Transfer of Alkoxycarbonyl from Alkyl Imidazolium-2-carboxylates to Benzyl Alcohol, a Cyclohexanone Enamine and Diethylamine

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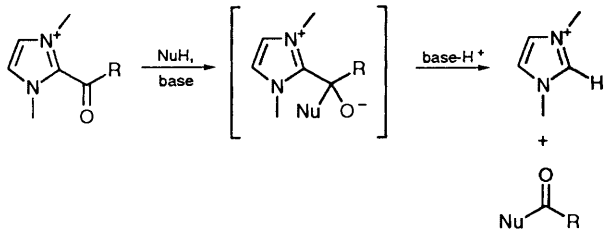
Alkylimidazole-2-carboxylates may be alkylated with methyl triflate to give the corresponding *N*-methylimidazolium salts. These salts react with benzyl alcohol in the presence of 1,4-diazabicyclo[2.2.2]octane, with 1-(pyrrolidin-1-yl)cyclohexene and with diethylamine to give benzyl alkyl carbonates, an enamino ester and a urethane respectively; in one case a tetrahedral intermediate is observed. The corresponding phenyl ester was consumed without attack by benzyl alcohol at the carbonyl group. A 2-cyanoimidazolium salt underwent similar ill-defined consumption whereas a 2-dimethylaminocarbonyl derivative remained unchanged. 2-Methylsulfonylimidazolium salts suffered attack by benzyl alcohol at the ring C-2.

Attack by nucleophiles at the carbonyl group of 2-imidazolium ketones and the subsequent ejection of the imidazolium moiety with consequent acylation of the nucleophile (Scheme 1) is a



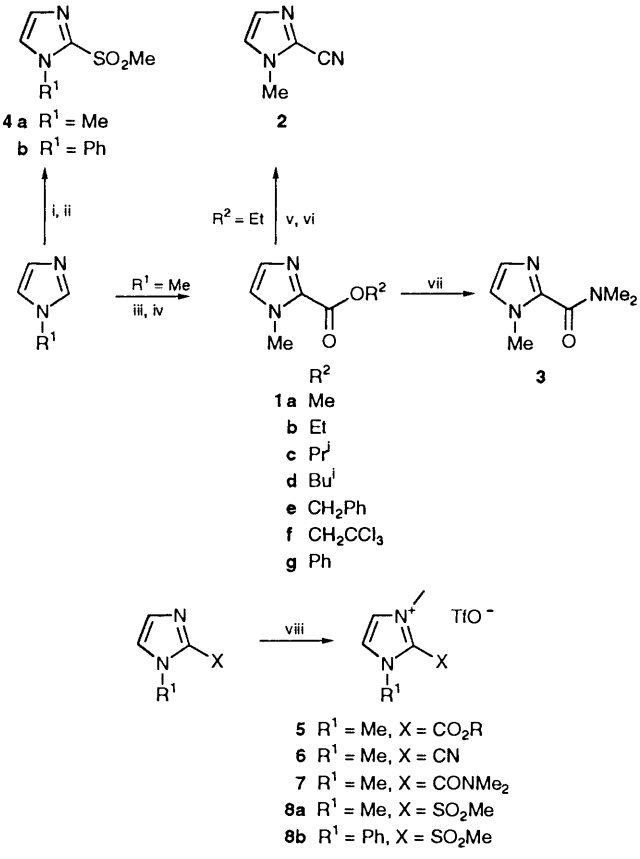
Scheme 1

well documented process[1] and mimics the biological chemistry of the corresponding thiazolium species of thiamine (vitamin B_1). In principle, similar attack on other carbonyl-containing groups at the 2-position of the imidazolium salt should also result in group transfer to the nucleophile and we were interested in determining the range of groups susceptible to such a reaction. This paper describes work on ester- and amide-containing imidazolium salts.

Results and Discussion

Synthesis of the Imidazolium Salts (Scheme 2).—Starting imidazole 2-esters **1** for the dealkoxycarbonylation were all made in one pot by the sequential reaction of 2-lithio-*N*-methylimidazole with trimethylsilyl chloride and an alkyl chloroformate. The prior addition of the silylating agent was essential for success of the reaction which presumably proceeds through the 2-trimethylsilyl derivative.[2] Aminolysis of the ethyl ester **1b**, followed by dehydration gave the 2-cyano derivative **2**. Treatment of **1b** with dimethylamine gave the amide **3**. Trapping 2-lithioimidazoles with dimethyl disulfide produced the 2-methylthio derivatives which could be oxidized to the sulfones **4**. *N*-Methylation of all these substrates with methyl triflate went smoothly and provided the desired imidazolium salts as stable, non-hygroscopic, white solids (esters **5**, cyanide **6**, amide **7** and sulphones **8**).

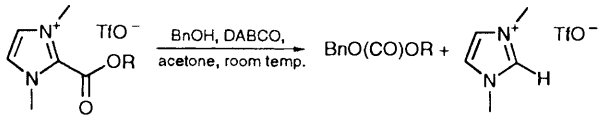
Dealkoxycarbonylation Reactions.—Reaction of the salts **5a–f** with benzyl alcohol in acetone in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) at room temperature under argon resulted in clean dealkoxycarbonylation to give good yields of the benzyl alkyl carbonates easily separated



Scheme 2 *Reagents and conditions:* i, BuLi, THF, −78 °C to −20 °C then MeSSMe, −78 °C to room temp.; ii, *m*CPBA, CH_2Cl_2, room temp.; iii, BuLi, THF, −78 °C to −20 °C then TMSCl, −78 °C to room temp.; iv, R^2OCOCl, −78 °C to room temp.; v, NH_3, MeOH; vi, $POCl_3$, py, PhMe, reflux; vii, aq. Me_2NH, MeOH; viii, MeOTf, CH_2Cl_2, room temp.

from the other product, *N*,*N*′-dimethylimidazolium triflate, by solvent extraction with dry ether after removal of the acetone (Scheme 3). Both the alcohol and base are required for the success of the reaction; neither reacted with **5** separately.

Formation of the benzyl carbonates occurs fairly rapidly. The half-lives for dealkoxycarbonylation of the methyl and isobutyl esters in [$^2H_6$]acetone at 30 °C was 33 and 926 min, respectively, by ^1H NMR spectroscopy. In the case of the ethyl



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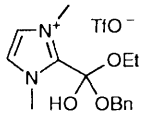
R	%
Me	74
Et	71
Pr^i	76
Bu^i	68
CH_2Ph	73
CH_2CCl_3	68

Scheme 3

ester, the ^1H NMR spectrum of the reaction mixture after 4 min showed the presence of *three* ethyl Me triplets in the region 1–1.5 ppm. Assuming one triplet peak was due to starting material and one due to product, the third is either an intermediate or a side-product. In addition, a quartet for an ethyl CH_2 appeared at 3.5 ppm, upfield from the ester ethyl CH_2 quartets at 3.8–4.3 ppm of the starting material and carbonate. Thus, this third material appears to contain an ethereal OEt group. Since it has disappeared by the end of the reaction an intermediate rather than a side-product is indicated and tetrahedral intermediate structure **9** seems likely. Earlier, we



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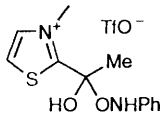

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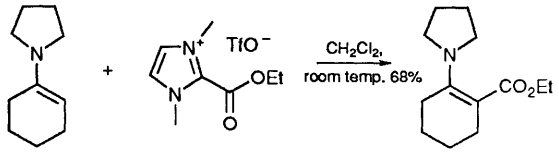
obtained stereochemical evidence consistent with the involvement of a tetrahedral intermediate in the cleavage of an acylimidazolium salt[3] and the tetrahedral intermediate **10** has been isolated in the *O*-acetylation of phenylhydroxylamine by 2-acetylthiazolium triflate.[4]

The nature of the alkyl group has little influence on the yields of these reactions although the rates of dealkoxycarbonylation are slower the larger the alkyl group (the reaction of the isopropyl ester takes 48 h for completion).

Looking at other nucleophiles, diethylamine readily effected demethoxycarbonylation of the ester **5a** in acetone in the absence of DABCO to give *N*,*N*-diethyl *O*-methyl carbamate (60%), but aniline failed to react. Carbon nucleophiles such as pentane-2,4-dione and 5,5-dimethylcyclohexane-1,3-dione and the ambident phenol all failed to react with the imidazolium esters either in the presence of DABCO or as sodio derivatives, although in the latter case the insolubility of the nucleophiles may have been the cause of the lack of reaction. However, the pyrrolidinyl enamine **11** cleanly effected deethoxycarbonylation of the ethyl ester **5b** in dichloromethane in the absence of DABCO (Scheme 4).

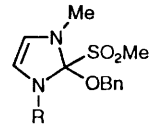


11 5b

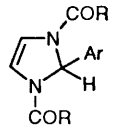
Scheme 4

In contrast to its alkyl counterparts, the phenyl ester **5g** reacted with benzyl alcohol and DABCO in a desultory manner and produced a complex mixture rather than any phenyl benzyl carbonate nor any imidazolium triflate. None of the products of this reaction could be isolated without decomposition. An alternative site of attack by nucleophiles for any of these substrates is C-2 of the imidazolium ring although this was never seen in the reactions of **5a–f**. Evidence against attack at C-2 of the imidazolium ring in **5g** too came from the results of reactions with the sulfones **8**.

The sulfones **8** certainly did appear to suffer attack at C-2 of the imidazolium ring. Thus, an olefinic singlet appeared in the ^1H NMR spectrum of the crude product from **8a** at 6.3 ppm simultaneously with the disappearance of the singlet at 7.95 ppm corresponding to the aromatic C-4(5) protons. This was even more clearly seen during the reaction of **8b** where the corresponding signals undergoing interchange were AB quartets from the aromatic region (8.1 ppm, *J* 1.5 Hz) in **8b** to the olefinic region (6.7 ppm, *J* 3.6 Hz) in the product. These chemical shifts and coupling constants are consistent with a 2,3-dihydroimidazole structure **12** for the products; in the related compounds **13** the enamido protons appear as AB



12 R = Me or Ph



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quartets at 6.3–6.9 ppm with *J* values 3 or 3.4 depending on the substituents.[5] Since the methylsulfone group is readily displaced by nucleophiles from C-2 of imidazoles[6] it is not unexpected that the imidazolium salts should suffer similar attack. Attempts to isolate the products of this attack led to their decomposition. The absence of olefinic peaks in the spectrum of the crude product mixture from **5g** suggested that intermediates of the type **12** were not present.

Neither cyano nor amide was cleaved from **6** or **7**, respectively, after treatment with benzyl alcohol and DABCO in acetone for 48 h. The amide **7** remained untouched whereas the cyano compound **6** was slowly consumed; again a complicated ^1H NMR spectrum of a mixture of unstable products resulted.

As far as we are aware the transfer of alkoxycarbonyl groups from 2-alkoxycarbonylimidazolium salts is the first demonstration of imidazolium behaving as a leaving group from any carbonyl other than a ketone or aldehyde.

Experimental

M.p.s. were determined on a Kofler hot-stage or Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer as thin film (oils) or as Nujol mulls (solids) unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q instrument, using tetramethylsilane as internal standard in $CDCl_3$ unless otherwise indicated. Coupling constants are given in Hz; signals are quoted as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), septet (sep), multiplet (m) and broad (br). Mass spectra were recorded on a VG Micromass 7070B machine by EI or FAB (thiodiethanol) methods.

Preparative gravity column chromatography was performed on Crosfield Sorbsil C60 silica gel. Petroleum refers to light petroleum of b.p. 40–60 °C. Ether refers to diethyl ether. Ether and tetrahydrofuran (THF) were distilled from sodium and potassium metal respectively under argon immediately prior to use. Dichloromethane was distilled from phosphorus pentoxide under argon just prior to use. Butyllithium was purchased from Aldrich Chemicals as solutions in hexanes. All other solvents and reagents were purified by standard methods.

General Synthesis of 2-Alkoxycarbonyl-1-methylimidazoles **1**.—To a solution (0.5 mol dm^{-3}) of 1-methylimidazole in dry

THF at −78 °C under argon was added butyllithium (1.6 mol dm^{-3}; 1.05 equiv.) dropwise. The reaction mixture was stirred for 30 min and then allowed to warm to −20 °C over 40 min when the yellow colour of the anion appeared. The mixture was cooled to −78 °C and chlorotrimethylsilane (1.05 equiv.) was added dropwise to it at such a rate that the temperature did not rise above −70 °C. The cold bath was removed and the mixture was allowed to warm to room temperature. After it had been stirred for 1 h, the mixture was cooled to −78 °C and the alkyl chlorofomate (1.05 equiv.) was added to it by syringe; the cold bath was then removed. After the temperature of the solution had reached ambient, the mixture was stirred for 12 h. Water was added to quench the reaction and the THF was removed on the rotary evaporator. The resultant slurry was taken up in dichloromethane (30 cm^3) and the mixture washed with water (2 × 20 cm^3) and the organic layer dried ($MgSO_4$). Removal of the drying agent and concentration gave the crude product which was purified on silica gel using petroleum–ether (3:1) as eluent. The following esters were made.

Methyl 1-methylimidazole-2-carboxylate[7,8] **1a** as a colourless oil (71%); ν_{max}(neat)/cm^{-1} 1713 (CO); δ_H 3.95 (3 H, s, OMe), 4.0 (3 H, s, NMe), 7.05 (1 H, fine d, J < 1, 4(5)-H) and 7.15 (1 H, fine d, J < 1, 4(5)-H); δ_C 36 (NMe), 52 (OMe), 126 [C-4(5)], 129 [C-4(5)], 136 (C-2) and 160 (CO); m/z 140 (M^+, 40%), 110 (32%), 109 (M^+ − OMe, 54%) and 82 (M^+ + H − CO_2Me, 100%).

Ethyl 1-methylimidazole-2-carboxylate[7,8] **1b** as a colourless oil (68%); ν_{max}/cm^{-1} 1711 (CO); δ_H 1.4 (3 H, t, CH_3CH_2O), 4.0 (3 H, s, NMe), 4.4 (2 H, q, CH_3CH_2O), 7.05 [1 H, fine d, J < 1, 4(5)-H] and 7.15 (1 H, fine d, J < 1, 4(5)-H); δ_C 14 (Me), 36 (NMe), 62 (CH_2O), 126 [C-4(5)], 129 [C-4(5)], 137 (C-2) and 159 (CO); m/z 154 (M^+, 11%), 110 (14%), 109 (M^+ − OEt, 19%) and 83 (M^+ + 2H − CO_2Et, 100%).

Isopropyl 1-methylimidazole-2-carboxylate **1c** as a colourless oil (63%) (Found: M^+, 168.0895. $C_8H_{12}N_2O_2$ requires M, 168.0898); ν_{max}(neat)/cm^{-1} 1714 (CO); δ_H 1.4 (6 H, d, J 7.2, $CHMe_2$), 4.0 (3 H, s, NMe), 5.25 (1 H, sep, J 7.2, $CHMe_2$), 7.0 [1 H, br s, 4(5)-H] and 7.15 [1 H, br s, 4(5)-H]; δ_C 22 (Me), 36 (NMe), 69 (CHO), 126 [C-4(5)], 129 [C-4(5)], 137 (C-2) and 159 (CO); m/z 168 (M^+, 20%), 110 (43%), 109 (M^+ − OPr^i, 50%) and 82 (M^+ + H − CO_2Pr^i, 100%).

Isobutyl 1-methylimidazole-2-carboxylate **1d** as a white crystalline solid, m.p. 45–46 °C (57%) (Found: M^+, 182.1055. $C_9H_{14}N_2O_2$ requires M, 182.1055); ν_{max}($CHCl_3$)/cm^{-1} 1711 (CO); δ_H 1.05 (6 H, d, J 7.2, $CHMe_2$), 2.2 (1 H, sep, $CHMe_2$), 4.0 (3 H, s, NMe), 4.15 (2 H, d, J 7.2, CH_2O), 7.0 (1 H, fine d, J < 1, 4(5)-H), and 7.15 [1 H, fine d, J < 1, 4(5)-H]; δ_C 19 (Me), 27 (CH), 35 (NMe), 71 (CH_2O), 126 [C-4(5)], 129 [C-4(5)], 136 (C-2) and 159 (CO); m/z 182 (M^+, 17%), 167 (M^+ − Me, 4%), 127 [M^+ + H − CH_2=$C(Me)_2$, 25%], 109 (M^+ − OBu^i, 98%) and 82 (M^+ + H − CO_2Bu^i, 100%).

Benzyl 1-methylimidazole-2-carboxylate **1e** as a white solid, m.p. 66–67 °C (52%) (Found: C, 66.4; H, 5.8; N, 12.8. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.59, N, 12.95%); ν_{max}(CH_2Cl_2)/cm^{-1} 1719 (CO); δ_H 3.98 (3 H, s, NMe), 5.4 (2 H, s, CH_2O), 7.0 [1 H, br s, 4(5)-H], 7.15 [1 H, br s, 4(5)-H] and 7.2–7.5 (5 H, m, Ph); δ_C 36 (NMe), 67 (CH_2), 126–136 (six peaks) and 159 (CO); m/z 216 (M^+, 4%), 110 (M^+ + H − OBn, 59%), 91 ($PhCH_2^+$, 84%) and 82 (M^+ + H − CO_2OBn, 100%).

2,2,2-*Trichloroethyl 1-methylimidazole-2-carboxylate* **1f** as a white solid, m.p. 38–39 °C (78%) (Found: C, 32.5; H, 2.7; N, 10.5. $C_7H_7Cl_3N_2O_2$ requires 32.65; H, 2.74; N, 10.88%); ν_{max}($CHCl_3$)/cm^{-1} 1727 (CO); δ_H 4.05 (3 H, s, NMe), 5.0 (2 H, s, CH_2O), 7.1 [1 H, br s, 4(5)-H] and 7.25 (1 H, br s, 4(5)-H); δ_C 36 (NMe), 74 (CH_2O), 95 (CCl_3), 127 [C-4(5)], 130 [C-4(5)], 135 (C-2) and 157 (CO); m/z 260 (1.5%), 258 (4.2%), 256 (4.6%) (M^+), 223 (11%), 221 (18%) (M^+ − Cl), 109 (M^+ − OCH_2CCl_3, 100%) and 82 (M^+ + H − $CO_2CH_2CCl_3$, 21%).

Phenyl 1-methylimidazole-2-carboxylate **1g** as a white crystalline solid (43%), m.p. 136–137 °C (lit.,[8] 142 °C); ν_{max}/cm^{-1} 1732 (CO); δ_H 4.1 (3 H, s, NMe) and 7.1–7.5 [7 H, m, 4(5)-H and Ph]; δ_C 36 (NMe), 115–130 (seven peaks) and 150 (CO); m/z 202 (M^+, 3%), 158 (M^+ − CO_2, 42%), 109 (M^+ − OPh, 100%) and 94 (38%).

2-*Cyano-1-methylimidazole*[9] **2**.—To an ice-cold solution of the ester **1b** (981 mg, 6.37 mmol) in methanol (20 cm^3) was slowly added aqueous ammonia (35% by wt.; 5 cm^3). The resultant solution was stirred at 0 °C for 2 h and then at room temperature overnight. The methanol was removed by rotary evaporation and the residue treated with water (10 cm^3) and extracted with ethyl acetate (2 × 5 cm^3). The combined extracts were dried ($MgSO_4$), filtered and rotary evaporated to give the crude amide as a solid. This was recrystallised from ethyl acetate to give 1-methylimidazole-2-carboxamide as a white solid (668 mg, 84%), m.p. 167–168 °C (lit.,[10] 165–167 °C or 170 °C); ν_{max}/cm^{-1} 3331, 2924 (NH_2) and 1666 (CO); δ_H 1.8 (2 H, s, NH_2), 4.05 (3 H, s, NMe) and 7.0 [2 H, m, 4(5)-H]. This solid (663 mg, 5.3 mmol) was dissolved in dry toluene (20 cm^3) containing dry pyridine (1.24 cm^3, 15.44 mmol) and then phosphorus oxychloride (2.37 g, 15.5 mmol) was added dropwise to the solution over 5 min. The solution was then heated to reflux for 2 h. After cooling, the toluene was removed by rotary evaporation and the residue was cooled in an ice-bath. Water (25 cm^3) was added very carefully to the cooled residue and the aqueous suspension was extracted with chloroform (3 × 10 cm^3). The combined extracts were washed with aqueous copper sulfate (5% by wt.; 5 × 5 cm^3) and water (5 cm^3) and dried (Na_2SO_4). Removal of the drying agent and evaporation of the solvent gave a yellow oil which was chromatographed on silica gel using ether–petroleum (1:1) as eluent to give the product as an oil (305 mg, 46%); ν_{max}/cm^{-1} 2236 (CN); δ_H 3.9 (3 H, s, NMe), 7.1 [1 H, s, 4(5)-H] and 7.2 [1 H, s, 4(5)-H]; δ_C 34 (NMe), 124 [C-4(5)], 132 (C-2); m/z 107 (M^+, 100%), 80 (M^+ − HCN, 9%), 66 (14%), 53 (15%) and 42 (62%).

1,*N*,*N*-*Trimethylimidazole-2-carboxamide* **3**.—To an ice-cold solution of the ester **1a** (511 mg, 3.65 mmol) in methanol (10 cm^3) was slowly added aqueous dimethylamine (40% by wt.; 10 cm^3). The resultant solution was stirred at 0 °C for 5 h and then at room temperature overnight. Methanol was removed by rotary evaporation and water (25 cm^3) was added to the residue. The aqueous suspension was extracted with ethyl acetate (3 × 8 cm^3) and the combined extracts were washed with water (1 × 10 cm^3) and dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed by rotary evaporation to give a colourless oil (469 mg, 84%) (Found: M^+, 153.0906. $C_7H_{11}N_3O$ requires M, 153.0902); ν_{max}/cm^{-1} 1618 (CO); δ_H 3.1 (3 H, s, CONMe), 3.4 (3 H, s, CONMe), 3.85 (3 H, s, NMe), 6.95 [1 H, fine d, J 1, 4(5)-H] and 7.0 [1 H, fine d, J 1, 4(5)-H]; δ_C 35 (NMe), 36 (NMe), 39 (NMe), 124 [C-4(5)], 127 [C-4(5)], 140 (C-2) and 161 (CO); m/z 153 (M^+, 10%), 139 (M^+ − CH_2, 6%), 109 (M^+ − NMe_2, 35%), 96 (65%) and 82 (M^+ + H − $CONMe_2$, 100%).

1-*Methyl-2-methylsulfonylimidazole* **4a**.—To a solution of 2-lithio-1-methylimidazole generated from 1-methylimidazole (1.07 g, 13.05 mmol) in dry THF (20 cm^3) at −78 °C under argon as above was added dimethyl disulfide (1.17 cm^3, 13.02 mmol) dropwise. The cold-bath was removed and the mixture was allowed to come to room temperature. It was then stirred overnight. After this, water (20 cm^3) was carefully added to

the mixture which was then rotary evaporated. The aqueous residue was extracted with ether (3 × 8 cm^3) and the combined extracts were washed with water (2 × 5 cm^3) and dried ($MgSO_4$). Removal of the drying agent and rotary evaporation of the solvent gave an oil which was chromatographed on silica gel using ether–petroleum (1:2) as eluent. The product was eluted as an oil (1.02 g, 61%) (Found: M^+, 128.0411. $C_5H_8N_2S$ requires *M*, 128.0408); ν_{max}/cm^{-1} 974; δ_H 1.55 (3 H, s, SMe), 3.6 (3 H, s, NMe), 6.85 [1 H, d, *J* 2, 4(5)-H] and 7.0 [1 H, d, *J* 2, 4(5)-H]; δ_C 16 (SMe), 33 (NMe), 122 [C-4(5)], 129 [C-4(5)] and 143 (C_2); *m/z* 128 (M^+, 100%), 113 (M^+ − Me, 20%), 95 (77%), 82 (M^+ + H − SMe, 32%), 72 (76%) and 42 (54%). The above sulfide (205 mg, 1.6 mmol) was dissolved in dichloromethane (15 cm^3) and treated dropwise at 0 °C under argon with a solution of *m*-chloroperoxybenzoic acid (50–60%; 1.65 g, 4.8 mmol) in dichloromethane (10 cm^3). After the addition, the solution was stirred at 0 °C for 1 h and then at room temperature for 10 h. After addition of water (25 cm^3) to the mixture, the layers were separated and the aqueous layer was extracted with ether (5 × 10 cm^3). The combined extracts were dried ($MgSO_4$), filtered and rotary evaporated to give a solid which was chromatographed on silica gel using ether–petroleum (2:1) as eluent. The product was obtained as a white crystalline solid (189 mg, 74%), m.p. 113–114 °C (lit.,[11] 117–118 °C); ν_{max}/cm^{-1} 1322 and 1125 (SO_2); δ_H 3.4 (3 H, s, SO_2Me), 4.0 (3 H, s, NMe), 7.0 [1 H, br s, 4(5)-H] and 7.1 [1 H, br s, 4(5)-H]; δ_C 35 (NMe), 43 (SO_2Me), 125 [C-4(5)], 129 [C-4(5)] and 143 (C-2); *m/z* 160 (M^+, 100%), 97 (M^+ + H − SO_2, 80%), 81 (M^+ − SO_2Me, 39%), 56 (41%), 54 (49%) and 42 (78%).

2-*Methylsulfonyl*-1-*phenylimidazole* **4b**.—A solution of 1-phenylimidazole[12] (630 mg, 4.38 mmol) in dry THF (20 cm^3) was treated dropwise under argon at −78 °C with butyllithium (1.6 mol dm^{-3}; 2.74 cm^3, 4.38 mmol) to give an orange coloured solution. This was allowed to warm to −50 °C over 40 min after which dimethyl disulfide (0.394 cm^3, 4.38 mmol) was added dropwise to it. After the addition, the cold-bath was removed and the mixture was stirred for 4 h. Water (30 cm^3) was then added to the mixture and the THF was removed by rotary evaporation. The residue was extracted with dichloromethane (4 × 10 cm^3) and the combined extracts were dried (Na_2SO_4), filtered and rotary evaporated. The residue was chromatographed on silica gel using dichloromethane as eluent to give the product as a solid (591 mg, 71%), m.p. 105–106 °C (Found: C, 63.2; H, 5.35; N, 14.75. $C_{10}H_{10}N_2S$ requires C, 63.13; H, 5.30; N, 14.72%); $\nu_{max}(CHCl_3)/cm^{-1}$ 967; δ_H 2.6 (3 H, s, NMe), 7.1 [2 H, ABq, *J* 2, 4(5)-H], 7.4 (5 H, m, Ph); δ_C 16 (SMe), 122, 125, 128 and 129 (2 peaks); *m/z* 190 (M^+, 20%), 175 (M^+ − Me, 3%), 91 (20%), 81 (18%), 77 (Ph^+, 12%), 32 (35%) and 28 (100%). The above sulfide (336 mg, 1.77 mmol) was oxidized to the sulfone using *m*-chloroperoxybenzoic acid (50–60%, 1.83 g, 5.32 mmol) as described for the 1-methyl analogue. The crude material was chromatographed on silica gel using ether–chloroform (1:1) as eluent to give the product as a white solid (247 mg, 63%), m.p. 96–97 °C (Found: C, 53.7; H, 4.05; N, 12.5. $C_{10}H_{10}N_2O_2S$ requires C, 54.05; H, 4.50; N, 12.61%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1322 and 1134 (SO_2); δ_H 3.3 (3 H, s, SO_2Me), 7.2 [2 H, ABq, *J* 1.5, 4(5)-H] and 7.45 (5 H, s, Ph); δ_C 43 (SO_2Me), 125.6, 126 and 129 (3 peaks); *m/z* 222 (M^+, 75%), 159 (M^+ + H − SO_2, 23%), 157 (M^+ − H − SO_2, 35%), 116 (63%), 91 (39%), 77 (Ph^+, 54%) and 28 (100%).

General Procedure for the N-*Methylation of Imidazoles*.—To a solution (0.1 mol dm^{-3}) of the imidazole in dichloromethane under argon at room temperature was added neat methyl triflate (1 equiv.) dropwise. The reaction was monitored by TLC and deemed finished with the disappearance of starting material and the appearance of a base-line spot. The solvent was rotary evaporated and the product was recrystallised from the designated solvent. The following salts were prepared.

2-*Methoxycarbonyl*-1,3-*dimethylimidazolium triflate* **5a** as a white crystalline solid from acetone–ether (76%), m.p. 96–97 °C (Found: C, 31.8; H, 3.6; N, 9.1. $C_8H_{11}F_3N_2O_5S$ requires C, 31.58; H, 3.64; N, 9.21%); ν_{max}/cm^{-1} 1744 (CO); $\delta_H([^2H_6]$-acetone) 4.0 (3 H, s, OMe), 4.15 (6 H, s, 2 × NMe) and 7.8 [2 H, s, 4(5)-H].

2-*Ethoxycarbonyl*-1,3-*dimethylimidazolium triflate* **5b** as a white crystalline solid from acetone–ether (81%), m.p. 115–116 °C (Found: C, 33.7; H, 4.0; N, 8.7. $C_9H_{13}F_3N_2O_5S$ requires C, 33.96; H, 4.12; N, 8.80%); ν_{max}/cm^{-1} 1745 (CO); $\delta_H([^2H_6]$acetone) 1.45 (3 H, t, *J* 8, *Me*CH_2O), 4.2 (6 H, s, 2 × NMe), 4.6 (2 H, q, *J* 8, CH_2O), 7.9 [2 H, s, 4(5)-H].

2-*Isopropoxycarbonyl*-1,3-*dimethylimidazolium triflate* **5c** as a white crystalline solid from acetone–ether (89%), m.p. 89–90 °C (Found: C, 36.1; H, 4.4; N, 8.4. $C_{10}H_{15}F_3N_2O_5S$ requires C, 36.15; H, 4.55; N, 8.43%); ν_{max}/cm^{-1} 1742 (CO); $\delta_H([^2H_6]$acetone) 1.4 (6 H, d, *J* 9, CH*Me*$_2$), 4.2 (6 H, s, 2 × NMe), 5.35 (1 H, sep, *J* 9, CHOCO) and 7.85 [2 H, s, 4(5)-H]; $\delta_C([^2H_6]$acetone) 21 (Me), 39 (NMe), 73 (CH) and 126 (C-4(5)).

2-*Isobutoxycarbonyl*-1,3-*dimethylimidazolium triflate* **5d** as a white crystalline solid from acetone–ether (85%), m.p. 96–97 °C (Found: C, 36.2; H, 4.45; N, 8.4. $C_{11}H_{17}F_3N_2O_5S$ requires C, 38.15; H, 4.95; N, 8.09%); ν_{max}/cm^{-1} 1742 (CO); $\delta_H([^2H_6]$-acetone) 1.0 (6 H, d, *J* 9, CH*Me*$_2$), 2.15 (1 H, d, sep, *J* 3, *J'* 9, C*H*Me_2), 4.2 (6 H, s, 2 × NMe), 4.6 (2 H, d, *J* 3, CH_2OCO) and 7.75 [2 H, s, 4(5)-H].

2-*Benzyloxycarbonyl*-1,3-*dimethylimidazolium triflate* **5e** as a white crystalline solid from acetone–ether (77%), m.p. 85–86 °C (Found: C, 44.1: H, 3.9; N, 7.1. $C_{14}H_{15}F_3N_2O_5S$ requires C, 44.21; H, 3.98; N, 7.37%); ν_{max}/cm^{-1} 1738 (CO); $\delta_H([^2H_6]$-acetone) 4.2 (6 H, s, 2 × NMe), 5.55 (2 H, s, CH_2OCO), 7.3–7.6 (5 H, m, Ph) and 7.9 [2 H, s, 4(5)-H].

1,3-*Dimethyl*-2-(2,2,2-*trichloroethoxycarbonyl*)*imidazolium triflate* **5f** as a white crystalline solid from acetone–ether (92%), m.p. 104–105 °C (Found: C, 25.9; H, 2.2; N, 6.3. $C_9H_{10}Cl_3F_3N_2O_5S$ requires C, 25.64; H, 2.39; N, 6.64%); ν_{max}/cm^{-1} 1758 (CO); $\delta_H([^2H_6]$acetone) 4.35 (6 H, s, 2 × NMe), 5.3 (2 H, s, CH_2) and 8.0 (2 H, s, 4(5)-H).

1,3-*Dimethyl*-2-*phenoxycarbonylimidazolium triflate* **5g** as a white solid from acetone–ether (81%), m.p. 102–103 °C (Found: C, 42.4; H, 3.35; N, 7.4. $C_{13}H_{13}F_3N_2O_5S$ requires C, 42.63; H, 3.58; N, 7.65%); ν_{max}/cm^{-1} 1744 (CO); $\delta_H([^2H_6]$acetone) 4.3 (6 H, s, 2 × NMe), 7.45 (5 H, br s, Ph) and 7.95 [2 H, s, 4(5)-H].

2-*Cyano*-1,3-*dimethylimidazolium triflate* **6** as a crystalline solid from acetone–ether (86%), m.p. 158–159 °C (Found: C, 31.0; H, 2.7; N, 15.35. $C_7H_8F_3N_3O_3S$ requires C, 31.00; H, 2.97; N, 15.49%); $\delta_H([^2H_6]$acetone) 4.2 (6 H, s, 2 × NMe) and 8.05 [2 H, s, 4(5)-H].

2-(*N*,*N*-*Dimethylaminocarbonyl*)-1,3-*dimethylimidazolium triflate* **7** as a crystalline solid from acetone–ether (91%), m.p. 126–127 °C (Found: C, 33.8; H, 4.35; N, 12.95. $C_9H_{14}F_3N_3O_4S$ requires C, 34.07; H, 4.45; N, 13.24%); ν_{max}/cm^{-1} 1681 (CO); $\delta_H([^2H_6]$acetone) 3.1 (3 H, s, CONMe), 3.2 (3 H, s, CONMe), 4.0 (6 H, s, 2 × NMe), 7.8 [2H, 4(5)-H]; $\delta_C([^2H_6]$acetone) 35 (NMe), 36 (NMe), 37 (NMe) and 124 (C-4(5)).

1,3-*Dimethyl*-2-*methylsulfonylimidazolium triflate* **8a** as a crystalline solid from acetone–ether (92%), m.p. 140–141 °C (Found: C, 25.9; H, 3.25; N, 8.3. $C_7H_{11}F_3N_2O_5S_2$ requires C, 25.93; H, 3.42; N, 8.64%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1378 and 1157 (SO_2); $\delta_H([^2H_6]$acetone) 3.75 (3 H, s, SO_2Me), 4.25 (6 H, s, 2 × NMe) and 8.0 [2 H, s, 4(5)-H]; $\delta_C([^2H_6]$acetone) 38 (NMe), 44(SO_2Me) and 127 (C4(5)).

1-Methyl-2-methylsulfonyl-3-phenylimidazolium triflate **8b** as a crystalline solid from acetone–ether (76%), m.p. 133–134 °C (Found: C, 36.8; H, 3.3; N, 7.1. $C_{12}H_{13}F_3N_2O_5S_2$ requires C, 37.30; H, 3.39; N, 7.25%); ν_{max}/cm^{-1} 1358 and 1153 (SO_2); δ_H([$^2H_6$]acetone) 3.6 (3 H, s, SO_2Me), 4.4 (3 H, s, NMe), 7.6–7.9 (5 H, m, Ph) and 8.1 (2 H, ABq, J 2, 4(5)-H).

Dealkoxycarbonylation: General Procedure.—To a solution of the 2-alkoxycarbonylimidazolium salt (1.5 mmol) in acetone (10 cm^3) under argon was added the substrate (benzyl alcohol (1 equiv.) and DABCO (1 equiv.) or pyrrolidin-1-ylcyclohex-1-ene (1.1 equiv.) or diethylamine (1.1 equiv.)] The mixture was stirred for the requisite time at room temperature after which the solvent was removed by rotary evaporation. The products were extracted from the residue by trituration with ether (3 × 5 cm^3). The ether extracts were combined and rotary evaporated to give the crude products which were purified by chomatography on silica gel using ether–petroleum (2:3) as eluent. The following were obtained.

Benzyl methyl carbonate[13] as a colourless oil (74%); ν_{max}/cm^{-1} 1752 (CO); δ_H 3.8 (3 H, s, OMe), 5.2 (2 H, s, CH_2) and 7.4 (5 H, s, Ph); δ_C 55 (OMe), 70 (CH_2), 128 (2 peaks), 135 and 156 (CO); *m/z* 166 (M^+, 38%), 107 (M^+ − MeOCO, 45%) and 91 ($PhCH_2^+$, 100%).

Benzyl ethyl carbonate as a colourless oil (71%) (Found: M^+, 180.0791. $C_{10}H_{12}O_3$ requires *M*, 180.0786); ν_{max}/cm^{-1} 1745 (CO); δ_H 1.25 (3 H, t, $OCH_2\mathit{Me}$), 4.15 (2 H, q, OCH_2Me), 5.1 (2 H, s, OCH_2Ph) and 7.35 (5 H, s, Ph); δ_C 14 (Me), 64 (CH_2O), 69 (CH_2O), 128 (3 peaks, Ph), 135 (Ph) and 155 (CO); *m/z* 180 (M^+, 43%), 108 ($PhCH_2OH^+$, 48%), 107 ($PhCH_2O^+$, 51%), 91 ($PhCH_2^+$, 100%) and 79 (65%).

Benzyl isopropyl carbonate as a colourless oil (76%) (Found: M^+, 194.0939. $C_{11}H_{14}O_3$ requires *M*, 194.0943); ν_{max}/cm^{-1} 1738 (CO); δ_H 1.3 (6 H, d, *J* 7.2, Me_2CHO), 4.9 (1 H, sep, *J* 7.2, $OC\mathit{H}Me_2$), 5.15 (2 H, s, OCH_2) and 7.4 (5 H, s, Ph); 22 (Me), 69 (OCH), 72 (OCH_2), 128 (2 peaks, Ph), 137 (Ph) and 156 (CO); *m/z* 194 (M^+, 18%), 152 ($M^+ + H - Pr^i$, 24%), 108 ($PhCH_2OH^+$, 45%), 107 ($PhCH_2O^+$, 50%), 91 ($PhCH_2^+$, 100%), 79 (45%) and 43 (Pr^{i+}, 23%).

Benzyl isobutyl carbonate as a colourless oil (68%) (Found: M^+, 208.1096. $C_{12}H_{16}O_3$ requires *M*, 208.1099); ν_{max}/cm^{-1} 1743 (CO); δ_H 0.95 (6 H, d, *J* 7.2, Me_2CH), 2.0 (1 H, apparent sep, *J* 7.2, $Me_2C\mathit{H}$), 3.95 (2 H, d, *J* 7.2, $OC\mathit{H}_2CH$), 5.2 (2 H, s, OCH_2Ph) and 7.4 (5 H, s, Ph); δ_C 19 (Me), 28 (CH), 69 (OCH_2), 74 (OCH_2), 128 (2 peaks, Ph), 136 (Ph) and 155 (CO); *m/z* 208 (M^+, 16%), 152 ($M^+ + H - Bu^i$, 16%), 108 ($PhCH_2OH^+$, 36%), 107 ($PhCH_2O^+$, 47%), 91 ($PhCH_2^+$, 100%), 57 (Bu^{i+}, 72%).

Dibenzyl carbonate[14] as a colourless oil (73%); ν_{max}/cm^{-1} 1748 (CO); δ_H 5.2 (4 H, s, OCH_2) and 7.4 (10 H, s, Ph); *m/z* 242 (M^+, 0.1%), 107 ($PhCH_2O^+$, 100%) and 92 (51%).

Benzyl 2,2,2-trichloroethyl carbonate as a colourless oil (68%) (Found: C, 42.2; H, 3.0. $C_{10}H_9Cl_3O_3$ requires C, 42.36; H, 3.20%); ν_{max}/cm^{-1} 1765 (CO); δ_H 4.75 (2 H, s, OCH_2CCl_3), 5.2 (2 H, s, OCH_2Ph) and 7.4 (5 H, s, Ph); δ_C 71 (CH_2), 77 (CH_2), 129 (3 peaks, Ph), 135 (Ph) and 154 (CO); *m/z* 286 + 284 + 282 (M^+, 3%, 9%, 9%), 107 ($PhCH_2O^+$, 41%), 91 ($PhCH_2^+$, 100%) and 79 (85%).

Ethyl 2-pyrrolidinylcyclohex-1-enecarboxylate[15] as a yellow oil (68%); ν_{max}/cm^{-1} 1704 (CO); δ_H 1.25 (3 H, t, $\mathit{Me}CH_2O$), 1.4–2.1 (8 H, m, CH_2), 2.2–2.6 (4 H, m, allylic CH_2), 3.35 (4 H, m, CH_2N) and 4.1 (2 H, q, CH_2O); *m/z* 223 (M^+, 2%), 210 (9%), 194 (M^+ − Et, 7%), 113 (25%) and 98 (100%).

N,N-Diethyl *O*-methyl carbamate[16] as a pale yellow oil; ν_{max}/cm^{-1} 1711 (CO); δ_H 1.0 (6 H, t, 2 × $\mathit{Me}CH_2N$), 3.2 (4 H, q, 2 × CH_2N) and 3.6 (3 H, s, OMe); δ_C 14 (Me), 41 (CH_2), 52 (OMe) and 156 (CO).

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Paper 3/05909J
Received 1st *October* 1993
Accepted 21st *October* 1993