, 240infl., and 330 nm (ε 8 670, 6 440, and 12 040); $\nu_{max.}$ 1 680 cm^{-1}; τ 1.83 and 3.00 (A_2B_2, J_{AB} 9 Hz, *p*-$EtOC_6H_4$), 5.84 (q, *J* 7 Hz, OCH_2-Me), and 8.57 (t, *J* 7 Hz, OCH_2Me).

Reactions of 3-*Phenyl*-1,2,3,4-*thiatriazolium*-5-*olate* (10a).—(a) *With sodium hydroxide.* Compound (10a) (2.0 g) was heated under reflux with 10% sodium hydroxide solution (50 ml) until evolution of ammonia ceased (2 h). Extraction with ether and evaporation gave phenyl azide (0.5 g) as a pale yellow oil, identical with an authentic sample.

(b) *With triethyloxonium tetrafluoroborate.* Compound (10a) (2.8 g) was added to a solution of triethyloxonium tetrafluoroborate (2.9 g) [18] in dichloromethane (25 ml) and the mixture was set aside at room temperature (24 h). Addition of ether to the chilled solution gave a precipitate which was recrystallised from ethanol–ether and identified as 5-*ethoxy*-3 *phenyl*-1,2,3,4-*thiatriazolium tetrafluoroborate* (17a) (3.9 g, 85%), m.p. 106° (Found: C, 36.5; H, 3.5; N, 14.4. $C_9H_{10}BF_4N_3OS$ requires C, 36.6; H, 3.4; N, 14.2%); $\lambda_{max.}$ 229infl., 278infl., and 313 nm (ε 5 080, 6 810, and 10 480); $\nu_{max.}$ (KBr) 1 020—1 120br and 1 660 cm^{-1}; τ($CDCl_3$ + $CF_3{\cdot}CO_2H$) 1.6—2.4 (m, Ph), 4.98 (q, *J* 7 Hz, OCH_2Me), and 8.38 (t, *J* 7 Hz, OCH_2Me); *m/e* 179 ($M^{\cdot+}$ − $EtBF_4$).

The following salts were similarly prepared: 5-*ethoxy*-3-p-*tolyl*-1,2,3,4-*thiatriazolium tetrafluoroborate* (17b) (4.0 g, 83%), needles from acetone–ether, m.p. 105° (Found: C, 39.0; H, 3.7; N, 13.8. $C_{10}H_{12}BF_4N_3OS$ requires C, 38.85;

H, 3.9; N, 13.6%); $\lambda_{max.}$ 237sh, 285infl., and 332 nm (ε 6 180, 5 920, and 16 600); $\nu_{max.}$ (KBr) 1 020—1 110br and 1 650 cm^{-1}; τ 1.88 and 2.60 (A_2B_2, J_{AB} 9 Hz, *p*-MeC_6H_4), 5.03 (q, *J* 7 Hz, OCH_2Me), and 8.42 (t, *J* 7 Hz, OCH_2Me); *m/e* 193 ($M^{\cdot+}$ − $EtBF_4$); 3-p-*chlorophenyl*-5-*ethoxy*-1,2,3,4-*thiatriazolium tetrafluoroborate* (17c) (4.4 g, 86%), lustrous needles from acetone–light petroleum (b.p. 40—60°), m.p. 137° (Found: C, 32.8; H, 2.85; N, 13.0. $C_9H_9BClF_4N_3OS$ requires C, 32.8; H, 2.7; N, 12.8%); $\lambda_{max.}$ 217sh, 236infl., 285infl., and 324 nm (ε 1 398, 8 730, 9 880, and 19 750); $\nu_{max.}$ (KBr) 1 020—1 120br and 1 650 cm^{-1}; τ($CDCl_3$ + $CF_3{\cdot}CO_2H$) 1.65 and 2.28 (A_2B_2, J_{AB} 9 Hz, *p*-ClC_6H_4), 5.00 (q, *J* 7 Hz, OCH_2Me), and 8.40 (t, *J* 7 Hz, OCH_2Me); *m/e* 213 (^{35}Cl) ($M^{\cdot+}$ − $EtBF_4$).

3-*Aryl*-1,2,3,4-*thiatriazolium*-5-*thiolates* (11).—5-Ethoxy-3-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate (17a) (0.2 g) was dissolved in a mixture of dimethylformamide (5 ml) and water (10 ml) and sodium sulphide (0.2 g) in water (5 ml) was added. After 2 h at room temperature, the orange solution was diluted with water (50 ml) and chilled. The orange precipitate was washed with water, dried, and recrystallised from light petroleum (b.p. 60—80°). The product was identified as 3-*phenyl*-1,2,3,4-*thiatriazolium*-5-*thiolate* (11a) (0.04 g, 30%), orange needles, m.p. 128° (Found: C, 43.15; H, 2.8; N, 21.7%; $M^{\cdot+}$, 195. $C_7H_5N_3S_2$ requires C, 43.1; H, 2.6; N, 21.5%; *M*, 195); $\lambda_{max.}$ 233, 292, and 450 nm (ε 3 940, 20 200, and 1 715); $\nu_{max.}$ 1 265 cm^{-1}; τ 1.6—2.5 (m, ArH).

The following compounds were similarly prepared: 3-p-*tolyl*-1,2,3,4-*thiatriazolium*-5-*thiolate* (11b) (0.04 g, 30%), deep orange plates, m.p. 142° (Found: C, 46.0; H, 3.6; N, 20.05%; $M^{\cdot+}$, 209. $C_8H_7N_3S_2$ requires C, 45 9; H, 3.4; N, 20.1%; *M*, 209); $\lambda_{max.}$ 239, 298, and 448 nm (ε 6 880, 24 900, and 2 370); $\nu_{max.}$ 1 270 cm^{-1}; τ 1.86 and 2.64 (A_2B_2, J_{AB} 8 Hz, *p*-MeC_6H_4), and 7.5 (s, Me); 3-p-*chlorophenyl*-1,2,3,4-*thiatriazolium*-5-*thiolate* (11c) (0.07 g, 34%), lustrous orange needles from ethanol–water, m.p. 188° [Found: C, 36.6; H, 1.85; N, 18.4%; $M^{\cdot+}$(^{35}Cl), 229. $C_7H_4ClN_3S_2$ requires C, 36.6; H, 1.8; N, 18.3%; *M*(^{35}Cl), 229]; $\lambda_{max.}$ 236, 297, and 456 nm (ε 6 130, 26 200, and 2 065); $\nu_{max.}$ 1 265 cm^{-1}; τ 1.6—3.1 (m, ArH).

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