The Chemistry of Nitrilium Salts. Part 3.[1] The Importance of Triazinium Salts in Houben–Hoesch Reactions Catalyzed by Trifluoromethanesulphonic Acid

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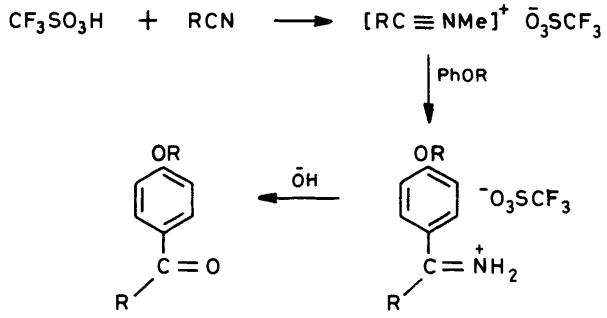
In the presence of trifluoromethanesulphonic (triflic) acid, isobutyronitrile reacts with anisole, 1,3-dimethoxybenzene, resorcinol, 1,3,5-trimethoxybenzene, and phloroglucinol at room temperature to give acylation products. A study of the reactions of acetonitrile and isobutyronitrile with triflic acid has shown that these modified Houben–Hoesch reactions occur by initial cyclotrimerization of the nitriles to 1,3,5-triazinium triflate salts followed by a slow reaction of the salts with the aromatic substrate. Support for this comes from the isolation of 2-(4-methoxyphenyl)-2,4,6-tri-isopropyl-1,2-dihydro-1,3,5-triazine from the reaction between anisole, triflic acid, and isobutyronitrile. Similar 1,2-dihydro-*s*-triazines and their salts have been prepared by reaction of trimethyl-*s*-triazinium triflate with 1,3-$(MeO)_2C_6H_4$, and tri-isopropyl-*s*-triazinium triflate with 1,3-$(RO)_2C_6H_4$ (R = H or Me) and 1,3,5-$(MeO)_3C_6H_3$; these salts are easily hydrolyzed to the corresponding aromatic ketones. The salt $[1,3,5\text{-}Me_3C_3N_3H_2]^+ 2\bar{O}_3SCF_3$ also reacts with *o*-phenylenediamine to give 2-methylbenzimidazolinium triflate in 83% yield. Nitrilium salts $[RC{\equiv}NMe]^+\bar{O}_3SCF_3$ (R = Me, Ph, or $PhCH_2$) undergo rapid reactions with 1,3-$(MeO)_2C_6H_4$ to form acylation products after hydrolysis, and *N*,*N*-dimethylaniline similarly affords 4-$Me_2NC_6H_4COMe$ on reaction with $[MeC{\equiv}NMe]^+\bar{O}_3SCF_3$ at room temperature.

Previously, we have shown[2] that aliphatic nitriles in the presence of trifluoromethane (triflic) acid react with phenols and phenol ethers to afford ketones in good yields. We supposed that this modified Houben–Hoesch reaction[3] involved the formation of an NH nitrilium salt as a key intermediate (Scheme 1) in accordance with the generally accepted mechanism for similar reactions.[3,4] Although many *N*-alkyl- and *N*-aryl-nitrilium salts have been synthesized[1] and their structures are well established,[5] information about NH nitrilium salts is restricted to reports of certain salts of complex anions, *e.g.* $2[PhC{=}NH]^+ SnCl_6^{2-}$, characterised mainly on the basis of conductivity measurements,[6,7] and n.m.r. studies of solutions of nitriles in strong acids.[5,8] As Zil'berman[9] and others[10,11] have shown, the reactions between nitriles and hydrogen halides can be quite complex, and, depending upon the conditions, a variety of monomeric and dimeric iminium salts can be produced as well as 1,3,5-triazinium salts.[11] A more detailed investigation of the reactions between acetonitrile and isobutyronitrile and phenol ethers in triflic acid has now been completed, and there is evidence that under the particular conditions of these reactions 1,3,5-triazinium salts, not NH nitrilium salts, are the key intermediates.



Scheme 1.

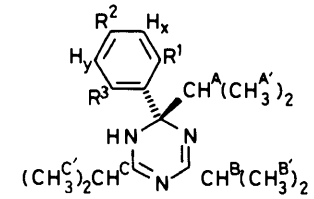
Results and Discussion

As previously established for other aliphatic nitriles,[2] acylation products are obtained in high yields only after premixing of an excess of triflic acid and the nitrile at room temperature for 2.5–3 h followed by addition of the phenol or phenol ether and hydrolysis and isolation of the ketones after 2—3 weeks at room temperature. The reactions of isobutyronitrile under similar conditions are entirely typical of those of other nitriles and afford the expected ketones with various phenol ethers as shown in Table 1. Phenol behaves anomalously with isobutyronitrile to give exclusively the kinetically controlled *O*-acylation product, rather than the thermodynamically favoured *C*-acylation product obtained with Pr^nCN and MeCN under similar conditions.[2] Reaction between anisole and Pr^iCN is very slow, and hydrolysis of the reaction mixture after 3 weeks gave a viscous oil shown by ^1H n.m.r. spectroscopy to be a mixture of the expected ketone, 4-$MeOC_6H_4COPr^i$, and the 1,2-dihydro-2,3,5-triazine derivative (1). These products could not be separated easily, but treatment of the mixture with triflic acid converted compound (1) into its

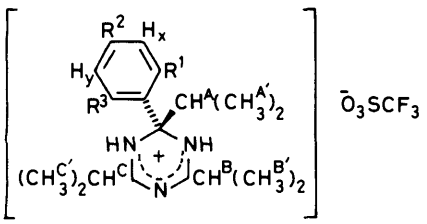
Table 1. Reaction of phenols and phenol ethers with isobutyronitrile and trifluoromethanesulphonic acid[a]

Aromatic substrate	Reaction time (days)	Product	Yield[b] (%)
C_6H_5OMe	15	4-$MeOC_6H_4COPr^i$	12
		+ (1)	24
C_6H_5OH	15	$C_6H_5OCOPr^i$	32
1,3-$(MeO)_2C_6H_4$	21	2,4-$(MeO)_2C_6H_3COPr^i$	77
1,3-$(HO)_2C_6H_4$	14	2,4-$(HO)_2C_6H_3COPr^i$	81
1,3,5-$(MeO)_3C_6H_3$	17	2,4,6-$(MeO)_3C_6H_2COPr^i$	41
1,3,5-$(HO)_3C_6H_3$	13	2,4,6-$(HO)_3C_6H_2COPr^i$, H_2O	41

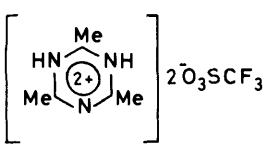
[a] All reactions were carried out at room temperature with a molar ratio of acid–nitrile–aromatic substrate of 3 : 1.5 : 1. [b] Yield of isolated product based on amount of aromatic substrate taken.



(1) $R^1 = H$, $R^2 = OMe$, $R^3 = H$
(8) $R^1 = H$ $R^2 = OMe$, $R^3 = OMe$
(10) $R^1 = H$, $R^2 = OH$, $R^3 = OH$



(2) $R^1 = H$, $R^2 = OMe$, $R^3 = H$
(7) $R^1 = H$, $R^2 = OMe$, $R^3 = OMe$
(9) $R^1 = OMe$, $R^2 = OMe$, $R^3 = OMe$



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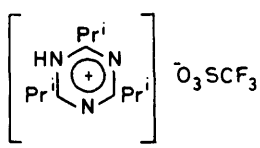

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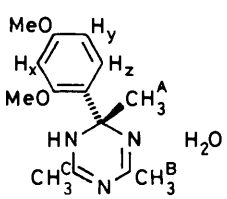

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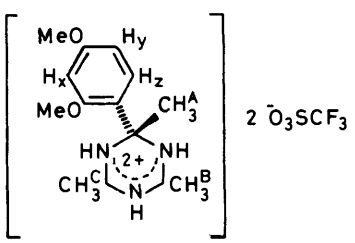
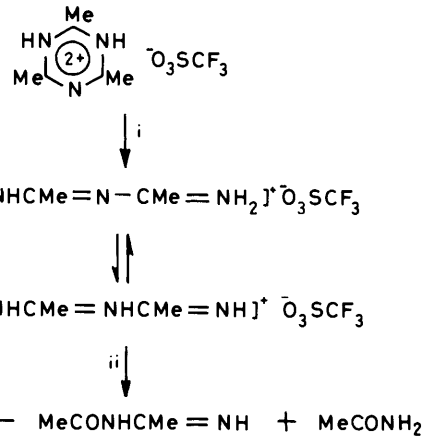


(6)

salt (2), which has been isolated and fully characterised. In view of this result it became important to establish whether triazine formation was merely a competing reaction leading to by-product formation, or whether it played a central mechanistic role.

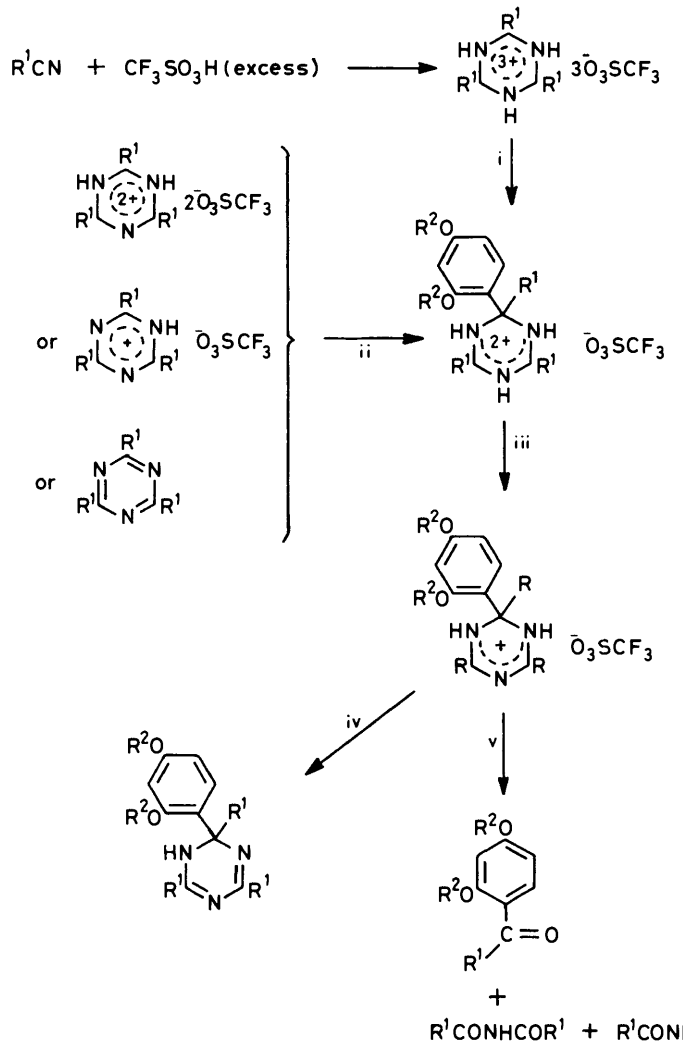
Contrary to an earlier report,[2] when dry acetonitrile (1 mol) was added dropwise to triflic acid (2 mol) at 0 °C there was no evidence for an i.r. band in the region of 2 300 cm^{-1} [$\nu(C\equiv\overset{+}{N}-)$] indicative of nitrilium salt formation, and after 2 h at room temperature addition of diethyl ether to the pale yellow solution gave the triazinium salt (3) in 58% yield. The same compound was also obtained in 41% yield after 3 h when triflic acid (1 mol) was added dropwise to acetonitrile (1 mol). When a mixture of triflic acid and acetonitrile was kept at room temperature for 23 h, and the precipitated salt (3) was then treated with pyridine, 2,4,6-trimethyl-1,3,5-triazine was isolated in 64% yield. Similarly, addition of triflic acid (1 mol) to Pr^iCN (1 mol) followed, after 20 h at room temperature, by addition of water gave the salt (4) in 28% yield. When this reaction was repeated using triflic acid–Pr^iCN (2 : 1 mol ratio) treatment with aqueous ammonia solution (*d* 0.880)



Scheme 2. *Reagents:* i, OH or H_2O; ii, H_2O

gave a 67% yield of 2,4,6-tri-isopropyl-1,3,5-triazine. The reaction between benzonitrile (1 mol) and triflic acid (1 mol) after 4 days at room temperature followed by addition of water gave 2,4,6-triphenyl-1,3,5-triazine in 95% yield. The cyclotrimerization of nitriles in the presence of Brønsted acids,[12] including triflic acid,[13] and HCl–Lewis acid catalysts,[14] is well known, and the cyclotrimerization of MeCN with triflic acid appears to be superior to other reported methods [15–17] for the synthesis of trimethyl-*s*-triazine. The importance of these experiments is that they demonstrate that under the conditions of the Houben–Hoesch reactions with triflic acid most of the nitrile must have been cyclotrimerized to triazinium salt *before* addition of the phenol or phenol ether. The degree of protonation of the product isolated from these cyclotrimerization reactions depends upon the acidity of the triazinium salts and the relative basicities of the added base, *i.e.* Et_2O, H_2O, NH_3, or C_5H_5N. Salt (3) is hygroscopic, slightly soluble in methanol and insoluble in benzene; it appears to react with acetone to give a yellow solution which darkens on standing. When refluxed with aqueous sodium carbonate it decomposes to give a mixture of acetamide and diacetamide, presumably *via* the intermediates shown in Scheme 2. The same products are also formed on treatment of a mixture of acetonitrile (1 mol) and triflic acid (2 mol) with either aqueous sodium carbonate or water after 2 h at room temperature. A similar hydrolysis may account for the low yield of compound (4) from the reaction of Pr^iCN and triflic acid where water was used during the work-up.

Addition of acetonitrile (1 mol) to triflic acid (1 mol) in benzene gave a homogeneous pale yellow solution, from which a yellow oil separated after 24 h at room temperature. On addition of 1,3-dimethoxybenzene the yellow oil turned deep red and, after 1 h at room temperature, hydrolysis of the mixture by addition of water and heating under reflux for 1.5 h gave 2,4-dimethoxyacetophenone in 71% yield. Significantly, treatment of the deep red oil with aqueous sodium carbonate at room temperature gave only a 12% yield of the ketone, the major product being the 1,2-dihydrotriazine derivative (5) isolated in 68% yield as its monohydrate. When 1,3-dimethoxybenzene was added to triflic acid and acetonitrile, which had been premixed for 0.5 h at 0 °C, and then, after 17 h at 0 °C, dry diethyl ether was added to the mixture, the 1,2-dihydrotriazinium salt (6) was isolated in 65% yield; the iminium salt, $[2,4\text{-}(MeO)_2H_4CMe{=}NH_2]^+\bar{O}_3SCF_3$, was also isolated in low yield from this reaction. In a separate experiment it has been shown that the salt (6) hydrolyses to give 2,4-dimethoxyacetophenone (91%), diacetamide, and acetamide on heating in water. The triazinium salt (3) in acetonitrile reacts only slowly with 1,3-dimethoxybenzene at



Scheme 3. *Reagents:* i, 1,3-$(R^2O)_2C_6H_4$; ii, 1,3-$(R^2O)_2C_6H_4$, CF_3SO_3H; iii, Et_2O; iv, aq. Na_2CO_3, room temp.; v, H_2O or Na_2CO_3, reflux

room temperature, to give 2,4-dimethoxyacetophenone (44%) and acetamide (20%) on hydrolysis after 4 days. This suggests that the yellow oil formed on mixing acetonitrile with triflic acid is probably the triprotonated triazine salt (7), and it is this, rather than the diprotonated species (3), which reacts with the phenol ether according to the reactions outlined in Scheme 3. The same yellow oil is also formed on treatment of (3) with triflic acid in benzene, but all attempts to isolate it as a pure species have been unsuccessful, since even weakly basic solvents, such as diethyl ether, are capable of removing a proton from the triazine salt (7) to precipitate the diprotonated species (3). The mechanism outlined in Scheme 3 would account for the need to premix the nitrile and triflic acid before addition of the phenol or phenol ether. It also explains why the use of an excess of acid over nitrile is beneficial, and why, as the triazinium salts of type (7) are only weak electrophiles, long reaction times are necessary, particularly for the less reactive aromatic substates, *e.g.* anisole. For the reasons outlined above we have been unable to prepare NH nitrilium salts and cannot directly compare their reactivity with those of triazinium salts. However, it has been shown that addition of the stable nitrilium salt $[MeC{\equiv}NMe]^+\bar{O}_3SCF_3$[2] to 1,3-dimethoxybenzene in acetonitrile at room temperature causes an immediate exothermic reaction and, after 20 min, ^1H n.m.r. spectroscopy indicated an 85% yield of the iminium salt $[2,4\text{-}(MeO)_2C_6H_3CMe{=}NHMe]^+\bar{O}_3SCF_3$, which was hydrolysed to 2,4-dimethoxyacetophenone with aqueous sodium carbonate. Even when an equimolar mixture of 1,3-dimethoxybenzene and triflic acid was added to solid $[MeC{\equiv}NMe]^+\bar{O}_3SCF_3$ the reaction was not inhibited and the iminium salt was formed in 84% yield after 15 min. Under similar conditions $[PhC{\equiv}NMe]^+\bar{O}_3SCF_3$ reacted with 1,3-dimethoxybenzene to give an 86% isolated yield of $[2,4\text{-}(MeO)_2C_6H_3CPh{=}NHMe]^+\bar{O}_3SCF_3$, which could be hydrolysed almost quantitatively to the ketone, and $[PhCH_2C{\equiv}NMe]^+\bar{O}_3SCF_3$ gave 2,4-$(MeO)_2C_6H_4COCH_2Ph$ in 86% yield; the intermediate ketimine salt was not isolated in this last case. *N,N*-Dimethylaniline also reacted rapidly with $[MeC{\equiv}NMe]^+\bar{O}_3SCF_3$ in benzene at room temperature to give 4-$Me_2NC_6H_4COMe$ after hydrolysis. The reactions of *N*-methylnitrilium salts are unlikely to be very different from those of NH nitrilium salts and the results of these experiments indicate that a mechanism such as that given in Scheme 1 can not explain the long reaction times necessary for the Houben–Hoesch reactions.

Further support for the involvement of triazinium salts in these reactions (Scheme 3) comes from the observation that

Table 2. ^{1}H N.m.r. spectra (chemical shifts in p.p.m. downfield from Me_4Si) [a]

Compound	Solvent	δ_HA	δ_HA′	δ_HB	δ_HB′	δ_HC	δ_HC′	$J_{AA'}$ [b]	$J_{BB'}$ [b]	$J_{CC'}$ [b]	Other bands
(1)	$CDCl_3$	2.06st	0.84d	2.32st	1.17d	2.32st	1.17d	7	7	7	3.72s (OCH_3), 6.84d (H_x, H_y, J 9 Hz), 7.94d (R^1, R^3) [c]
(2)	$CDCl_3$	2.53st	0.92d	2.98st	1.33d	2.98st	1.33d	7	7	7	3.82s (OCH_3), 6.93d (H_x, H_y, J 8.5 Hz), 7.44d (R^1, R^3), 8.8br (NH), 10.1br (NH)
(5)	$CDCl_3$	1.68s		1.96s		1.96s					3.77s (4-OCH_3), 3.84s (2-OCH_3), 6.46dd (H_y, J_{yz} 9 Hz, J_{xz} 2.5 Hz), 6.50d (H_x), 7.46d (H_z), 5.63br (NH + H_2O)
(6)	$(CD_3)_2CO$	2.38s		2.72s		2.72s					3.88s (4-OCH_3), 4.03s (2-OCH_3), 6.67dd (H_y, J_{yz} 8 Hz, J_{xy} 2.5 Hz), 6.82s (H_x), 7.53d (H_z), 11.7br (NH)
(7)	$CDCl_3$	2.78st	0.76d (3H) 1.02d (3H)	3.13st	1.35d (6H)	3.13st	1.35d (3H) 1.37 (3H)	7	7	7	3.87s (4-OCH_3), 4.0s (2-OCH_3), 6.54dd (H_y, J_{yz} 9 Hz, J_{xy} 2 Hz), 6.60d (H_x), 7.35d (H_z), 9.13br (NH), 10.66br (NH)
(8)	$CDCl_3$	2.40st	0.73d (3H) 0.99d (1H)	2.40st	1.25d	2.40st	1.25d (3H) 1.14d (3H)	7	7	7	3.82s (4-OCH_3), 3.90s (2-OCH_3), 6.54dd (H_y, J_{yz}, 9 Hz, J_{xy} 2 Hz), 6.49d (H_x), 7.62d (H_z), 6.54br (NH)
(9)	$(CD_3)_2CO$	2.5—2.3m	1.1d	2.5—3.4m	1.24d	2.5—3.4m	1.24d	7	7	7	3.86s (4-OCH_3), 3.95s (2- and 6-OCH_3), 6.46s (H_x, H_y), 9.9br (NH)
(10)	$(CD_3)_2CO$	2.48st	0.88d	2.48st	1.22d (6H)		1.22d (3H) 1.26d (3H)	7	7	7	6.27dd (H_y, J_{yz} 9 Hz, J_{xy}, 2 Hz), 6.22d (H_x), 7.37d (H_z)

[a] Compounds numbered as in displayed formulae; d = doublet, s = singlet, st = septet, dd = double doublet, br = broad. [b] In Hz. [c] NH Band not observed.

although neither the tri-isopropyl-*s*-triazine nor the triazinium salt (4) react with 1,3-dimethoxybenzene in benzene at room temperature during several hours, addition of triflic acid (1 mol) to a mixture of (4) (1 mol) and the ether (1 mol) in benzene gave a quantitative yield of compound (7) after 1.5 h at room temperature; the same product was also obtained in 94% yield from the reaction of tri-isopropyl-*s*-triazine, 1,3-dimethoxybenzene, and triflic acid at room temperature for 1.5 h in benzene. Treatment of (7) with aqueous sodium hydrogen carbonate gave the 1,2-dihydrotriazine (8). Under similar conditions, reaction between tri-isopropyl-*s*-triazine, triflic acid, and 1,3,5-trimethoxybenzene gave a quantitative yield of the triflate salt (9). The reaction with anisole was slow and only a 24% yield of (2) could be isolated, while resorcinol gave compound (10) in 78% yield. Triphenyl-*s*-triazine in the presence of triflic acid did not react with 1,3-dimethoxybenzene during several hours, and this is consistent with the low reactivity of benzonitrile in the triflic acid catalyzed Houben–Hoesch reactions. Under standard conditions [2] benzonitrile failed to react with anisole after 17 days at room temperature and the only product isolated after hydrolysis was triphenyl-*s*-triazine. With phenol, hydrolysis of the reaction mixture after 14 days gave mainly triphenyl-*s*-triazine formed together with phenyl benzoate (34%). Even with resorcinol after 17 days the major product was the triazine, although a low yield of 2,4-dihydroxybenzophenone (10%) was also isolated from this reaction.

These reactions of triazinium triflate salts with aryl ethers suggest that under suitable conditions it may be possible to use them as a substitute for the elusive NH nitrilium salts in the synthesis of heterocyclic compounds. This idea has not yet been explored in any detail, but when the salt (3) is heated with *o*-phenylenediamine in chloroform for 2 h, it forms 2-methylbenzimidazolinium triflate in 83% yield.

The ^{1}H n.m.r. spectra of the new 1,2-dihydro-2,4,6-triazines and triazinium salts show some interesting features (Table 2). The spectra of the 1,2-dihydrotriazines (1) and (5) clearly show that the alkyl group in the 2-position of the 1,2-dihydrotriazine ring is in a different environment from those in the 4 and 6 positions. The fact that the alkyl groups in 4 and 6 positions are equivalent in these compounds indicates that the NH proton moves rapidly between the three N atoms. The alkyl substituents in the 4 and 6 positions of the triazinium ring of the salts (2) and (6) are also equivalent, but have a different chemical shift from that in the 2-position. The spectra of compounds (7), (8), and (10) are different; not only are all three isopropyl substituents non-equivalent, but the two methyl groups of the isopropyl substituents on C-2 are also non-equivalent causing non-equivalence of the methyl groups of the isopropyl substituents on C-4 and C-6.

The NH protons are no longer equivalent and do not exchange, suggesting that in these compounds there is hydrogen bonding between the NH protons and the O atom of the *o*-methoxy or -hydroxy substituent in the aryl ring, thus restricting free rotation of the aryl group. A variable temperature study of the ^{1}H n.m.r. spectrum of compound (7) in both $(CD_3)_2SO$ and chlorobenzene over the range +35 to +120 °C has shown that the NH signals broaden and at 120 °C coalesce into a single, broad band centred at *ca.* δ 9.4.

Experimental

Isobutyronitrile and acetonitrile were commercial samples purified by distillation from P_2O_5 and then from CaH_2, and the phenols and phenol ethers were purified by recrystallisation or distillation. I.r. spectra were recorded on Perkin-Elmer 197 or 397 instruments, ^{1}H n.m.r. spectra were recorded either on a Perkin-Elmer R12 (60 MHz) or on a R32 (90 MHz) instrument with Me_4Si as internal standard; mass spectra were obtained using an MS45 mass spectrometer operating at an ionising electron-beam energy of 70 ev.

Acetylation Reactions with Isobutyronitrile.—Triflic acid (22.5 g, 0.15 mol) was added dropwise to isobutyronitrile (5.2 g, 0.075 mol) during 40 min with stirring and the mixture was left at room temperature for 3 h. The phenol or phenol ether (0.05 mol) was then added during 40 min as a solution in the nitrile (13—20 cm^3). The mixture was stored at room temperature for 13—21 days before refluxing with water (50 cm^3) for 1.5 h. The crude product was isolated by ether extraction, and the extract was washed with aqueous sodium hydrogen carbonate and then water, dried ($MgSO_4$), the solvent removed and the residue purified by either recrystallisation or chromatography (Al_2O_3, 100—200 mesh). The results are given in Table 1, and the products were identified by the following data. 2,4-$(HO)_2C_6H_3COPr^i$: m.p. 66—67 °C (from light petroleum) (lit.,[18] m.p. 67—68.5 °C), δ ($CDCl_3$) 1.24 (6 H, d, CH_3, *J* 7 Hz), 3.39 (1 H, sept., CH), 6.26 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz), 6.78 (1 H, br s, OH), 7.50 (1 H, d, 6-H, $J_{5,6}$ 9 Hz), and 12.8 (1 H, s, OH); *m/z* 180 ($M^{+\cdot}$, 30.6%); $\nu_{max.}$ 3 257 (OH) and 1 634 cm^{-1} (C=O). 2,4,6-$(HO)_3C_6H_2COPr^i\cdot H_2O$: m.p. 65—66.5 °C (from H_2O) (lit.,[19] m.p. 68 °C), δ [$(CD_3)_2CO$] 1.16 (6 H, d, CH_3, *J* 7 Hz), 3.88 (1 H, sept., CH), 5.86 (2 H, s, 3-H and 5-H) and 10.8 (2 H, br s, OH); the signal from the third OH group could not be detected; *m/z* 196 ($M^{+\cdot}$, 15.6%); $\nu_{max.}$ 3 571—3 077 br (OH) and 1 629 cm^{-1} (C=O). 2,4,6-$(MeO)_3C_6H_2COPr^i$: m.p. 57—60 °C (from 1 : 1 diethyl ether–light petroleum) (lit.,[20] m.p. 62—62.5 °C), δ ($CDCl_3$) 1.15 (6 H, d, CH_3, *J* 7 Hz), 3.02 (1 H, sept., CH), 3.77 (6 H, s, OCH_3), 3.87 (3 H, s, OCH_3), and 6.13 (2 H, s, 3-H and 5-H); *m/z* 238 ($M^{+\cdot}$, 8.2%); $\nu_{max.}$ 1 695 cm^{-1} (C=O). 2,4-$(MeO)_2C_6H_3COPr^i$: m.p. 35—37 °C (from Et_2O) (lit.,[20] b.p. 116—117/0.2 mmHg); δ ($CDCl_3$) 1.15 (6 H, d, CH_3, *J* 7 Hz), 3.55 (1 H, sept., CH), 3.82 (3 H, s, OCH_3), 3.86 (3 H, s, OCH_3), 6.50 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz), and 7.65 (1 H, d, 6-H, $J_{5,6}$ 9 Hz); *m/z* 208 ($M^{+\cdot}$, 11.5%); $\nu_{max.}$ 1 667 cm^{-1} (C=O). 4-$MeOC_6H_4COPr^i$: δ ($CDCl_3$) 1.15 (6 H, d, CH_3, *J* 7 Hz), 3.55 (1 H, sept., CH), 3.78 (3 H, s, OCH_3), 6.92 (2 H, d, A part of AA′XX′ spectrum, J_{AX} 9 Hz), and 7.94 (2 H, d, X part); *m/z* 178 ($M^{+\cdot}$, 10.1%); $\nu_{max.}$ 1 706 cm^{-1} (C=O). 2,4,6-Tri-isopropyl-2-(4-methoxyphenyl)-1,2-dihydro-1,3,5-triazine (1): *m/z* 315 ($M^{+\cdot}$, 0.1%), 272 ([M − Pr^i]$^+$, 100), 134 ([$MeOC_6H_4C{\equiv}NH$]$^+$ 79.1), 133 ([$MeOC_6H_4CN$]$^{+\cdot}$ 12.5), 70 ([$Pr^iC{\equiv}NH$]$^+$ 27.9), 69 ([Pr^iCN]$^{+\cdot}$ 4.6), and 43 ([C_3H_7]$^+$ 34.2); $\nu_{max.}$ 3 356w (NH), 1 675m cm^{-1} (C=N). 2,4,6-Tri-isopropyl-2-(4-methoxyphenyl)-1,2-dihydrotriazinium triflate (2): white crystals from MeOH, m.p. 117—120 °C, *m/z* (no $M^{+\cdot}$), 272 [(M − CF_3SO_3H–Pr^i)$^+$ 79.7], 134 ([$MeOC_6H_4C{\equiv}NH$]$^+$ 73.5), 133 ([$MeOC_6H_2CN$]$^{+\cdot}$ 6.2), 70 ([$Pr^iC{\equiv}NH$]$^+$, 21.8), 69 ([Pr^iCN]$^{+\cdot}$, 40.3), 44 ([C_3H_8]$^{+\cdot}$, 100), and 43 ([C_3H_7]$^+$, 41.8) (Found: C, 51.8; H, 6.4; F, 12.4; N, 8.9; S, 6.85. $C_{20}H_{30}F_3N_3O_4S$ requires C, 51.6; H, 6.45; F, 12.26; N, 9.03; S, 6.88%).

Preparation of 2,4,6-*Trimethyl*-1,3,5-*triazine.*—Dry acetonitrile (1.56 g, 38.05 mmol) was added dropwise to freshly distilled triflic acid (6.76 g, 45.07 mmol), cooled at 0 °C under nitrogen. The mixture was then stirred at room temperature for 23 h before dry diethyl ether (4 cm^3) was added *via* a syringe with ice-cooling to give a yellow suspension. Dropwise addition of pyridine (3.75 g, 45.07 mmol) gave white crystals of 2,4,6-trimethyl-1,3,5-triazine (1.00 g, 8.13 mmol, 64%), m.p. 56—57 (lit.,[15] m.p. 55—56 °C), δ ($CDCl_3$) 2.57 (CH_3) (Found: C, 58.6; H, 7.7; N, 34.1. Calc. for $C_6H_9N_3$: C, 58.5; H, 7.4; N, 34.1%).

Preparation of 2,4,7-*Tri-isopropyl*-1,3,5-*triazine.*—A mixture of isobutyronitrile (4.1 g, 0.06 mol) and triflic acid (17.0 g, 0.113 mol) was stirred at room temperature for 20 h before treatment with ammonia solution (*d* 0.880; 50 cm^3), and extraction with diethyl ether (3 × 50 cm^3) gave 2,4,6-tri-isopropyl-1,3,5-triazine (2.77 g, 13.4 mmol, 67%) as a pale yellow oil, b.p. 70—71 °C/2 mmHg (lit.,[13] b.p. 68 °C/2 mmHg), δ ($CDCl_3$) 1.36 (18 H, d, CH_3, *J* 7 Hz) and 2.97 (3 H, sept.); *m/z* 207 ($M^{+\cdot}$, 51.1%) (Found: C, 69.6; H, 10.2; N, 20.1. Calc. for $C_{12}H_{21}N_3$: C, 69.5; H, 10.2; N, 20.3%).

Preparation of 2,4,6-*Triphenyl*-1,3,5-*triazine.*—Benzonitrile (2.6 g, 0.025 mol) was added to triflic acid (7.5 g, 0.05 mol) and the bright yellow solution was stored at room temperature for 4 days before addition of ice–water (50 cm^3) to precipitate the triazine (2.5 g, 0.238 mol, 95%) as white needles, m.p. 230—231 °C (lit.,[12] m.p. 232 °C).

Preparation of 1H,3H-2,4,6-*Trimethyl*-1,3,5-*triazinium Triflate* (3).—Dry acetonitrile (0.78 g, 19.02 mmol) was added dropwise during 30 min to triflic acid (4.23 g, 28.16 mmol) cooled at 0 °C under nitrogen, and the mixture was stirred at room temperature for 2 h before addition of diethyl ether (5 cm^3) which caused precipitation of *compound* (3) (1.56 g, 3.69 mmol, 58%) as white crystals, m.p. 141—143 °C (from 1 : 1 : 1 MeOH–$CHCl_3$–Et_2O) (Found: C, 22.4; H, 2.8; F, 26.5; N, 9.6. $C_8H_{11}F_3N_3O_6S_2$ requires C, 22.7; H, 2.6; F, 26.9; N, 9.9%); *m/z* (no $M^{+\cdot}$) 123 [(M^+ − $2CF_3SO_3H$), 46.4%]; $\nu_{max.}$ 3 170br, 3 070br, 1 705s, 1 680s, 1 540s, 1300—1 200br ($CF_3SO_3^-$), 1 160vs ($CF_3SO_3^-$), 1 150sh, 1 030s ($CF_3SO_3^-$), 995m, 890m, 760w, 660m, 640s cm^{-1} ($CF_3SO_3^-$). No ^{1}H n.m.r. spectrum was taken as the compound was insoluble in $CDCl_3$ and reacted with $(CD_3)_2CO$.

When triflic acid (2.54 g, 16.9 mmol) was added dropwise to dry acetonitrile (0.69 g, 16.9 mmol) followed by diethyl ether after 3 h the yield of (3) was (0.97 g, 2.29 mmol, 41%).

Preparation of 1H-2,4,6-*Tri-isopropyl*-1,3,5-*triazinium Triflate* (4).—When triflic acid (4.4 g, 0.03 mol) was added to isobutyronitrile (2.1 g, 0.03 mol) at 0 °C with intermittent shaking, and the orange reaction mixture was allowed to stand at room temperature for 20 h before being shaken with water (20 cm^3) and extracted with ether (3 × 25 cm^3); removal of the solvent from the extract gave *compound* (4) (1.0 g, 28%) as white plates, m.p. 161—164 °C (from Et_2O), δ ($CDCl_3$) 1.45 (18 H, d, CH_3, *J* 7 Hz) and 3.49 (3 H, sept., CH); the NH proton was not observed; *m/z* (no $M^{+\cdot}$) 208 [(M − CF_3SO_3)$^+$, 4.1%] and 207 [(M − CF_3SO_3H)$^{+\cdot}$, 29]; $\nu_{max.}$ 3 215w (NH), 1 534 (C=N), 1 289s, 1 160s, 1 025s, and 626 cm^{-1} ($CF_3SO_3^-$)

(Found: C, 43.6; H, 6.2; F, 15.9; N, 11.5. $C_{13}H_{22}F_3N_3O_3S$ requires C, 43.7; H, 6.2; F, 16.0; N, 11.8%).

Reactions of N-*Methylacetonitrilium Triflate*.—(a) *With* 1,3-*dimethoxybenzene*. 1,3-Dimethoxybenzene (2.08 g, 15.06 mmol) was added to solid *N*-methylacetonitrilium triflate (3.09 g, 15.06 mmol), followed by dry acetonitrile (2 cm^3), inside a dry box. The salt dissolved immediately and the yellow solution gradually turned deep red with evolution of heat. A ^1H n.m.r. spectrum on the neat mixture after 20 min showed unchanged 1,3-dimethoxybenzene (*ca.* 15%) and *N*-(2,4-dimethoxy-α-methylbenzylidene)methylammonium triflate [δ 2.48 (3 H, s, CCH_3), 2.97 (3 H, d, *J* 5.5 Hz, NCH_3), 3.6 (3 H, s, 4-OCH_3), 3.66 (3 H, s, 2-OCH_3), 6.43 (2 H, d overlapping with dd, 3-H and 5-H, $J_{3,5}$ 2.5 Hz, $J_{5,6}$ 9 Hz), and 7.2 (1 H, d, 6-H); δ(^{19}F) −0.4 p.p.m. relative to CF_3CO_2H]. After 2 days at room temperature the mixture was heated under reflux with water (20 cm^3) for 10 min followed by dropwise addition of 2M-sodium carbonate solution until the mixture reached pH 10, then extraction with chloroform (4 × 25 cm^3) gave crude 2,4-dimethoxyacetophenone (2.51 g, 13.91 mmol, 92%), which was purified by chromatography (SiO_2, 230—400 mesh, $CHCl_3$ eluant).

By addition of light petroleum (b.p. 40—60 °C) to the reaction mixture before hydrolysis, *N*-(2,4-dimethoxy-α-methylbenzylidene)methylammonium triflate salt could be isolated from this reaction as white crystals, m.p. 98—102 °C (from Et_2O) (Found: C, 42.1; H, 5.0; F, 16.2; N, 4.3; S, 9.6. $C_{12}H_{16}F_3NO_5S$ requires C, 41.98; H, 4.7; F, 16.6; N, 4.08; S, 9.33%).

(*b*) *With* N,N-*dimethylaniline*. Freshly distilled *N*,*N*-dimethylaniline (1.96 g, 0.0162 mol) in dry benzene (15 cm^3) was added to the nitrilium salt (3.3 g, 0.0161 mol) to form a deep red oil. After 24 h the solvent was removed and the residue was boiled with 1M KOH solution (30 cm^3) for 30 min, before being extracted with chloroform. The extract was washed several times with water, dried (K_2CO_3), and after removal of the solvent the residue was chromatographed [SiO_2, 1 : 2 Et_2O–light petroleum (b.p. 40—60 °C) as eluant] to give 4-*N*,*N*-dimethylaminoacetophenone (0.8 g, 0.005 mol, 31%) as a white solid, m.p. 104—105 °C (lit.,[21] m.p. 105 °C).

Reactions of N-*Methylbenzonitrilium Triflate*.—(*a*) *With* 1,3-*dimethoxybenzene*. Under similar conditions a solution of 1,3-dimethoxybenzene (2.24 g, 0.016 mol) and the nitrilium salt (4.34 g, 0.016 mol) in benzene after 24 h at room temperature gave, on treatment with 1M-KOH solution and extraction with chloroform, *N*-(2,4-dimethoxy-α-phenylbenzylidene)-methylamine as a yellow oil (3.56 g, 86%), which was purified by chromatography [SiO_2, light petroleum (b.p. 40—60 °C) as eluant] [δ ($CDCl_3$) 3.25 (3 H, s, NCH_3), 3.69 (3 H, s, 4-OCH_3), 3.85 (3 H, s, 2-OCH_3), 6.56 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 3 Hz, $J_{5,6}$ 9 Hz), 6.85 (1 H, d, 6-H), and 7.2—7.9 (5 H, m, C_6H_5); $\nu_{max.}$ 1 625vs cm^{-1} (C=N)]. When the oil was dissolved in methanol (20 cm^3) and heated under reflux with dilute hydrochloric acid for 3 h, extraction with chloroform, followed by chromatography of the extract [Florisil, light petroleum (b.p. 40—60 °C) as eluant] gave 2,4-dimethoxybenzophenone (3.1 g, 96% based on ketimine) as white crystals, m.p. 90 °C (lit.,[22] m.p. 87—88 °C).

(*b*) *With* N,N-*dimethylaniline*. Treatment of *N*-methylbenzonitrilium triflate (4.27 g, 0.016 mol) with *N*,*N*-dimethylaniline (1.94 g, 0.016 mol) resulted in an exothermic reaction to give light yellow crystals of 4-*N*,*N*-dimethylaminobenzophenone (2.67 g, 0.012 mol, 72%).

Reaction of N-*Methylphenylacetonitrilium Triflate with* 1,3-*Dimethoxybenzene*.—Reaction between the nitrilium salt (2.17 g, 7.7 mmol) and 1,3-dimethoxybenzene (1.1 g, 7.7 mmol) in dry benzene (10 cm^3) during 24 h, followed by heating with aqueous KOH, gave 2,4-dimethoxyphenylacetophenone [crude yield 1.9 g, 100%; after chromatography on Florisil with 5 : 1 diethyl ether–light petroleum (b.p. 40—60 °C) as eluant, 1.3 g, 68%], m.p. 42 °C (lit.,[23] m.p. 39—40 °C); δ ($CDCl_3$) 3.82 (3 H, s, 4-OCH_3), 3.87 (3 H, s, 2-OCH_3), 4.3 (2 H, s, CH_2CO), 6.5 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 3 Hz, $J_{5,6}$ 9 Hz), 7.26 (5 H, s, C_6H_5), and 7.71 (1 H, d, 6-H).

Preparation of 2,4,6-*Trimethyl*-2-(2,4-*dimethoxyphenyl*)-1,2-*dihydro*-1,3,5-*triazine* (5).—Dry acetonitrile (0.78 g, 19.2 mmol) was added dropwise to a suspension of triflic acid (2.85 g, 19.02 mmol) in dry benzene (10 cm^3) under dry nitrogen and after 1 week at room temperature the initially homogeneous solution gradually turned yellow and a yellow oil separated. Dropwise addition of 1,3-dimethoxybenzene (0.88 g, 6.34 mmol) caused the rapid development of a deep red colour with evolution of heat, and after vigorous stirring for 1 h at room temperature removal of the solvent gave a deep red oil. Basification of this to pH 8—9 with aqueous sodium carbonate and extraction with chloroform gave a pale yellow oil, shown by ^1H n.m.r. spectroscopy to be a mixture of unchanged 1,3-dimethoxybenzene (0.169 g, 1.22 mmol, 19%), 2,4-dimethoxyacetophenone (0.137 g, 0.76 mmol, 12%), and compound (5) (1.21 g, 4.29 mmol, 68%). 2-(2,4-*Dimethoxyphenyl*)-2,4,6-*trimethyl*-1,2-*dihydro*-1,3,5-*triazine hydrate* (5) (1.04 g, 3.99 mmol, 63%) was isolated by chromatography [Florisil, 200—300 mesh, using Et_2O, Et_2O–$CHCl_3$ (4 : 1), and finally Et_2O–$CHCl_3$ (1 : 1) as eluants] as a white solid, m.p. 46—51 °C (Found: C, 59.5; H, 7.4; N, 14.9. $C_{14}H_{19}N_3O_2{\cdot}H_2O$ requires C, 60.2; H, 7.6; N, 15.0%); *m/z* 261 ($M^{+\cdot}$, 1.4%), 264 [(M − CH_3)$^+$, 100%], 164 {[$(MeO)_2C_6H_3C{\equiv}NH$]$^+$, 34.1}, 163 {[$(MeO)_2C_6H_3CN$]$^{+\cdot}$, 7.1], 137 {[$(MeO)_2C_6H_3$]$^+$, 65.6}, and 41 [$(CH_3CN)^{+\cdot}$, 13.3].

When a solution of (5) (0.506 g, 0.9 mmol) in water (4 cm^3) was heated under reflux for 1.5 h before being basified to pH 8—9 with aqueous sodium carbonate and extracted with chloroform, the products were 2,4-dimethoxyacetophenone (0.15 g, 0.82 mmol, 91%), acetamide (0.003 g, 0.046 mmol, 2.5%), and diacetamide (0.005 g, 0.046 mmol, 5%). These products were characterised by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples.

Preparation of 1H,3H,5H-2,4,6-*Trimethyl*-2-(2,4-*dimethoxyphenyl*)-1,2-*dihydro*-1,3,5-*triazinium Triflate* (6).—Following the procedure described in the previous experiment, a mixture of acetonitrile (1.56 g, 38.05 mmol) and triflic acid (6.76 g, 45.07 mmol) was stirred at room temperature for 3 h before addition of 1,3-dimethoxybenzene (1.75 g, 12.68 mmol), and the mixture was stored at 0 °C for 17 h. Addition of dry diethyl ether (10 cm^3) with cooling precipitated *compound* (6) (4.59 g, 8.17 mmol, 65%) as white crystals, m.p. 202—205 °C (decomp.), which were recrystallised from MeOH–Et_2O (1 : 1) (Found: C, 34.2; H, 3.8; N, 7.5. $C_{16}H_{21}F_6N_3O_8S_2$ requires C, 34.2; H, 3.8; N, 7.5%), *m/z* ($M^{+\cdot}$ not seen), ($M^{+\cdot}$ − $2CF_3SO_3H$ not seen), 138 [(M − $2CF_3SO_3H$ − $C_6H_9N_3$)$^+$ 100%], 123 [$(C_6H_9N_3)^{+\cdot}$, 13.6], 82 {[$M^{+\cdot}$ − $2CF_3SO_3H$ − $(MeO)_2C_6H_3$ − MeCN], 48.9}, and 69 [$(CF_3)^+$, 6.0].

The diethyl ether was removed from the filtrate and the residue was dissolved in water and extracted with chloroform to give a brown oil (0.64 g), containing mainly unchanged 1,3-dimethoxybenzene, but on standing *N*-(2,4-dimethoxy-α-methylbenzylidene)methylammonium triflate (0.07 g, 0.21 mmol, 1.7%) separated as pale yellow needles, m.p. 128—130 °C, *m/z* 179 [($M^{+\cdot}$ − CF_3SO_3H), 16.9%] and 164 [(M −

$CF_3SO_3H - CH_3)^+$, 100]; $\nu_{max.}$ 3 320m (NH), 1 620vs (C=N), 1 300—1 240br, 1 030vs, 640vs cm^{-1} ($CF_3SO_3^-$).

When a solution of compound (6) (0.57 g, 1.01 mmol) in water (4 cm^3) was basified to pH 8—9 with aqueous sodium carbonate, extraction with chloroform gave compound (5) (0.18 g, 1.00 mmol, 99%).

Reactions of 1H,3H-2,4,6-*Trimethyl*-1,3,5-*triazinium Triflate* (3).—(*a*) *With water.* A solution of compound (3) (0.196 g, 0.46 mmol) in water (5 cm^3) was heated at 90—100 °C for 15 min, before being cooled and basified to pH 8—9 with aqueous sodium carbonate. Extraction with chloroform (5 × 10 cm^3) gave a yellow oil, shown by ^1H n.m.r. spectroscopy to be a mixture of diacetamide (0.018 g, 40% δ 2.31), and acetamide (0.004 g, 5% δ 2.03).

(*b*) *With* 1,3-*dimethoxybenzene.* A solution of 1,3-dimethoxybenzene (0.57 g, 4.10 mmol) in dry acetonitrile was added to a suspension of (3) (0.87 g, 2.05 mmol) in the same solvent (5 cm^3) under nitrogen and a yellow colour developed immediately. The mixture was stored at room temperature for 15 h, heated under reflux for 9 h, and allowed to stand at room temperature for a further 3 days before being refluxed with water (15 cm^3) for 1.5 h. The mixture was then basified with aqueous Na_2CO_3, and extraction with chloroform gave a yellow oil (0.737 g), shown by ^1H n.m.r. spectroscopy to be a mixture of unchanged 1,3-dimethoxybenzene (0.375 g, 2.72 mmol, 66%), 2,4-dimethoxyacetophenone (0.16 g, 0.91 mmol, 44%), and acetamide (0.071 g, 1.21 mmol, 20%).

(*c*) *With* o-*phenylenediamine.* A solution of *o*-phenylenediamine (0.171 g, 1.58 mmol) in dry chloroform (10 cm^3) was added to (3) (0.223 g, 0.53 mmol) in chloroform, and on heating the suspension under reflux a homogeneous solution was obtained; then, gradually over 1 h, 2-methylbenzimidazolinium triflate (0.246 g, 0.87 mmol, 83%) precipitated as a white solid, m.p. 203—205 °C (Found: C, 38.1; H, 3.2; N, 9.8; S, 11.3. Calc. for $C_9H_9F_3N_2O_3S$: C, 38.2; H, 3.2; N, 9.9; S, 11.4%), δ [$(CD_3)_2CO$] 3.0 (3 H, s, CH_3), 7.4—7.95 (4 H, m, ArH); the NH protons were not observed; *m/z* ($M^{+\cdot}$) not observed, 132 [$(M^{+\cdot} - CF_3SO_3H)$ 100%].

When an aqueous solution of the salt (1.0 g, 3.55 mmol) was basified with aqueous KOH a quantitative yield of 2-methylbenzimidazole, m.p. 173 °C (lit.,[24] 175—176 °C) was obtained.

Reaction of 2,4,6-*Tri-isopropyl*-1,3,5-*triazine.*—(*a*) *With* 1,3-*dimethoxybenzene.* Triflic acid (3.0 g, 18.0 mmol), the triazine (1.89 g, 9.1 mmol), and 1,3-dimethoxybenzene (1.28 g, 9.3 mmol) were dissolved in benzene (10 cm^3) at room temperature and after 1.5 h the solvent was evaporated, and the residue was washed thoroughly with ether to give 2-(2,4-*dimethoxyphenyl*)-2,4,6-*tri-isopropyl*-1,2-*dihydro*-1,3,5-*triazinium triflate* (7) (4.39 g, 8.87 mmol, 97%), as white crystals, m.p. 168—170 °C (Found: C, 50.8; H, 6.5; F, 12.0; N, 8.3; S, 6.3. $C_{21}H_{32}F_3N_3O_5S$ requires C, 50.9; H, 6.5; F, 11.5; N, 8.5; S, 6.5%), *m/z* (no $M^{+\cdot}$) 346 [$(M - CF_3SO_3H)$ 0.1%], 302 [$(M - CF_3SO_3H - Pr^i)^+$, 100], 164 {$[(MeO)_2C_6H_3CNH]^+$, 75.4}, 163 {$[(MeO)_2C_6H_3CN]^{+\cdot}$, 6.6}, 70 [$(Pr^iCNH)^+$, 55.2], 69 [$(Pr^iCN)^{+\cdot}$, 8.0], 44 [$(C_3H_8)^{+\cdot}$, 6.3], and 43 [$(C_3H_7)^+$, 52.5]; $\nu_{max.}$ 3 185m (NH), 1 706s (C=N), 1 258s, 1 031s, and 629s cm^{-1} ($CF_3SO_3^-$).

Extraction of a solution of (7) (1.0 g, 2.0 mmol) in chloroform (50 cm^3) with a saturated solution of sodium hydrogen carbonate (4 × 20 cm^3) followed by washing with water (3 × 15 cm^3), and removal of the solvent from the organic phase, gave 2-(2,4-*dimethoxyphenyl*)-2,4,6-*tri-isopropyl*-1,2-*dihydro*-1,3,5-*triazine* (8) (0.65 g, 18.78 mmol, 94%) as a white solid, m.p. 62—65 °C (Found: C, 69.6; H, 9.3; N, 12.0. $C_{20}H_{31}N_3O_3$ requires C, 69.6; H, 8.98; N, 12.17%), *m/z* (no $M^{+\cdot}$), 302 [$(M - Pr^i)^+$, 84.6%], 164 {$[(MeO)_2C_6H_3CNH)]^+$, 39.0}, 163 {$[(MeO)_2C_6H_3CN]^{+\cdot}$, 12.5}, 70 [$(Pr^iCNH)^+$, 27.3], 69 [$(Pr^iCN)^{+\cdot}$, 3.5], 44 [$(C_3H_8)^{+\cdot}$, 100], and 43 [$(C_3H_7)^+$, 40.1]; $\nu_{max.}$ 3 367m (NH) and 1 650 cm^{-1} (C=N).

(*b*) *With resorcinol.* When triflic acid (1.7 g, 11.0 mmol) was added to a mixture of resorcinol (0.4 g, 4.0 mmol) and 2,4,6-tri-isopropyl-1,3,5-triazine (1.1 g, 5.0 mmol) in nitromethane (5 cm^3) and the mixture was stirred at 0 °C for 4 h a pale yellow solid precipitated. This was chromatographed (Florisil, 100—200 mesh; Et_2O and MeOH as eluants) to give 2-(2,4-*dihydroxyphenyl*)-2,4,6-*tri-isopropyl*-1,2-*dihydro*-1,3,5-*triazine* (10) (0.8 g, 3.12 mmol, 78% based on resorcinol) as a pale yellow solid, m.p. 132 °C (with decomp.) (Found: C, 68.2; H, 8.5; N, 13.4. $C_{18}H_{27}H_3O_2$ requires C, 68.14; H, 8.52; N, 13.25%), *m/z* (no $M^{+\cdot}$), 274 [$(M - Pr^i)^+$, 14.1%], 231 [$(M - 2Pr^i)^+$, 49.4], 216 [$(M - 2Pr^i - CH_3)^+$, 45.6], 188 [$(M - 3Pr^i)^+$, 27.5], 136 {$[(HO)_2C_6H_3CNH]^+$, 16.5}, 135 {$[(HO)_2C_6H_3CN]^{+\cdot}$, 12.2}, 70 [$(Pr^iCNH)^+$, 13.2], 69 [$(Pr^iCN)^{+\cdot}$, 26.0], and 43 [$(Pr^i)^+$, 100]; $\nu_{max.}$ 3 322m (NH), 3 175br m (OH), and 1 650m cm^{-1} (C=N).

(*c*) *With* 1,3,5-*trimethoxybenzene.* A mixture of triflic acid (2.7 g, 18.0 mmol), triazine (1.86 g, 9.0 mmol), and 1,3,5-trimethoxybenzene (1.5 g, 9.0 mmol) in benzene (10 cm^3) at room temperature for 1.5 h gave 2,4,6-*tri-isopropyl*-2-(2,4,6-*trimethoxyphenyl*)-1,2-*dihydro*-1,3,5-*triazinium triflate* (9) (4.38 g, 8.33 mmol, 93%), as a white solid, m.p. 100—101 °C (Found: C, 50.1; H, 6.6; F, 10.9; N, 8.0. $C_{22}H_{34}F_3N_3O_6S$ requires C, 50.28; H, 6.47; F, 10.86; N, 8.0%); *m/z* (C.I., NH_3) ($M^{+\cdot}$ not seen) 208 [$(Pr^iC_3N_3H)^+$, 100%]; $\nu_{max.}$ 3 230m (NH) and 1 600s cm^{-1} (C=N).

Reaction of 2,4,6-*Tri-isopropyl*-1,3,5-*triazinium Triflate with* 1,3-*Dimethoxybenzene.*—Triflic acid (0.5 g, 3.0 mmol) was added to a mixture of 1,3-dimethoxybenzene (0.4 g, 3.0 mmol) and compound (4) (0.9 g, 3.0 mmol) in dry benzene, and the mixture was shaken intermittently during 1.5 h at room temperature. Evaporation of the solvent gave a red solid residue which was washed with ether (2 × 5 cm^3) to give compound (7) (1.7 g, 3.0 mmol, 100%).

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