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FLUOROCARBON DERIVATIVES OF NITROGEN. PART 19. SYNTHESIS AND MASS SPECTROMETRIC ANALYSIS OF SOME PYRIDINIUM (TETRAFLUORO-4-PYRIDYL)-METHYLIDES

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SUMMARY

Nine new pyridinium methylides have been synthesised via S_NAr displacement of the 4-fluorine from pentafluoropyridine with pyridinium phenacylide [→ $\overset{+}{py}—\bar{C}(COPh)C_5F_4N$-4] and a range of pyridinium alkoxycarbonylmethylides [→ $\overset{+}{py}—\bar{C}(CO_2R)C_5F_4N$-4, R = Me, Et, Pr^n, Pr^i, CH_2CCl_3, CH_2CF_3, CH_2Ph, CH_2CH_2Ph]. A detailed analysis of the mass spectrometric fragmentation patterns for the alkoxycarbonyl compounds has been carried out. Spectroscopic data has also been obtained for pyridinium methylides synthesised from pyridinium ethoxycarbonylmethylide and 3-chlorotetrafluoropyridine or octafluorotoluene.

INTRODUCTION

During studies on reactions between pyridinium methylides and alkenes, alkynes, or nitriles of the fluorocarbon class [1], we have assessed nucleophilic index at methylidic carbon by testing the ability of several pyridinium ylides to displace fluorine as fluoride from pentafluoropyridine and related polyfluoroaromatic substrates. We report here on the participation of pyridinium phenacylide (**1**) and several of its alkoxycarbonyl congeners (**2** - **9**) in S_NAr reactions

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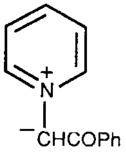

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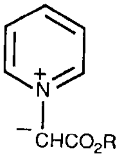
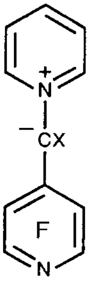


R = Me (**2**), Et (**3**), Pr^n (**4**),
Pr^i(**5**), CH_2CCl_3 (**6**), CH_2CF_3 (**7**),
CH_2Ph (**8**), CH_2CH_2Ph (**9**), Bu^t (**10**)



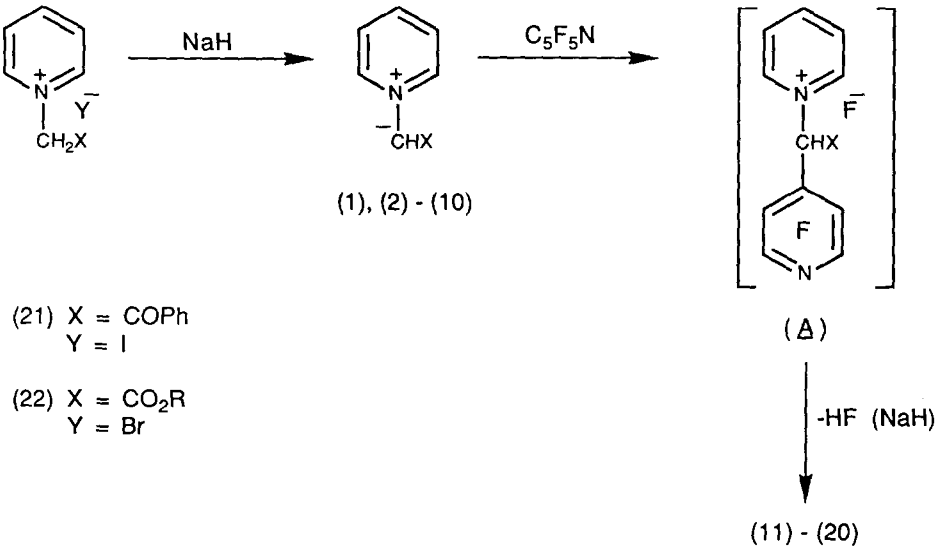
X = COPh (**11**), CO_2Me (**12**), CO_2Et (**13**),
CO_2Pr^n (**14**), CO_2Pr^i (**15**), CO_2Bu^t (**16**),
$CO_2CH_2CCl_3$ (**17**), $CO_2CH_2CF_3$ (**18**),
CO_2CH_2Ph (**19**), $CO_2CH_2CH_2Ph$ (**20**)

with pentafluoropyridine, and on the mass spectral data for the range of pyridinium alkoxycarbonyl(tetrafluoro-4-pyridyl)methylides (**12** - **20**) thereby available to us {the t-butylated compound (**16**) had been prepared previously from methylide **10** and pentafluoropyridine [2]}.

DISCUSSION

Preparation of Pyridinium (Tetrafluoro-4-pyridyl)methylides

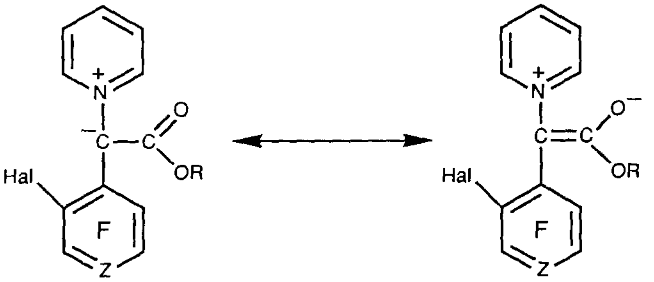
Owing to its instability [3], pyridinium phenacylide (**1**) was generated in cold DMF from phenacylpyridinium iodide (**21**) and sodium hydride, and treated *in situ* with pentafluoropyridine (see Scheme 1). This produced a hygroscopic orange precipitate which, after being dried, proved to be almost pure (by elemental analysis) pyridinium benzoyl(tetrafluoro-4-pyridyl)methylide (**11**) (50% yield). As expected from this result, the phenacylide (**1**) did attack perfluoropropene and other fluorinated dipolarophiles to give fluorinated indolizines, as described earlier [4].



Scheme 1.

Similar <u>in situ</u> treatment of pentafluoropyridine with a range of pyridinium (alkoxycarbonyl)methylides (**2** - **9**), generated by dehydrobromination of the corresponding <u>N</u>-(alkoxycarbonylmethyl)-pyridinium bromides (**22**) with sodium hydride in DMF, gave the corresponding new tetrafluoro-4-pyridyl compounds [(**12**) - (**15**) and (**17** - **20**); see Scheme 1] in unoptimised yields ranging from 27 to 61%. A 1:2:1 molar ratio of (**22**) : NaH : C_5F_5N was employed, the second equivalent of the hydride being added to act as an HF-sink. {This technique had been used previously to procure the t-butoxy compound (**16**) in 85% yield [2].} The ethoxycarbonylmethylide (**3**) like its t-butoxy counterpart (**10**) [2], also displaced fluorine from 3-chlorotetrafluoropyridine [→ (**23**), 63% yield] and octafluorotoluene [→ (**24**), 44%] at 0-20 °C in DMF, but not from the less reactive fluoroaromatic substrate hexafluorobenzene.

Spectroscopically, all three related (ethoxycarbonyl)polyfluoroarylmethylides [(**13**), (**23**), and (**24**)] showed ultraviolet



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(**23**) R = Et, Z = N, Hal = Cl

(**24**) R = Et, Z = CCF_3, Hal = F

(**26**) R = Bu^t, Z = N, Hal = Cl

(**27**) R = Bu^t, Z = CCF_3, Hal = F

absorption maxima in the ranges 240-250 and 340-350 nm, carbonyl (stretching) bands in the infrared at frequencies ca. 150 cm^{-1} higher than N-(ethoxycarbonylmethyl)pyridinium bromide (**22**, X = Et) indicative of significant contributions from enolate canonical forms (**25**), and NMR bands fully consistent with the structures assigned. Thus, the UV, IR and NMR data compared well with that for analogues prepared from pyridinium t-butoxycarbonylmethylide (**10**) generated from (**22**) where X = CO_2Bu^t and Y^- = ClO_4^- [3]. The mass spectra proved to be more interesting and were studied in some detail, as described below.

Mass Spectral Studies

In the EI mass spectra, the molecular ions for all three ethoxycarbonyl compounds [(**13**), (**23**), (**24**)] are relatively strong compared with those of their t-butoxy counterparts [(**16**), (**26**), (**27**)]; *e.g.* for methylides **13** and **16** the relative abundances of $\underline{M}^{+\cdot}$ were 54 and 9 % respectively. The base peak in the spectrum of **16** is due to loss of isobutene, whereas in the case of **13** it arises from loss of both ethene and CO_2. It was this latter observation which prompted us to synthesise specifically for mass spectral analysis the other compounds of the pyridinium alkoxycarbonyl(tetrafluoro-4-pyridyl) methylide class containing β-hydrogens (**14**, **15**, and **20**), and some without the structural feature (**12**, **17**, **18**, and **19**).

Methylides (**12**) - (**20**) were analyzed mass spectrometrically using both positive and negative ionization modes. The *m/z* data for the common fragments are listed in Tables 1 and 2. Entirely consistent positive-ion data were obtained for the ethoxycarbonyl compounds **23** and **24** derived from 3-chlorotetrafluoropyridine and octafluorotoluene, respectively (see the Experimental Section).

Positive-ion spectra. The three ethoxycarbonyl methylides [(**13**),(**23**), and (**24**)] all gave similar spectra (Table 3) with an intense molecular ion, the most prominent simple cleavage being the loss of the ethoxy radical (m/z = 269), whereas the McLafferty rearrangement to give loss of ethene (m/z = 286), followed by loss of CO_2 (m/z = 242) affords in each case the base ion, which, in effect, is the molecular ion of the unsubstituted methylide (Scheme 2). The molecular ion of the methylide **13** gives a metastable peak due to decomposition to give $C_5H_5^+$ (m/z = 65) and the radical $HN{=}\dot{C}{-}C_5F_4N$ (**29**).

In the case of the t-butoxycarbonyl methylides [(**16**),(**26**) and (**27**)], the initial McLafferty rearrangement predominates, presumably due to the larger mass of the isobutene molecule lost compared to the ethene from the corresponding ethoxycarbonyl methylides.

TABLE 1

Relative abundances/% of the twelve most abundant ions observed in the **positive-ion mass spectra** of pyridinium alkoxycarbonyl(tetrafluoro-4-pyridyl)methylides, $py^+\text{-}\bar{C}(CO_2R)C_5F_4N\text{-}4$

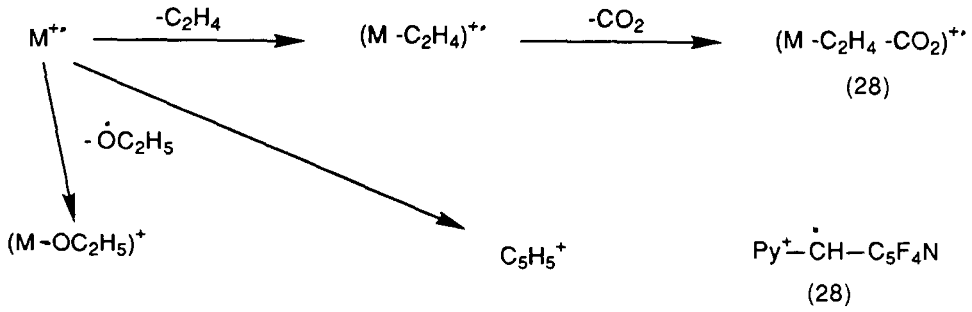
Compound No.		(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
	R	Me	Et	Pr^n	Pr^i	Bu^t	CH_2CCl_3	CH_2CF_3	CH_2Ph	CH_2CH_2Ph
$\underline{m}/\underline{z}$	Fragment									
	$\underline{M}^{+\cdot}$	100	54	66	30	9	49	80	48	45
286	$\underline{M} - R(+ H)^{+\cdot}$	-	11	40	100	100	14	<1	2	52
269	$\underline{M} - OR^+$	6	32	39	31	25	100	56	9	26
242	$\underline{M} - CO_2\ R(+ H)^{+\cdot}$	12	100	100	27	9	69	92	100	100
241	$\underline{M} - CO_2R^+$	2	9	9	7	8	12	11	5	5
150	$\underline{M} - pyC(CO_2R)^+$	2	3	2	2	4	8	16	4	<1
91	$\underline{M} - (CO_2R)C_5F_4N^+$	31	5	<1	3	2	1	3	88	20
79	$\underline{M} - C(CO_2R)C_5F_4N^{+\cdot}$	11	33	23	14	41	4	58	11	23
65	$C_5H_5^+$	18	56	37	40	40	8	100	24	24
44	$CO_2^{+\cdot}$	7	7	1	2	26	2	28	2	3
39	$C_3H_3^+$	10	21	11	32	66	2	53	6	4
29	$C_2H_5^+$	4	5	2	1	33	<1	20	1	<1

TABLE 2

Relative abundances/% of the common ions observed in the **negative-ion mass spectra** of pyridinium alkoxycarbonyl(tetrafluoro-4-pyridyl)methylides $py^{+}\text{—}\bar{C}(CO_2R)C_5F_4N$-4

Compound No.	(12)	(13)	(14)	(15)	(17)	(18)	(19)
R	Me	Et	Pr^n	Pr^i	CH_2CCl_3	CH_2CF_3	CH_2Ph
Ion mass no.							
$\underline{M}^{\cdot -}$	100	100	100	100	a	100	100
$\underline{M}$-63$^-$	-	5.5	4	30	-	2	1.5
$\underline{M}$-78$^{\cdot -}$	6	9	15	19	8	13	15
$\underline{M}$-81$^-$	-	2	3	16	-	-	-
$\underline{M}$-123$^-$	-	-	-	-	-	0.5	5
$\underline{M}$-137$^-$	-	-	3	4	-	-	-
$\underline{M}$-149$^-$	-	-	1	4	-	-	-
$\underline{M}$-173$^-$	6	-	-	-	-	-	-
$\underline{M}$-178$^{\cdot -}$	-	-	1	6	-	1	
$\underline{M}$-179$^-$	-	-	1	5	-	-	6

[a] The base ion corresponded to $(\underline{M}\text{-Cl})^-$.



Scheme 2.

The spectra of the new methylides synthesised for this study show a marked contrast between those with a β-hydrogen on the alkyl group, and those not having one (Table 4). The abundances indicate that while loss of olefin most probably arises by the conventional McLafferty rearrangement, the loss of both olefin and CO_2, involving the transfer of an α-hydrogen, must occur by an alternative process. The driving force behind this α-transfer is ascribed to the formation of the radical ion of the unsubstituted methylide (**28**), the positive charge no doubt being located on the pyridine moiety, with the radical being stabilised by the tetrafluoropyridyl substituent.

As well as the radical ion at m/z = 242, all spectra exhibited a further radical ion at m/z = 222 due to loss of HF from the fragment corresponding to the unsubstituted methylide (**28**), probably forming the radical ion of the heterotricycle **30**.

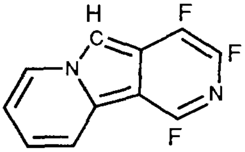


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TABLE 3

Relative abundances/% of significant positive ions observed in the mass spectra of ethoxycarbonyl methylides

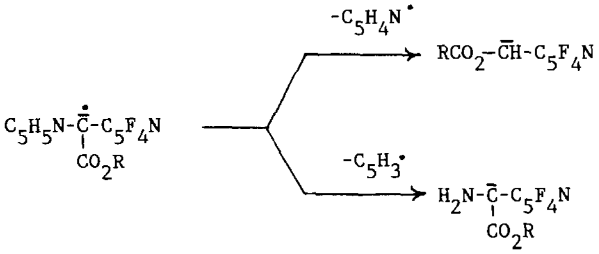
Compound	**13**	**23***	**24**
$M^{+\cdot}$	54	87	50
$(M-C_2H_4)^{+\cdot}$	11	6	11
$(M-OC_2H_5)^{+\cdot}$	32	40	31
$(M-C_2H_4-CO_2)^{+\cdot}$	100	100	100
$(M-C_2H_5-CO_2)^{+}$	9	4	3

*Σ chlorine isotopes.

TABLE 4

Compound	$M^{+\cdot}$	$(M\text{-olefin})^{+\cdot}$	$(M\text{-olefin-}CO_2)^{+\cdot}$	$(M\text{-alkoxy})^{+\cdot}$
β-hydrogen present				
13	54	11	100	32
14	66	40	100	39
15	30	100	27	31
16	9	100	9	25
20	45	52	100	26
β-hydrogen absent				
12	100	-	12	6
17	49	14	69	100
18	80	-	92	56
19	48	2	100	9

Negative ion spectra. These were obtained using isobutene as the chemical ionisation reagent. In all except the case of the trichloroethyl ester (**17**) the molecular ion was the base ion; **17** exhibited a pseudo molecular ion $(M + Cl)^{-\cdot}$ as the base ion. Very few fragment ions were observed, and in no case was cleavage of the alkyloxy group detected. The most abundant common fragment (M-78, average intensity = 12%) was that due to the loss of the pyridyl radical, resulting in a radical-anion (**31**) stabilised by both the carboxyalkyl group and the tetrafluoropyridyl substituent.



(**31**)

(**32**)

It is interesting to note that the respective characteristic fragment ions in the positive spectra arise by loss of the alkoxycarbonyl group (see Table 1), and in the case of the negative spectra by loss of the pyridyl radical (Table 2). Negative ions are also observed through the loss of C_5H_3, giving the ion **32**.

EXPERIMENTAL

Spectroscopic Analyses

IR spectra were recorded with Perkin-Elmer 298 or 720 spectrophotometers, NMR spectra with a Perkin-Elmer R32 instrument operating at 84.6 (^{19}F; ext. CF_3CO_2H ref., absorptions to high field being assigned negative values) or 90 (^{1}H; ext. Me_4Si ref.) MHz, mass spectra with a Kratos MS45 spectrometer (ionizing voltage 70 eV; data processed by a Kratos DS55 Aquisition Interface System, resolution 1 in 1500 mass units), and UV spectra with a Cary 118 spectrophotometer. Only the twelve most abundant mass spectral peaks are listed unless others of great significance were observed.

Starting Materials

Pentafluoropyridine was used as received from Fluorochem Ltd. (Glossop, U.K.).

Phenacylpyridinium iodide (**21**), m.p. 214-215 °C (lit.[5,6], 215-216, 215-219 °C) possessing a correct elemental composition (CHN) was prepared in 92% yield via the King reaction (pyridine + acetophenone + iodine), as described in the literature [5]. Analytically pure (CHBrN) N-(ethoxycarbonylmethyl)pyridinium bromide (**22**, R = Et), m.p. 134-136 °C (lit. [7], 135-136 °C), was obtained in 67% yield by treating ethyl bromoacetate with a two-molar proportion of pyridine in boiling ethanol, as reported previously [4]. However, a somewhat better yield (73%) was achieved simply by adding the bromoacetic ester (10.0 g, 60 mmol) to stirred pyridine (9.93 g, 120 mmol) at a rate so that the spontaneous exothermic reaction did not run out of control. The latter method was also used to prepare (on a 5-10 gramme scale) samples of N-(methoxycarbonylmethyl)pyridinium bromide (**22**, R = Me) (68% yield), m.p. (dec.) 174-175 °C (recrystallised from 1:1 v/v Pr^iOH-EtCOMe), N-(propyloxycarbonylmethyl)pyridinium bromide (**22**, R = Pr^n) (82%), m.p. 110 °C (purified by trituration with Et_2O) N-(isopropyloxycarbonylmethyl)pyridinium bromide (**22**, R = Pr^i) (33%), m.p. 79-81 °C (crude liquid product washed with Et_2O then left to crystallize; crystals washed with EtCOMe), N-(2,2,2-trichloro-ethoxycarbonylmethyl)pyridinium bromide (**22**, R = CCl_3CH_2) (65%), m.p. 161-163 °C (recrystallised from Me_2CHOH-MeCOEt), N-(2,2,2-trifluoroethoxycarbonylmethyl)pyridinium bromide (**22**, R = CF_3CH_2) (93%) which failed to solidify and was used straightway to generate the corresponding methylide (**7**), N-(benzyloxycarbonyl methyl)pyridinium bromide (**22**, R = $C_6H_5CH_2$) (100%) which also failed to solidify and was used immediately to generate the methylide **8**, and N-(phenylethyloxycarbonylmethyl)pyridinium bromide (**22**, R = $PhCH_2CH_2$) (*ca*. 100%) which also failed to solidify and was used immediately to generate the corresponding methylide (**9**). Satisfactory combustion analyses (CHN) were obtained for bromides **22**, where R = Me, Et, Bu^t, CCl_3CH_2 (the others were not analysed), and all the samples possessed IR and ^1H NMR spectra fully consistent with the identities assigned.

Preparation of Pyridinium (Tetrafluoro-4-pyridyl)methylides, $\overset{+}{py} - \bar{C}X(C_5F_4N\text{-}4)$

(a) X = COPh (**11**)

Sodium hydride (0.12 g, 5.0 mmol) was added to a cold (5 °C) magnetically-stirred solution of phenacylpyridinium iodide (1.62 g, 5.0 mmol) in dry dimethylformamide (DMF; 12.5 cm^3) under an atmosphere of dry nitrogen. The pale brown mixture turned yellow then yellowish brown when stirred for 20 minutes; it was then cooled to 0 °C before a solution of pentafluoropyridine (0.84 g, 5.0 mmol) in dry DMF (5 cm^3) was added dropwise. The reaction mixture was stirred at 0 °C for 30 minutes, at 20 °C for 30 minutes, then treated with water (60 cm^3). The precipitate which appeared was recovered by filtration, washed with water, then dried *in vacuo* over phosphorus pentoxide to provide pale orange, hygroscopic pyridinium benzoyl (2,3,5,6-tetrafluoro-4-pyridyl)methylide (**11**) (*nc*) (0.88 g, 2.5 mmol, 50%), m.p. 112-113 °C, with a somewhat unsatisfactory elemental composition [Found: C, 61.7; H, 3.3; N, 7.5%. $C_{18}H_{10}F_4N_2O$ requires C, 62.4; H, 2.9; N, 8.0%], λ_{max} (mull) 1600 cm^{-1} (C = O str.), δ_F (35% w/v in $CDCl_3$) -17.8 (m;, 2-,6-F), -65.5 (m; 3-,5-F) p.p.m., δ_H (same soln.) 7.25 (s; C_6H_5) and C_5H_5N absorptions at 7.86 (t; 3-,5-H), 8.26 (t;, 4-H), and 8.94 (d; 2-, 6-H) p.p.m., _m/z_ 346 ($C_{18}H_{10}F_4N_2O^+$, 100%), 327 ($C_{18}H_{10}F_3N_2O^+$, 26), 267 ($C_{13}H_5F_4NO$, 19), 239 ($C_{12}H_5F_4N$, 23.5), 220 ($C_{12}H_5F_3N$, 30.5), 105 ($C_7H_5O^+$, 65), 79 ($C_5H_5N^+$, 64) 77, ($C_6H_5^+$, 99), 65 ($C_5H_5^+$, 47), 51 ($C_4H_3^+$, 39), 39 ($C_3H_3^+$, 30.5), 29 (CHO^+, 15.5).

(b) X = CO_2Et (**13**)

Pentafluoropyridine (1.69 g, 10 mmol) in dry DMF (10 cm^3) was added dropwise to a cold (_ca_. 5 °C), stirred, dark orange mixture containing pyridinium ethoxycarbonylmethylide which had been prepared by treating _N_-(ethoxycarbonylmethyl)pyridinium bromide (2.45 g, 10 mmol) in dry DMF (25 cm^3) with sodium hydride (0.48 g, 20 mmol); the methylide generation system was stirred at _ca_. 5 °C for 20 minutes prior to the addition of the pentafluoropyridine, and the apparatus was equipped for the exclusion of moist air. The reaction mixture, which slowly became deep red, was kept at 0 °C for 30 minutes and then at room temperature for 30 minutes before being cooled to 0 °C and treated cautiously with water (10 cm^3); more water (100 cm^3) was then added before the orangy rust-coloured precipitate which had appeared was recovered, washed with more water, and dried (_in vacuo_ over P_4O_{10}). This provided bright orange microcrystals of pyridinium ethoxycarbonyl(2,3,5,6-tetrafluoro-4-pyridyl)methylide (**13**) (n.c.) (1.1 g, 3.5 mmol, 35%) [Found: C, 53.8; H, 3.0; N, 8.9%; $\underline{M}^{+\cdot}$, 314. $C_{14}H_{10}F_4N_2O_2$ requires C, 53.5; H, 3.2; N, 8.9%; _M_, 314], m.p. 117-119 °C, λ_{max} (mull) 1610 cm^{-1} (C=O, str.), λ_{max} (EtOH) 240 (ε_{max} 8511), 336 (20334), 452 (8393) nm (see Table 5 for NMR data).

(c) Other Alkoxycarbonyl(tetrafluoro-4-pyridyl)methylides

The previous experiment [(b) above] was repeated, using the appropriate _N_-(alkoxycarbonylmethyl)pyridinium bromide (**22**), to yield the following products (see Table 5 for NMR data).

(i) R = Me (**12**) (n.c.), pyridinium methoxycarbonyl-(2,3,5,6-tetrafluoro-4-pyridyl)methylide (35% yield) [Found: C, 52.0; H, 2.6; N, 9.3%; $M^{+\cdot}$, 300. $C_{13}H_8F_4N_2O_2$ requires C, 52.0; H, 2.7; N, 9.3%; M, 300], red solid, m.p. 159-160 °C, λ_{max} (mull) 1600 cm^{-1} (C=O str.), λ_{max} (EtOH) 240 (ε_{max} 9230), 335 (21230), 450 (8769) nm.

(ii) R = Pr^n (**14**) (n.c.), pyridinium n-propyloxycarbonyl(2,3,5,6-tetrafluoro-4-pyridyl)methylide (31% yield) [Found: C, 54.9; H, 3.7; N, 8.5%; $M^{+\cdot}$, 328. $C_{15}H_{12}F_4N_2O_2$ requires C, 54.9; H, 3.65; N, 8.5%, M, 328], orange microcrystals, m.p. 106-108 °C, λ_{max} (mull) 1590 cm^{-1} (C=O str.), λ_{max} (EtOH) 246 (ε_{max} 8200), 336 (20090), 454 (8610) nm.

(iii) R = Pr^i (**15**) (n.c.), pyridinium i-propyloxycarbonyl(2,3,5,6-tetrafluoro-4-pyridyl)methylide (47% yield) [Found: C, 54.9; H, 3.7; M, 8.4%; $M^{+\cdot}$, 328. $C_{15}H_{12}F_4N_2O_2$ requires C, 54.9; H, 3.65; N, 8.5%; M, 328], an orange powder, m.p. 109-110 °C, λ_{max} (mull) 1580 cm^{-1} (C=O str.), λ_{max} (EtOH) 240 (ε_{max} 37962), 336 (87314), 454 (36823) nm.

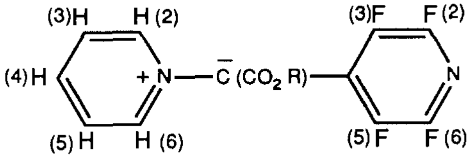
(iv) R = CH_2CCl_3 (**17**) (n.c.), pyridinium 2,3,5,6-tetrafluoro-4-pyridyl(2,2,2-trichloroethoxycarbonyl)methylide (54% yield) [Found: C, 39.2; H, 1.6; N, 6.5%; $M^{+\cdot}$, 416. $C_{14}H_7Cl_3F_4N_2O_2$ requires C, 40.3; H, 1.7; N, 6.5%; M, 416], a yellowish-brown powder, m.p. (dec.) 166-168 °C, λ_{max} (mull) 1620 cm^{-1} (C=O str.), λ_{max} (EtOH) 240 (ε_{max} 8767), 331 (17534), 440 (6651) nm.

(v) R = CH_2CF_3 (**18**) (n.c.), pyridinium 2,3,5,6-tetrafluoro-4-pyridyl(2,2,2-trifluoroethoxycarbonyl)methylide (45% yield) [Found: C, 45.6; H, 2.0; N, 7.6%; $M^{+\cdot}$, 368. $C_{14}H_7F_7N_2O_2$ requires C, 45.6; H, 1.9; N, 7.6%; M, 368], a brown microcrystalline solid, m.p. (dec.) 153-155°C, λ_{max} (mull) 1610 cm^{-1} (C=O str.), λ_{max} (EtOH) 238 (ε_{max} 9092), 330 (17918), 438 (16935) nm.

(vi) R = CH_2Ph (**19**) (n.c.) pyridinium benzyloxycarbonyl(2,3,5,6-tetrafluoro-4-pyridyl)methylide (61% yield) [Found: C, 60.7; H, 3.5; N, 7.4%; $M^{+\cdot}$, 376. $C_{19}H_{12}F_4N_2O_2$ requires C, 60.6; H, 3.2; N, 7.4%; M, 376], reddish brown flakes, m.p. 136-138 °C, λ_{max} (mull) 1620 cm^{-1} (C=O str.), λ_{max} (EtOH) 235 (ε_{max} 13065), 450 (6184) nm.

TABLE 5

NMR chemical shift/p.p.m. data for pyridinium alkoxycarbonyl(tetrafluoro-4-pyridyl)methylides in $CDCl_3$ (35% w/v) (TFA = CF_3CO_2H, TMS = Me_4Si)



Compd. No.	δ_F(TFA)		δ_H(TMS)		
	F-2,6[a]	F-3,5[a]	H-3,5 and 4[b]	H-2,6[c]	
(12)	-15.8	-62.8	7.42-7.92	8.62	3.70 (CH_3)
(13)	-15.8	-62.5	7.64-7.85	8.67	1.28 (CH_3),4.25 (CH_2)
(14)	-16.0	-62.8	7.40-7.85	8.65	0.93 (CH_3), 1.68 ($C\underline{H}_2CH_3$) 4.11 (CH_2O)
(15)	-16.0	-62.0	7.40-7.85	8.60	1.25 ($2xCH_3$),5.08 (CH)
(17)	-16.0	-63.3	7.45-7.90	8.72	4.82 (CH_2)
(18)[e]	-15.0	-62.5	7.30-8.00	8.48	4.32 (CH_2)
(19)	-16.7	-64.4	7.46-8.80 (incl.Ph)		5.30 (CH_2)
(20)	-16.3	-63.2	7.40-8.85 (incl.Ph)		3.08 (CH_2Ph), 4.50 (CH_2O)

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[a] AA'XX' type multiplets. [b] Overlapping multiplets. [c] Doublet.

[e] Triplet, δCF_3 4.9 ppm, $^{3}\underline{J}_{F,H}$ 9.3 Hz.

(vii) $\underline{\mathrm{R = CH_2CH_2Ph}}$ (**20**) (n.c.) analytically-impure (CHN) pyridinium 2-phenylethoxycarbonyl(2,3,5,6-tetrafluoro-4-pyridyl)methylide (27% yield) [Found: C, 62.65; H, 3.85; N, 6.55%; $\underline{M}^{+\cdot}$, 390. $C_{20}H_{14}F_4N_2O_2$ requires C, 61.5; H, 3.6; N, 7.2%; $\underline{M}$, 390], a dark red powder, m.p. 86-88 °C, λ_{max} (mull) 1620 cm^{-1} (C=O str.), λ_{max} (EtOH) 238 (ε_{max} 7977), 336 (14359), 450 (6040) nm.

Reactions of Pyridinium Ethoxycarbonylmethylide with 3-Chlorotetrafluoropyridine and Octafluorotoluene

The experiments were carried out as described for pentafluoropyridine [(b) X = CO$_2$Et, above] to give
(i) pyridinium 3-chloro-2,5,6-trifluoro-4-pyridyl(ethoxycarbonyl)-methylide (**23**) (n.c.) (63% yield) [Found: C, 49.7; H, 2.6; N, 8.1%. $C_{14}H_{10}ClF_3N_2O_2$ requires C, 50.8; H, 3.0; N, 8.4%], an orange solid, m.p. 146-147 °C, λ_{max} (mull) 1600 cm^{-1} (C = O str.), m/z (EI) (^{35}Cl isotope peaks shown; correct-abundance ^{37}Cl peaks present) 330 ($\underline{M}^{+\cdot}$, 86.5), 302 ($\underline{M}$ - Et + H, 5.5), 285 ($\underline{M}$ - OEt, 40), 258 ($\underline{M}$ - CO$_2$Et + H, 100%), 223 (31), 166 ($\underline{M}$-pyCCO$_2$Et, 4), 91 (C_6H_5N, 2), 65 (C_5H_5, 78.5), 39 (C_3H_3, 41), δ_F (CDCl$_3$) + 3.2 (dd, 2-F), -13.6 (dd, 6-F), -60.4 (t, 5-F) p.p.m. (rel.int. 1:1:1) ($\underline{J}_{2,5}$ $\underline{J}_{5,6}$ 22 Hz, $\underline{J}_{2,6}$ 12 Hz), δ_H (same soln.), 1.24 (t, CH$_3$), 4.18 (q, CH$_2$), 7.4-7.75 (complex 3-,4-,5-H), 8.55 (d, 2-,6-H) p.p.m. (rel.int. 3:2:3:2) (no impurity bands observed despite the unsatisfactory elemental analysis); and (ii) pyridinium ethoxycarbonyl(heptafluoro-4-tolyl)methylide (**24**) (n.c.) (44% yield after the original precipitate had been freed from a red gum with warm aqueous methanol then dried) [Found: C, 50.1; H, 2.4; N, 3.6%, $C_{16}H_{10}F_7NO_2$ requires C, 50.4; H, 2.6; N, 3.7%], as red crystals, m.p. 93-94 °C, λ_{max} (mull) 1600 cm^{-1} (C=O str.). λ_{max} (EtOH) 250 (ε_{max} 8572), 349 (16827), 456 (9207) nm, $\underline{m}/\underline{z}$ (EI) 381 ($\underline{M}^{+\cdot}$, 50%), 353 ($\underline{M}$ - Et + H, 11), 336 ($\underline{M}$ - OEt, 31), 309 ($\underline{M}$ - CO$_2$Et + H, 100), 290 ($\underline{M}$ - CO$_2$Et + H - F, 13), 217 ($\underline{M}$ - pyCO$_2$Et, 5), 91 [$\underline{M}$ - CO$_2$Et(C_7F_7), 6], 80 (C_5H_6N, 33), 69 (CF$_3$, 16), 65 (C_5H_5N, 68), 52 (C_4H_4, 13), 39 (C_3H_3, 26), δ_F (CDCl$_3$) +22.9 (t, $\underline{J}$ 21 Hz, CF$_3$), -58.2 (mult., 2-, 6-F), -64.3 (mult. 3-,5-F) p.p.m. (rel.int. 3:2:2), δ_H (same soln.) 1.18 (t, CH$_3$), 4.13 (q, CH$_2$), 7.4-7.65 (complex 3-,4-,5-H), 8.66 (d, 2-,6-H) p.p.m. (rel.int. 3:2:3:2).

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