Reactions of 4-Halogeno- and 4-Methylthio-imidazolium Salts with Sulphide and Methanethiolate Ions

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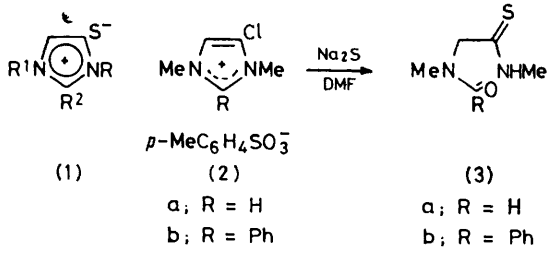
1,3-Dimethyl-substituted 4-halogeno- or 4-methylthio-substituted imidazolium salts undergo reaction with sulphur nucleophiles accompanied by (i) ring cleavage to give *N*-methylthioamides (chloro derivatives with sulphide ions), (ii) replacement of halogen (chloro derivatives with methanethiolate), or (iii) reduction (bromo or methylthio derivatives with sulphide or methanethiolate ions). Subsequent thiation at C-2 leads to 2-thiones, the 4-bromo derivative yielding 1,3-dimethylimidazoline-2-thione, the 4-methylthio derivative 1,3-dimethyl-4-methylthioimidazoline-2-thione. The 4-methylthio-substituted imidazolium salt undergoes selective *N*-demethylation on heating in pyridine.

KNOWN 1,3-disubstituted anhydro-4-mercaptoimidazolium hydroxides (1) are few [1a,2] and not readily accessible. The fact that such mesoionic systems serve as 1,3-dipoles [1a] prompted the present exploration of general and convenient synthetic routes to (1).

4-Chloro-1,3-dimethylimidazolium toluene-*p*-sulphonate (2a), obtained on treatment of 5-chloro-1-methylimidazole [3] with methyl toluene-*p*-sulphonate, reacted with sodium sulphide * in a fashion different from that of its 2-aza analogue, in which halogen replacement led to the 2-aza analogue of (1).[1b] In the present series, however, the linear aldehyde (3a) was produced in 75% yield under the same conditions (Scheme 1). Two stable



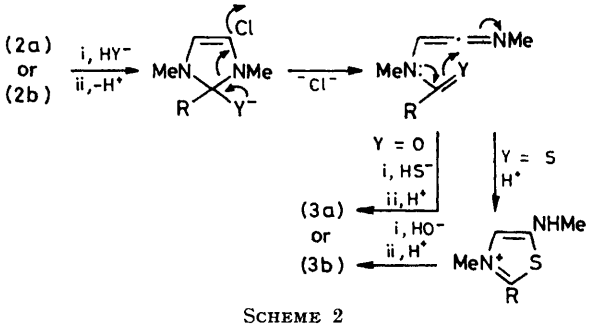
(1) (2) (3)
a; R = H a; R = H
b; R = Ph b; R = Ph

SCHEME 1

rotamers of the latter could be distinguished in solution (see Experimental section). Analogously, the 2-phenyl salt (2b) yielded (3b) in 78% yield. Since the mesoionic system (1) is unaffected by sodium sulphide,[4] (1) is excluded as an intermediate in the conversion of (2) into (3). A likely course of reaction, therefore, is an initial attack of sulphide or hydroxide ions at C-2, followed by ring fission. In the case of hydroxide addition, subsequent addition of sulphide ions could produce (3a). A similar sequence, involving sulphide addition, ring fission, and a second sulphide addition, can be excluded since it would result in the thio-analogue of (3a), known to produce the stable, mesoionic compound (1a) under the reaction conditions.[4] A conceivable alternative route to (3a) involves addition of sulphide ions, ring fission, ring closure to a thiazolium ion, and, finally, hydrolysis of the latter, a known and ready reaction [4,5] (Scheme 2).

* Since the imidazolium salt (2a) was available only as dihydrate, no efforts were made to apply water-free sulphide in the reaction.

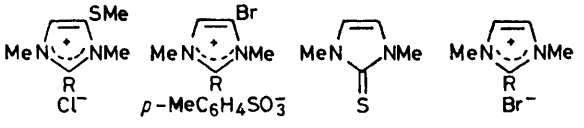
In contrast to the reaction with hydrated sodium sulphide, conversion of (2a and b) into the substitution



SCHEME 2

products (4a and b) proceeded quantitatively on treatment with methanethiolate ions at room temperature. Unfortunately, attempts at selective *S*-demethylation of (4a and b) were of no avail.

Exposure of the bromine-substituted salt (5a) to reaction with excess sodium sulphide (3 mol. equiv.) in methanol resulted in the production of the imidazoline-thione (6) (67% yield). When only one molar equivalent of sodium sulphide was employed, the imidazolium salt (7a) was isolated in 42% yield, along with (6), elemental sulphur, and a small quantity of (3a). In the phenyl series, (5b) afforded (7b), in 77% yield, under similar conditions. Most likely, rapid sulphide reduction of (5a and b), to give (7a and b), is followed, in the case of

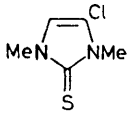


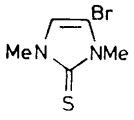
(4) (5) (6) (7)
a; R = H a; R = H a; R = H
b; R = Ph b; R = Ph b; R = Ph

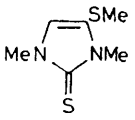
(7a), by proton abstraction and thiation of the anion to give (6) in a known reaction.[6]

In the chlorine-substituted series, thiation dominated over ring cleavage, (8) being formed, virtually quantitatively, when (2a) was treated with sodium sulphide and sulphur. When (5a) was subjected to similar conditions, reduction with formation of (7a) and (6) prevailed over thiation into (9).

Treatment of (5a) with methanethiolate (1 mol. equiv.) afforded, in 82% yield, the reduced product (7a),


(8)


(9)


(10)

while excess methanethiolate led to thiation of (7a) to give (6), most likely effected by dimethyl disulphide, formed in the redox process, and known to be able to transform (7a) into (6) in the presence of base.[7]

Redox processes, rather than demethylation, were prominent also when the 4-methylthio salt (4a) was treated with methanethiolate ions, yielding equimolar quantities of (7a) and (10), the formation of the latter suggesting the intermediacy of 2-methylthio-substituted species. Pyridine at 200 °C effected demethylation of (4a) to give a mixture of 1-methyl-4-methylthioimidazole and 1-methyl-5-methylthioimidazole; no methyl–sulphur cleavage was detectable.

Alternative successful routes to 1,3-disubstituted anhydro-4-mercaptoimidazolium hydroxides provide the subject of a forthcoming publication.[4]

EXPERIMENTAL

Solvents were removed *in vacuo*. Chromatography was carried out as described previously.[8] The purity and identity of all compounds were secured through m.p., i.r., ^{1}H n.m.r., and mass spectra. ^{1}H and ^{13}C n.m.r. spectra were recorded on Bruker HX-90 and WH-90 instruments, respectively. Low and high resolution mass spectra were obtained on a Perkin-Elmer 270 and an A.E.I. MS 3074 instrument, respectively.

Starting Materials.—Sodium sulphide (60—62% Na_2S; Riedl de Haën) and a 55% suspension of sodium hydride in mineral oil (Pract.; Fluka) were employed.

5-Chloro-1-methylimidazole [3] was heated to 100 °C with 1.2 equiv. of methyl toluene-*p*-sulphonate for 3 h. Washing with ether and recrystallization from methanol–ether gave 98% of 4-*chloro*-1,3-*dimethylimidazolium tosylate* (2a) as crystals, m.p. 104—105 °C (Found: C, 42.8; H, 5.2; N, 8.4; S, 9.5; Cl, 10.45. $C_{12}H_{15}ClN_2O_3S,2H_2O$ requires C, 42.55; H, 5.65; N, 8.25; S, 9.45; Cl, 10.45%), δ(D_2O) 8.69br (1 H, s, H-2), 7.98 (1 H, d, *J* 1.9 Hz, H-5), 3.85 (3 H, s, NCH_3), and 3.77 (3 H, s, NCH_3).

4-Bromo-1-methylimidazole [9] and methyl toluene-*p*-sulphonate similarly produced 94% of 4-*bromo*-1,3-*dimethylimidazolium tosylate* (5a), crystals, m.p. 121—122 °C (Found: C, 41.55; H, 4.3; N, 7.95; Br, 23.2. $C_{12}H_{15}BrN_2O_3S$ requires C, 41.5; H, 4.35; N, 8.05; Br, 23.0%), δ(D_2O) 8.82br (1 H, s, H-2), 7.58 (1 H, d, *J* 1.9 Hz, H-5), 3.88 (3 H, s, NCH_3), and 3.80 (3 H, s, NCH_3).

2-Phenylimidazole (9.64 g) was suspended in aqueous sodium hydroxide (8%; 61 ml). Methyl iodide (4.2 ml) in acetone (110 ml) was added with stirring during 5 min. Stirring was continued for 1 h, and the mixture was heated to reflux for 15 min. After cooling, methyl iodide (4.2 ml) was added and the mixture stirred for 15 min at 20 °C and for 15 min at reflux temperature. Ether (365 ml) was added and the aqueous solution extracted twice with ether (100 ml). The combined ether solutions were dried, the ether was removed, and the residue distilled to give 1-methyl-2-phenylimidazole (4.3 g, 42%), b.p. 161 °C at 0.4 kPa (lit.,[10] 175 °C at 2.0 kPa).

The selective monochlorination was capricious but proceeded satisfactorily under the following conditions. 1-Methyl-2-phenylimidazole (1.04 g) in tetrachloromethane (47 ml) containing triethylamine (4.6 ml) was cooled to −30 °C; chlorine in tetrachloromethane (22 ml), was then added with stirring until the starting material was consumed (*ca.* 1 h; t.l.c.). Stirring was continued at −30 °C for 1 h and then at −20 °C for 1/2 h. Cyclohexene (1.3 ml) was added to trap excess chlorine and the temperature was allowed to rise to 20 °C. Ammonia (25%; 15 ml) was added, the organic phase isolated, and the aqueous solution extracted with dichloromethane (20 ml). The combined organic solutions were extracted four times with hydrochloric acid (5%; 30 ml). After concentration to *ca.* 30 ml, ammonia (25%; 10 ml) was added and the mixture extracted with dichloromethane (3 × 20 ml). The solvent was removed and the residue chromatographed on silica gel (30 g) using chloroform as eluant to give 5-*chloro*-1-*methyl*-2-*phenylimidazole* (1.14 g, 90%).* Recrystallization (ligroin) yielded crystals, m.p. 116—117 °C (Found: C, 62.4; H, 4.8; N, 14.65; Cl, 18.35. $C_{10}H_9ClN_2$ requires C, 62.2; H, 4.7; N, 14.55; Cl, 18.4%), δ($CDCl_3$) 7.6—7.3 (5 H, m, C_6H_5), 7.00 (1 H, s, H-5), and 3.60 (3 H, s, NCH_3).

5-*Bromo*-1-*methyl*-2-*phenylimidazole* * was prepared analogously in 51% yield, m.p. 104—105 °C (Found: C, 50.65; H, 3.95; N, 11.65; Br, 33.95. $C_{10}H_9BrN_2$ requires C, 50.65; H, 3.85; N, 11.8; Br, 33.7%), δ($CDCl_3$) 7.7—7.4 (5 H, m, C_6H_5), 7.17 (1 H, s, H-5), and 3.62 (3 H, s, NCH_3).

5-Chloro-1-methyl-2-phenylimidazole, when treated with methyl toluene-*p*-sulphonate as above, produced 4-*chloro*-1,3-*dimethyl*-2-*phenylimidazolium tosylate* (2b) (94%) as crystals, m.p. 110—112 °C (Found: C, 56.85; H, 4.9; N, 7.25; S, 8.55; Cl, 9.3. $C_{18}H_{19}ClN_2O_3$ requires C, 57.05; H, 5.05; N, 7.4; S, 8.45; Cl, 9.35%), δ(D_2O) 8.0—7.8 (6 H, m, H-5 and C_6H_5), 3.80 (3 H, s, NCH_3), and 3.64 (3 H, s, NCH_3).

5-Bromo-1-methyl-2-phenylimidazole and methyl toluene-*p*-sulphonate gave analogously 4-*bromo*-1,3-*dimethyl*-2-*phenylimidazolium tosylate* (5b) (98%), crystals, m.p. 139—140 °C (Found: C, 51.2; H, 4.6; N, 6.45; S, 7.7; Br, 18.8. $C_{18}H_{19}BrN_2O_3S$ requires C, 51.05; H, 4.55; N, 6.6; S, 7.6; Br, 18.9%), δ(D_2O) 7.9—7.6 (6 H, m, H-5 and C_6H_5), 3.73 (3 H, s, NCH_3), and 3.68 (3 H, s, NCH_3).

4-*Halogenoimidazolium Salts and Sodium Sulphide*.—(*a*) 4-Chloro-1,3-dimethylimidazolium tosylate (2a) (3.27 g) and finely ground sodium sulphide (2.74 g) were stirred in dimethylformamide (or methanol) (11 ml) for 12 h. The solvent was then removed at 40 °C and the residue extracted with boiling ethyl acetate (5 × 20 ml). The extract was filtered through silica gel (Merck; 0.05—0.2 mm) (10 g) and then through activated carbon. Removal of the solvent furnished N-*methyl*-(N-*formyl*-N-*methylamino*)*thioacetamide* (3a) (1.18 g, 75%) as crystals, m.p. 83—84 °C. Recrystallization (ethyl acetate–ether) did not change the m.p. (Found: C, 41.15; H, 7.0; N, 19.3; S, 22.05. $C_5H_{10}N_2OS$ requires C, 41.05; H, 6.9; N, 19.15; S, 21.95%), *m/e* 146 (M^+), δ($CDCl_3$) conformer A, *ca.* 8.76br (1 H, s,

* The position of the halogen follows from the coupling (3.3 Hz) between the halogen-substituted carbon atom and the methyl protons. The hydrogen-carrying ring carbon atom does not couple with the methyl protons. These characteristics obtain for C-5 and -4, respectively, in 1-methylimidazole.[11]

exchangeable, NH), 8.17 (1 H, s, CHO), 4.40 (2 H, s, CH_2), 3.16 (3 H, d, *J* 4.9 Hz, collapses on irradiation at δ 8.78, CH_3 in thioamide), and 3.13 (3 H, s, CH_3 in amide); conformer B, δ *ca.* 9.03, 8.10, 4.40, 3.22 (*J* 4.7 Hz), and 2.86 (the ratio A : B is 2 : 1), $\delta_C(CDCl_3)$ conformer A, 197.5 (s, C=S), 163.5 (d, C=O), 56.6 (t, CH_2), 35.6 (q, CH_3), and 32.6 (q, CH_3); conformer B, δ_C 197.0, 163.8, 60.5, 32.6, and 30.4; $\nu_{max.}$(KBr) 3 260 (NH) and 1 675 (C=O) cm^{-1}.

(*b*) 4-Chloro-1,3-dimethyl-2-phenylimidazolium tosylate (2b) and sodium sulphide likewise afforded *N-methyl-(N-benzoyl-N-methylamino)thioacetamide* (3b) (78%) as crystals, m.p. 159—160 °C. Recrystallization (ethyl acetate–ether) gave m.p. 162—163 °C (Found: C, 59.4; H, 6.45; N, 12.45; S, 14.35. $C_{11}H_{14}N_2OS$ requires C, 59.45; H, 6.35; N, 12.6; S, 14.4%), *m/e* 222 (M^+), $\delta(CDCl_3)$ 9.18br (1 H, s, exchangeable, NH), 7.46 (5 H, s, C_6H_5), 4.54 (2 H, s, CH_2), 3.1 (3 H, d, *J* 5.2 Hz, collapses on irradiation at 9.18, CH_3 in thioamide), and 3.14 (3 H, s, CH_3 in amide), $\nu_{max.}$(KBr) 3 220 (NH) and 1 610 (C=O) cm^{-1}.

(*c*) 4-Bromo-1,3-dimethylimidazolium tosylate (5a) (146 mg) and sodium sulphide (169 mg, 3 equiv.) in methanol (0.4 ml) were refluxed with stirring for 3 h. Removal of the solvent, extraction with ethyl acetate (7 × 4 ml), and removal of ethyl acetate gave 1,3-dimethyl-Δ^4-imidazoline-2-thione (6) (36 mg, 67%), m.p. 164—170 °C. Recrystallization (ethyl acetate) gave m.p. 180 °C (lit.,[12] 182 °C).

(*d*) 4-Bromo-1,3-dimethylimidazolium tosylate (5a) (828 mg) and sodium sulphide (610 mg, 1 equiv.) in methanol (2.4 ml) were stirred for 3 h at 20 °C and the mixture worked up as described under (*c*). The ethyl acetate extract contained 146 mg of a mixture of (6) and (3a) (4 : 1, according to ^1H n.m.r.). The residue from the extraction with ethyl acetate was acidified with hydrobromic acid. Evaporation to dryness, extraction with carbon disulphide (4 × 5 ml), and removal of the solvent gave sulphur (2 mg), identified through its mass spectrum. The residue was extracted with boiling dichloromethane (4 × 5 ml). Removal of the solvent gave 1,3-dimethylimidazolium bromide (7a) (179 mg, 42%), m.p. 116 °C, identical with a specimen obtained from the tosylate [13] by ion exchange (Amberlite IRA 400, in the Br^- form).

(*e*) 4-Bromo-1,3-dimethyl-2-phenylimidazolium tosylate (5b) (174 mg), sodium sulphide (106 mg, 3 equiv.), and methanol were stirred at 20 °C for 3 h. The mixture was acidified with hydrobromic acid, the solvent removed, and the residue extracted with boiling dichloromethane. Removal of the solvent and washing with carbon disulphide (4 × 5 ml) left 1,3-dimethyl-2-phenylimidazolium bromide (7b) (99 mg, 77%), sublimed at 282—286 °C, identical with a specimen obtained from the tosylate [13] by ion exchange (Amberlite IRA 400, in the Br^- form).

(*f*) 1,3-Dimethylimidazolium tosylate (336 mg), sulphur (478 mg), sodium sulphide (508 mg), and methanol (1.5 ml) were heated to reflux with stirring for 6 days. Removal of the solvent, extraction with boiling ethyl acetate (4 × 5 ml), filtering after cooling to 20 °C, and removal of the ethyl acetate gave 114 mg (71%) of 1,3-dimethyl-Δ^4-imidazoline-2-thione (6), m.p. 169—171 °C. Filtering through activated carbon and recrystallization (ethyl acetate) gave a product with m.p. 180 °C.

(*g*) 4-Chloro-1,3-dimethylimidazolium tosylate (2a) (447 mg), sulphur (575 mg), sodium sulphide (594 mg), and methanol (1.8 ml) were heated to reflux with stirring for 3 h. The mixture was worked up as in (*e*). The crude product was dissolved in dichloromethane (20 ml), the solution washed with water (3 × 2 ml), dried, the solvent removed, the residue dissolved in methanol, the solution filtered through activated carbon, and the solvent removed to give off-white *4-chloro-1,3-dimethyl-Δ^4-imidazoline-2-thione* (8) (206 mg, 93%), m.p. 143 °C. Recrystallization (dichloromethane–ether) gave an analytical sample, m.p. 145 °C (Found: C, 36.85; H, 4.3; N, 16.95; S, 19.8; Cl, 21.6. $C_5H_7ClN_2S$ requires C, 36.9; H, 4.35; N, 17.25; S, 19.7; Cl, 21.8%), $\delta(CDCl_3)$ 6.80 (1 H, s, H-5), 3.63 (3 H, s, NCH_3), and 3.60 (3 H, s, NCH_3).

(*h*) 4-Bromo-1,3-dimethylimidazolium tosylate (5a), sulphur, sodium sulphide, and methanol were heated under similar conditions. The mixture was then acidified with hydrobromic acid, filtered through activated carbon, the solvent removed, and the residue extracted with methanol [4 × 5 ml per 0.5 g of (5a)]. Removal of the methanol, extraction with ethyl acetate as in (*g*), removal of the solvent, and chromatography (25 g silica gel per 120 mg of crude product; ethyl acetate) gave first *4-bromo-1,3-dimethyl-Δ^4-imidazoline-2-thione* (9) (42%), m.p. 176—179 °C. Recrystallization (ethyl acetate) did not raise the m.p. (Found: C, 29.15; H, 3.4; N, 13.45; S, 15.4; Br, 38.6. $C_4H_7BrN_2S$ requires C, 29.0; H, 3.4; N, 13.5; S, 15.5; Br, 38.5%), $\delta(CDCl_3)$ 6.82 (1 H, s, H-5) and 3.67 (6 H, s, 2 × NCH_3). The next fraction contained 1,3-dimethyl-Δ^4-imidazoline-2-thione (6) (8%), m.p. 176—179 °C, identical with the material described above. The residue from the extraction with ethyl acetate was extracted with boiling dichloromethane [4 × 10 ml per 0.5 g of (5a)]. Removal of the solvent gave 1,3-dimethylimidazolium bromide (7a) (41%), identical with the material above.

4-Halogenoimidazolium Salts and Sodium Methanethiolate.—(*a*) Under dry nitrogen, 4-chloro-1,3-dimethylimidazolium tosylate (2a) (614 mg), carefully dried at 1.3 Pa over phosphorus pentaoxide, and sodium hydride suspension (97 mg, 1.05 equiv.) were cooled to −80 °C, and methanethiol (1 ml), distilled from molecular sieve (3 Å), was condensed in the flask. The mixture was stirred at 20 °C for 1 h, during which time sodium hydride dissolved with hydrogen evolution. The mixture was heated to 50 °C for 10 min, collecting the evaporating methanethiol in a receiver cooled to −80 °C. Dry dimethylformamide [14] (1.5 ml) (or dry methanol) was introduced and the mixture stirred at 20 °C for 3 days. Dimethylformamide was removed at 40 °C, the residue washed with ether (4 × 10 ml), dissolved in 2N-hydrochloric acid (10 ml), passed through an ion exchanger [Amberlite IRA 400 in the Cl^- form (50 ml)], the solvent removed, and the residue extracted with boiling dichloromethane (6 × 10 ml). The dichloromethane solution contains the product, which was dissolved in water. Filtration through activated carbon, removal of the water, and reprecipitation from dichloromethane–ether afforded *1,3-dimethyl-4-methylthioimidazolium chloride* (4a) (362 mg, 97%), crystals, m.p. 144—146 °C (Found: C, 33.95; H, 5.8; N, 13.3; S, 15.3; Cl, 16.6. $C_6H_{11}ClN_2S,2H_2O$ requires C, 33.55; H, 7.05; N, 13.05; S, 14.95; Cl, 16.5%), $\delta(D_2O)$ 8.65br (1 H, s, H-2), 7.47 (1 H, d, *J* 1.9 Hz, H-5), 3.81 (3 H, s, NCH_3), 3.80 (3 H, s, NCH_3), and 2.38 (3 H, s, SCH_3).

(*b*) 4-Bromo-1,3-dimethylimidazolium tosylate (5a), sodium hydride, and methanethiol were treated analogously using dry methanol as the solvent, acidifying with hydrobromic acid, and omitting ion-exchange to give 1,3-dimethylimidazolium bromide (7a) (82%), identical with the material above.

(*c*) When 2.1 equiv. of sodium hydride were used, and

the mixture worked up as in (*d*) above, omitting extraction with carbon disulphide, (5a) afforded (6) (65%) and (7a) (30%).

(*d*) 4-Chloro-1,3-dimethyl-2-phenylimidazolium tosylate (2b) was treated as described in (*a*) to produce *1,3-dimethyl-2-phenyl-4-methylthioimidazolium chloride* (4b) (100%), an oil, δ(D_2O) 7.86 (5 H, s, C_6H_5), 3.79 (3 H, s, NCH_3), 3.76 (3 H, s, NCH_3), and 2.58 (3 H, s, SCH_3).

(*e*) To (4a) (79 mg) and sodium hydride suspension (21 mg, 1 equiv.), under dry nitrogen, methanethiol was added and excess removed as above. Dry dimethylformamide (0.8 ml) was introduced and the mixture stirred at 20 °C for 2 h. Acetic acid (0.04 ml) was added, the solvent removed at 40 °C, the residue extracted with boiling ethyl acetate (4 × 5 ml), the solvent removed, the residue washed with hexane (3 × 1 ml) at 0 °C, and chromatographed (p.l.c.) on silica gel with ethyl acetate–ether–hexane (1 : 2 : 1). The main fraction (R_F 0.52) contained *1,3-dimethyl-4-methylthio-Δ⁴-imidazoline-2-thione* (10) (38 mg, 50%), m.p. 115 °C. Recrystallization (ethyl acetate–hexane) did not raise the m.p. (Found: C, 41.5; H, 5.85; N, 16.15; S, 36.6. $C_6H_{10}N_2S_2$ requires C, 41.35; H, 5.8; N, 16.05; S, 36.8%), δ($CDCl_3$) 6.95 (1 H, s, H-5), 3.64 (3 H, s, NCH_3), 3.61 (3 H, s, NCH_3), and 2.29 (3 H, s, SCH_3). The residue from the extraction with ethyl acetate was dissolved in water. Sodium bromide (100 mg) was added, the water removed, the dry residue extracted with boiling dichloromethane (4 × 5 ml), and the solvent removed to give 1,3-dimethylimidazolium bromide (7a) (34 mg, 44%), identical with the material above.

Dealkylation of 1,3-*Dimethyl-4-methylthioimidazolium Chloride*.—Compound (4a) (77 mg) was heated with dry pyridine (0.5 ml) in a sealed tube to 200 °C for 3 h. Removal of the solvent, extraction with ethyl acetate (3 × 10 ml), filtering through activated carbon, and removal of the ethyl acetate left an oil. P.l.c. (ethyl methyl ketone saturated with water) gave *1-methyl-4-methylthioimidazole* (12 mg, 28%) (R_F 0.51), oil (Found: *m/e*, 128.041. $C_5H_8N_2S$ requires *M*, 128.041), δ($CDCl_3$) 7.66br (1 H, s, H-2), 7.21 (1 H, d, H-5, *J* 1.0 Hz), 3.70 (3 H, s, NCH_3), and 2.28 (3 H, s, SCH_3), and *1-methyl-5-methylthioimidazole* (17 mg, 52%) (R_F 0.42), oil (Found: *m/e*, 128.041), δ($CDCl_3$) 7.47br (1 H, s, H-2), 6.89 (1 H, d, H-4, *J* 1.3 Hz), 3.67 (3 H, s, NCH_3), and 2.43 (3 H, s, SCH_3). The isomers were distinguished by their ring proton shifts and cross-ring coupling constants.[15]

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