Fluorocarbon Derivatives of Nitrogen. Part 13.[1] Reaction of Perfluoroalkanenitriles with Pyridinium Alkoxycarbonylmethylides: Synthesis of Perfluoroalkylated Imidazo[1,2-*a*]pyridines (1-Azaindolizines).[2] *X*-Ray Molecular Structure of Pyridinium 4,5-Dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide

Ronald E. Banks,* Robin G. Pritchard (in part), and Julie Thomson
Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Pyridinium t-butoxycarbonylmethylide, generated *in situ* by treatment of *N*-(t-butoxycarbonylmethyl)-pyridinium perchlorate with sodium hydride (in acetonitrile) or triethylamine (in dichloromethane), reacts with trifluoroacetonitrile to yield 3-(t-butoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]-pyridine, *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate, and pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide. The corresponding heptafluoropropyl compounds can be prepared in the same way, starting from heptafluorobutyronitrile; in both cases, the relative yields of the three types of product can be varied by changing the reactant ratios. Treatment of *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate with heptafluorobutyronitrile in the presence of triethylamine gives 2-(heptafluoropropyl)-4,5-dihydro-4-oxo-6-(trifluoromethyl)pyrimidin-5-ylide. Trapping of pyridinium ethoxycarbonylmethylide with trifluoroacetonitrile provides the known 3-(ethoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine, plus pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide. Reduction (zinc–acetic acid) of the latter, for which a detailed *X*-ray crystallographic analysis has been performed, gave 4-hydroxy-2,6-bis(trifluoromethyl)pyrimidine. A stepwise mechanism is proposed to account for the cycloaddition step involved in formation of perfluoroalkylated imidazo[1,2-*a*]pyridines from pyridinium alkoxycarbonylmethylides and the perfluoroalkanenitriles CF_3CN and n-C_3F_7CN.

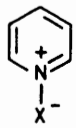
The results reported in detail[2] here stemmed from our continuing interest in reactions between *N*-heteroaromatic oxides,[3] imines,[4,5] or methylides[1,6] and unsaturated compounds of the fluorocarbon class. Having found that *N*-iminopyridinium ylide (**1**) attacks trifluoroacetonitrile to provide a mixture of 2-(trifluoromethyl)[1,2,4]triazolo[1,5-*a*]pyridine (**5**) and one of its dihydro analogues [either (**6**) or (**7**)][5] we turned our attention to the corresponding situation with pyridinium t-butoxycarbonylmethylide (**2**)—a reactive intermediate which can be generated ($p\overset{+}{y}CH_2CO_2Bu^t$ ClO_4^- + NaH) and utilized, without apparent complications, in the *hydrocarbon* nitrile MeCN as solvent.[7] At the outset, no reports could be found in the literature for reactions between nitriles and *N*-heteroaromatic methylides; later, a brief account[8] appeared of cycloadditions between trifluoroacetonitrile and some isoquinolinium methylides [(**8**) ⟶ (**12**); (**9**) ⟶ (**13**) + (**15**); (**10**) ⟶ (**14**); (**11**) ⟶ (**14**) + (**16**) + (**17**)] and pyridinium ethoxycarbonylmethylide [(**3**) ⟶ (**18**)].†

Reasons why pyridinium t-butoxycarbonylmethylide (**2**) was chosen for study and not pyridinium methylide (**4**) itself have been stated previously;[1,2,6] the imidazo[1,2-*a*]pyridine (**19**) described here has been used[6] to illustrate the point about replacement of a t-butoxycarbonyl group in a final product by hydrogen [(**19**) + CF_3CO_2H ⟶ (**20**) ⟶ (when heated) (**21**)].

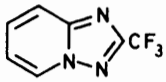
Synthetic and Structural Aspects.—Addition of pentafluoropyridine or octafluorotoluene to the orange-yellow solution obtained when *N*-(t-butoxycarbonylmethyl)pyridinium perchlorate (**23**) was stirred in cold (0—5 °C), dry acetonitrile with sodium hydride, followed by storage of the mixtures at room temperature, enabled very good yields (>85%) of ylides (**25**) derived from pyridinium t-butoxycarbonylmethylide (**2**) to be obtained.[1] Use of trifluoroacetonitrile (b.p. −64 °C) in place of a fluoroaromatic substrate—the solution containing the methylide being stirred under an atmosphere of the nitrile—provided a complex product when either a stoicheiometric proportion of the nitrile [CF_3CN:(**23**):NaH] (1:1:1) or a molar excess (2:1:1) was employed; no reaction occurred in the absence of sodium hydride, and some of the minor products were unknown compounds formed when trifluoroacetonitrile was treated with sodium hydride alone in acetonitrile. The two major organic products formed in the stoicheiometric situation were isolated chromatographically and found to be 3-(t-butoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**19**) (16% yield‡) and *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate (**26**) (27%); doubling the proportion of trifluoroacetonitrile decreased the yields of these products to 9 and 18%, respectively, and provided, as major product, a third novel compound, namely pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (29%). When the reaction involving a two-

† Unfortunately this imidazo[1,2-*a*]pyridine was not named in the publication[8] and its structure was inadvertently drawn [Y. Kobayashi, personal communication (dated 20 January 1982) in reply to a letter from R. E. B. (23 September 1981) stating that structure (**19**) had been assigned to the imidazopyridine derived from (**2**)] as that of the alternative regioisomeric end-product of the reaction, *i.e.*, the imidazo[1,5-*a*]pyridine (**22**).

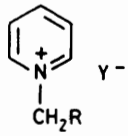
‡ Unless stated otherwise, yields refer to analytically pure specimens.



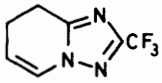
(1) X = NH
(2) X = $CHCO_2Bu^t$
(3) X = $CHCO_2Et$
(4) X = CH_2



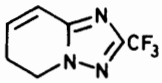
(5)



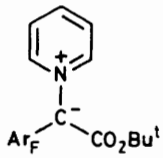
(23) R = CO_2Bu^t, Y = ClO_4
(24) R = CO_2Et, Y = Br



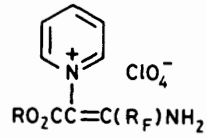
(6)



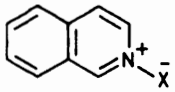
(7)



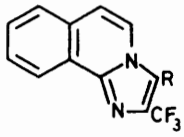
(25) Ar_F = 4-C_5F_4N, 4-$C_6F_4CF_3$



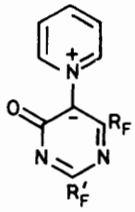
(26) $R_F = CF_3$, R = Bu^t
(27) R_F = n-C_3F_7, R = Bu^t
(28) $R_F = CF_3$, R = Et



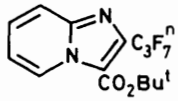
(8) X = $CHCO_2Et$
(9) X = CHCOPh
(10) X = CHCN
(11) X = $C(CO_2Me)CN$



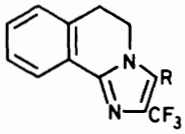
(12) R = CO_2Et
(13) R = COPh
(14) R = CN



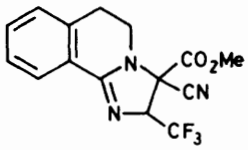
(29) $R_F = R_F' = CF_3$
(30) $R_F = R_F'$ = n-C_3F_7
(31) $R_F = CF_3$, R_F' = n-C_3F_7



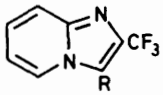
(32)



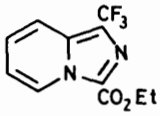
(15) R = COPh
(16) R = CN



(17)



(18) R = CO_2Et
(19) R = CO_2Bu^t
(20) R = CO_2H
(21) R = H



(22)

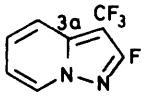
molar proportion of trifluoroacetonitrile was repeated with its higher homologue heptafluorobutyronitrile, the heptafluoropropyl analogues [(**32**), (**27**), and (**30**) respectively] of the trifluoromethylated products (**19**), (**26**), and (**29**) were the major components of the complex mixture obtained, and they were isolated in 16 (**27**), 6.5 (**30**), and 23% (**32**) yield. This established the generality of the reaction in terms of product range.

In view of these results, it was decided to re-examine the reaction of pyridinium ethoxycarbonylmethylide (**3**) with trifluoroacetonitrile, which, in Japanese hands,[8] provided only 3-(ethoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**18**). No experimental details were given except that ethoxycarbonylmethylpyridinium bromide (**24**) had been treated with trifluoroacetonitrile in the presence of triethylamine in dichloromethane. The yield of the imidazopyridine (**18**) was said to be 18%, and 'other pyridinium methylides gave a very complex mixture of products.'[8] We found that the complex product produced when the bright yellow mixture formed by addition of triethylamine to ethoxycarbonylmethylpyridinium bromide in dichloromethane was stirred under an atmosphere of trifluoroacetonitrile did contain the imidazo[1,2-*a*]pyridine (**18**) (major product), the yield of isolated material being 29% when the molar ratio of potential pyridinium ethoxycarbonylmethylide (**3**):CF_3CN was 1:1, and 19% when the ratio was 1:2. In the latter case the major product was pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (42%), *i.e.*, the main product obtained under comparable conditions from pyridinium t-butoxycarbonylmethylide (**2**). In neither reaction involving the ethoxycarbonyl system was the ethoxycarbonyl analogue (**28**) of the propenylpyridinium perchlorate (**26**) encountered, but both of the crude products contained, *inter alia*, small amounts of unknown compounds shown by separate experiment to arise from attack of triethylamine on trifluoroacetonitrile.

No attempt was made to study the effect of using sodium hydride to generate pyridinium ethoxycarbonylmethylide (**3**) from the corresponding pyridinium bromide (**24**). However, triethylamine was used as the base to set up reactions between pyridinium t-butoxycarbonylmethylide (**2**) and trifluoroacetonitrile or heptafluorobutyronitrile in dichloromethane. In the case of the lower homologue, and with an equimolar ratio of reactants [CF_3CN:(**23**):Et_3N (1:1:1) in CH_2Cl_2], the complex product was shown by n.m.r. and quantitative h.p.l.c. analysis to comprise mainly 3-(t-butoxycarbonyl)-2-(trifluoromethyl)-imidazo[1,2-*a*]pyridine (**19**) (28%) and *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate (**26**) (44%), and to contain only traces of pyridinium 4,5-

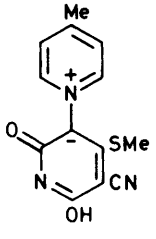
dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**); allowing for losses during isolation, this result compares well with the identical situation with sodium hydride as the base [yields: 16% (**19**), 27% (**26**), trace (**29**)]. Use of heptafluorobutyronitrile in a two-molar proportion [C_3F_7CN:(**23**):Et_3N (2:1:1) in CH_2Cl_2] provided the same three major products (isolated chromatographically), namely a C_3F_7-substituted imidazo[1,2-*a*]pyridine (**32**), perchlorate salt (**27**), and pyrimidin-5-ylide (**30**), in higher overall total yield than when sodium hydride (in MeCN) was employed as the base under identical conditions, and with a notable difference in individual yield only where the pyrimidinylide was concerned: (**32**), 14 *vs.* 23%; (**27**) 16 *vs.* 14%; (**30**) 25 *vs.* 6.5%.

The structures of the three crystalline imidazo[1,2-*a*]pyridines (**18**), (**19**), and (**32**) were established by elemental analysis and spectroscopic techniques [i.r., u.v., mass, and n.m.r. (^{13}C, ^{1}H, ^{19}F)]. ^{1}H N.m.r. spectra showed the pattern typical for ring protons in such imidazo[1,2-*a*]pyridines,[9] and the ^{13}C and ^{19}F spectral data correlated well with those published for analogous compounds [including (**5**)].[5,10] Our failure to detect coupling between fluorines of a perfluoroalkyl group and the bridgehead nucleus C-8a in any of the compounds militated strongly against adoption of alternative regioisomeric structures [such as (**22**)] because CF_3-to-bridgehead carbon (C-3a) coupling (q, $^{3}J_{C,F}$ 2.5 Hz) has been observed in the ^{13}C n.m.r. spectrum of 2-fluoro-3-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine (**33**);[4] additionally, the t-butoxy-compound (**19**) was converted into the known 2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**21**) by conventional techniques (see above).[6]



(**33**)

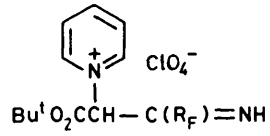
X-Ray crystallography (see below) was used to confirm the structure of pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**), deduced initially from spectroscopic data, elemental analysis, mode of formation, and reductive cleavage with zinc dust in glacial acetic acid[11] to 4-hydroxy-2,6-bis(trifluoromethyl)pyrimidine (48% yield; a known compound[12]). The structure of the bis(heptafluoropropyl) analogue (**30**) followed from its spectroscopic properties and elemental composition. In terms of structure, the closest analogy to ylides (**29**) and (**30**) appears to be the pyridinium compound (**34**) formed when the dinitrile $CH_2(CN)_2$ is treated



(**34**)

with the pyridinium iodide 4-$MeC_5H_4\overset{+}{N}C(CO_2Et)=C(SMe)_2$ I^- in the presence of potassium carbonate in a dipolar aprotic solvent.[13]

N-[2-Amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate (**26**) and its heptafluoropentenyl analogue (**27**) were fully characterized by elemental analysis and spectroscopic measurements; n.m.r. data indicated the presence of only one geometrical isomer in each case. The tautomeric structures (**35**) and (**36**) were discounted on the basis of i.r. and ^{1}H n.m.r. spectroscopy (NH_2 group present in each case); also, the off-resonance decoupled ^{13}C n.m.r. spectrum of the trifluoromethyl compound was fully consistent with structure (**26**), nucleus C-1 of the *N*-pyridinium substituent giving rise to a singlet not a doublet (much further upfield) as would have been the case with an isomer of structure (**35**).

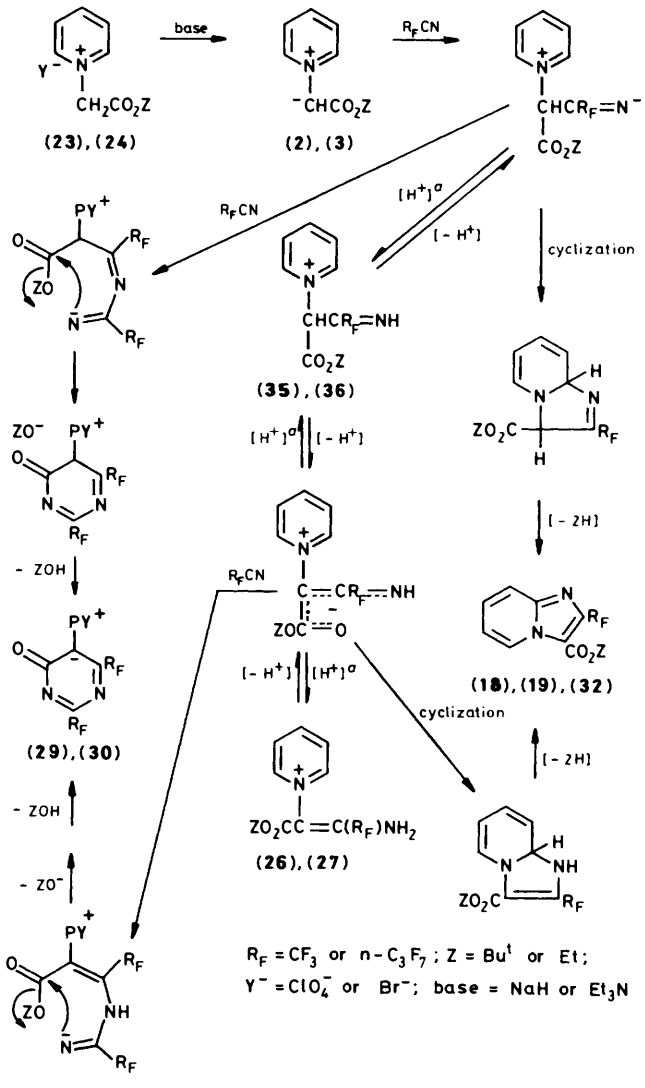


(**35**) $R_F = CF_3$
(**36**) $R_F = n\text{-}C_3F_7$

Mechanisms.—The relatively few reports concerning 1,3-cycloadditions involving pyridinium methylides that mention mechanisms normally favour stepwise ring-closure to yield di- or tetra-hydroindolizines (depending on the type of C–C multiple bonding in the dipolarophile) which, on occasion, have been isolated;[14] these initial adducts often aromatize 'spontaneously' *via* hydrogen transfer to the dipolarophile, disproportionation, 1,4-elimination, or undefined 'oxidation' processes. An analogous situation exists for cycloadditions between *N*-iminopyridinium ylide (**1**) and organic nitriles, and the case of the formation of the triazolopyridine (**5**) and its dihydro-analogue (**6**) or (**7**) from trifluoroacetonitrile has been discussed.[5] Mechanisms for the formation of imidazoisoquinolines (**12**)—(**14**) from isoquinolinium methylides and trifluoroacetonitrile were not discussed except that 'oxidation' of dihydro analogues formed first [and isolated in some cases, see (**15**) and (**16**)] was proposed, and 1,4-elimination of the elements of HCN and HCO_2Me from the presumptive initial adduct derived from methylide (**11**) were indicated.[8]

Isolation of only the two triazolopyridines (**5**) and (**6**) or (**7**) from the product formed *via* attack of *N*-iminopyridinium ylide (**1**) on trifluoroacetonitrile did not allow a decision to be reached regarding the type of mechanism (*i.e.*, concerted or stepwise) operating in the cycloaddition process. By contrast, excellent support for a stepwise mechanism is available here in the case of attack by pyridinium alkoxycarbonylmethylides (**2**) and (**3**) on trifluoroacetonitrile or heptafluorobutyronitrile through the isolation of alkenylpyridinium salts (**26**) and (**27**) and pyrimidinylides (**29**) and (**30**). A complete mechanistic scenario is presented in the Scheme. Clearly, when the molar ratio of nitrile to methylide is increased, the yield of pyrimidinylic product should also increase—as is observed; likewise, treatment of the propenylpyridinium perchlorate (**26**) (i) with sodium hydride in acetonitrile *did* yield the corresponding imidazo[1,2-*a*]pyridine (**19**); and (ii) with triethylamine in the presence of trifluoroacetonitrile (in CH_2Cl_2) *did* give the corresponding pyrimidinylide (**29**) (80% yield) [addition of NaH as the base *followed* by CF_3CN gave only traces of compound (**29**), the main product being (**19**) (32%)].

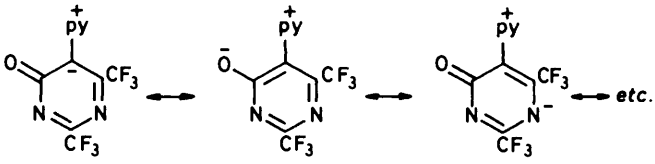
Finally, a synthetic application of the mechanistic proposal outlined in the Scheme has been demonstrated through the synthesis in 68% yield of the (mixed perfluoroalkyl)pyrimidinylide (**31**) *via* simultaneous treatment of the trifluoropropenylpyridinium perchlorate (**26**) with triethylamine and heptafluorobutyronitrile. Possible extensions of this result are obvious, and are being pursued.



Scheme.
[a] Several 'built-in' proton sources are obvious

Crystallographic Discussion

The *X*-ray molecular structure of compound (**29**) was determined as described in the Experimental section. The pyrimidine ring is contained in a crystallographic mirror plane, which bisects the pyridinium substituent at right angles (Figure). Its dimensions are as expected for a delocalized system, agreeing with reported pyrimidine structures[15] except for the region adjoining the oxygen substituent [N(3)–C(4) 1.365(5), C(4)–C(5) 1.444(5) Å; N(3)–C(4)–C(5) 115.7(4), C(4)–C(5)–C(6) 120.8(4)°; *cf.* the mean values of 1.338, 1.373 Å; 122.6, 116.3° respectively in pyrimidine itself]. The ring distortions are reminiscent of those occurring in the picrate



(**29a**) (**29b**) (**29c**)

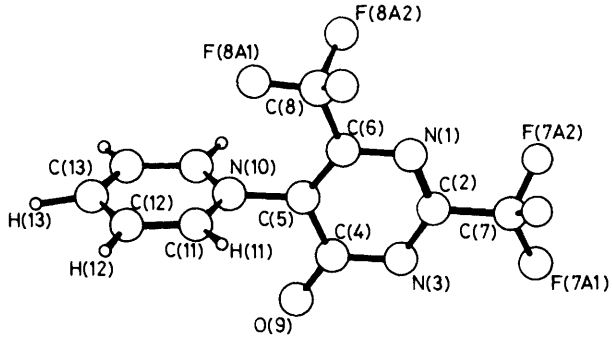


Figure. Geometry of a molecule of compound (**29**).

anion,[16] which, together with similar carbonyl C=O lengths [1.229(4) Å; *cf.*,[16] 1.243(7), 1.239(6) Å respectively for potassium and ammonium 2,4,6-trinitrophenoxide] suggest comparable delocalization of negative charge in the two systems [(**29a**) ⟷ (**29b**) ⟷ *etc.*]. There is no indication of conjugation between the pyrimidine and the pyridinium ring, the dimensions of which are close to reported values.[17] Trifluoromethyl disorder, represented by superimposed major (A) and minor (B) configurations [C(7) 0.664:0.336; C(8) 0.702:0.298], produced a wide scatter in C–F bond lengths, but their weighted mean, 1.294 Å, is as expected.

Experimental

X-Ray Crystallography.—CAD4 Diffractometer, ambient temperature, $\omega/2\theta$ mode with ω scan width 1.00 + 0.35tanθ and scan speed varied according to the intensity gathered in an initial pre-scan from 0.5 to 5 deg min^{-1}, graphite monochromatized Mo-K_α radiation; 997 unique reflections measured ($I > 0$; $1° \leqslant \theta \leqslant 27°$, $+h$, $+k$, $+l$) yielding 812 $F \geqslant 3\sigma(F)$. Negligible variation in intensity of three standards measured at hourly intervals. L_p corrections applied, absorption ignored. All atoms, with the exception of fluorine and hydrogen, were found by direct methods (MULTAN 80[18]). A difference map revealed hydrogens and a pair of disordered CF_3 groups, each of which were represented by two superimposed configurations in the subsequent full-matrix least-squares refinement (SHELX 76[19]). All non-hydrogen atoms were treated anisotropically and hydrogens isotropically. Final $R = 0.062$ [$R_w = 0.068$, $w = 1.9433/(\sigma(F_o)^2 + 0.001F_o^2$; $\sigma(F_o)$ from counting statistics]. Fluctuations in the final difference map were $< \pm 0.25$ e Å^{-3}. Computations were carried out on the joint CDC 7 600/Amdahl 470 system of the University of Manchester Regional Computing Centre. Neutral-atom scattering factors[20] were employed throughout. The Cambridge Crystallographic Database was surveyed using the Crystal Structure Search and Retrieval[21] interactive system accessed *via* the UMIST link to the VAX at Daresbury. Final atomic co-ordinates are listed in Table 1, and some details of molecular geometry and non-bonded distances are presented in Table 2; the Figure shows an asymmetric unit, including the atomic numbering scheme, and was plotted using the PLUTO program.[22] Tables of additional molecular geometry (including torsion angles), non-hydrogen atom anisotropic thermal parameters, and hydrogen-atom co-ordinates and isotropic thermal parameters are deposited as Supplementary Publication No. SUP 56627 (4 pp.).*

* For details of the Supplementary Publications Scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans. 1*, 1986, issue 1.

Table 1. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms

	x	*y*	*z*
N(1)	5 330(4)	4 348(2)	2 500
C(2)	4 282(6)	3 800(2)	2 500
N(3)	2 560(4)	3 760(2)	2 500
C(4)	1 664(6)	4 379(2)	2 500
C(5)	2 717(5)	5 006(2)	2 500
C(6)	4 502(5)	4 965(2)	2 500
C(7)	5 254(9)	3 109(2)	2 500
F(7A1)	4 344(9)	2 564(3)	2 500
F(7A2)	6 338(9)	3 063(3)	1 176(7)
F(7B1)	6 603(23)	3 096(9)	2 500
F(7B2)	4 458(19)	2 701(5)	1 278(16)
C(8)	5 688(6)	5 586(2)	2 500
F(8A1)	4 941(8)	6 185(3)	2 500
F(8A2)	6 743(6)	5 571(2)	1 202(4)
F(8B1)	7 244(19)	5 463(9)	2 500
F(8B2)	5 378(20)	6 008(6)	1 298(14)
O(9)	65(4)	4 402(1)	2 500
N(10)	1 773(4)	5 661(2)	2 500
C(11)	1 279(4)	5 946(2)	3 966(4)
C(12)	290(4)	6 541(2)	3 989(5)
C(13)	−225(6)	6 845(2)	2 500

X-*Ray Structure Determination for Pyridinium* 4,5-*Dihydro*-4-*oxo*-2,6-*bis*(*trifluoromethyl*)*pyrimidin*-5-*ylide* (**29**).—*Crystal data.* $C_{11}H_5F_6N_3O$ (**29**), M_r = 309.17, T = 293 K, orthorhombic, a = 7.679(2), b = 19.065(3), c = 7.970(2) Å, V = 1 166.8 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $9 < \theta < 12$, λ = 0.710 69 Å), space group *Pbcm* (No. 57), Z = 4, D_c = 1.76 Mg m^{-3}, F(000) = 616; crystal: colourless triangular prism, *ca.* 0.5 × 0.5 × 0.3 mm, μ = 0.13 mm^{-1}.

Spectroscopic Analyses.—Details of the instruments used to record spectra have been given previously.[1] N.m.r. chemical shifts were measured relative to Me_4Si (int.; ^1H and ^{13}C) or CF_3CO_2H (ext.; ^{19}F), positive values being assigned to absorptions appearing downfield from reference signals.

Starting Materials.—Perfluoroalkanenitriles were prepared from commercial (FluoroChem) samples of the corresponding acids *via* standard recipes [$R_FCO_2H \longrightarrow R_FCO_2Et \longrightarrow R_FCONH_2 \longrightarrow R_FCN$ (R_F = CF_3, n-C_3F_7)].[23] Analytically pure samples of *N*-t-butoxycarbonylmethylpyridinium perchlorate[7] and *N*-ethoxycarbonylmethylpyridinium bromide[24] were procured according to the literature methods; the perchlorate was stored until required in a wide-mouthed screw-topped glass jar kept underneath a heavy steel dome provided with a safety vent, and was subjected to minimal mechanical disturbance at all times.

Reactions of Trifluoroacetonitrile.—(a) *With pyridinium t-butoxycarbonylmethylide* (**2**) (i) With sodium hydride to generate the methylide. With care taken to exclude moisture, sodium hydride (0.24 g, 10 mmol) was added to a cold (0 °C), magnetically stirred solution of *N*-(t-butoxycarbonylmethyl)-pyridinium perchlorate (**23**) (2.94 g, 10 mmol) in dry acetonitrile (50 cm^3) contained in a Pyrex ampoule (300 cm^3) equipped with a PTFE–glass Rotaflo valve; production of pyridinium t-butoxycarbonylmethylide (**2**) was marked by the evolution of hydrogen and the formation of an orange-yellow solution, which was subsequently (after 20 min) cooled to −196 °C and degassed (*via* several pump–thaw–freeze cycles) before trifluoroacetonitrile (0.95 g, 10 mmol) was condensed into the cold (−196 °C) tube. The reaction vessel was then placed in a blast-proof cabinet, allowed to warm to room temperature, and left with the magnetic stirrer in motion for 2 days. After removal of gaseous material [shown by i.r. spectroscopy to be trifluoroacetonitrile (0.1 mmol)] from the tube, the liquid product was filtered to remove a small amount of inorganic material, then evaporated to provide a multi-component [2 major and numerous minor products according to h.p.l.c. analysis (reverse-phase partisil 10 ODS column, 25 cm × 5 mm; mobile phase MeCN–water (7:3 v/v)] red-brown solid (3.71 g); subjection of this residue to flash chromatography (silica, 15 × 5 cm; $CHCl_3$, Me_2CO, then MeOH) provided two major fractions [yellow (0.61 g) and orange (2.12 g), respectively] which were purified (as stated below) to give 3-(*t-butoxycarbonyl*)-2-(*trifluoromethyl*)*imidazo*[1,2-a]*pyridine* (**19**) (recrystallized from 50% aqueous EtOH; 0.45 g, 16%) (Found: C, 54.5; H, 4.4; F, 20.0; N, 9.7. $C_{13}H_{13}F_3N_2O_2$ requires C, 54.5; H, 4.5; F, 19.9; N, 9.8%) as white crystals, m.p. 102—103 °C; $\nu_{max.}$(mull) 1 695 cm^{-1} (C=O str); $\lambda_{max.}$(EtOH) 234.5 (ε 26 450), 241 (25 750), 289 (9 900), and 300 nm (9 470); m/z 286 ($M^{+\cdot}$, 16%) and 230 ($M^{+\cdot} - C_4H_8$, 100); δ_F (20% soln in $CDCl_3$) 17.3 p.p.m. (s); δ_H (same soln) 1.63 (s, Bu^t), 7.14 (td, 6-H), 7.51 (ddd, 7-H), 7.82 (dt, 8-H), and 9.39 (dt, 5-H) (rel. int. 9:1:1:1:1) ($J_{7,8}$ 9.0, $J_{5,6} \approx J_{6,7} \approx$ 7.2, $J_{5,7} \approx J_{6,8} \approx$ 1.2, $J_{5,8}$ 1.0 Hz); δ_C (50% soln in $CDCl_3$;

Table 2. Selected bond lengths (Å), angles (°), and interatomic distances (Å)

N(1)–C(2)	1.319(5)	N(1)–C(6)	1.338(4)
C(2)–N(3)	1.325(5)	C(2)–C(7)	1.514(6)
N(3)–C(4)	1.365(5)	C(4)–C(5)	1.444(5)
C(4)–O(9)	1.229(4)	C(5)–C(6)	1.373(5)
C(5)–N(10)	1.444(5)	C(6)–C(8)	1.494(5)
C(7)–F(7A1)	1.252(8)	C(7)–F(7A2)	1.347(7)
C(7)–F(7B1)	1.037(17)	C(7)–F(7B2)	1.388(14)
C(8)–F(8A1)	1.277(6)	C(8)–F(8A2)	1.314(4)
C(8)–F(8B1)	1.218(14)	C(8)–F(8B2)	1.273(11)
N(10)–C(11)	1.343(3)	C(11)–C(12)	1.365(4)
C(12)–C(13)	1.379(4)		

C(6)–N(1)–C(2)	114.0(3)	N(3)–C(2)–N(1)	130.9(4)
C(7)–C(2)–N(1)	112.9(4)	C(7)–C(2)–N(3)	116.3(4)
C(4)–N(3)–C(2)	117.0(3)	C(5)–C(4)–N(3)	115.7(4)
O(9)–C(4)–N(3)	122.3(4)	O(9)–C(4)–C(5)	122.0(4)
C(6)–C(5)–C(4)	120.8(4)	N(10)–C(5)–C(4)	115.8(3)
N(10)–C(5)–C(6)	123.4(3)	C(5)–C(6)–N(1)	121.7(3)
C(8)–C(6)–N(1)	114.0(3)	C(8)–C(6)–C(5)	124.3(3)
F(7A1)–C(7)–C(2)	116.6(6)	F(7A2)–C(7)–C(2)	111.1(3)
F(7A2)–C(7)–F(7A1)	107.0(4)	F(7B1)–C(7)–C(2)	120.8(11)
F(7B2)–C(7)–C(2)	105.7(6)	F(7B2)–C(7)–F(7B1)	115.3(9)
F(7A2)–C(7)–F(7A2)^{I}	103.1(8)	F(7B2)–C(7)–F(7B2)^{I}	89.2(11)
F(8A1)–C(8)–C(6)	115.8(4)	F(8A2)–C(8)–C(6)	111.0(3)
F(8A2)–C(8)–F(8A1)	107.3(3)	F(8B1)–C(8)–C(6)	116.4(9)
F(8B2)–C(8)–C(6)	112.7(5)	F(8B2)–C(8)–F(8B1)	107.8(9)
F(8A2)–C(8)–F(8A2)^{I}	103.8(5)	F(8B2)–C(8)–F(8B2)^{I}	97.6(14)
C(11)–N(10)–C(5)	119.4(2)	C(11)–N(10)–C(11)	120.9(3)
C(12)–C(11)–N(10)	120.3(3)	C(13)–C(12)–C(11)	119.9(3)
C(12)–C(13)–C(12)^{I}	118.7(4)		

C(2)^{II} ··· F(8B2)	3.06(2)
C(4)^{II} ··· F(8A2)	3.20(1)
C(5)^{II} ··· F(8A2)	3.18(1)
F(7A1)^{III} ··· F(8A1)	2.69(2)
F(7A2)^{II} ··· F(8B2)	2.96(2)
F(7A2)^{IV} ··· F(7A2)	2.85(2)
F(7A2)^{IV} ··· F(7B2)	2.34(2)
F(7A2)^{V} ··· C(11)	3.17(1)
F(7B2)^{IV} ··· F(7B2)	2.18(3)
F(8B1)^{VI} ··· O(9)	2.96(2)
O(9)^{VII} ··· C(11)	3.07(1)

^{I} $x, y, \frac{1}{2} - z$; ^{II} $1 - x, 1 - y, -z$; ^{III} $1 - x, \frac{1}{2} + y, z$; ^{IV} $x, \frac{1}{2} - y, -\frac{1}{2} - z$; ^{V} $1 - x, 1 - y, \frac{1}{2} + z$; ^{VI} $-1 + x, y, z$; ^{VII} $-x, 1 - y, 1 - z$.

broadband decoupled) 27.7 (s, *Me*$_3$C), 83.1 (s, Me$_3$*C*), 114.2 (s, C-3), 115.2 (s, C-6 or -8), 118.2 (s, C-8 or -6), 120.9 [q, ^1J(CF$_3$) 270 Hz, CF$_3$], 127.8 (s, C-7), 128.1 (s, C-5), 139.8 (q, $^2J_{CF}$ 38 Hz, C-2), 145.1 (s, C-8a), and 158.4 p.p.m. (s, C=O); and cream-coloured N-[2-*amino*-3,3,3-*trifluoro*-1-(*t-butoxycarbonyl*)*prop*-1-*enyl*]*pyridinium perchlorate* (**26**) [precipitated from MeCO$_2$Et by addition of light petroleum (b.p. 40—60 °C)] (1.11 g, 27%) (Found: C, 40.1; H, 4.2; Cl, 9.0; F, 14.6; N, 7.1. $C_{13}H_{16}ClF_3N_2O_6$ requires C, 40.15; H, 4.1; Cl, 9.1; F, 14.7; N, 7.2%), m.p. 141.5—142.5 °C (decomp.); $\nu_{max.}$(mull) 3 440, 3 320 (d, N–H str), 1 690 (C=O str), and 1 645 cm^{-1} (N–H def); $\lambda_{max.}$(EtOH) 263 nm (ε 17 450); *m/z* 186 (top mass peak; $C_8H_5F_3N^+$, 15%), 79 ($C_5H_5N^+$, 20), 56 ($C_4H_8^+$, 50), 44 (CO_2^+, 100), and 41 ($C_3H_5^+$, 70.5); δ_F [20% soln in (CD$_3$)$_2$SO] 14.5 p.p.m. (s); δ_H (same soln) 1.31 (s, Bu^t), 8.31 (br dd, 3- and 5-H), 8.7 (br s, NH$_2$), 8.84 (t, 4-H), and 9.26 (br, d, 2- and 6-H) (rel. int. 9:2:2:1:2) ($J_{3,4} = J_{4,5} = 8.0$, $J_{2,3} = J_{5,6} = 6.0$ Hz); δ_C (40% soln in CD$_3$CN; broadband decoupled) 28.1 (s; *Me*$_3$C), 85.2 (s, Me$_3$*C*), 107.5 (s, C-1′), 120.6 [q, ^1J(CF$_3$) 278 Hz, CF$_3$], 129.4 (s, C-3 and -5), 146.9 [q, $^2J_{CF}$ 33 Hz, C-2′], 149.5 (s, C-4), 150.6 (s, C-2 and -6), and 164.2 p.p.m. (s, C=O). Other fractions were shown by t.l.c. and h.p.l.c. to be mixtures of unidentified minor components [one of which was found later to be the pyrimidinylide (**29**)]; additionally, sodium perchlorate contaminated with organic material, including the propenylpyridinium perchlorate (**26**), was eluted.

The reaction was repeated (same techniques and work-up procedure) on twice the scale [*N*-(t-butoxycarbonylmethyl)-pyridinium perchlorate (5.87 g, 20 mmol), sodium hydride (0.48 g, 20 mmol), and acetonitrile (100 cm^3) in a 540 cm^3 'Rotaflo tube'] but with a molar excess of trifluoroacetonitrile (3.80 g, 40 mmol) during 2 days at room temperature. This yielded 3-(t-butoxycarbonyl)-2-(trifluoromethyl)imidazo-[1,2-*a*]pyridine (**19**) (0.49 g, 9%), *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate (**26**) (1.37 g, 18%), and a pale brown solid (2.69 g, the final fraction) which was re-chromatographed (flash method; silica, 15 × 5 cm; Me$_2$CO then MeOH) to provide a pale orange solid that, when triturated with acetone, gave *pyridinium* 4,5-*dihydro*-4-*oxo*-2,6-*bis*(*trifluoromethyl*)*pyrimidin*-5-*ylide* (**29**) (1.82 g, 29%) (Found: C, 42.6; H, 1.4; F, 36.9; N, 13.7. $C_{11}H_5F_6N_3O$ requires C, 42.7; H, 1.6; F, 36.9; N, 13.6%) as white crystals, m.p. 266—267 °C (decomp.); $\nu_{max.}$(mull) 1 640 and 1 620 cm^{-1}; $\lambda_{max.}$(EtOH) 229 (ε 17 000), 259 (8 050), and 299.5 nm (3 800); *m/z* 309 ($M^{+\cdot}$, 100%), 308 ($M^{+\cdot}$ − H, 51), 281 ($M^{+\cdot}$ − CO, 90), 79 ($C_5H_5N^+$, 30.5), and 69 (CF_3^+, 27.5); δ_F [10% soln in (CD$_3$)$_2$CO] 6.0 (s) and 12.8 p.p.m. (s) (rel. int. 1:1); δ_H (same soln) 8.45 (t, 3- and 5-H), 8.95 (tt, 4-H), and 9.14 (d, 2- and 6-H) (rel. int. 2:1:2) ($J_{3,4} = J_{4,5} = 8.0$; $J_{2,4} = J_{4,6} = 1.6$; $J_{2,3} = J_{5,6} = 6.0$ Hz).

(ii) With triethylamine to generate pyridinium t-butoxycarbonylmethylide. Triethylamine (0.50 g, 5 mmol) was added to a suspension of *N*-(t-butoxycarbonylmethyl)pyridinium perchlorate (**23**) (1.47 g, 5 mmol) in dichloromethane (25 cm^3) contained in a cold (0 °C) Pyrex tube (300 cm^3) equipped with a Rotaflo valve; a bright orange-yellow precipitate appeared immediately. The contents of the sealed tube were stirred magnetically for 20 min, then the tube was cooled to −196 °C, the contents were degassed, and trifluoroacetonitrile (0.48 g, 5 mmol) was condensed in. After the tube had warmed to room temperature (in an explosion-proof box), magnetic stirring was resumed and was continued for 2 days. No trifluoroacetonitrile was recovered, and evaporation of the liquid reaction product (which contained no insoluble matter), followed by n.m.r. and quantitative h.p.l.c. analysis (calibrated 25 × 5 mm reverse-phase Partisil 10 ODS column; 50% aqueous MeCN) of the orange-brown residual solid (2.35 g), showed it to contain 3-(t-butoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**19**) (0.4 g, 28%), *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]pyridinium perchlorate (**26**) (0.85 g, 44%), traces of the pyrimidinylide (**29**), unknown products arising from the action of triethylamine on trifluoroacetonitrile, triethylammonium perchlorate, and several minor unidentified components.

The experiment was repeated with *N*-(t-butoxycarbonylmethyl)pyridinium perchlorate (10 mmol, 2.94 g) suspended in dichloromethane (50 cm^3), triethylamine (20 mmol, 2.01 g), and trifluoroacetonitrile (20 mmol, 1.90 g). None of the nitrile was recovered, and the reddish brown liquid product contained a solid which proved to be analytically pure pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (0.85 g, 28%), m.p. 266—267 °C; the filtrate obtained during recovery of this pyrimidinylide was evaporated to give a multi-component (at least 8 by h.p.l.c.) orange-brown solid (4.50 g) which was chromatographed (flash method; 15 × 15 cm silica eluted with CHCl$_3$, Me$_2$CO, and MeOH in that order) to provide the imidazo[1,2-*a*]pyridine (**19**) (0.15 g, 5% after recrystallization from aqueous ethanol), m.p. 102—103 °C (pure according to i.r. analysis), triethylammonium perchlorate (not weighed), and a further quantity of the pyrimidinylide (**29**) (1.21 g, 39% after a second pass through the chromatographic column; total yield 67%). Several other minor products were not identified, and only a trace of the propenylpyridinium perchlorate (**26**) was detected in an intermediate fraction.

(b) *With pyridinium ethoxycarbonylmethylide* (**3**). With care taken to exclude moisture, triethylamine (1.01 g, 10 mmol) was added to a cold (0 °C), stirred (magnetically) suspension of *N*-(ethoxycarbonylmethyl)pyridinium bromide (**24**) (2.46 g, 10 mmol) in dichloromethane (50 cm^3) in a Pyrex Rotaflo tube (300 cm^3). The bright yellow mixture was stirred for 20 min, then degassed before trifluoroacetonitrile (1.90 g, 20 mmol) was condensed into the cold (−196 °C) tube. The tube was stored at room temperature for 2 days with the stirrer in motion before unchanged trifluoroacetonitrile (not measured) was removed and the reaction solution was filtered to provide pure (after being washed with dichloromethane) pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (0.70 g, 23%) (Found: C, 42.6; H, 1.3; F, 37.3; N, 13.7%), m.p. 267—268 °C, which was identified spectroscopically (i.r., n.m.r., and mass). Evaporation of the filtrate (Rotavapor) gave dichloromethane coloured yellow by an unidentified contaminant (the solution turned Prussion blue overnight) and a complex (9 components by h.p.l.c. analysis) orange-brown solid (3.91 g) shown by n.m.r. analysis to comprise mainly the pyrimidinylide (**29**), the imidazopyridine (**19**), and triethylammonium bromide. The solid was added to acetone prior to chromatographic work-up, and the insoluble triethylammonium bromide (1.23 g, 68%) (Found: C, 39.6; H, 8.9; Br, 44.0; N, 7.7. Calc. for $C_6H_{16}BrN$: C, 39.6; H, 8.8; Br, 43.9; N, 7.7%) was removed by filtration; the filtrate was absorbed on silica, and the components were eluted (flash method; 15 × 5 cm silica; CHCl$_3$, Me$_2$CO, and MeOH) to provide 3-(ethoxycarbonyl)-2-(trifluoromethyl)imidazo-[1,2-*a*]pyridine (**18**) (0.49 g, 19% after recrystallization from 50% aqueous ethanol) (Found: C, 51.4; H, 3.2; F, 22.0; N, 11.0. Calc. for $C_{11}H_9F_3N_2O_2$: C, 51.2; H, 3.5; F, 22.1; N, 10.9%), m.p. 101—103 °C (lit.,[8] 102—103 °C); $\nu_{max.}$(mull) 1 695 cm^{-1} (C=O str); $\lambda_{max.}$(EtOH) 234 (ε 27 070), 240.5 (25 430), 289 (9 770), and 300 nm (9 580); *m/z* 258 ($M^{+\cdot}$, 56%), 230 ($M^{+\cdot}$ − C_2H_4, 38), and 186 ($M^{+\cdot}$ − C_2H_4 − CO_2, 100); δ_F (20% soln in CDCl$_3$) 17.0 p.p.m. (s); δ_H (same soln) 1.44 (t, Me), 4.48 (q, CH$_2$), 7.18 (td, 6-H), 7.56 (ddd, 7-H), 7.85 (dt, 8-H), and 9.38 (dt, 5-H) (rel. int. 3:2:1:1:1:1) (J_{CH_2,CH_3} 7.4, $J_{7,8}$ 9.0, $J_{5,6} \approx J_{6,7} \approx 6.8$, $J_{5,7} \approx J_{6,8} \approx 1.2$, $J_{5,8} = 1.0$ Hz), two fractions comprising mixtures (by h.p.l.c. and n.m.r.) of unknown compounds, and pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) [0.58 g, 19% (total yield 42%) after further chromatographic purification and trituration

with Me_2CO], m.p. 266—267 °C, identified by i.r. spectroscopy.

When the reaction was repeated, except that only 10 mmol of trifluoroacetonitrile were used, only 3-(ethoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**18**) (0.75 g, 29%) and triethylammonium bromide (1.20 g, 66%) were recovered from the highly complex reaction product.

Reaction of Heptafluorobutyronitrile with Pyridinium t-Butoxycarbonylmethylide (**2**).—(a) *With sodium hydride to generate the methylide.* Heptafluorobutyronitrile (7.8 g, 40 mmol) was condensed, under reduced pressure, into a cold (−196 °C) Pyrex Rotaflo tube (300 cm^3) containing a degassed bright orange solution of the methylide produced *in situ* by stirring together *N*-(t-butoxycarbonylmethyl)pyridinium perchlorate (**23**) (5.87 g, 20 mmol), sodium hydride (0.48 g, 20 mmol), and acetonitrile (100 cm^3) in the absence of moisture for 30 min. The tube was sealed, warmed to room temperature, and the contents were stirred magnetically for 5 days; the orange solution turned maroon. After gaseous material [C_3F_7CN (*ca.* 12 mmol) contaminated with MeCN, according to i.r. spectroscopy] had been removed from the tube, the liquid product was filtered to remove traces of a solid (not examined) then evaporated (Rotavapor), leaving a sticky maroon solid (11.3 g), shown by t.l.c. and h.p.l.c. analysis to comprise three major and numerous minor components. The former were isolated by flash chromatography [three separate batches of the crude material; silica, 15 × 5 cm; eluted with CH_2Cl_2–light petroleum (b.p. 40—60 °C), starting with a 1:1 v/v mixture and increasing the CH_2Cl_2 content, then Me_2CO, and finally MeOH] and found to be 2-(*heptafluoropropyl*)-3-(*t-butoxycarbonyl*)*imidazo*[1,2-a]*pyridine* (**32**) [first fraction; (1.76 g, 23% after recrystallization from 50% aqueous ethanol)] (Found: C, 46.6; H, 3.4; F, 34.5; N, 7.4. $C_{15}H_{13}F_7N_2O_2$ requires C, 46.6; H, 3.4; F, 34.5; N, 7.25%) as white crystals, m.p. 91—92 °C; $\nu_{max.}$(mull) 1 695 cm^{-1} (C=O str); $\lambda_{max.}$(EtOH) 235 (ε 25 300), 241 (22 200), and 288.5 nm (9 100); *m/z* 386 ($M^{+\cdot}$, 11%) and 330 ($M^{+\cdot} - C_4H_8$, 100); δ_F (20% soln in $CDCl_3$) −1.5 (t, CF_3), −28.4 (q, $CF_2CF_2CF_3$), and −46.2 p.p.m. (s, $CF_2CF_2CF_3$) (rel. int. 3:2:2) ($^4J_{F,F}$ 10.2 Hz); δ_H 1.62 (s, Bu^t), 7.12 (td, 6-H), 7.50 (ddd, 7-H), 7.83 (dt, 8-H), and 9.40 (dt, 5-H) (rel. int. 9:1:1:1:1); δ_C (40% soln in $CDCl_3$; broadband decoupled) 27.4 (s, Me_3C), 83.1 (s, Me_3C), 108.9 (tsex, $^1J_{CF}$ 266 Hz, $CF_2CF_2CF_3$), 112.9 (tt, $^1J_{C,F}$ 255, $^2J_{C,F}$ 32.3 Hz, $CF_2CF_2CF_3$), 114.8 (s, C-6 or -8), 116.5 (s, C-3), 118.0 (qt, $^1J_{C,F}$ 288, $^2J_{C,F}$ 34.2 Hz, CF_3), 118.1 (s, C-8 or -6), 127.9 (s, C-5 and -7), 137.6 (t, $^2J_{C,F}$ 28.0 Hz, C-2), 145.4 (s, C-8a), and 158.5 p.p.m. (s, C=O); *N*-[2-amino-3,3,4,4,5,5,5-heptafluoro-1-(t-butoxycarbonyl)pent-1-enyl]-pyridinium perchlorate (**27**) [third fraction; (1.55 g, 16% after trituration with ethyl acetate)], m.p. 172—174 °C; and pyridinium 2,6-bis(heptafluoropropyl)-4,5-dihydro-4-oxopyrimidin-5-ylide (**30**) [fifth fraction; (0.65 g, 6.5% after further chromatography with Me_2CO, then MeOH, as eluant)], the last two being identical spectroscopically (i.r., n.m.r.) with the samples described below. Impure sodium perchlorate [fourth fraction; (2.55 g)] was also recovered; the second fraction (0.38 g) was a multi-component (h.p.l.c.) orange-brown tarry solid.

(b) *With triethylamine to generate t-butoxycarbonylmethylide* (**2**). The reaction of this methylide with trifluoroacetonitrile [experiment (a) above] was repeated on one-quarter the scale but with triethylamine (5 mmol) as the base, dichloromethane (50 cm^3) as solvent, and a 2-day reaction period. None of the nitrile was recovered, and work-up of the reddish black solution, as before, afforded 2-(heptafluoropropyl)-3-(t-butoxycarbonyl)imidazo[1,2-*a*]pyridine (**32**) (0.28 g, 14%), m.p. 91—92 °C, with correct i.r. and n.m.r. spectra; N-[2-*amino*-3,3,4,4,5,5,5-*heptafluoro*-1-(*t-butoxycarbonyl*)*pent*-1-*enyl*]-*pyridinium perchlorate* (**27**) (0.32 g, 14%) (Found: C, 37.0; H, 3.1; F, 27.3; N, 5.8. $C_{15}H_{16}ClF_7N_2O_6$ requires C, 36.8; H, 3.3; F, 27.2; N, 5.7%), off-white crystals; m.p. 173—174 °C; $\nu_{max.}$(mull) 3 360, 3 260, 3 210, (N–H str), 1 690 (C=O str), and 1 630 cm^{-1} (N–H def); *m/z* 286 (top mass peak; $C_{10}H_5F_7N_2^+$, 16.5%), 167 ($C_8H_7F_2N_2^+$, 33), 79 ($C_5H_5N^+$, 6), 56 ($C_4H_8^+$, 68), 44 (CO_2^+, 57), and 41 ($C_3H_5^+$, 100); δ_F [20% soln in $(CD_3)_2CO$] −3.0 (t, CF_3), −36.1 (q, $CF_2CF_2CF_3$), and −47.8 p.p.m. (s, $CF_2CF_2CF_3$) (rel. int. 3:2:2) ($^4J_{F,F}$ 11.0 Hz); δ_H (same soln) 1.37 (s, Bu^t), 8.43 (t, 3- and 5-H), 8.5 (br s, NH_2), 8.99 (t, 4-H), and 9.29 (d, 2-and 6-H) (rel. int. 9:2:2:1:2) ($J_{3,4} = J_{4,5}$ = 8.0, $J_{2,3} = J_{5,6}$ = 6.0 Hz); and *pyridinium* 2,6-*bis*(*heptafluoropropyl*)-4,5-*dihydro*-4-*oxopyrimidin*-5-*ylide* (**30**) (0.63 g, 25%) (Found: C, 35.2; H, 0.7; F, 52.4; N, 8.6. $C_{15}H_5F_{14}N_3O$ requires C, 35.4; H, 1.0; F, 52.3; N, 8.25%), m.p. 189—190 °C; $\nu_{max.}$(mull) 1 630 and 1 610 cm^{-1}; $\lambda_{max.}$(EtOH) 232.5 (ε 13 720), 259 (8 350), and 307.5 nm (4 170); *m/z* 509 ($M^{+\cdot}$, 27 %), 481 ($M^{+\cdot} - CO$, 5), 362 ($M^{+\cdot} - CO - C_2F_5$, 100), 79 ($C_5H_5N^+$, 5), and 69 (CF_3^+, 6); δ_F [20% soln in $(CD_3)_2CO$] − 3.0 (t, $^4J_{F,F}$ 10.2 Hz, CF_3), −3.5 (t, $^4J_{F,F}$ 8.5 Hz, CF_3), −33.9 (q, $^4J_{F,F}$ 10.2 Hz, $CF_2CF_2CF_3$), −38.3 (q, $^4J_{F,F}$ 8.5 Hz, $CF_2CF_2CF_3$), −48.0 (s, $CF_2CF_2CF_3$), and −48.9 (s, $CF_2CF_2CF_3$) (rel. int. 3:3:2:2:2:2); δ_H (same soln) 8.50 (t, 3-and 5-H), 8.99 (t, 4-H), and 9.14 (d, 2- and 6-H) (rel. int. 2:1:2) ($J_{3,4} = J_{4,5}$ = 7.2, $J_{2,3} = J_{5,6}$ = 6.0 Hz). Numerous unidentified minor products were detected by h.p.l.c., 'tar' was present, and crude triethylammonium perchlorate (0.69 g) was isolated.

Reactions of N-[2-*Amino*-3,3,3-*trifluoro*-1-(*t-butoxycarbonyl*)*prop*-1-*enyl*]*pyridinium Perchlorate* (**26**).—(a) *With sodium hydride.* A cold (0 °C), magnetically stirred solution of the perchlorate (0.78 g, 2.0 mmol) in dry acetonitrile (10 cm^3) contained in a Pyrex Rotaflo tube (130 cm^3) effervesced and turned dark red when treated with sodium hydride [0.05 g(?), 2.1 mmol]. After 30 min (moisture was excluded from the apparatus), the tube was cooled to −196 °C, the contents were degassed, and the sealed tube was stored at room temperature (with the stirrer activated) for 2 days. Flash chromatographic work-up (15 × 3 cm, silica; $CHCl_3$, Me_2CO) of the crude organic product provided 3-(t-butoxycarbonyl)-2-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**19**) (0.13 g, 23%) and *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]-pyridinium perchlorate (**26**) (0.43 g, 55% recovery), both identified spectroscopically (i.r., n.m.r.). Failure to effect more extensive conversion of the perchlorate into the imidazopyridine presumably reflects the difficulty of introducing the correct amount of sodium hydride on the scale of this experiment.

(b) *With sodium hydride and trifluoroacetonitrile.* The experiment was repeated except that trifluoroacetonitrile (0.19 g, 2.0 mmol) was condensed into the cold (−196 °C) Rotaflo tube after the reaction was degassed. Much trifluoroacetonitrile was recovered (1.5 mmol, 75%), and the crude reaction product was shown by n.m.r. spectroscopy to comprise mainly starting material (**26**) and the imidazopyridine (**19**). Quantitative h.p.l.c. analysis revealed the presence of pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (4% yield), and showed the yield of the imidazopyridine (**19**) to be 32%.

(c) *With triethylamine and perfluoroalkanenitriles.* (i) Using trifluoroacetonitrile. Triethylamine (0.25 g, 2.5 mmol), then trifluoroacetonitrile (0.24 g, 2.5 mmol), were condensed, under reduced pressure, into a cold (−196 °C), evacuated, Pyrex Rotaflo tube (130 cm^3) containing a degassed suspension of *N*-[2-amino-3,3,3-trifluoro-1-(t-butoxycarbonyl)prop-1-enyl]-pyridinium perchlorate (**26**) (0.97 g, 2.5 mmol) suspended in dichloromethane (12.5 cm^3) and a PTFE-coated magnetic stirrer follower. The tube was sealed, allowed to warm to room temperature, then left for 2 days with the stirrer in motion; as the tube warmed up the contents became bright yellow, changing to orange as room temperature was attained. After removal of traces of trifluoroacetonitrile plus some dichloromethane from

the tube, the contents were filtered to collect a solid product, shown by t.l.c. and spectroscopic (i.r., n.m.r.) analysis to be pure 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)pyrimidin-5-ylide (**29**) (0.29 g, 26%). Evaporation of the filtrate left an orange-yellow solid (1.01 g), shown by n.m.r. analysis to contain the pyrimidinylide (**29**), triethylammonium perchlorate, and a small amount of unchanged starting material (**26**); h.p.l.c. analysis confirmed this, and also revealed the presence of traces of the imidazopyridine (**19**) and several unidentified compounds; quantitative h.p.l.c. showed the yield of the pyrimidinylide (**29**) to be 54%, making the total yield 80%.

(ii) Using heptafluorobutyronitrile. The previous experiment (i) was repeated with heptafluorobutyronitrile (0.49 g, 2.5 mmol) in place of trifluoroacetonitrile. The reaction mixture (which became orange then dark maroon in colour) was worked up by flash chromatography (silica, 15 × 4 cm; eluted with $CHCl_3$ followed by increasing amounts of Me_2CO and finally MeOH) to provide triethylammonium perchlorate contaminated with starting material (**26**) and *pyridinium* 2-(*heptafluoropropyl*)-4,5-*dihydro*-4-*oxo*-6-(*trifluoromethyl*)*pyrimidin*-5-*ylide* (**31**) (0.69 g, 68% after trituration with ethyl acetate) (Found: C, 38.3, H, 0.9; F, 46.3; N, 10.3. $C_{13}H_5F_{10}N_3O$ requires C, 38.1; H, 1.2; F, 46.45; N, 10.3%), a white solid, m.p. 267—268 °C; $\nu_{max.}$(mull) 1 620 and 1 605 cm^{-1}; $\lambda_{max.}$(EtOH) 230 (ε 13 930), 257 (8 130), and 304 nm (3 940); *m/z* 409 ($M^{+\cdot}$, 26.5%), 408 ($M^{+\cdot}$ − H, 14) 262 ($M^{+\cdot}$ − CO − C_2F_5, 100), 79 ($C_5H_5N^+$, 9), and 69 (CF_3^+, 8); δ_F [20% soln in $(CD_3)_2CO$] 12.2 (s, CF_3), −3.2 (t, $^4J_{C,F}$ 8.5 Hz, $CF_3CF_2CF_2$), −38.0 (q, $^4J_{F,F}$ 8.5 Hz, $CF_3CF_2CF_2$), and −48.6 p.p.m. (s, $CF_2CF_2CF_3$) (rel. int. 3:3:2:2); δ_H (same soln) 8.50 (t, 3- and 5-H), 8.97 (t, 4-H), and 9.18 (d, 2- and 6-H) (rel. int. 2:1:2).

Reaction of Pyridinium 4,5-*Dihydro*-4-*oxo*-2,6-*bis*(*trifluoromethyl*)*pyrimidin*-5-*ylide* (**29**) *with Zn–Acetic Acid.*—The mixture turned orange and evolved much heat when zinc powder (3 g) then glacial acetic acid (10 cm^3) were added to a stirred suspension of the ylide (**29**) (1.55 g, 5.0 mmol) in diethyl ether (25 cm^3). After 2 h, the mixture was filtered and the filtrate was worked up by standard techniques to provide impure 4-hydroxy-2,6-bis(trifluoromethyl)pyrimidine (0.55 g, 48%) [Found: C, 31.0; H, 0.6; F, 49.4; N, 12.4%; $M^{+\cdot}$, 232. Calc. for $C_6H_2F_6N_2O$: C, 31.0; H, 0.9; F, 49.1; N, 12.1%; *M*, 232], m.p. 112—113 °C (after sublimation, *in vacuo*, at 60 °C) (lit.,[12] 117—118 °C). Comparison of the ^1H (impurity band at δ 6.1) and ^{19}F (impurity bands at δ_F +8.0 and +12.2) n.m.r. spectra of this material with those of an authentic sample revealed the presence of small amounts of an unidentified impurity; the i.r. spectrum contained two extra weak N–H stretch absorptions at 3 350 and 3 400 cm^{-1}.

Acknowledgements

We are deeply indebted to the S.E.R.C. for providing J. T.'s studentship and for financing the CAD4 diffractometer, and to Dr. B. Beagley (UMIST) for his interest in the *X*-ray study.

References

1 Part 12, R. E. Banks and J. Thomson, *J. Chem. Res.*, 1985, (*S*) 33; (*M*) 0671.
2 Preliminary publication: R. E. Banks and J. Thomson, *J. Fluorine Chem.*, 1983, **22**, 589.
3 R. E. Banks, R. N. Haszeldine, and J. M. Robinson, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1226.
4 R. E. Banks and S. M. Hitchen, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1593.
5 R. E. Banks and S. M. Hitchen, *J. Fluorine Chem.*, 1982, **20**, 373.
6 R. E. Banks and J. Thomson, *J. Fluorine Chem.*, 1984, **26**, 499.
7 J. B. Bapat, J. Epsztajn, A. R. Katritzky, and B. Plau, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1692.
8 Y. Kobayashi, I. Kumadaki, and E. Kobayashi, *Heterocycles*, 1981, **15**, 1223.
9 J. P. Paolini and R. K. Robins, *J. Heterocycl. Chem.*, 1965, **2**, 53; W. W. Paudler and H. L. Blewitt, *Tetrahedron*, 1965, **21**, 353.
10 R. J. Pugmire, M. J. Robins, D. M. Grant, and R. K. Robins, *J. Am. Chem. Soc.*, 1971, **93**, 1887.
11 *Cf.* C. A. Henrick, E. Ritchie, and W. C. Taylor, *Austr. J. Chem.*, 1967, **20**, 2441, 2445, 2467.
12 S. Inoue, J. Saggiomo, and E. A. Nodiff, *J. Org. Chem.*, 1961, **26**, 4505.
13 Y. Tominaga, H. Fujito, K. Mizuyama, Y. Matsuda, and G. Kobayashi, *Chem. Pharm. Bull.*, 1977, **25**, 1519.
14 I. Zugrăvescu and M. Petrovanu, 'N-Ylid Chemistry,' McGraw-Hill, New York, 1976.
15 M. Martinez-Ripoll and H. P. Lorenz, *Acta Crystallogr., Sect. B*, 1973, **29**, 2260; 1974, **30**, 793; P. J. Wheatley, *ibid.*, 1960, **13**, 80.
16 K. Maartmann-Moe, *Acta Crystallogr., Sect B*, 1969, **25**, 1452.
17 P. J. Wheatley, *Acta Crystallogr.*, 1957, **10**, 182.
18 P. J. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN 80: A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-ray Diffraction Data,' Universities of York (England) and Louvain (Belgium), 1980.
19 G. M. Sheldrick, 'SHELX 76: Program for Crystal Structure Determination,' University of Cambridge (England), 1976.
20 'International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.
21 'Crystal Structure Search and Retrieval' (Instruction Manual), Daresbury Laboratory, England, 1984.
22 W. D. S. Motherwell and W. Clegg, 'PLUTO Program for Plotting Molecular and Crystal Structures,' University of Cambridge, 1974.
23 H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, 1943, **65**, 1459; R. N. Haszeldine, *J. Chem. Soc.*, 1950, 2789.
24 F. Kröhnke, *Ber. Dtsch. Chem. Ges.*, 1937, **70**, 543.

Received 28*th November* 1985; *Paper* 5/2086