Studies on Mesoionic Compounds. Part 6.[1] Synthesis of Three New Mesoionic Heterocyclic Systems; Sulphur-containing Analogues of Sydnone

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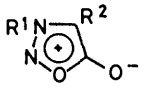
The synthesis of three new classes of mesoionic heterocycle, 1,2,3-oxadiazolium-5-thiolate (3), 1,2,3-thiadiazolium-5-olate (4), and 1,2,3-thiadiazolium-5-thiolate (6), from the Meerwein alkylation product of sydnone is described.

SINCE Earl and Mackney [2] reported the formation of sydnone in 1935, other five-membered mesoionic compounds have been widely studied.[3] Although a large number of derivatives of sydnone and sydnone imine have been synthesised, those analogues containing an exocyclic sulphur atom instead of oxygen or nitrogen, or an endocyclic oxygen atom have not yet been described. A principal difficulty in the synthesis of those compounds could be that the amino dithio and thiocarbonic acids are not stable. Attempts to prepare the above analogues from sydnone directly were all unsuccessful.[4] Recently Ollis *et al.*[5] reported a useful method for introducing a sulphur atom into the 1,2,3,4-oxatriazolium-5-olate system by reaction of its *O*-alkyl derivative with sodium



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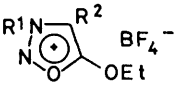

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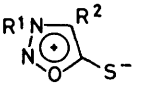

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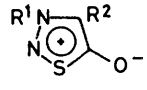

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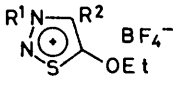

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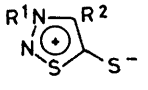

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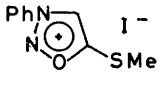
a; R^1 = Ph, R^2 = H; b; R^1 = Ph, R^2 = Me
c; R^1 = R^2 = Ph; d; R^1 = Me, R^2 = Ph



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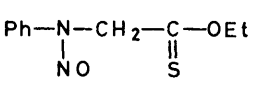

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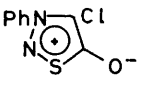

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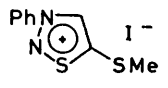

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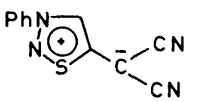

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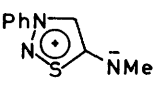

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sulphide. In connection with our synthetic studies on mesoionic compounds, we now report an improved procedure of this method for the synthesis of the 1,2,3-oxadiazolium-5-thiolates (3), derivatives of a new class of mesoionic compound related to sydnone, and their conversion into further new mesoionic heterocyclic systems, 1,2,3-thiadiazolium-5-olates (4) and 1,2,3-thiadiazolium-5-thiolates (6).

According to the method reported by Potts *et al.*,[6] the sydnones (1) were alkylated with triethyloxonium tetrafluoroborate [7] to give the corresponding salts (2). Treatment of compound (2a) with sodium sulphide [5] resulted in many unidentified products, whereas on treatment of the salt (2a) with sodium hydrosulphide [8] in ethanol the desired 1,2,3-oxadiazolium-5-thiolate (3a) was obtained as yellow crystals. Elemental analysis supported the composition of (3a). The i.r. spectrum of the compound (3a) showed a strong absorption at 1 450 cm^{-1}, attributed to thione stretching. In the n.m.r. spectrum the chemical shifts of the phenyl (δ 7.7) and H-4 (δ 7.5) protons were very similar to those of 3-phenylsydnone (1a) (δ 7.7 and 6.8, respectively).[9] The presence of an exocyclic sulphur atom in (3a) was further confirmed by reaction with methyl iodide to give the methiodide (7). These results, while not being conclusive, support the formulation of (3a) as a mesoionic compound. An oily by-product of the reaction was thought to be, by its spectral features, the thiocarboxylate (8). At a lower temperature, formation of this compound could be largely prevented. In the same way the salts (2b—d) yielded the corresponding mesoionic 1,2,3-oxadiazolium-5-thiolates (3b—d).

This successful synthesis encouraged us to prepare another new class of mesoionic compound. Interesting examples of isomerisation of mesoionic heterocycles involving exchange between endocyclic and exocyclic hetero atoms have been described by Ollis *et al.*; these include 1,3,4-oxadiazolium-2-thiolates,[10] 1,3,4-thiadiazolium-2-aminides,[11] and 1,2,4-triazolium-3-aminides [12] into 1,3,4-thiadiazolium-2-olates, 1,2,4-triazolium-3-thiolates, and isomeric 1,2,4-triazolium-3-aminides, respectively. All these isomerisations occurred on heating the substrates in ethanol. A similar interconversion of a 1,2,3,4-oxatriazolium system to tetrazolium [13] and 1,2,3,4-thiatriazolium systems [5] has been established. These cases would involve base-catalysed rearrangements. Our novel 1,2,3-oxadiazolium-5-thiolates (3) were similarly treated. Although compounds (3) failed to transform to 1,2,3-thiadiazolium-5-olates (4) on heating in ethanol, treatment with hot ethanol–

ammonium hydroxide[5] was successful in formation of the crystalline compounds (4). This reaction proceeded also in the absence of ethanol. The i.r. spectra of compounds (4) exhibited strong absorption bands in the region 1 590—1 640 cm^{-1} attributed to carbonyl stretching. These were absent in the spectra of compounds (3). Although the mass spectra of these isomers (3) and (4) showed similar patterns to each other, they revealed clearly their structural differences; the fragment ions $M^{\cdot+}$ — NO· and $M^{\cdot+}$ — NS· were observed in the spectra of (3) and (4), respectively. This observation is reminiscent of the mesoionic 1,2,3,4-oxa- and thia-triazole derivatives.[5] Two derivatives of the 1,2,3-thiadiazolium-5-olate (4) system, substituted at the 4-position with chlorine, have been synthesised recently by Burmistrov and Kozinskii[14] in an alternative route. 3-Aryl-4-carboxymethylsydnones were treated with thionyl chloride in the presence of catalytic amounts of dimethylformamide and then with hydrogen peroxide to yield 3-phenyl- and 3-*p*-tolyl-4-chloro-1,2,3-thiadiazolium-5-olates. Since the starting sydnones are structurally limited, it is assumed that this synthesis is not a general route to the mesoionic system (4). The chlorination product (9), obtained by treatment of the compound (4a) with *N*-chlorosuccinimide, was identical with the corresponding product prepared by the method of Burmistrov and Kozinskii.

The exocyclic oxygen atoms of compounds (4) were alkylated with Meerwein's reagent to afford quantitatively the salts (5). These, as well as (2), gave the new mesoionic system, 1,2,3-thiadiazolium-5-thiolates (6), on treatment with sodium hydrosulphide. These compounds (6) were orange and gave the methiodide (10) on reaction with methyl iodide. Their mass spectra also showed the fragment ion $M^{\cdot+}$ — NS·. Furthermore, the salt (5a) reacted with malononitrile in the presence of triethylamine[15] to give the dicyanomethanide derivative (11), and the methiodide (10) afforded the methylaminide derivative (12) in the reaction with methylamine. It should be possible to synthesise some new classes of mesoionic heterocycle in the reaction of the salts mentioned above with other nucleophiles.

EXPERIMENTAL

M.p.s were determined with a Yanagimoto hot-stage apparatus. I.r. and u.v. spectra were measured with JASCO IRA-1 and Hitachi 124 spectrophotometers, respectively, n.m.r. spectra were obtained with a JNM-PMX-60 spectrometer (tetramethylsilane as internal standard), and mass spectra were recorded with a JEOL JMS-O1SG-2 instrument.

Preparation of 5-Ethoxy-1,2,3-oxadiazolium Tetrafluoroborates (2).—By the procedure described by Potts, *et al.*,[6] the following salts (2) were prepared from 3-phenylsydnone (1a),[1] 4-methyl-3-phenylsydnone (1b),[16] 3,4-diphenylsydnone (1c),[17] and 3-methyl-4-phenylsydnone (1d),[17] respectively: 5-ethoxy-3-phenyl-1,2,3-ozadiazolium · tetrafluoroborate (2a) (80%), m.p. 65—68° (lit.,[6] 68—70°); 5-ethoxy-4-methyl-3-phenyl-1,2,3-oxadiazolium tetrafluoroborate (2b) (75%), m.p. 106—107° (lit.,[6] 107—109°); 5-ethoxy-3,4-diphenyl-1,2,3-oxadiazolium tetrafluoroborate (2c) (100%), colourless oil; 5-ethoxy-3-methyl-4-phenyl-1,2,3-oxadiazolium tetrafluoroborate (2d) (100%), colourless oil. The salts (2c and 2d) were used in the next step without purification.

3-Phenyl-1,2,3-oxadiazolium-5-thiolate (3a).—To a stirred suspension of the salt (2a) (2.8 g) in ethanol (60 ml) was added a solution of sodium hydrosulphide[8] (672 mg) in ethanol (20 ml) at −70 °C. After 45 min the ethanol was evaporated off. Addition of water, extraction with chloroform, evaporation, and recrystallisation from isopropyl alcohol gave the 1,2,3-*oxadiazolium-5-thiolate* (3a) (1.0 g, 56%) as yellow needles, m.p. 167—168° (Found: C, 53.95; H, 3.1; N, 15.5. $C_8H_6N_2OS$ requires C, 53.91; H, 3.39; N, 15.72%), $\lambda_{max.}$ (EtOH) 262 (log ε 4.33) and 396 nm (3.81), δ($CDCl_3$) 7.5 (1 H, s, 4-H) and 7.7 (5 H, s, Ph), *m/e* 178 (86%), 148 (30), 104 (100), and 77 (73).

4-Methyl-3-phenyl-1,2,3-oxadiazolium-5-thiolate (3b).—A suspension of the salt (2b) (2.2 g) in ethanol (15 ml) was treated with sodium hydrosulphide (484 mg) in ethanol (10 ml) and worked up as above. The 1,2,3-*oxadiazolium-5-thiolate* (3b) (710 mg, 56%) was obtained as yellow needles, m.p. 125—126° (from isopropyl alcohol) (Found: C, 56.45; H, 4.35; N, 14.65. $C_9H_8N_2OS$ requires C, 56.23; H, 4.19; N, 14.57%), $\lambda_{max.}$ (EtOH) 253 (log ε 4.14) and 387 nm (3.92), δ($CDCl_3$) 2.3 (3 H, s, Me) and 7.4—7.9 (5 H, m, Ph), *m/e* 192 (78%), 162 (9), 118 (100), and 77 (53).

3,4-Diphenyl-1,2,3-oxadiazolium-5-thiolate (3c).—To a stirred suspension of the crude salt (2c) (1.7 g) in ethanol (5 ml) was added sodium hydrosulphide (269 mg) in ethanol (5 ml) at −5 °C. After 30 min the mixture was worked up as above to give the 1,2,3-*oxadiazolium-5-thiolate* (3c) [281 mg, 29% based on (1c)] as yellow cubes, m.p. 234—235° (from methanol) (Found: C, 66.35; H, 3.75; N, 10.75. $C_{14}H_{10}N_2OS$ requires C, 66.12; H, 3.96; N, 11.02%), $\lambda_{max.}$ (EtOH) 238 (log ε 4.05), 290sh (3.77), 370 (3.50), and 480 nm (3.24), δ($CDCl_3$) 7.2—7.7 (m + s, 2 × Ph), *m/e* 254 (60%), 238 (10), 224 (27), 180 (100), and 77 (42).

3-Methyl-4-phenyl-1,2,3-oxadiazolium-5-thiolate (3d).—To a stirred suspension of the crude salt (2d) (312 mg) in ethanol (2 ml) was added sodium hydrosulphide (120 mg) in ethanol (2 ml) at −5 °C. After 1 h the mixture was worked up as above, and the product was chromatographed on silica gel (Merck, 70—230 mesh) (2 g). Elution with chloroform gave the 1,2,3-*oxadiazolium-5-thiolate* (3d) [105 mg, 51% based on (1d)] as yellow leaflets, m.p. 164—165° (from isopropyl alcohol) (Found: C, 56.05; H, 3.95; N, 14.6. $C_9H_8N_2OS$ requires C, 56.23; H, 4.19; N, 14.57%), $\lambda_{max.}$ (EtOH) 252 (log ε 3.74), 341 (3.49), and 428 nm (2.88), δ($CDCl_3$) 4.15 (3 H, s, NMe) and 7.55 (5 H, s, Ph), *m/e* 192 (77%), 162 (18), 118 (100), and 77 (36).

1,2,3-Thiadiazolium-5-olates (4).—(*a*) A mixture of the 1,2,3-oxadiazolium-5-thiolate (3a) (1.5 g), 28% ammonium hydroxide (20 ml), and ethanol (30 ml) in a sealed tube was heated at 110—120 °C for 45 h. Dilution with water, extraction with chloroform, evaporation, and recrystallisation from cyclohexane–benzene gave *3-phenyl-1,2,3-thiadiazolium-5-olate* (4a) (1.28 g, 85%) as needles, m.p. 118—119° (Found: C, 53.95; H, 3.55; N, 15.95. $C_8H_6N_2OS$ requires C, 53.91; H, 3.39; N, 15.72%), $\nu_{max.}$ (KBr) 1 630 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 264 (log ε 3.99) and 342 nm (3.58), δ($CDCl_3$), 7.4—7.8 (5 H, m, Ph) and 7.85 (1 H, s, 4-H), *m/e* 178 (12%), 149 (3), 132 (6), 104 (100), and 77 (94).

(*b*) Similarly, a mixture of the 1,2,3-oxadiazolium-5-thiolates (3b—d) (500 mg), 28% ammonium hydroxide (10 ml), and ethanol (15 ml) was heated at 120 °C for 15 h.

Work-up as above gave *4-methyl-3-phenyl-1,2,3-thiadiazolium-5-olate* (4b) (370 mg, 74%) as needles, m.p. 123—124° (from isopropyl ether) (Found: C, 56.05; H, 4.05; N, 14.6. $C_9H_8N_2OS$ requires C, 56.23; H, 4.19; N, 14.57%), $\nu_{max.}$ (KBr) 1 600 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 233 (log ε 3.88) and 340 nm (3.75), δ($CDCl_3$) 2.2 (3 H, s, Me) and 7.5 (5 H, s, Ph), *m/e* 192 (80%), 176 (1.5), 146 (0.5), 118 (100), and 77 (84); *3,4-diphenyl-1,2,3-thiadiazolium-5-olate* (4c) (210 mg, 42%) as pale yellow sticks, m.p. 142—143° (from isopropyl alcohol) (Found: C, 66.3; H, 3.9; N, 11.0. $C_{14}H_{10}N_2OS$ requires C, 66.12; H, 3.96; N, 11.02%), $\nu_{max.}$ (KBr) 1 640 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 242 (log ε 4.01) and 353 nm (3.81), δ($CDCl_3$) 7.2 (5 H, s, Ph) and 7.35 (5 H, s, Ph), *m/e* 254 (89%), 238 (8), 208 (0.3), 180 (100), and 77 (50); and *3-methyl-4-phenyl-1,2,3-thiadiazolium-5-olate* (4d) (300 mg, 60%) as pale yellow needles, m.p. 123—124° (from isopropyl alcohol) (Found: C, 56.4; H, 4.25; N, 14.75. $C_9H_8N_2OS$ requires C, 56.23; H, 4.19; N, 14.57%), $\nu_{max.}$ (KBr) 1 590 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 255 (log ε 3.76) and 342 nm (3.63), *m/e* 192 (100%), 176 (2.5), 118 (54), and 77 (20).

5-Ethoxy-3-phenyl-1,2,3-thiadiazolium Tetrafluoroborate (5a).—To a solution of the 1,2,3-thiadiazolium-5-olate (4a) (537 mg) in dichloromethane (2 ml) was added a solution of triethyloxonium tetrafluoroborate (746 mg) in dichloromethane (2 ml) with stirring at room temperature. After 3 h the solvent was evaporated off. Washing of the residue with ether and recrystallisation from isopropyl alcohol gave the *1,2,3-thiadiazolium tetrafluoroborate* (5a) (860 mg, 97%), leaflets, m.p. 71—72° (Found: C, 40.9; H, 3.8; N, 9.5. $C_{10}H_{11}BF_4N_2OS$ requires C, 40.84; H, 3.77; N, 9.53%), $\nu_{max.}$ (KBr) 1 120—1 040 cm^{-1}, δ([$^2H_6$]acetone) 1.6 (3 H, t, Me), 4.8 (2 H, q, OCH_2), 7.5—8.3 (5 H, m, Ph), and 9.9 (1 H, s, 4-H).

5-Ethoxy-4-methyl-3-phenyl-1,2,3-thiadiazolium Tetrafluoroborate (5b).—A mixture of the 1,2,3-thiadiazolium-5-olate (4b) (192 mg) and triethyloxonium tetrafluoroborate (253 mg) in dichloromethane (2 ml) was stirred at room temperature for 15 h. The mixture was worked up as above to give the *1,2,3-thiadiazolium tetrafluoroborate* (5b) (307 mg, 100%) as leaflets, m.p. 82—83° (from cyclohexane–isopropyl alcohol) (Found: C, 42.65; H, 4.35; N, 8.9. $C_{11}H_{13}BF_4N_2OS$ requires C, 42.88; H, 4.25; N, 9.09%), $\nu_{max.}$ (KBr) 1 050 cm^{-1}, δ([$^2H_6$]acetone) 1.7 (3 H, t, Me), 2.5 (3 H, s, Me), 4.8 (2 H, q, OCH_2), and 7.8 (5 H, s, Ph).

1,2,3-Thiadiazolium-5-thiolates (6).—To a stirred suspension of the salt (5a) (294 mg) in ethanol (2 ml) was added a solution of sodium hydrosulphide (56 mg) in ethanol (2 ml) at −70 °C. After 30 min, addition of water, extraction with chloroform, evaporation, and recrystallisation from isopropyl alcohol gave *3-phenyl-1,2,3-thiadiazolium-5-thiolate* (6a) (126 mg, 65%) as reddish orange leaflets, m.p. 170—171° (Found: C, 49.7; H, 3.25; N, 14.35. $C_8H_6N_2S_2$ requires C, 49.46; H, 3.11; N, 14.42%), $\lambda_{max.}$ (EtOH) 285 (log ε 3.99) and 440 nm (3.22), δ($CDCl_3$) 7.5—8.0 (5 H, m, Ph) and 8.5 (1 H, s, 4-H), *m/e* 194 (72%), 178 (2), 148 (16), 104 (100), and 77 (72). Similarly, from the salt (5b) (308 mg) and sodium hydrosulphide (56 mg), *4-methyl-3-phenyl-1,2,3-thiadiazolium-5-thiolate* (6b) (110 mg, 53%) was obtained as orange leaflets, m.p. 144—146° (from isopropyl alcohol) (Found: C, 51.65; H, 3.65; N, 13.3. $C_9H_8N_2S_2$ requires C, 51.89; H, 3.85; N, 13.45%), $\lambda_{max.}$ (EtOH) 272 (log ε 3.82) and 428 nm (2.99), δ($CDCl_3$) 2.4 (3 H, s, Me) and 7.2—7.75 (5 H, m, Ph), *m/e* 208 (100%), 192 (4), 162 (0.5), 118 (50), and 77 (52).

5-Methylthio-3-phenyl-1,2,3-oxadiazolium Iodide (7).—A mixture of the 1,2,3-oxadiazolium-5-thiolate (3a) (178 mg) and methyl iodide (1 ml) in chloroform (5 ml) was stirred at room temperature for 6 h. Concentration and recrystallisation of the residue from ethanol gave the *methiodide* (7) (252 mg, 79%) as orange-yellow needles, m.p. 120—122° (Found: C, 33.9; H, 3.0; N, 8.6. $C_9H_9IN_2OS$ requires C, 33.76; H, 2.83; N, 8.75%), δ([$^2H_6$]-DMSO) 3.0 (3 H, s, SMe), 7.7—8.3 (5 H, m, Ph), and 10.0 (1 H, s, 4-H).

4-Chloro-3-phenyl-1,2,3-thiadiazolium-5-olate (9).—(*a*) A mixture of the 1,2,3-thiadiazolium-5-olate (4a) (178 mg) and *N*-chlorosuccinimide (134 mg) in carbon tetrachloride (15 ml) was refluxed for 2 h. Filtration, concentration of the filtrate, and recrystallisation from cyclohexane gave the *4-chloro-compound* (9) (162 mg, 76%) as needles, m.p. 116—118° (Found: C, 45.4; H, 2.4; N, 12.95. $C_8H_5ClN_2OS$ requires C, 45.18; H, 2.37; N, 13.17%), $\nu_{max.}$ (KBr) 1 580 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 260 (log ε 3.78) and 350 nm (3.78), *m/e* 218 (M^+).

(*b*) By the procedure described by Burmistrov and Kozinskii,[14] 4,5-dichloro-3-phenyl-1,2,3-thiadiazolium chloride was prepared from 4-carboxymethyl-3-phenylsydnone [18] in 39% yield, m.p. 264—268° (decomp.) (from carbon tetrachloride–isopropyl alcohol) [lit.,[14] 250° (decomp.)]. In our investigation an improved method was used for the following oxidation reaction. A mixture of the above chloride (100 mg), *m*-chloroperbenzoic acid (75 mg), and chloroform (5 ml) was kept at room temperature for 28 days. Washing with 5% aqueous sodium hydrogencarbonate and evaporation gave an oily residue. The oil was triturated with n-hexane several times, and the combined n-hexane solutions were evaporated. Recrystallisation of the residue from isopropyl alcohol gave the *4-chloro-1,2,3-thiadiazolium-5-olate* (9) (12 mg, 15%), m.p. 116—117° (lit.,[14] 116—117°), identical with the product obtained in (*a*) (i.r. and mixed m.p.).

5-Methylthio-3-phenyl-1,2,3-thiadiazolium Iodide (10).—A mixture of the 1,2,3-thiadiazolium-5-thiolate (6a) (100 mg) and methyl iodide (1 ml) in chloroform (5 ml) was stirred at room temperature for 2 h. Concentration and recrystallisation from ethanol gave the *methiodide* (10) (170 mg, 98%) as orange–yellow needles, m.p. 146—148° (Found: C, 32.4; H, 3.0; N, 8.6. $C_9H_9IN_2S_2$ requires C, 32.15; H, 2.70; N, 8.33%), δ([$^2H_6$]-DMSO) 2.9 (3 H, s, SMe), 7.5—8.3 (5 H, m, Ph), and 10.1 (1 H, s, 4-H).

3-Phenyl-1,2,3-thiadiazolium-5-dicyanomethanide (11).—To a cooled solution of the salt (5a) (405 mg) and malononitrile (86 mg) in acetonitrile (5 ml) was added with stirring a solution of triethylamine (131 mg) in acetonitrile (2 ml). After 30 min, concentration, addition of water, extraction with chloroform, and evaporation gave a crystalline residue. Recrystallisation from ethanol yielded the *dicyanomethanide* (11) (120 mg, 38.5%) as orange–yellow needles, m.p. 255—258° (Found: C, 58.45; H, 2.65; N, 24.7. $C_{11}H_6N_4S$ requires C, 58.39; H, 2.67; N, 24.76%), $\nu_{max.}$ (KBr) 2 200 and 2 170 cm^{-1} (CN), $\lambda_{max.}$ (EtOH) 287 (log ε 4.33) and 464 nm (3.91).

3-Phenyl-1,2,3-thiadiazolium-5-methylaminide (12).—A mixture of the methiodide (10) (335 mg), 30% ethanolic methylamine (1 ml), and methanol (5 ml) was stirred at room temperature for 1.5 h. After concentration of the mixture, the residue was washed with ether and recrystallised from isopropyl alcohol to give the *hydroiodide* of (12) (138 mg, 43%) as yellow leaflets, m.p. 189—190° (Found: C, 34.05; H, 2.9; N, 13.0. $C_9H_{10}IN_3S$ requires C, 33.87;

H, 3.16; N, 13.17%), δ([$^2H_6$]acetone) 3.4 (3 H, s, NMe), 7.6—8.3 (5 H, m, Ph), and 9.4 (1 H, s, 4-H).

The above hydroiodide (175 mg) was added with stirring to a saturated aqueous potassium carbonate (2 ml). Extraction with chloroform, evaporation, and recrystallisation from isopropyl ether gave the *methylaminide* (12) (60 mg, 57%) as yellow needles, m.p. 122—124° (Found: C, 56.45; H, 4.45; N, 21.85. $C_9H_9N_3S$ requires C, 56.52; H, 4.74; N, 21.97%), $\nu_{max.}$ (KBr) 1 580 cm^{-1} (C=N), δ($CDCl_3$) 3.1 (3 H, s, NMe), 7.3—7.9 (5 H, m, Ph), and 8.1 (1 H, s, 4-H), *m/e* 191 (62%), 145 (10), 104 (100), and 77 (68).

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