Acetone Oxime α-Triphenylphosphonium Bromide (2g). A solution of chloroacetone (9.25 g, 0.100 mol) and hydroxylamine hydrochloride (10.42 g, 0.150 mol) was allowed to stand at room temperature for 12 h. After the solution was extracted with methylene chloride (3 × 50 mL), 2,2-dimethoxypropane (10.4 g, 0.100 mol) and *p*-toluenesulfonic acid monohydrate (0.050 g) were added. The resulting solution was boiled under reflux for 24 h. The acid was neutralized by washing the solution with 1% sodium bicarbonate (3 × 100 mL). After the mixture was dried, the product was distilled to give (2-methoxy-2-propyl)-α-chloroacetone *syn*-*O*-oxime (**3g**) (12.10 g, 67%) as a colorless oil: bp 40 °C (0.10 mm); NMR ($CDCl_4$) δ 4.07 (s, 2 H), 3.12 (s, 3 H), 1.95 (s, 3 H), 1.40 (s, 6 H); *m/e* 148 (5), 147 (8), 92 (10), 91 (30), 72 (50), 71 (15).

Anal. Calcd for $C_7H_{14}ClNO_2$: C, 46.80; H, 7.86. Found: C, 46.88; H, 7.83.

3g (1.805 g, 0.010 mol) and triphenylphosphine (2.623 g, 0.010 mol) in dry acetone (10 mL) were boiled under reflux in the presence of triethylamine (1 drop) for 75 h. Addition of ether gave an oil which was dissolved in 95% ethanol (10 mL), and concentrated hydrochloric acid (10 drops) was added. Addition of ether after 5 h gave a colorless solid which was recrystallized from a mixture of absolute ethanol and ether (1:4 (v/v)) to give **2g** (1.2 g, 32.4%): mp 223 °C (lit.[3] mp 223 °C).

3-Methyl-5,5,5-triphenyl-4,5-dihydro-1,2,5-oxazaphosphole (5g). Triethylamine (10.1 g, 0.100 mol) was added at once to a suspension of a pure sample of **2g** (36.98 g, 0.100 mol) at 0 °C with vigorous stirring. The suspended **2g** dissolved and within a few minutes **5g** precipitated (31.5 g, 95%) as pale yellow crystals. An analytical sample[12] was prepared by rapid recrystallization from a mixture of methylene chloride and ether (1:4) to give **5g** as tan crystals: mp 117–119 °C dec; NMR ($CDCl_3$) δ 7.35 (m, 15 H), 3.08 (d, 2 H, J_{HP} = 11 Hz), 2.12 (s, 3 H); *m/e* 278 (84), 277 (100).

Anal. Calcd for $C_{21}H_{20}NOP$: C, 75.66; H, 6.05. Found: C, 75.76; H, 6.07.

2-Methylazirine (6g). **5g** (3.33 g, 0.010 mol) was pyrolyzed as in the case of **6f** to give 2-methylazirine (**6g**) (0.35 g, 63.6%). Redistillation gave a pure sample as a colorless liquid: bp 42–43 °C (1 atm); IR (NaCl) 1772 ($\nu_{C=N}$); NMR ($CDCl_3$) δ 2.50 (s, 3 H), 1.35 (s, 2 H); *m/e* (70 eV) 55 (84), 54 (100), 53 (7), 52 (22), 51 (15), 41 (18), 40 (30), 39 (15), 38 (11); *m/e* (15 eV) 55 (100), 54 (88).

2,5,6-Trimethyl-3,4-diphenyl-3*H*-azepine (13). A solution of 2-methylazirine (**6g**) (0.220 g, 0.0040 mol) and 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer (**12**) (0.520 g, 0.0010 mol) in chloroform (25 mL) was heated in a Fischer–Porter tube at 100 °C for 48 h. Evaporation of the solvent, followed, by addition of pentane (50 mL) gave **12** (0.031 g, 6%). Concentration of the filtrate to a final volume of 10 mL and cooling gave the azepine **13** (0.14 g, 22%) as a pale yellow solid: NMR ($CDCl_3$) δ 7.50–6.90 (m, 10 H), 6.66 (s, 1 H), 5.10 (s, 1 H), 2.16 (s, 3 H), 1.90 (s, 3 H), 1.67 (s, 3 H); *m/e* 288 (22), 278 (70), 286 (100), 272 (17), 260 (12), 246 (16).

4,4-Dideuterio-3,5,5,5-tetraphenyl-4,5-dihydro-1,2,5-oxazaphosphole (5a-d_2). Deuterium bromide (47%) in deuterium oxide (17.5 g) was added to a suspension of **5a** (39.5 g, 0.100 mol) in a mixture of dry dimethylformamide (100 mL) and deuterium oxide (50 mL) at 0 °C over a period of 10 min with stirring. The reaction mixture was warmed to dissolve the solid, filtered, and cooled to 0 °C. Dry triethylamine (ca. 30 mL) was then added to the cold solution and the colorless precipitate was collected and washed with methanol-*d*. Rapid recrystallization of the product from a mixture of methylene chloride and ether (1:4) gave **5a**-d_2 (26.5 g, 67%) containing 5% monodeuterated **5a**-*d* (by NMR).

2-Phenyl-3,3-dideuterioazirine (6a-d_2). **5a**-d_2 (3.97 g, 0.0100 mol) was pyrolyzed as in **6f** to give 2-phenyl-3,3-dideuterioazirine (**6a**-d_2) (0.52 g, 44%) containing 6% **6a**-*d* (by NMR): *m/e* (15 eV) 119 (100%).

Acknowledgment. Support of this research by NCI Grant CA 19203 from DHEW is gratefully acknowledged.

Registry No. 1a, 17082-13-2; **1b**, 71426-50-1; **1c**, 71426-51-2; **1d**, 71426-52-3; **1e**, 71426-53-4; **1f**, 71426-54-5; **2a**, 71426-55-6; **2b**, 71426-56-7; **2c**, 71426-57-8; **2d**, 71426-58-9; **2e**, 71426-59-0; **2g**, 71426-60-3; **3a**, 50314-87-9; **3b**, 71426-61-4; **3c**, 71426-62-5; **3d**, 71426-63-6; **3e**, 71426-64-7; **3f**, 71426-65-8; **3g**, 71426-66-9; **4a**, 71426-67-0; **4b**, 71426-68-1; **4c**, 71426-69-2; **4d**, 71486-17-4; **4e**, 71426-70-5; **5a**, 14264-70-1; **5a**-d_2, 71426-71-6; **5b**, 71426-72-7; **5c**, 17631-19-5; **5d**, 71426-73-8; **5e**, 71426-74-9; **5f**, 71426-75-0; **5g**, 17631-21-9; **6a**-d_2, 71426-76-1; **6f**, 71426-77-2; **6g**, 71426-78-3; **7**, 71463-33-7; **8**, 71426-79-4; **12**, 26307-17-5; **13**, 71426-80-7; hydroxylamine sulfate, 10039-54-0; triphenylphosphine, 603-35-0; 2,2-dimethoxypropane, 77-76-9; α-bromoacetophenone, 70-11-1; α-bromo-*p*-chloroacetophenone, 536-38-9; α,*p*-dibromoacetophenone, 99-73-0; α-bromo-*p*-methylacetophenone, 619-41-0; α-bromo-*p*-methoxyacetophenone, 2632-13-5; 1-bromo-3,3-dimethyl-2-butanone, 5469-26-1; 1-bromo-2-propanone, 598-31-2.

Supplementary Material Available: Analytical data on compounds **1b–e** → **5b–e** and **4a** (4 pages). Ordering information is given on any current masthead page.

(12) A previous attempt[3] to obtain **5g** in pure form has been unsuccessful.

Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Effects of Hydrogen Bonding and Protonation on Nitrogen Chemical Shifts in Imidazoles[1a]

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The ^{15}N chemical shifts of imidazoles, *N*-methylimidazole and 4-methylimidazole, have been measured in acidic and neutral nonaqueous media. Both hydrogen bonding and protonation of the imidazoles result in upfield shifts of the average of the nitrogen resonances, but the magnitudes of the protonation shifts far exceed those associated with hydrogen bonding. The less-than-normal shifts of the imidazolium ions in nonaqueous media suggest ion-pair formation resulting from interion hydrogen bonding. Such effects diminish in solvents of higher dielectric constant and greater solvating power for salts.

The imidazole unit in the histidyl residues of several enzymes plays a major role in hydrolytic bond cleavage in peptides. A study of the behavior of free imidazole and its derivatives toward hydrogen-bonding and protonating

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Table I. ^{15}N Chemical Shifts[a] of *N*-Methylimidazole at 25 °C in Hydrogen-Bonding and Protonating Media

solvent	$\delta^{15}N$ N1	$\delta^{15}N$ N3	$\delta^{15}N^b$	$\Delta\delta$ (N1 − N3)[c]
C_6H_6[d]	215.7	111.4	163.6	104.3
$CHCl_3$[e]	215.1	119.3	167.2	95.8
CH_3OH[d]	212.5	127.8	170.2	84.7
H_2O[f]	211.5	128.5	169.9	83.0
CF_3CH_2OH[h]	214.0	127.8	170.9	86.2
CH_3CO_2H[h]	213.0	134.2	173.6	78.8
CF_3CO_2H[h]	205.8	189.8	197.8	16.0
CH_3CO_2H	203.1	198.0	200.6	5.1
CH_3OH[d,g]	202.5	200.7	201.6	1.8
H_2O[f,g]	204.1	203.6	203.9	0.5

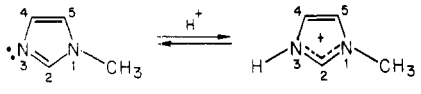
[a] Of 2 M solutions of 1 or 2 in ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] Average shifts of nitrogens. [c] Difference between the shifts of N1 and N3. [d] Unpublished research by R. O. Duthaler. [e] Unpublished research by C. Dyllick-Brenzinger. [f] Reference 7. [g] *N*-methylimidazolium chloride used in place of *N*-methylimidazole. [h] 2 M in $CHCl_3$.

media is therefore important to an understanding of the function of the imidazoyl ring in biological environments. Nuclear magnetic resonance spectroscopy, because of its applicability to a wide variety of solvent systems, offers special advantages for elucidating such medium effects.

The ^{13}C chemical shifts of a few imidazoles have been measured as functions of solvent,[2-4] shift reagents,[5] and acid concentration in aqueous solution.[4a] However, nitrogen NMR should be still more informative because the imidazole nitrogens are the active sites for solvent and acid interactions. This is amply supported by the extant data on the effects of solvent on ^{14}N chemical shifts of imidazole and *N*-methylimidazole[6] and on ^{15}N protonation shifts of several imidazoles in aqueous solution.[7] The present paper is concerned with hydrogen-bonding and protonation shifts of the ^{15}N resonances of imidazoles in nonaqueous media.

Results and Discussion

N-Methylimidazole (1) shows two ^{15}N NMR resonances:

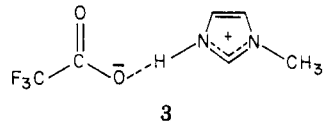


1 2

one at low field corresponding to the "pyridine" nitrogen, N3, and the other at higher field, the "pyrrole" nitrogen, N1. The difference in these shifts in neutral solutions is very large and, depending on the solvent, ranges from about 80 to 100 ppm.

Hydrogen bonding causes the N3 (pyridine-like) resonance of *N*-methylimidazole to shift upfield while the N1 (pyrrole-like) resonance shifts downfield, although to a much smaller extent. The net result of hydrogen bonding is a smaller difference between the chemical shifts of N1 and N3 and an upfield movement of their average (Table I). Thus, the change from a solution of 1 in cyclohexane to a solution in chloroform containing 1 equiv of trifluoroethanol causes the shift difference to decrease by 18 ppm and the average of the shifts to move upfield by 7.3 ppm. Substitution of 1 equiv of the more strongly hydrogen-bonding acetic acid for trifluoroethanol in chloroform results in a reduction of 7.4 ppm in the shift difference and a further upfield shift of the average by 2.7 ppm.

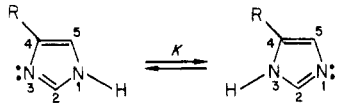
Protonation of *N*-methylimidazole (2) converts both N1 and N3 into amidinium nitrogens with nearly equal ^{15}N shifts. In water, the N1 − N3 shift difference of 2 is only 0.5 ppm. The average of the nitrogen shifts of 2 in water is about 34 ppm upfield of the value for 1. When trifluoroethanol is replaced by 1 equiv of trifluoroacetic acid in a 2 M solution of 1 in chloroform, the average nitrogen shift moves upfield by about 27 ppm, and the shift difference becomes 16 ppm. That full protonation of the base occurs in this medium, however, is indicated by the replacement of the infrared carboxyl absorption of trifluoroacetic acid at 1774 cm^{-1} with that of the carboxylate anion at 1668 cm^{-1} (0.6 M each of 1 and trifluoroacetic acid in chloroform). The deviations of the difference and the average nitrogen shifts in this medium from the values in water seem better attributed[7] to the effect of a small amount of charge transfer from the cation to a nearby carboxylate anion via hydrogen bonding (3) than to in-



3

complete proton transfer. The resulting electrical asymmetry is in the proper direction to account for the difference in the shifts of N1 and N3. The type of ion-pair association represented by 3 is expected to diminish in solvents with better solvating capabilities for salts. Accordingly, the shift difference, $\Delta\delta$ (N1 − N3), for 3 is 5.1 ppm in acetic acid, 1.8 ppm in methanol, and 0.5 ppm in water (see Table I).

Imidazoles with a labile N–H bond exist in solution as an equilibrium mixture of rapidly interconverting tautomers (eq 1). The ^{15}N shift of each nitrogen, N1 and N3,[8]



(1)

4a, R = H **4b**, R = H
5a, R = CH_3 **5b**, R = CH_3

is therefore the weighted average of its value in each of the two tautomers. When R = H, for which the equilibrium constant *K* is unity, the average shifts are equivalent, and imidazole therefore exhibits only one peak in its ^{15}N spectrum.[9] That this shift is a composite of pyridine- and pyrrole-type resonances, as found for *N*-methylimidazole, is indicated by the fact that the imidazole resonance and the average of the N1 and N3 shifts of 1 differ by less than 2 ppm in solvents in which imidazole (4) is like 1 in not being highly self-associated. It is not surprising, then, that the single ^{15}N resonance of imidazole behaves in the same

(1) (a) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences. (b) On sabbatical leave from Pennsylvania State University, Ogontz Campus.

(2) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 3543–9.
(3) Reynolds, W. F.; Peat, I. E.; Freedman, M. H.; Lyerla, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 328–31.
(4) (a) Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 4232–8; (b) Pugmire, R. J.; Grant, D. M. *Ibid.* **1971**, *93*, 1880–7.
(5) Elguero, J.; Marzin, C.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 357–63.
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(7) Bachovchin, W. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8041–7.

(8) The numbering system we use here is designed to keep the R group located on the lowest numbered ring carbon. In view of the rapid equilibration of the tautomers, it is not logical to use the IUPAC numbering of the imidazole ring where the NH nitrogen is always assigned the lowest number. In the biochemist's lexicon, N1 would be the τ nitrogen and N3 would be the π nitrogen.

(9) This is true even in dimethyl sulfoxide, in which solvent slow intermolecular N–H proton exchange is, however, evident with pyrazole; unpublished experiments of Dr. C. Dyllick-Brenzinger.

Table II. ^{15}N Chemical Shifts[a] of Imidazole at 25 °C in Hydrogen-Bonding and Protonating Media

solute	concn, M	solvent	$\delta^{15}N$
4	2	$CHCl_3$	166.4
4	2	H_2O[b]	171.0
4	2	CF_3CH_2OH[d]	172.4
4	2	CF_3CH_2OH	176.2
4	2	CH_3CO_2H[d]	180.6
4	2	CH_3CO_2H	199.8
4·HCl	1.2	CH_3OH	200.3
4·HCl		H_2O[b]	202.0
$6{\cdot}I^-$	1.4	CH_3OH	204.5[c]

[a] In ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] Reference 7. [c] As the iodide salt. [d] 2 M in $CHCl_3$.

Table III. ^{15}N Chemical Shifts[a] of 4-Methylimidazole in Hydrogen-Bonding and Protonating Media at 25 °C

concn, M	solvent	$\delta^{15}N$[b] N1	$\delta^{15}N$[b] N3	$\delta^{15}N$[c]	$\Delta\delta$ (N1 − N3)[d]
1.5	$CHCl_3$	167.0	161.5	164.3	5.5
	H_2O[e]	172.8	164.4	168.6	8.4
2	CF_3CH_2OH[g]	173.3	167.0	170.2	6.3
2	CF_3CO_2H[g]	199.1	195.0	197.0	4.1
2	CH_3CO_2H	201.3	197.3	199.3	4.0
	H_2O[e,f]	202.6	198.6	200.6	4.0

[a] In ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] N1 and N3 were identified by their splitting patterns in the proton-coupled spectrum: a triplet for N1 [J(N1-N2) ≈ J(N1-H5) = 8.7 Hz] and a broadened doublet for N3 [J(N3-H2) = 9.4 Hz]. See: Blomberg, F.; Maurer, W.; Rüterjans, H. *J. Am. Chem. Soc.* **1977** *99*, 8149, for an analysis of nitrogen-proton splittings in histidine. [c] Average of the averaged shifts of N1 and N3. [d] Differences between the averaged shifts of N1 and N3. [e] Reference 7. [f] 4-Methylimidazolium chloride is the solute. [g] 2 M in $CHCl_3$.

way toward hydrogen-bonding and protonating solvents as the average of the nitrogen shifts of *N*-methylimidazole. Thus, changing the solvent, from chloroform to chloroform containing 2 M trifluoroethanol and then to neat trifluoroethanol, results in successive upfield shifts of the nitrogen resonances of 6.0 and 3.8 ppm, respectively, as the degree of hydrogen bonding increases (Table II). It is likely that the average ^{15}N shift of imidazole is no more influenced by self-association in chloroform solution at the 2 M concentration used here than it is by hydrogen bonding to the solvent itself because it differs from the average of the *N*-methylimidazole resonances in the same solvent by only 0.8 ppm.

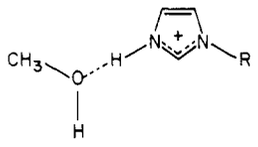
The shift of the imidazolium ion is like that of **2**, being far upfield at 202 ppm in water.[7] The resonance of imidazole in chloroform containing 1 equiv of acetic acid (181 ppm) is much lower, and this value is surely the result of incomplete protonation. The evidence is the presence of the infrared carboxyl absorption of *both* the hydrogen-bonded acid at 1700 cm^{-1} and the carboxylate anion at 1550 cm^{-1}. The extent of protonation in this medium may be estimated to be on the order of 17% from the ^{15}N shifts of strongly hydrogen-bonded (in trifluoroethanol) and fully protonated imidazole.

The effect of decreasing ion-pair association for the salts of the imidazolium ion is again demonstrated by the upfield shift of its nitrogen resonance with a change of medium toward more strongly solvating solvents (Table II).

The small, but consistent, downfield trend of the average nitrogen shifts in the series of imidazolium ions **6** → **2** → **7** with decreasing methylation at nitrogen suggests a small

6, 204.5 ppm 2, 201.6 ppm 7, 200.3 ppm

amount of charge dispersal from the cation to the solvent through hydrogen bonding to an NH hydrogen (**8**) similar



8, R = H or CH_3

to that postulated for the ion pair, **3**. Rapid tautomeric equilibration (eq 1) of 4-methylimidazole (**5**) in solution causes an averaging of the ^{15}N shifts of the two isomeric forms. The average shifts for N1 and N3 are not equal because N1 and N3 are not equivalent. If we assume that the shifts of **5** in the absence of equilibration would be those of *N*-methylimidazole, the equilibrium constant for eq 1 is about 0.8 and is relatively insensitive to solvent changes.

The effect of hydrogen bonding with solvent is to produce upfield shifts of both nitrogen resonances of **5**, as was the case for the nitrogens of imidazole itself (Table III).

Formation of the 4-methylimidazolium ion **9** in chloroform containing 1 equiv of trifluoroacetic acid is clearly evident from the much larger upfield shifts of the N1 and N3 resonances relative to their shifts in weakly acidic but hydrogen-bonding solvents. The less-than-normal shifts of the trifluoroacetate salt of **9** in chloroform (average nitrogen shift of 197.0 ppm relative to 200.6 ppm in water) can be accommodated by assumption of ion pairing as for

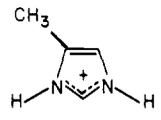


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Table IV. Proton Chemical Shifts[a] of Imidazole and *N*-Methylimidazole in Deuteriochloroform

compd	concn, M	δ(H5,H4)[b]	δ(H2)	δ(NH)	δ(N-CH_3)
1	1.3	6.81, 6.96	7.36		3.63
1	0.6	6.84, 7.01	7.40		3.66
1	0.6, + 0.6 M CH_3CO_2H	6.84, 7.02	7.58	13.02[c,e]	3.67
1	0.6, + 0.6 M CF_3CH_2OH	6.84, 6.96	7.39	6.89[d,f]	3.67
1	0.6, + 0.6 M CF_3CO_2H	7.15, 7.30	8.75	15.29[g,h]	3.90
4	0.6	7.10	7.69	12.03	
4	0.6, + 0.6 M CH_3CO_2H	7.10	8.00	14.58[g]	
4	0.6, + 0.6 M CF_3CH_2OH	7.00	7.58	9.11[g]	

[a] In ppm downfield from Me_4Si. [b] Assignments uncertain. [c] OH proton resonance of the CH_3CO_2H present in the solution. [d] OH proton resonance of the CF_3CH_2OH present in the solution. [e] OH proton resonance of CH_3CO_2H (0.6 M) in $CDCl_3$ is 10.64 ppm. [f] OH proton resonance of CF_3CH_2OH (0.6 M) in $CDCl_3$ is 2.64 ppm. [g] Averaged position of OH and NH resonances. [h] OH proton resonance of CF_3CO_2H (0.6 M) in $CDCl_3$ is 10.28 ppm.

3. The upfield shifts of the nitrogen resonances of **9**, on changing solvent from chloroform to acetic acid to water, again reflects diminishing ion pairing.

Proton Chemical Shifts. Table IV summarizes proton chemical shifts of imidazole and *N*-methylimidazole in several hydrogen-bonding and protonating solvents. Of the nonexchanging protons, only that at C2 appears to be sensitive to hydrogen bonding at nitrogen. Protonation affects all resonances, shifting them downfield, with H2 experiencing the largest change.

Addition of trifluoroethanol to a solution of imidazole in chloroform causes an upfield shift of the H2 proton, a possible result of disruption of the hydrogen bonds in associated imidazoles by the alcohol. This is supported by a change in the broad imidazole infrared absorption in the region 3400–2400 cm^{-1}. Furthermore, while the change of solvent from chloroform to trifluoroethanol in chloroform has no sizable effect on the proton resonances of *N*-methylimidazole, the infrared spectrum in the presence of trifluoroethanol shows a broad absorption from 3400 to 2400 cm^{-1} attributable to hydrogen bonds at nitrogen that is not present in the infrared spectra of either *N*-methylimidazole or trifluoroethanol by themselves. From this it appears that the position of the H2 resonance is not much affected by changes in hydrogen bonding at the pyridine-type nitrogen.

Hydrogen bonding and protonation of imidazoles strongly affect the proton resonances of the hydrogen-bonding and protonating agents. Thus, hydrogen bonding of trifluoroethanol, acetic acid, and trifluoroacetic acid with *N*-methylimidazole in chloroform causes downfield shifts of their OH resonances by 4.3, 2.4, and 5.0 ppm, respectively, relative to their positions in chloroform alone.

Experimental Section

The ^{15}N NMR spectra were obtained with a Bruker WH-180 NMR spectrometer operating at 18.25 MHz as previously described.[10] The shifts were measured relative to external 1 M $D^{15}NO_3$ in D_2O, using 25 mL of 2 M solutions of imidazoles and imidazolium salts in 25-mm o.d. spinning sample tubes. The reference was contained in a 5-mm o.d. NMR tube held in the center of the sample tube by means of a Teflon plug. The deuterium in the reference provided the field-frequency lock signal. The temperature was held near 25 °C, but the shifts reported are corrected to this temperature in cases where the temperature deviated from this value. Because of the long relaxation times and small, unfavorable nuclear Overhauser effects of the pyridine-type nitrogens in imidazoles, a pulse width of 12 μs was used with a repetition rate of 20 s and proton noise decoupling only during data acquisition, with an average of 500 accumulations at a sweep width of 7000 Hz. Continuous proton noise decoupling and faster pulsing were used in the measurements of the salts.

N-Methylimidazole and 4-methylimidazole were distilled under reduced pressure. Spectrograde chloroform was dried over anhydrous potassium carbonate and distilled. A center cut was stored over molecular sieves and used within a few days. Acetic acid was distilled and the fraction, boiling at 117.5–118.0 °C, stored in a desiccator and used within 1 day.

The hydrochloride and methyl iodide salts were prepared as previously described.[11]

Registry No. 1, 616-47-7; 4, 288-32-4; 4·HCl, 1467-16-9; 5, 822-36-6; 6, 4333-62-4.

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Reactions of Quinuclidine *N*-Oxide and Other Amine Oxides with Sulfur Dioxide. Structure of Quinuclidine Sulfur Trioxide

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Passage of SO_2 gas through solutions of quinuclidine *N*-oxide in water or undried organic solvents at ambient temperature resulted in precipitation of sparingly soluble colorless platelets of quinuclidine sulfur trioxide in 85–90% yields. Reaction in dry benzene gave a mixture of QN–SO_3, QN–OSO_3, and QN·H_2SO_3 (QN = quinuclidine). Addition of SO_2 to a mixture of oxides of triethylenediamine in H_2O yielded $O_3SN(CH_2CH_2)_3NSO_3$. A kinetic study showed that hydrolysis of QN–SO_3 in water is exceedingly slow, even at 86 °C. The hydrolysis is first order and occurs at a rate (9.3×10^{-7} s^{-1}) which is *280* times slower than the analogous rate for Et_3N–SO_3. Alkaline hydrolysis of QN–SO_3 was moderately fast, yielding QN and sulfate. A single-crystal X-ray structure determination of QN–SO_3 confirmed the expected sulfamic acid type coordination of SO_3 to QN (N–S = 1.831(6) Å). Cell data: space group $P2_1/m$, a = 7.955 (4), b = 8.829 (3), c = 6.100 (4) Å, β = 96.03 (4)°, R = 0.052, R_w = 0.031 for 491 diffractometer-collected reflections with $I \geq 3\sigma(I)$ and symmetry-parameterized rigid-body model refinement.

The reaction of amine oxides with sulfur dioxide has been studied sporadically over the past several decades and found to give products quite dependent on both reaction condition and the nature of the oxide.[1,2] For example, trimethylamine oxide and SO_2 in dry benzene yield the sulfitoamine, Me_3N–OSO_2,[2] but in aqueous solution dimethylamine and formaldehyde result, presumably due to decomposition of the sulfitoamine intermediate via a Polonovski-type reaction.[3] Triethylamine oxide undergoes similar reaction with SO_2 in aqueous media, but, in dry benzene, triethylamine oxide–sulfur trioxide (Et_3NO–SO_3) was found to be a product.[3] Formation of the latter was rationalized by the reaction sequence in eq 1.

$$Et_3N\text{–}O + SO_2 \rightarrow Et_3N\text{–}SO_3$$
$$Et_3N\text{–}O + Et_3N\text{–}SO_3 \rightarrow Et_3N\text{–}OSO_3 + Et_3N \quad (1)$$

The ability of Et_3N–O to take SO_3 from Et_3N–SO_3 was in

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