

## The Chemistry of Nitrilium Salts. Part 2.<sup>1</sup> The Preparation of Nitrilium Trifluoromethanesulphonate Salts and Their Reactions with Some Oxygen and Sulphur Nucleophiles

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The syntheses of the nitrilium salts  $[\text{RC}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$  [R = Me, Pr<sup>i</sup>, PhCH<sub>2</sub>, Ph, CH<sub>2</sub>=CHCH<sub>2</sub>, NC-(CH<sub>2</sub>)<sub>3</sub>, and CH<sub>2</sub>=CH] by reaction of MeO<sub>3</sub>SCF<sub>3</sub> with the corresponding nitriles are described. The similar reaction between (*E*)-PhCH=CHCN and MeO<sub>3</sub>SCF<sub>3</sub> gives a mixture of [(*E*)-PhCH=CHC≡NMe]<sup>+</sup>  $\bar{\text{O}}_3\text{SCF}_3$  and the *s*-triazinium salt  $[\{(E)\text{-PhCH=CH}\}_3\text{C}_3\text{N}_3\text{H}]^+ \bar{\text{O}}_3\text{SCF}_3$ , which hydrolyzes to give (*E*)-PhCH=CHCONHMe and the triazine. The compound CF<sub>3</sub>SO<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CN, prepared from I(CH<sub>2</sub>)<sub>4</sub>CN and AgO<sub>3</sub>SCF<sub>3</sub>, does not form a cyclic nitrilium salt, but slowly dimerizes at room temperature to  $[\text{CF}_3\text{-SO}_3(\text{CH}_2)_4\text{C}\equiv\text{N}(\text{CH}_2)_4\text{CN}]^+ \bar{\text{O}}_3\text{SCF}_3$ . Both I(CH<sub>2</sub>)<sub>4</sub>CN and CF<sub>3</sub>SO<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CN can be converted into the salt  $[\text{CF}_3\text{SO}_3(\text{CH}_2)_4\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ , but this does not form a dinitrilium salt on reaction with acetonitrile. On heating benzophenone oxime with CF<sub>3</sub>SO<sub>3</sub>H Beckmann rearrangement products are obtained, but conversion of  $[\text{MeC}(\text{OH})=\text{NPh}]^+ \bar{\text{O}}_3\text{SCF}_3$  into the nitrilium salt  $[\text{CH}_3\text{C}\equiv\text{NPh}]^+ \bar{\text{O}}_3\text{SCF}_3$  occurs in only low yield even after 8 h at 130 °C under high vacuum. The nitrilium salts with R = Ph, Me, Pr<sup>i</sup>, and PhCH<sub>2</sub> undergo rapid exothermic reactions with phenol, thiophenol, alcohols, and thiols to give the corresponding imidate and thioimidate salts in high yields. 4,4-Dimethyl-2-phenyl-1,3-oxazoline is obtained in 74% yield on heating  $[\text{PhC}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$  with H<sub>2</sub>NCMe<sub>2</sub>CH<sub>2</sub>OH, and both this and 2,4,4-trimethyloxazoline react with MeO<sub>3</sub>SCF<sub>3</sub> to give almost quantitative yields of the corresponding *N*-methyloxazolium salts, which can be reduced to the oxazolines with NaBH<sub>4</sub>. *N*-Methyloxazolium salts have also been obtained from the reactions of nitrilium salts (R = Ph or Me) with ethylene oxide.

Nitrilium ions have long been recognised as playing an important role in several heterocyclization reactions,<sup>2</sup> and more recently interest in these species has been stimulated by work on the stereospecificity of their formation and reactions with nucleophiles.<sup>3</sup> The first stable, isolable nitrilium salts were synthesized independently in 1955 by Klages<sup>4</sup> and by Meerwein,<sup>5</sup> and there are now several practical routes available for their preparation: these include the reactions of *N*-aryl-substituted imidoyl chlorides<sup>4,6-8</sup> and nitrile-HCl adducts<sup>9</sup> with Lewis acids; nitrile-Lewis acid adducts with simple secondary and tertiary alkyl halides;<sup>6,7,10</sup> the alkylation of nitriles with trialkyloxonium salts,<sup>6</sup> dialkoxy-carbonium fluoroborates,<sup>11,12</sup> bromoethane and silver tetrafluoroborate,<sup>13</sup> and methyl fluorosulphonate;<sup>14</sup> and the thermal decomposition of diazonium salts in the presence of nitriles. There have been two brief reports that benzyl<sup>15</sup> and methyl<sup>16</sup> trifluoromethanesulphonate (triflate) esters react with acetonitrile, presumably to form acetonitrilium salts *in situ*, but the use of triflate esters to prepare isolable nitrilium salts has not been described previously. We were attracted to the use of the triflate esters in the knowledge that they are powerful alkylating agents,<sup>17</sup> which are readily available from alcohols,<sup>15,18</sup> alkenes,<sup>19</sup> alkynes,<sup>20</sup> alkyl halides,<sup>21</sup> diazoesters,<sup>15</sup> and carbonyl compounds.<sup>22</sup>

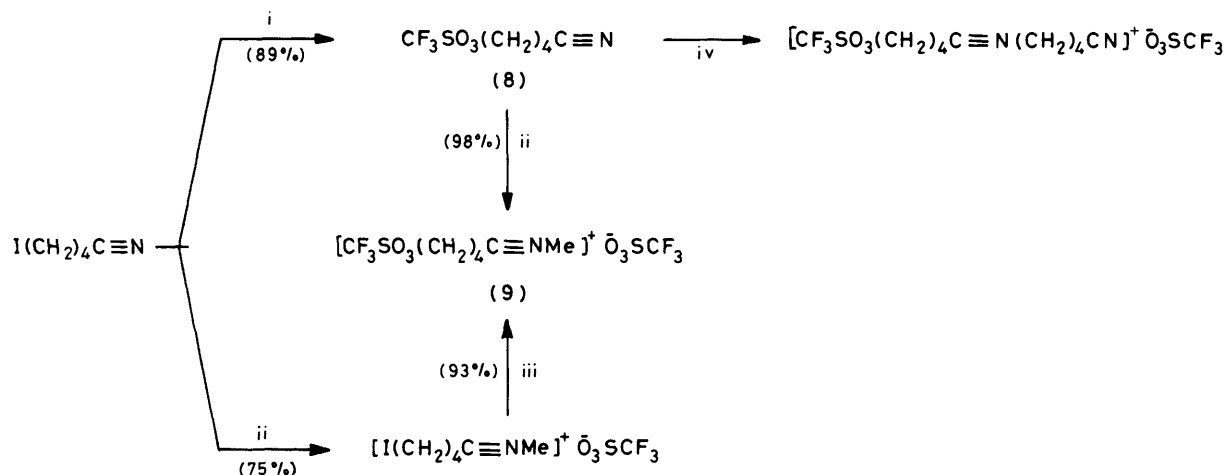
We now report the preparation of some *N*-methylnitrilium triflate salts, and some reactions with nucleophiles leading to heterocyclic products. Part of this work has been reported in a preliminary communication.<sup>23</sup>

### Results and Discussion

**Preparation of *N*-Methylnitrilium Triflate Salts.**—Addition of acetonitrile to an equimolar amount of methyl triflate at room temperature gave pale yellow crystals of *N*-methylacetonitrilium triflate (1) in 94% yield after 18 h. An alternative procedure, which gave a similar yield, was to add the

nitrile in benzene to a solution of methyl triflate in the same solvent at room temperature, but the reaction time was longer and complete crystallization often took several days. The reaction could be accelerated by heating the mixture at 70–80 °C, and, under these conditions, was usually complete in 15–20 min. Unlike alkylation with trialkyloxonium<sup>6</sup> or dialkoxy-carbonium salts,<sup>11,12</sup> which form ether or alkyl-formate by-products, the reactions of methyl triflate usually afford clean products in high yield. Similar reactions between methyl triflate and isobutyronitrile, phenylacetonitrile, and 3-cyanopropene gave the nitrilium salts (2)–(4) respectively (see Table). Compounds (2) and (4) were obtained as red, viscous oils and were characterised only by their spectroscopic data. All the isolated nitrilium salts are converted into the corresponding amides in moist air and at all times they must be handled in dry apparatus in a dry inert atmosphere. They are insoluble in carbon tetrachloride, hydrocarbons, and diethyl ether, slightly soluble in chloroform, and soluble in nitromethane; they form deep red solutions in acetone or dimethyl sulphate. The nitrilium triflate salts all show a characteristic<sup>7,24,25</sup>  $\nu(\text{C}\equiv\text{N})$  band in the i.r. region of 2 350–2 400 cm<sup>-1</sup> in addition to bands at 1 220–1 300, 1 160, 1 030, and 630 cm<sup>-1</sup> for the triflate anion. The <sup>1</sup>H n.m.r. spectra (Table) are comparable with those of the BF<sub>4</sub> salts reported by Olah and Kiovsky,<sup>25</sup> but the low solubility in deuteriochloroform resulted in poor resolution, and in some cases no spectrum could be obtained; as noted above, the salts appear to react with [<sup>2</sup>H<sub>6</sub>]acetone and [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide and this limits the choice of solvent.

Nitriles having electron-withdrawing substituents, *e.g.* ClCH<sub>2</sub>CN, CCl<sub>3</sub>CN, 4-ClC<sub>6</sub>H<sub>4</sub>CN, 2- or 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CN, and 1,2-, 1,3-, or 1,4-(NC)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> did not react with methyl triflate even after several days at 50–60 °C. Not surprisingly malonitrile and succinonitrile also failed to react under these conditions, but with glutaronitrile methylation occurred during 18 h to give compound (5) as a red, viscous oil.



**Scheme.** Reagents: i,  $\text{AgO}_3\text{SCF}_3$ ,  $\text{C}_6\text{H}_6$ , 23 h, room temp.; ii,  $\text{MeO}_3\text{SCF}_3$ , 18 h, room temp.; iii,  $\text{AgO}_3\text{SCF}_3$ ,  $\text{CH}_3\text{NO}_2$ , 16 h, room temp.; iv, 3 days, room temp.

**Table.** I.r. and n.m.r. spectroscopic data for nitrilium triflate salts (1)–(7)

| Compound   | $\nu(\text{C}\equiv\text{N})/\text{cm}^{-1}$ | $^1\text{H}$ N.m.r./ $\delta$  | $^{19}\text{F}$ N.m.r./p.p.m. |
|--|--|--|-------------------------------|
| $[\text{MeC}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (1)                        | 2400   | 2.03 (br s, 3 H, $\text{CCH}_3$ ), 4.0 (br s, 3 H, $\text{NCH}_3$ )  | -0.3                          |
| $[\text{Pr}^i\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (2)               | 2350   | 1.7 (d, 6 H, $J$ 7 Hz, $\text{CH}_3$ ), 3.7 (sept., 1 H, $\text{CHCH}_3$ ), 4.05 (s, 3 H, $\text{NCH}_3$ ) | -0.3                          |
| $[\text{PhCH}_2\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (3)             | 2390   | 3.8 (br s, 3 H, $\text{NCH}_3$ ), 4.6 (br s, 2 H, $\text{CH}_2$ ), 7.35 (s, 5 H, $\text{C}_6\text{H}_5$ )  | -0.3                          |
| $[\text{CH}_2=\text{CHCH}_2\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (4) | 2350   |  |                               |
| $[\text{NC}(\text{CH}_2)_3\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (5)  | 2375   |  |                               |
| $[\text{PhC}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (6)                        | 2350   | 4.13 (s, 3 H, $\text{NCH}_3$ ), 7.2–8.4 (m, 5 H, $\text{C}_6\text{H}_5$ )                                  | -0.23                         |
| $[\text{CH}_2=\text{CHC}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ (7)            | 2355   | 3.8 (s, 3 H, $\text{NCH}_3$ ), 7.64–6.8 (m, 3 H, $\text{CH}_2=\text{CH}$ )                                 | -0.3                          |

Attempts to methylate the second nitrile group by using an excess of methyl triflate were unsuccessful, presumably because of the increased inductive withdrawal of the nitrilium group. Benzonitrile and acrylonitrile reacted only slowly with methyl triflate to give the salts (6) and (7), respectively, and the products were contaminated by small amounts (typically <5%) of the corresponding *s*-triazinium triflate salts. These are thought to be formed by competing cyclotrimerization reactions of the nitriles, catalyzed by traces of triflic acid present in the methyl triflate.<sup>26</sup> When stringent precautions were taken to remove any acid (distillation of the methyl triflate several times in flame-dried apparatus under dry nitrogen) the yields of *s*-triazinium triflate salts were reduced to negligible amounts. In the case of cinnamonitrile, cyclotrimerization competes so effectively with methylation that we have been unable to obtain the pure nitrilium salt. Even taking the most stringent precautions, reaction at 50 °C for 45 min gave a viscous orange oil shown by  $^1\text{H}$  n.m.r. and i.r.

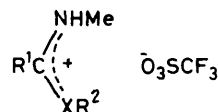
spectroscopy to contain a mixture of the nitrilium salt [ $\nu(\text{C}\equiv\text{N})$  2 320  $\text{cm}^{-1}$ ] and the *s*-triazinium triflate salt, which on alkaline hydrolysis gave (*E*)- $\text{PhCH}=\text{CHCONHMe}$  (43%) and the corresponding triazine (45%).

Cyclic nitrilium intermediates have been postulated for several heterocyclization reactions involving treatment of unsaturated nitriles,<sup>27,28</sup>  $\omega$ -ketonitriles,<sup>29–38</sup> and dinitriles,<sup>2c,39,40</sup> with acids, but, to our knowledge, such salts have never been isolated, and a recent attempt to prepare a seven-membered cyclic nitrilium salt by treatment of  $\epsilon$ -caprolactam with phosphorus pentachloride in benzene was unsuccessful.<sup>2b</sup> It was of some interest to prepare the ester  $\text{CF}_3\text{SO}_3(\text{CH}_2)_4\text{CN}$  (8) in order to examine whether it could undergo a 6-*endo-digonal*<sup>41</sup> ring-closure. Initial attempts to prepare the ester by the reaction between commercially available 5-chlorovaleronitrile and silver triflate in benzene or nitromethane gave no visible conversion after 85 days at room temperature. In contrast, 5-iodovaleronitrile, obtained from the chloro-derivative by reaction with sodium iodide either in toluene at 100 °C in the presence of alumina<sup>42</sup> (100% yield after 46 h), or in acetone under reflux (95% yield after 20 h), reacted with silver triflate in benzene to give compound (8) as a pale yellow oil in 89% yield after 23 h at room temperature. Compound (8) showed no tendency to cyclize at room temperature, but slowly dimerized during 3 days to give a product tentatively identified as  $[\text{CF}_3\text{SO}_3(\text{CH}_2)_4\text{C}\equiv\text{N}(\text{CH}_2)_4\text{CN}]^+ \bar{\text{O}}_3\text{SCF}_3$ , on the basis of its i.r. spectrum [ $\nu$  2 215  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ), 2 360s ( $\text{C}\equiv\text{N}^-$ ), 1 140–1 300br, 1 160, 1 030 and 630  $\text{cm}^{-1}$  ( $\text{CF}_3\text{SO}_3$  groups)]; a  $^1\text{H}$  n.m.r. spectrum could not be obtained owing to its low solubility in deuteriochloroform. Treatment of compound (8) with methyl triflate in benzene at room temperature gave the nitrilium salt  $[\text{CF}_3\text{SO}_3(\text{CH}_2)_4\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$  (9) in 98% yield; the same product was also obtained by methylation of iodovaleronitrile to give  $[\text{I}(\text{CH}_2)_4\text{C}\equiv\text{NMe}]^+ \bar{\text{O}}_3\text{SCF}_3$ , followed by reaction with silver triflate in nitromethane for 16 h at room temperature (see Scheme). An attempt to convert compound (9) into the dinitrilium salt  $[\text{MeC}\equiv\text{N}(\text{CH}_2)_4\text{C}\equiv\text{NMe}]^{2+} 2\bar{\text{O}}_3\text{SCF}_3$  by reaction with acetonitrile was unsuccessful, even after 14 days at room temperature.

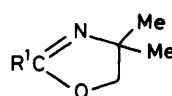
*N*-Arylnitrilium salts have proved to be useful intermediates in heterocyclization reactions,<sup>4</sup> and we were interested in a general route to the triflate analogues. Aryl triflates are readily available from phenols, but they have been shown to be extremely stable towards solvolysis even at elevated temper-

atures<sup>43</sup> and were considered unlikely to react with nitriles to form nitrilium salts. *N*-Phenylbenzotriazolium hexachloroantimonate and tetrafluoroborate salts are reported to be formed on heating benzophenone oxime with boron trifluoride at 120–130 °C.<sup>6</sup> There is also a report,<sup>25</sup> based on n.m.r. spectroscopic evidence, that *N*-phenylnitrilium salts are formed on Beckmann rearrangement of benzophenone oxime in HO<sub>3</sub>SF–SbF<sub>5</sub>–SO<sub>2</sub> solution or neat fluorosulphonic acid after only 30 min at 100 °C. An equimolar mixture of acetophenone oxime and triflic acid gave only the protonated oxime [PhMeC=NHOH]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$ , either after 15 h at room temperature, or on heating for 2 h at 100 °C. The Beckmann rearrangement products [MeC(OH)=NHPh]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$  (90%) and [PhC(OH)=NHMe]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$  (10%) were obtained only after heating at 130 °C under reduced pressure for 0.5 h. On further heating at this temperature, for a total of 8 h under continuous vacuum, the yield of protonated acetanilide fell to 61% while that of protonated *N*-methylbenzamide remained approximately constant at 12%. In addition, the <sup>1</sup>H n.m.r. spectrum showed the presence of a new compound [ $\delta$  2.39s (CCH<sub>3</sub>) and 7.33s (C<sub>6</sub>H<sub>5</sub>)] formed in ca. 26% yield, which is believed to be the desired nitrilium salt [CH<sub>3</sub>C≡NPh]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$ . Alkaline hydrolysis of this final product mixture gave *N*-methylbenzamide (11%) and acetanilide (85%), supporting the assumption that the nitrilium salt is formed. Similar results were also obtained starting from acetanilide. An equimolar mixture of triflic acid and acetanilide at room temperature gave a quantitative yield of protonated acetanilide, which on heating at 130 °C for 8 h gave a mixture of [MeC(OH)=NHPh]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$  (60%) and the nitrilium salt [CH<sub>3</sub>C≡NPh]<sup>+</sup>  $\bar{O}_3\text{SF}$  is produced after only 30 min on heating a mixture of acetophenone oxime and fluorosulphonic acid at 100 °C in a sealed n.m.r. tube. Recently, Fry and Ott<sup>44</sup> have demonstrated that the *N*-phenylbenzamide–BF<sub>3</sub> adduct does not rearrange to [PhC≡NPh]<sup>+</sup>  $\bar{B}F_4$  at room temperature after several weeks. In the light of our experience it may be that temperatures in excess of 130 °C are also necessary for this conversion.

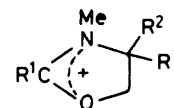
**Some Reactions of Nitrilium Triflate Salts.**—The salts (1) and (6) did not react with aliphatic nitriles over several days at room temperature, and there was no reaction between 2-nitrophenol and (1) even on heating under reflux for several hours. Stronger nucleophiles, however, such as PhOH, CH<sub>2</sub>=CHCH<sub>2</sub>OH, CH<sub>2</sub>=CHCH<sub>2</sub>SH and PhSH, underwent rapid, exothermic reactions to give the imidate and thioimidate salts (10)–(14). When the nitrilium salt (6) was heated with 2-amino-2-methylpropan-1-ol in nitromethane for 6 h, 4,4-dimethyl-2-phenyl-1,3-oxazoline (15) was produced in 74% yield together with [H<sub>3</sub>NCMe<sub>2</sub>CH<sub>2</sub>OH]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$  and [MeNH<sub>3</sub>]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$ . This represents a facile synthesis of oxazolines when compared with the usual method of heating an ethanolamine derivative with a carbonyl acid.<sup>45</sup> In our hands the reaction between 2-amino-2-



- (10) R<sup>1</sup> = R<sup>2</sup> = Ph, X = O  
 (11) R<sup>1</sup> = Pr<sup>i</sup>, R<sup>2</sup> = CH<sub>2</sub>CH=CH<sub>2</sub>, X = O  
 (12) R<sup>1</sup> = PhCH<sub>2</sub>, R<sup>2</sup> = CH<sub>2</sub>CH=CH<sub>2</sub>, X = O  
 (13) R<sup>1</sup> = Pr<sup>i</sup>, R<sup>2</sup> = CH<sub>2</sub>CH=CH<sub>2</sub>, X = S  
 (14) R<sup>1</sup> = R<sup>2</sup> = Ph, X = S



- (15) R<sup>1</sup> = Ph  
 (16) R<sup>1</sup> = Me



- (17) R<sup>1</sup> = Ph, R<sup>2</sup> = Me  
 (18) R<sup>1</sup> = Me, R<sup>2</sup> = Me  
 (19) R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 (20) R<sup>1</sup> = Me, R<sup>2</sup> = H

methylpropan-1-ol and benzoic acid required a temperature of 190 °C for 20 h to give compound (15) in only 50% yield. The reaction of acetic acid with 2-amino-2-methylpropan-1-ol was faster and gave 2,4,4-trimethyl-1,3-oxazoline (16) in 70% yield after 2 h at 175 °C. Both compounds (15) and (16) reacted rapidly with methyl triflate at room temperature to form the respective *N*-methyloxazolinium salts (17) and (18) in almost quantitative yield as thermally and hydrolytically stable white, crystalline solids. A similar synthesis of the oxazolinium salt (19) has been reported recently.<sup>46</sup> As demonstrated for the corresponding iodide salts,<sup>47</sup> the triflate derivatives (17) and (18) are reduced to the corresponding oxazolines using sodium borohydride in methanol. *N*-Methyloxazolinium salts (19) and (20) have also been obtained by addition of ethylene oxide to suspensions of the nitrilium salts (6) and (1), respectively, in dry benzene at 5–10 °C. In these cases the products were contaminated with viscous liquid by-products which have strong i.r. absorptions in the region of 3 600–2 700 cm<sup>-1</sup> and a weak-medium band at 1 710 cm<sup>-1</sup>, and are possibly mixtures of salts of aminoesters [RCO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>Me]<sup>+</sup>  $\bar{O}_3\text{SCF}_3$  and amido-alcohols RCONMeCH<sub>2</sub>CH<sub>2</sub>OH. It has so far proved impossible to separate the oxazolinium triflate salts from these contaminants, but addition of NH<sub>4</sub>PF<sub>6</sub> or KPF<sub>6</sub> to methanolic solutions containing (19) or (20) resulted in precipitation of white crystalline solids. From the i.r. spectra and elemental analyses of these it is apparent that anion exchange is not quantitative and the precipitated salts contained a mixture of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts. Similar problems were experienced in the reactions of the nitrilium salts (1), (3), and (6) with propene oxide and styrene oxide. Reaction undoubtedly occurs to give the expected oxazolinium salts, but the products were always contaminated with a deep brown oil, and it has so far proved impossible to separate the salts from the by-products.

### Experimental

Liquid nitriles were purified and dried by distillation from P<sub>2</sub>O<sub>5</sub> and then from CaH<sub>2</sub>,<sup>48</sup> and all solvents were dried by recognised procedures.<sup>48</sup> Methyl triflate was obtained from triflic acid and dimethyl sulphate<sup>19</sup> and was freshly distilled under dry nitrogen in a flame-dried apparatus immediately before each reaction. All reactions involving nitrilium tri-

flate salts were either carried out in a dry box or in flame-dried apparatus purged with nitrogen dried by passage through  $P_2O_5$  and passed over heated copper oxide. I.r. spectra were recorded on Perkin-Elmer 197 or 397 instruments.  $^1H$  N.m.r. spectra were recorded on a Perkin-Elmer R12 (60 MHz) or R32 (90 MHz) spectrometer with  $Me_4Si$  as internal standard, and  $^{19}F$  n.m.r. spectra (R32 instrument at 84.6 MHz) were run with external  $CF_3CO_2H$  reference (values to low field of the reference are designated negative).

**General Procedures for the Preparation of N-Methylnitrilium Triflate Salts.**—(a) *At room temperature.* The nitrile was added dropwise with stirring to an equimolar amount of methyl triflate, and after complete addition the flask was cooled to  $-196^\circ C$  and evacuated using the freeze-thaw technique before allowing the contents to warm up to room temperature. Complete crystallization of solid salts usually occurred between 1 and 5 days, and liquid nitrilium salts were usually left for 5–6 days before work-up. The salts were washed several times with dry benzene inside a dry box, before removal of the last traces of benzene under high vacuum.

If a diluent was necessary benzene was the solvent of choice as both nitriles and methyl triflate are soluble but the nitrilium salts are insoluble.

(b) *At elevated temperature.* An equimolar mixture of nitrile and methyl triflate was prepared as in (a), and after evacuating the flask, the mixture was heated in a water bath at  $70-80^\circ C$  for 5–10 min, before being cooled to room temperature; the nitrilium salt usually crystallized and was washed with benzene as in (a).

The following compounds were obtained. *N-Methylacetonitrilium triflate* (1), light yellow crystals, m.p.  $54-60^\circ C$  (10.23 g, 0.05 mol, 100%) (Found: C, 23.2; H, 2.8; F, 27.3; S, 15.4.  $C_4H_6F_3NO_3S$  requires C, 23.42; H, 2.95; F, 27.8; S, 15.6%). Obtained from acetonitrile (2.05 g, 0.05 mol) and methyl triflate (8.2 g, 0.05 mol) after 18 h at room temperature. A yield of 88% was obtained on heating at  $70-80^\circ C$  for 10–15 min. *N-Methylisobutyronitrilium triflate* (2), light yellow crystals, m.p.  $64-66^\circ C$  (5.80 g, 0.025 mol, 98%) (Found: C, 30.3; H, 4.3; N, 6.0; S, 14.2.  $C_6H_{10}F_3NO_3S$  requires C, 30.9; H, 4.3; N, 6.0; S, 13.7%). From isobutyronitrile (1.82 g, 0.026 mol) and methyl triflate (4.1 g, 0.025 mol) after 2 days at room temperature, or 6 days at room temperature using benzene as a solvent. *N-(Methyl)phenylacetonitrilium triflate* (3), a red oil (4.96 g, 0.018 mol, 72%) from phenylacetonitrile (2.95 g, 0.025 mol) and methyl triflate (4.1 g, 0.025 mol) after 3 days at room temperature, or 7 days using benzene as solvent. *N-Methylbut-3-enonitrilium triflate* (4), a red oil (5.4 g, 0.023 mol, 94%) from but-3-enonitrile (1.67 g, 0.025 mol) and methyl triflate (4.1 g, 0.025 mol) after 18 h at room temperature. *4-Cyano-N-methyl-n-butyronitrilium triflate* (5), a red oil (2.3 g, 0.01 mol, 100%) from glutaronitrile (0.94 g, 0.01 mol) and methyl triflate (3.28 g, 0.02 mol) after 2 days at room temperature. *N-Methylbenzonitrilium triflate* (6), pale yellow crystals, m.p.  $84-86^\circ C$  (5.12 g, 0.0192 mol, 96%) (Found: C, 40.3; H, 3.2; N, 5.5; S, 12.0.  $C_9H_8F_3NO_3S$  requires C, 40.4; H, 2.99; N, 5.24; S, 12.0%). From benzonitrile (2.06 g, 0.02 mol) and methyl triflate (3.28 g, 0.02 mol) after 15 min at  $70-80^\circ C$ . *N-methylacrylonitrilium triflate* (7), yellow solid, m.p.  $52-54^\circ C$  (2.57 g, 12.0 mmol, 78%) from acrylonitrile (0.81 g, 15.0 mmol) and methyl triflate (2.50 g, 15.0 mmol) at  $80-90^\circ C$  for 20 min.

*N-Methylcinnamonitrilium Triflate.*—Methyl triflate (0.695 g, 4.24 mmol) was added quickly to dry cinnamonitrile (0.54 g,

4.27 mmol), and the mixture heated at  $70-80^\circ C$  for 45 min to give a viscous orange oil, which was washed with benzene ( $3 \times 5\text{ cm}^3$ ) and diethyl ether ( $5\text{ cm}^3$ ) to give an orange gum (0.76 g) [ $\nu(C\equiv N^-)$  2 320s  $cm^{-1}$ ]. This was treated with water ( $10\text{ cm}^3$ ) followed by drops of 2M-KOH until the solution reached pH 10. The aqueous solution was extracted with diethyl ether ( $6 \times 10\text{ cm}^3$ ) and dichloromethane ( $3 \times 10\text{ cm}^3$ ), and the extracts were combined and dried ( $MgSO_4$ ) before the bulk of the solvent was removed to precipitate *N-methylcinnamide* (0.18 g, 1.12 mmol, m.p.  $109-110^\circ C$  (lit.,<sup>49</sup> m.p.  $110-111^\circ C$ );  $\delta(CDCl_3)$  2.96 (d, 3 H,  $J_{CH_3-NH}$  5 Hz,  $NHCH_3$ ), 6.2 (br s, 1 H, NH), 7.01 (d, 1 H,  $J$  16 Hz,  $CHCONHMe$ ), 7.72 (d, 1 H,  $CHPh$ ), and 7.2–7.6 (m, 5 H,  $C_6H_5$ ), having an i.r. spectrum identical with that reported.<sup>50</sup> The filtrate was chromatographed ( $SiO_2$ , 60 mesh,  $CHCl_3$  as eluant) to give 2,4,6-tristyryl-1,3,5-triazine (0.09 g, 0.23 mmol) recrystallised from  $CHCl_3-Et_2O$  (1 : 1) as white needles, m.p.  $219-220^\circ C$  (lit.,<sup>51</sup> m.p.  $224-226^\circ C$ ) which had identical i.r. and  $^1H$  n.m.r. spectra with those of an authentic sample [prepared in 98% yield by heating a mixture of cinnamonitrile (0.864 g, 6.69 mmol) and triflic acid (0.338 g, 2.23 mmol) at  $70-80^\circ C$  for 45 min].

**Preparation of 5-Iodovaleronitrile.**—Neutral alumina (21.26 g) and sodium iodide (31.87 g, 0.2 mol) were suspended in a solution of 5-chlorovaleronitrile (5.00 g, 0.04 mol) in toluene ( $165\text{ cm}^3$ ) and the mixture was heated with vigorous stirring at  $90^\circ C$  until g.l.c. analysis (1.5 m PEGA,  $200^\circ C$ ) indicated a quantitative conversion (46 h). After filtration the solvent was removed, and the pale yellow oil was distilled to give 5-iodovaleronitrile (5.74 g, 0.03 mol, 65%), b.p.  $98^\circ C/1\text{ mmHg}$ , shown to be 99% pure by g.l.c.,  $\nu_{max}$  (liquid film) 2 210s  $cm^{-1}$  ( $C\equiv N$ );  $\delta(CDCl_3)$  3.49 (br t, 2 H,  $J$  7 Hz,  $ICH_2$ ), 2.65 (br t, 2 H,  $J$  7 Hz,  $CH_2CN$ ), 1.8–2.3 (br m, 4 H,  $CH_2CH_2$ );  $m/z$  209 (15.9%) [ $M$ ]<sup>+</sup>, 127 (11.5) [ $I$ ]<sup>+</sup>, 82 (100) [ $M - I$ ]<sup>+</sup>, 55 (89.7) [ $M - I - HCN$ ]<sup>+</sup>, and 54 (38.5) [ $M - I - H_2CN$ ]<sup>+</sup>.

**Preparation of 4-Cyanobutyl Triflate.**—A solution of 5-iodovaleronitrile (2.09 g, 10.00 mmol) in dry benzene ( $5\text{ cm}^3$ ), added dropwise to a suspension of silver triflate (2.57 g, 10.00 mmol) in dry benzene ( $15\text{ cm}^3$ ) at room temperature, gave a precipitate of silver iodide (2.32 g, 99%) which was filtered off, and the solvent removed from the filtrate to give 4-cyanobutyl triflate (8) as a yellow oil (2.06 g, 8.91 mmol, 89%);  $\nu_{max}$  (liquid film) 2 215m ( $C\equiv N$ ), 1 260–1 200br, 1 145s, 1 030s, and 960  $cm^{-1}$  ( $CF_3SO_3$ );  $\delta(CDCl_3)$  4.60 (br t, 2 H,  $J$  7 Hz,  $CF_3SO_3CH_2$ ), 2.44 (br t, 2 H,  $J$  7 Hz,  $CH_2CN$ ), and 1.70–2.10 (br m, 4 H,  $CH_2CH_2$ ).

After 3 days at room temperature the oil had turned into a yellow gum (1.92 g, 4.14 mmol, 93%) which was washed with benzene ( $5\text{ cm}^3$ ) and dried *in vacuo*. This product is believed to be *N*-(4-cyanobutyl)-5-(trifluoromethylsulphonyl)valeronitrilium triflate.

**Reaction between 5-Iodovaleronitrile and Methyl Triflate.**—Methyl triflate (0.70 g, 4.24 mmol) was added quickly to the nitrile (0.89 g, 4.24 mmol) and the flask was then cooled to  $-196^\circ C$ , evacuated, and allowed to warm to room temperature. After 18 h at this temperature, *N*-methyl-5-iodovaleronitrilium triflate (1.18 g, 3.16 mmol, 75%) was formed as a viscous, pale yellow oil, which was washed with benzene ( $2 \times 5\text{ cm}^3$ ) and dried *in vacuo*;  $\nu_{max}$  (liquid film) 2 370m ( $C\equiv N^-$ ), 1 300–1 160br, 1 030s, and 970s  $cm^{-1}$  ( $CF_3SO_3^-$ );  $\delta(CDCl_3)$  3.79 (s, 3 H,  $N^+CH_3$ ), 3.2–3.5 (br m,  $ICH_2$  and  $-N^+=CCH_2$ ), and 2.0–2.3 (br m,  $CH_2CH_2$ ).

*Preparation of N-Methyl-5-(trifluoromethylsulphonyl)valeronitrilium Triflate.*—(a) From 4-cyanobutyl triflate. After 3 days at room temperature a mixture of methyl triflate (0.26 g, 1.6 mmol) and 4-cyanobutyl triflate (0.37 g, 1.6 mmol) gave the nitrilium salt (9) as a pale yellow oil (0.59 g, 1.5 mmol, 93%) after being washed with benzene (3 cm<sup>3</sup>) and dried *in vacuo*.  $\nu_{\max}$ . (liquid film) 2400s (C≡N<sup>+</sup>), 1300—1140br, 1030s, 930s cm<sup>-1</sup> (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>).

(b) From 5-iodo-N-methylvaleronitrilium triflate. Addition of a solution of 5-iodo-N-methylvaleronitrilium triflate (1.18 g, 3.16 mmol) in dry nitromethane (4 cm<sup>3</sup>) to a suspension of silver triflate (0.81 g, 3.16 mmol) in the same solvent gave silver iodide (0.70 g, 2.98 mmol, 95%) which was filtered off. The solvent was removed from the filtrate to give the product as a light brown oil (1.22 g, 3.09 mmol, 98%), having an i.r. spectrum identical with that of compound (9) obtained in the previous experiment.

*Reaction of Acetophenone Oxime with Triflic Acid.*—(a) At room temperature. A strongly exothermic reaction occurred upon dropwise addition of triflic acid (0.85 g, 5.63 mmol) to acetophenone oxime (0.76 g, 5.63 mmol) under dry nitrogen (1 atm) at room temperature which gave a light brown oil; this slowly turned into a semi-solid when left for 15 h at room temperature. This product was identified as protonated acetophenone oxime on the basis of spectroscopy [ $\nu_{\max}$ . (neat liquid) 1670m (C=N<sup>+</sup>), 1300—1200br, 1120s, 1030s, and 960br s cm<sup>-1</sup> (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>);  $\delta$ (CDCl<sub>3</sub>) 2.75 (s, 3 H, CH<sub>3</sub>) 7.9—7.47 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 11.97 (br s, 1 H, possibly NH), and 13.61 (br s, 1 H, possibly OH);  $\delta$ (<sup>19</sup>F) (CDCl<sub>3</sub>) -0.05 p.p.m.].

(b) At 100 °C. The product obtained on heating a mixture of triflic acid (0.85 g, 5.63 mmol) and acetophenone oxime (0.76 g, 5.63 mmol) at 100 °C for 2 h with a high vacuum continuously applied had identical i.r., and <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra with those obtained for the product of the previous experiment.

(c) At 130 °C. A mixture of triflic acid (0.64 g, 4.29 mmol) and acetophenone oxime (0.58 g, 4.29 mmol) heated at 130 °C for 30 min under a continuous high vacuum gave a dark brown oil, shown by <sup>1</sup>H n.m.r. spectroscopy to be a mixture of protonated acetanilide (90%);  $\delta$  2.53 (s, CH<sub>3</sub>), 7.33 (s, C<sub>6</sub>H<sub>5</sub>), 10.61 (br s, NH), and 13.62 (br s, possibly OH); and protonated N-methylbenzamide (10%);  $\delta$  3.05 (br s, CH<sub>3</sub>) and 7.33 (s, C<sub>6</sub>H<sub>5</sub>); the OH and NH signals were not observed.

Heating at 130 °C was continued for a further 7.5 h and the <sup>1</sup>H n.m.r. spectrum then showed a singlet at  $\delta$  2.39 (possibly CH<sub>3</sub>C≡N<sup>+</sup>) (26%) in addition to the bands due to protonated acetanilide (61%) and protonated N-methylbenzamide (12%); the aromatic protons of the species [CH<sub>3</sub>C≡NPh]<sup>+</sup> appear at  $\delta$  7.33 together with those for the other two compounds. The spectrum also showed a signal at  $\delta$  8.49br which could not be assigned.

The oil was then hydrolysed by shaking with 2M-KOH solution (5 cm<sup>3</sup>) for 5—10 min, and extracted with diethyl ether (6 × 10 cm<sup>3</sup>). The combined extracts were dried (MgSO<sub>4</sub>) and the solvent was removed to give acetanilide (0.49 g, 3.63 mmol, 85%) and N-methylbenzamide (0.06 g, 0.47 mmol, 11%). The N-methylbenzamide was identified by comparison of its <sup>1</sup>H n.m.r. spectrum with that of an authentic sample, and by addition of D<sub>2</sub>O to the mixture which caused the doublet at  $\delta$  2.92 (J 5 Hz, NHCH<sub>3</sub>) to collapse to a singlet.

*Reaction of Acetanilide with Triflic Acid.*—(a) At room temperature. A strongly exothermic reaction occurred on dropwise addition of triflic acid (0.17 g, 1.13 mmol) to acetanilide (0.15 g, 1.13 mmol) at room temperature which gave

protonated acetanilide as a pale yellow oil;  $\delta$ (neat liquid) 2.52 (s, 3 H, CH<sub>3</sub>), 7.32 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 10.33 (br s, 1 H, NH), and 12.95 (br possibly s, OH).

(b) At 130 °C. When the mixture was heated at 130 °C for 8 h under a continuous vacuum a new band appeared at  $\delta$  2.39 in the <sup>1</sup>H n.m.r. spectrum and was assigned to [CH<sub>3</sub>C≡NPh]<sup>+</sup> (40%). Hydrolysis of the product mixture with 2M-NaOH, followed by extraction with ether (2 × 25 cm<sup>3</sup>) and chloroform (2 × 25 cm<sup>3</sup>), gave, after drying of the combined extracts (MgSO<sub>4</sub>) and evaporation of the solvent, acetanilide (1.80 g, 13.95 mmol, 82%) together with a small amount of a dark red tar.

*Reactions of N-Methylbenzonitrilium Triflate.*—(a) With water. A vigorous, exothermic reaction occurred on treatment of compound (6) (1.95 g, 0.073 mol) with water (50 cm<sup>3</sup>), and extraction of the aqueous solution with chloroform gave white crystals of N-methylbenzamide (0.96 g, 0.007 mol, 96%), m.p. 76—77 °C (lit.,<sup>52</sup> 78—82 °C), recrystallised from light petrol-um (b.p. 40—60 °C).

(b) With phenol. A solution of phenol (1.02 g, 0.011 mol) in dry benzene (20 cm<sup>3</sup>) was added to a stirred suspension of the nitrilium salt (1.91 g, 0.011 mol) in benzene (10 cm<sup>3</sup>), and after 10 min white crystals of N-( $\alpha$ -phenoxybenzylidene)-methylammonium triflate (10) (3.54 g, 0.01 mol, 90%), m.p. 175—178 °C, precipitated, and were recrystallised from hot benzene (Found: C, 49.4; H, 4.1; F, 15.9; N, 4.1. C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>4</sub>S requires C, 49.9; H, 3.9; F, 15.8; N, 3.9%);  $\nu_{\max}$ . (Nujol mull) 1680vs cm<sup>-1</sup> (C=N<sup>+</sup>);  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>CO] 3.6 (s, 3 H, NCH<sub>3</sub>), 7.4 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 7.3—7.9 (m, 5 H, OC<sub>6</sub>H<sub>5</sub>), and 11.78 (br s, 1 H, NH);  $\delta$ (<sup>19</sup>F) -0.3 p.p.m. (s); m/z 211 (1.2%, M - CF<sub>3</sub>SO<sub>3</sub>H), 119 (20.8, PhCNHMe<sup>+</sup>), 118 (100, PhC≡NMe<sup>+</sup>), 103 (16.2, PhCN<sup>+</sup>), 94 (17.2, PhOH<sup>+</sup>), 77 (45.3, C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 69 (26.2, CF<sub>3</sub><sup>+</sup>), and 51 (19.6, C<sub>4</sub>H<sub>3</sub><sup>+</sup>).

(c) With thiophenol. Reaction between the nitrilium salt (2.98 g, 0.011 mol) and thiophenol (1.23 g, 0.11 mol) in benzene (15 cm<sup>3</sup>) at room temperature for 10 min gave white crystals of N-( $\alpha$ -phenylthiobenzylidene)methylammonium triflate (14) (4.0 g, 0.01 mol, 96%), m.p. 108—110 °C, which were filtered off, washed with benzene, and dried *in vacuo* (Found: C, 48.0; H, 4.0; F, 15.2; N, 3.7; S, 17.1. C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>3</sub>S<sub>2</sub> requires C, 47.7; H, 3.7; F, 15.1; N, 3.7; S, 17.0%)  $\nu_{\max}$ . (Nujol mull) 1620vs cm<sup>-1</sup> (C=N<sup>+</sup>);  $\delta$ (CDCl<sub>3</sub>) 3.56 (br s, 3 H, NCH<sub>3</sub>), 7.24 (s, 5 H, C<sub>6</sub>H<sub>5</sub>-C), 7.05—7.5 (m, 5 H, S-C<sub>6</sub>H<sub>5</sub>), and 11.92 (br s, 1 H, NH);  $\delta$ (<sup>19</sup>F) -0.5 p.p.m.; m/z 227 (M - CF<sub>3</sub>SO<sub>3</sub>H not seen), 119 (25.4%, PhCNHMe<sup>+</sup>), 118 (100, PhC≡NMe<sup>+</sup>), 110 (27.1, PhSH<sup>+</sup>), 103 (23.1, PhCN<sup>+</sup>), 77 (55.4, C<sub>6</sub>H<sub>5</sub><sup>+</sup>), 69 (72.3, CF<sub>3</sub><sup>+</sup>), and 51 (24.6, C<sub>4</sub>H<sub>3</sub><sup>+</sup>).

(d) With 2-amino-2-methylpropan-1-ol. A mixture of the nitrilium salt (3.07 g, 0.011 mol) and 2-amino-2-methylpropan-1-ol (1.02 g, 0.011 mol) in nitromethane (10 cm<sup>3</sup>) was heated under reflux for 6 h. Removal of most of the solvent under reduced pressure and addition of chloroform gave, after cooling to 0 °C, a white precipitate (0.77 g) which was a mixture of the salt [NH<sub>3</sub>CMe<sub>2</sub>CH<sub>2</sub>OH]<sup>+</sup> O<sub>3</sub>SCF<sub>3</sub>, m.p. 98—100 °C (Found: C, 25.2; H, 5.15; N, 6.1; S, 13.5. C<sub>5</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>4</sub> requires C, 25.1; H, 5.02; N, 5.9; S, 13.4%);  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>SO] 1.15 [s, 6 H, (CH<sub>3</sub>)<sub>2</sub>C] and 7.0—7.8 (br 3 H, NH<sub>3</sub>); the OH band was not observed; and the salt [MeNH<sub>3</sub>]<sup>+</sup> O<sub>3</sub>SCF<sub>3</sub>, m.p. 144—145 °C (Found: C, 13.5; H, 3.6; N, 7.7; S, 17.5. C<sub>2</sub>H<sub>6</sub>F<sub>3</sub>NO<sub>3</sub>S requires C, 13.3; H, 3.3; N, 7.7; S, 17.7%)  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>CO] 2.75 (s, 3 H, CH<sub>3</sub>) and 3.38 (s, 3 H, NH<sub>3</sub>); addition of D<sub>2</sub>O caused the last band to disappear. After

filtration, and removal of the solvent from the filtrate, the residue was washed with dilute aqueous NaOH, extracted with diethyl ether ( $3 \times 10 \text{ cm}^3$ ), and the ether extract dried ( $\text{MgSO}_4$ ) before removal of the solvent to give 4,4-dimethyl-2-phenyl-1,3-oxazoline (15) as a pale yellow oil (1.48 g, 0.0085 mol, 74%), shown by g.l.c. (2-m SE 30 column at  $200^\circ \text{C}$ ) to be 98% pure, and having i.r. and  $^1\text{H}$  n.m.r. spectra identical with an authentic sample (prepared in 50% yield by heating 2-amino-2-methylpropan-1-ol and benzoic acid at  $190^\circ \text{C}$  for 20 h<sup>45</sup>).

(e) *With ethylene oxide.* Ethylene oxide (2.77 g, 0.063 mol), previously condensed into a weighed, tapped ampoule containing dry benzene ( $10 \text{ cm}^3$ ), was added dropwise to a stirred suspension of the nitrilium salt (11.93 g, 0.045 mol) in dry benzene ( $50 \text{ cm}^3$ ) contained in a three-necked flask fitted with a low-temperature condenser. After being stirred at  $5\text{--}10^\circ \text{C}$  for 2 h, the solution had turned pale yellow. Solid  $\text{KPF}_6$  (8.22 g, 0.045 mol) was added in portions and the mixture was stirred at room temperature for 3 h to give an *N*-methyl-2-phenyl-1,3-oxazolinium salt (10.62 g, 0.035 mol, 77%) as a white solid (m.p.  $133\text{--}135^\circ \text{C}$ ) shown by i.r. spectroscopy and elemental analysis to be a ca. 40:60 mixture of the  $\text{CF}_3\text{SO}_3^-$  and  $\text{PF}_6^-$  salts (Found: C, 38.6; H, 3.9; F, 29.6; N, 4.4. Calc. for  $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NO}_4\text{S}$ : C, 42.44; H, 3.89; F, 18.31; N, 4.5%. Calc. for  $\text{C}_{10}\text{H}_{12}\text{F}_6\text{NOP}$ : C, 39.10; H, 3.94; F, 37.11; N, 4.56%);  $\nu_{\text{max}}$ . 1 660s ( $\text{C}=\text{N}^+$ ), 1 300—1 240br s, 1 1145s, 1 025s, ( $\text{CF}_3\text{SO}_3$ ), and 860—800br s  $\text{cm}^{-1}$  ( $\text{PF}_6^-$ );  $\delta[(\text{CD}_3)_2\text{CO}]$  3.62 (s, 3 H,  $\text{NCH}_3$ ), 4.57 (t, 2 H,  $J$  9 Hz,  $\text{CH}_2\text{N}$ ), 5.21 (t, 2 H,  $\text{CH}_2\text{O}$ ), and 8.07—7.76 (m, 5 H,  $\text{C}_6\text{H}_5$ ).

*Reaction of N-Methylacetoneitrilium Triflate with Ethylene Oxide.*—Reaction between ethylene oxide (0.92 g, 0.019 mol) and the nitrilium salt (3.89 g, 0.019 mmol) in dry benzene ( $25 \text{ cm}^3$ ) at  $5\text{--}10^\circ \text{C}$  for 2 h, followed by 20 min at room temperature, gave a viscous, orange oil. After removal of the benzene layer, addition of an ethanolic solution of ammonium hexafluorophosphate (4.86 g, 0.019 mol), and stirring for several hours at room temperature, a pale yellow solid (3.07 g, 0.013 mol, 66%) was obtained, m.p.  $162\text{--}164^\circ \text{C}$  (with decomp.), after removal of the solvent and addition of methanol. This solid was shown by i.r. and  $^1\text{H}$  n.m.r. spectroscopy to be mainly 2,3-dimethyl-1,3-oxazolinium hexafluorophosphate, contaminated with a small amount of the triflate salt;  $\nu_{\text{max}}$ . 1 685s ( $\text{C}=\text{N}^+$ ), 1 300—1 200br m, 1 150w, 1 030m ( $\text{CF}_3\text{SO}_3$ ), and 860—800br vs  $\text{cm}^{-1}$  ( $\text{PF}_6^-$ );  $\delta[(\text{CD}_3)_2\text{CO}]$  2.53 (s, 3 H,  $\text{CCH}_3$ ), 3.47 (s, 3 H,  $\text{NCH}_3$ ), 4.31 (t, 2 H,  $J$  9 Hz,  $\text{CH}_2\text{N}$ ), and 5.06 (t, 2 H,  $\text{CH}_2\text{O}$ ).

*Reactions of N-Methylisobutyronitrilium Triflate.*—(a) *With allyl alcohol.* Dropwise addition of a cooled solution of allyl alcohol (0.96 g, 0.0165 mol) in dry benzene ( $10 \text{ cm}^3$ ) to a stirred suspension of the nitrilium salt (3.86 g, 0.0166 mol) in benzene ( $10 \text{ cm}^3$ ) gave an exothermic reaction with precipitation of *N*-(2-methyl-1-prop-1-enylthioxypropylidene)methylammonium triflate (11) (4.8 g, 0.0165 mol, 100%) as a white solid, m.p.  $72\text{--}74^\circ \text{C}$ , which was recrystallised from benzene (Found: C, 37.5; H, 5.6; F, 19.6; N, 4.9; S, 10.9.  $\text{C}_9\text{H}_{16}\text{F}_3\text{NO}_4\text{S}$  requires C, 37.1; H, 5.5; F, 19.6; N, 4.8; S, 11.0%);  $\nu_{\text{max}}$ . 1 660br s  $\text{cm}^{-1}$  ( $\text{C}=\text{N}^+$ );  $\delta(\text{CDCl}_3)$  1.45 [d, 6 H,  $J$  7 Hz,  $(\text{CH}_3)_2\text{CH}$ ], 3.15 (d, 3 H,  $J$  5 Hz,  $\text{CH}_3\text{NH}$ ), 3.18 [sept., 1 H,  $(\text{CH}_3)_2\text{CH}$ ], 5.16 (d, 2 H,  $J$  5 Hz,  $\text{OCH}_2$ ), 5.45 (dd, 1 H,  $J_{\text{cis}}$  7 Hz,  $J_{\text{gem}}$  1 Hz,  $=\text{CH}_2$ ), 5.6 (dd, 1 H,  $J_{\text{trans}}$  11 Hz,  $J_{\text{gem}}$  1 Hz,  $=\text{CH}_2$ ), 5.7—6.4 (m, 1 H,  $\text{CH}_2\text{CH}=\text{}$ ), and 10.2 (br, 1 H,  $\text{NHCH}_3$ );  $\delta(^{19}\text{F}) -0.3$  p.p.m.

(b) *With prop-2-enethiol.* Reaction between prop-2-enethiol

(0.79 g, 0.011 mol) and the nitrilium salt (2.59 g, 0.011 mol) in benzene ( $20 \text{ cm}^3$ ) at room temperature for 5 min gave *N*-(2-methyl-1-prop-1-enylthioxypropylidene)methylammonium triflate (13) as a pale yellow oil (2.1 g, 0.0069 mol, 63%);  $\nu_{\text{max}}$ .

1 610vs  $\text{cm}^{-1}$  ( $\text{C}=\text{N}^+$ );  $\delta(\text{CDCl}_3)$  1.42 [d, 6 H,  $J$  7 Hz,  $(\text{CH}_3)_2\text{CH}$ ], 3.32 (d, 3 H,  $J$  5 Hz,  $\text{NHCH}_3$ ), 3.35 [sept., 1 H,  $(\text{CH}_3)_2\text{CH}$ ], 4.05 (d, 2 H,  $J$  7 Hz,  $\text{CH}_2\text{S}$ ), 5.42 (dd, 1 H,  $J_{\text{cis}}$  6 Hz,  $J_{\text{gem}}$  1 Hz,  $=\text{CH}_2$ ), 5.58 (dd, 1 H,  $J_{\text{trans}}$  11 Hz,  $J_{\text{gem}}$  1 Hz,  $=\text{CH}_2$ ), 5.95 (m, 1 H,  $\text{CH}_2\text{CH}=\text{}$ ) and 10.6—11.2 (br,  $\text{NHCH}_3$ );  $\delta(^{19}\text{F}) -0.4$  p.p.m.;  $m/z$  160 (6.1%,  $M - \text{CF}_3\text{SO}_3\text{H}$ ).

*Reaction of N-(Methyl)phenylacetoneitrilium Triflate with Allyl Alcohol.*—Addition of allyl alcohol (1.03 g, 0.0177 mol) to the nitrilium salt (4.97 g, 0.0177 mol) in benzene ( $10 \text{ cm}^3$ ) gave crystals of compound (12) (5.9 g, 0.017 mol, 100%), m.p.  $52\text{--}56^\circ \text{C}$ , which were recrystallised from benzene (Found: C, 46.0; H, 5.1; F, 16.3; N, 4.2; S, 9.0.  $\text{C}_{13}\text{H}_{16}\text{F}_3\text{NO}_4\text{S}$  requires C, 46.0; H, 4.8; F, 16.8; N, 4.1; S, 9.4%);  $\nu_{\text{max}}$ . 1 680vs  $\text{cm}^{-1}$  ( $\text{C}=\text{N}^+$ );  $\delta(\text{CDCl}_3)$  3.23 (d, 3 H,  $J$  5 Hz,  $\text{NHCH}_3$ ), 4.35 (s, 2 H,  $\text{PhCH}_2$ ), 5.04 (d, 2 H,  $J$  6 Hz,  $\text{OCH}_2$ ), 5.35 (dd, 1 H,  $J_{\text{cis}}$  7 Hz,  $J_{\text{gem}}$  1 Hz,  $=\text{CH}_2$ ), 5.5 (dd, 1 H,  $J_{\text{trans}}$  11 Hz,  $=\text{CH}_2$ ), 5.7—6.3 (m, 1 H,  $\text{CH}_2\text{CH}=\text{}$ ), 7.4 (s, 5 H,  $\text{C}_6\text{H}_5$ ), and 10.8 (br, 1 H,  $\text{NHCH}_3$ );  $\delta(^{19}\text{F}) -0.3$  p.p.m.;  $m/z$  189 (1.2%,  $M - \text{CF}_3\text{SO}_3\text{H}$ ).

*Preparation of 2,3,4,4-Tetramethyl-1,3-oxazolinium Triflate.*—Dropwise addition of methyl triflate (1.39 g, 0.0085 mol) to 2,4,4-trimethyl-1,3-oxazoline (0.96 g, 0.0085 mol) gave a very exothermic reaction with immediate formation of the oxazolinium salt (18) (2.20 g, 0.0079 mol, 93%) as a white solid, m.p.  $100\text{--}102^\circ \text{C}$ , which was recrystallised from chloroform-diethyl ether (1:1);  $\nu_{\text{max}}$ . 1 670s  $\text{cm}^{-1}$  ( $\text{C}=\text{N}^+$ );  $\delta(\text{CDCl}_3)$  1.57 [s, 6 H,  $\text{C}(\text{CH}_3)_2$ ], 2.52 (s, 3 H,  $\text{CCH}_3$ ), 3.29 (s, 3 H,  $\text{NCH}_3$ ), and 4.70 (s,  $\text{CH}_2$ );  $\delta(^{19}\text{F}) -0.4$  p.p.m.

*Preparation of 3,4,4-Trimethyl-2-phenyl-1,3-oxazolinium Triflate.*—Methyl triflate (6.95 g, 0.042 mol) and 4,4-dimethyl-2-phenyl-1,3-oxazoline (7.42 g, 0.042 mol) reacted to give 3,4,4-trimethyl-2-phenyl-1,3-oxazolinium triflate (17) (14.3 g, 0.042 mol, 99%) as a white solid, m.p.  $80\text{--}81^\circ \text{C}$ , which was recrystallised from chloroform-diethyl ether (1:1);  $\nu_{\text{max}}$ . 1 640s  $\text{cm}^{-1}$  ( $\text{C}=\text{N}^+$ );  $\delta(\text{CDCl}_3)$  1.84 [s, 6 H,  $(\text{CH}_3)_2\text{C}$ ], 3.62 (s, 3 H,  $\text{NCH}_3$ ), 5.07 (s, 2 H,  $\text{CH}_2$ ), and 7.60—8.30 (m, 5 H,  $\text{C}_6\text{H}_5$ );  $\delta(^{19}\text{F}) -0.4$  p.p.m.

*Preparation of 2,3,4,4-Tetramethyl-1,3-oxazolidine.*—A solution of 2,3,4,4-tetramethyl-1,3-oxazolinium triflate (11.08 g, 0.04 mol) in dry methanol ( $40 \text{ cm}^3$ ) was maintained below  $5^\circ \text{C}$  while sodium borohydride (0.76 g, 0.02 mol) was added in portions during 1 h. After being stirred at  $5^\circ \text{C}$  for 2 h, the reaction mixture was diluted with 5% aqueous sodium hydroxide ( $80 \text{ cm}^3$ ) and extracted with diethyl ether ( $5 \times 25 \text{ cm}^3$ ). The extract was dried and the residue was distilled to give the oxazolidine (2.99 g, 0.032 mol, 80%), b.p.  $86\text{--}94^\circ \text{C}$ ;  $\delta(\text{neat liquid})$  0.72 (s, 3 H, *gem*- $\text{CH}_3$ ), 0.85 (s, 3 H, *gem*- $\text{CH}_3$ ), 0.92 (d, 3 H,  $J$  5 Hz,  $\text{CHCH}_3$ ), 1.88 (s, 3 H,  $\text{NCH}_3$ ), 3.31 (s, 2 H,  $\text{OCH}_2$ ), and 3.86 (q, 1 H,  $\text{CHCH}_3$ );  $\nu_{\text{max}}$  (liquid) 1 315m, 1 265w, 1 245w, 1 175m, 920w, 905w, 815m, and 820w  $\text{cm}^{-1}$ , shown by g.l.c. to be  $>98\%$  pure.

*Preparation of 3,4,4-Trimethyl-2-phenyl-1,3-oxazolidine.*—Under similar conditions to those described in the previous experiment, reaction between 3,4,4-trimethyl-2-phenyl-1,3-oxazolinium triflate (13.65 g, 0.04 mol) and sodium borohydride (0.76 g, 0.02 mol) in methanol gave 3,4,4-trimethyl-

2-phenyl-1,3-oxazolidine (3.12 g, 0.016 mol, 41%), b.p. 69—80 °C/1 mmHg, having i.r. and <sup>1</sup>H n.m.r. spectra identical with those reported.<sup>47</sup>

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