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FLUOROCARBON DERIVATIVES OF NITROGEN. PART 18 [1]. SYNTHESIS OF FLUORINATED INDOLIZINES THROUGH REACTIONS OF PYRIDINIUM ETHOXYCARBONYLMETHYLIDE OR PYRIDINIUM PHENACYLIDE WITH PERFLUOROPROPENE, PERFLUOROBUT-2-YNE AND 3,3,3-TRIFLUOROPROPYNE

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SUMMARY

3-Ethoxycarbonyl-2-fluoro-1-trifluoromethylindolizine (**6**), 3-ethoxycarbonyl-1,2-(bistrifluoromethyl)indolizine (**8**), 3-ethoxycarbonyl-1-trifluoromethylindolizine (**10**) and 3-ethoxycarbonyl-2-perfluoroheptylimidazo[1,2-a]pyridine (**12**) have been obtained via trapping of pyridinium ethoxycarbonylmethylide with perfluoropropene, perfluorobut-2-yne, 3,3,3-trifluoropropyne and perfluorooctanenitrile respectively. Similarly, 2-fluoro-1-trifluoromethyl-3-phenacylindolizine (**7**), 1,2-bis(trifluoromethyl)-3-phenacylindolizine (**9**),and 3-phenacyl-1-trifluoromethylindolizine (**11**), have been obtained via reaction of pyridinium phenacylide with perfluoropropene, perfluorobut-2-yne, and 3,3,3-trifluoropropyne respectively. Alkaline hydrolysis of (**8**) gave 1,2-bis(trifluoromethyl)indolizine-3-carboxylic acid (**16**), which was decarboxylated thermally to 1,2-bis(trifluoromethyl)-indolizine (**15**).

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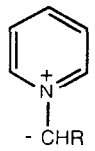
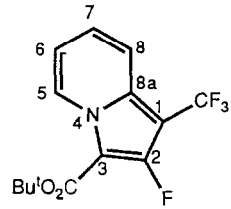
INTRODUCTION





(1) R = CO_2Bu^t

(3) R = CO_2Et

(4) R = COPh

(5) R = H

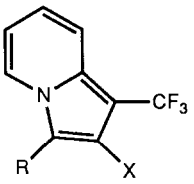
(2)

Having shown in a detailed study [2] that perfluoropropene is attacked by pyridinium t-butoxycarbonylmethylide (**1**) to give, inter alia, 3-(t-butoxycarbonyl)-2-fluoro-1-(trifluoromethyl)indolizine (**2**), we decided to widen our experience of this type of route to fluorinated indolizines first by carrying out reactions between perfluoropropene and pyridinium ethoxycarbonyl- (**3**) and benzoyl-methylide (**4**; pyridinium phenacylide), then to attempt to trap these methylides with fluorinated acetylenes. Success in the latter piece of work prompted experimentation with the parent methylide **5** , as will be recounted. For preliminary accounts of related studies with fluorinated pyridinium methylides [R (as in **1-5**) = $COCF_3$ and CF_3], see reference 3.

RESULTS AND DISCUSSION

As described elsewhere [1], solutions of the unstable methylides **3** and **4** were prepared by the action of sodium hydride on DMF solutions of appropriate pyridinium halides [py^+-CH_2R X^- (R = CO_2Et, X = Br ; R = COPh, X = I)]. When these solutions were shaken mechanically under atmospheres of perfluoropropene at ambient temperature for about 2 days, complex reaction products were formed from which the hoped-for indolizines (**6** and **7**) were isolated by simple dry-column flash chromatography in yields of 13 and 12%

respectively. Attempts were made neither to optimize the yields nor to discover the fate of all the perfluoropropene consumed. The decision to adopt this attitude was made in the light of our previous experience not only with the complex mixtures from the perfluoropropene-pyridinium t-butoxycarbonylmethylide (**1**) reaction [2] but also with the corresponding reactions where trifluoroacetonitrile was used to trap both pyridinium t-butoxycarbonylmethylide (**1**) and its ethoxycarbonyl analogue (**3**). In short, we were satisfied simply to have established that indolizinic products (**6** and **7**) consistent with the previous results, and hence with the mechanistic implications thereof [2,4], are obtainable in this fashion.

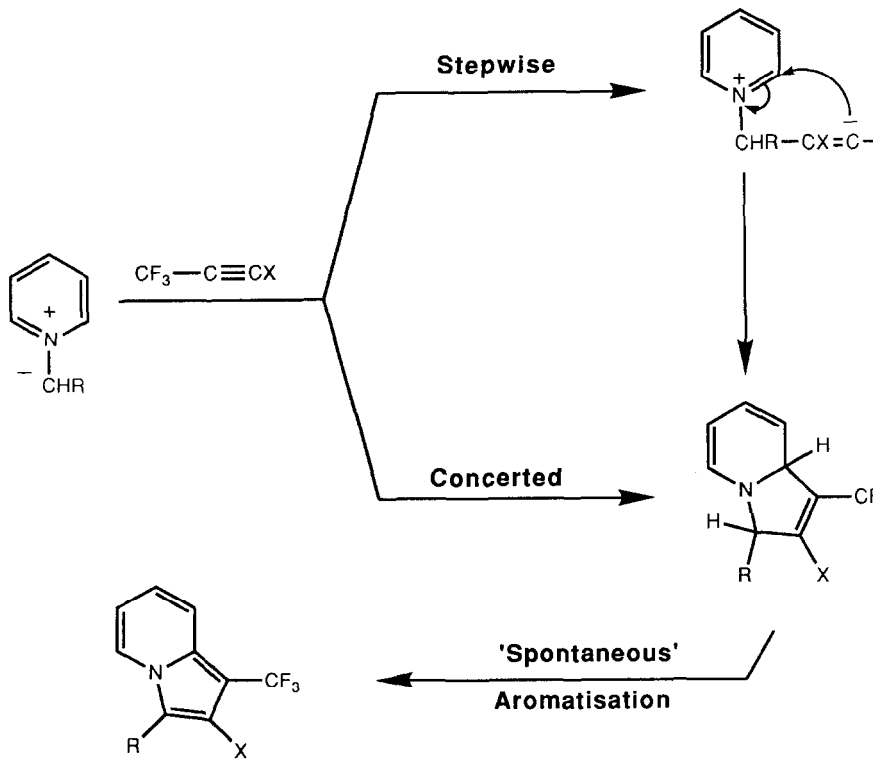


(**6**) R = CO_2Et, X = F
(**7**) R = COPh, X = F
(**8**) R = CO_2Et, X = CF_3
(**9**) R = COPh, X = CF_3
(**10**) R = CO_2Et, X = H
(**11**) R = COPh, X = H

Both pyridinium ethoxycarbonyl methylide (**3**) and its phenacyl analogue (**4**) were also found to react in a complex manner with perfluorobut-2-yne and 3,3,3-trifluoropropyne. Again, efforts were made to isolate only the new indolizines **8** (24% yield) and **9** (13%) from the complex reaction products obtained in two isolated experiments. X-Ray analysis [5] established that the product (22% yield) from the reaction between 3,3,3-trifluoropropyne and pyridinium ethoxycarbonylmethylide possessed structure **10**, i.e. that the compound was not the alternative 2-trifluoromethyl regioisomer; the same substituent orientation was therefore adopted for the indolizine (**11**; isolated in 14% yield) obtained from 3,3,3-trifluoropropyne and pyridinium phenacylide.

Like the reaction between perfluoropropene and pyridinium methylides **1**, **3**, and **4** (all of which are sufficiently nucleophilic to attack pentafluoropyridine and octafluorotoluene in S_NAr fashion

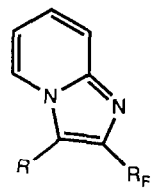
[1,2]), we suspect [cf. ref 2] that these reactions involving acetylenic traps [cf. ref.6] proceed via stepwise rather than concerted mechanisms. Further work is required to resolve this matter, however, and particularly so where 3,3,3-trifluoropropyne is concerned owing to problems with the acidity of the hydrogen substituent under the reaction conditions used here. Also, nothing concrete can be said about the mechanism of the aromatisation stages of the reactions (see the Scheme), a matter which has been commented upon previously [2,4,7].



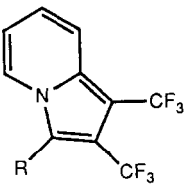
R = CO_2Et, COPh; X = H, CF_3

Scheme.

Pyridinium ethoxycarbonylmethylide (**3**) can also be trapped with the 'aza-acetylene' $C_7F_{15}C{\equiv}N$ to give, inter alia, the imidazo[1,2-a]pyridine **12** (isolated in 20% yield). The structure was assigned on the basis of the formation of the azaindolizines **13** and **14** from t-butoxycarbonylmethylide and the nitriles CF_3CN and C_3F_7CN via cycloadditions thought to involve a stepwise mechanism [4].



(**12**) $R_F = C_7F_{15}$
(**13**) $R_F = CF_3$
(**14**) $R_F = C_3F_7$



(**15**) R = H
(**16**) R = CO_2H
(**17**) R = $COCF_3$

Attempts to utilize pyridinium methylide itself (**5**; generated via the reaction CsF + py^+-CH_2SiMe_3 ^-OTF in $MeOCH_2CH_2OMe$ [8]) for the synthesis of fluorinated indolizines have failed in our hands so far. Thus, although NMR analysis of the crude complex product suggested that formation of 1,2-bis(trifluoromethyl)indolizine (**15**) had occurred in a reaction involving perfluorobut-2-yne, none could be isolated. The product in question was easily obtained (51% yield), however, by thermal decarboxylation of 1,2-bis(trifluoromethyl)-indolizine-3-carboxylic acid (**16**) produced in 91% yield by alkaline hydrolysis of its ethyl ester (**8**). Its identity was established by comparing its n.m.r. spectra (^1H, ^{19}F) with those of a sample prepared by treatment of the trifluoroacetylindolizine **17** (synthesised from pyridinium trifluoroacetylmethylide and perfluorobut-2-yne) with hot ethanolic sodium hydroxide [12].

EXPERIMENTAL

Spectroscopic Analyses

I.r., u.v., and mass spectra were recorded with the aid of Perkin-Elmer 298 or 720 spectrophotometers, a Cary 118 spectrophotometer, and a Kratos MS45 spectrometer (electron beam energy, 70 eV) respectively. N.m.r. spectra were obtained using

Perkin-Elmer R32 (^{1}H, 90; ^{19}F 84.6 MHz) and R34 (^{1}H 220 MHz), and Bruker WP80 (^{13}C, 20.1 MHz) instruments; absorptions to low field of reference signals [int. $Me_4Si(^{1}H)$, CF_3CO_2H (^{19}F), Me_4Si (^{13}C)] have been assigned positive chemical shift values.

Starting Materials

Perfluoropropene, perfluorobut-2-yne, 3,3,3-trifluoropropyne, and perfluoro-octanoic acid were used as received from Fluorochem Ltd (Glossop, U.K.). The acid was converted to perfluoro-octanenitrile according to the literature ($C_7F_{15}CO_2H \rightarrow C_7F_{15}CO_2Ag \rightarrow C_7F_{15}CO_2Et \rightarrow C_7F_{15}CONH_2 \rightarrow C_7F_{15}CN$), to give a sample (Found: C, 24.8; N, 3.3. Calc. for $C_8F_{15}N$: C, 24.3; N, 3.5%) which distilled in the range 98-102 °C (lit.[**9**], b.p. 100 ±2 °C). The methylide precursors N-ethoxycarbonylmethylpyridinium bromide and phenacylpridinium iodide were synthesised by known procedures [10,11] and their purities checked by spectroscopic methods and elemental analysis (C, H and N).

Reactions of Pyridinium Ethoxycarbonylmethylide (3)

(a) With perfluoropropene

The ylide (**3**) was generated by stirring N-ethoxycarbonyl-methylpyridinium bromide (2.45g, 10 mmol) in dry dimethylformamide (DMF; 25 cm^3) with sodium hydride (0.48 g, 20 mmol) at 0 °C under nitrogen. After 20 minutes, the mixture (now orange-brown in colour) was transferred (under a blanket of nitrogen) to a Pyrex tube (800 cm^3) equipped with a Rotaflo stopcock. The tube was then cooled (-196 °C) and the contents degassed (three freeze-pump-thaw cycles) before perfluoropropene (1.87 g, 12.5 mmol) was condensed into the vessel. The stopcock was then closed and the tube warmed to room temperature (whilst in a blast-proof cabinet) and shaken mechanically (behind a blast screen) for 50 h. Gaseous material was pumped out of the tube and the involatile content was filtered to remove solid material; the filtrate was evaporated *in vacuo* to yield a viscous dark red liquid (2.6 g) which was worked up by dry-column flash chromatography [DCFC; 15 x 5 cm, silica; CH_2Cl_2-light petroleum (b.p. 40-60 °C) mixtures as

eluants] to provide (first fraction) pale yellow 3-ethoxycarbonyl-2-fluoro-1-(trifluoromethyl)indolizine (**6**) (n.c.) (0.35 g, 1.27 mmol, 13%) (Found: C, 52.5; H, 3.2; N, 4.8. $C_{12}H_9F_4NO_2$ requires C, 52.4; H, 3.3; N, 5.1%), m.p. 100 - 102 °C, λ_{max} (mull) 1695 cm^{-1} (C=O str.), m/z 276 [$(M + 1)^+$, 14%], 275 (M^+, 100%), 256 [$(M-F)^+$, 17%], 247 [$(M-C_2H_4)^+$, 30%], 230 [$(M-C_2H_5O)^+$, 41%], δ_F (in $CDCl_3$) 24.0 [d, $^4J(F,F)$ 10 Hz; CF_3], -60.1 (q; CF) p.p.m., δ_H (same soln.) 1.43 (t; CH_3), 4.48 (q; CH_2), 7.06 (t; H-6), 7.38 (t; H-7), 7.75 (d; H-8), 9.58 (d; H-5) p.p.m. Two other fractions were subsequently eluted, both of which contained (by t.l.c. and n.m.r. analysis) the indolizine (**6**) and several other components; these were abandoned.

(b) With perfluorobut-2-yne

The previous experiment [(a)] was repeated using 7.35 g (30.0 mmol) of N-ethoxycarbonylmethylpyridinium bromide in DMF (30 cm^3), 1.44 g (60.0 mmol) of sodium hydride, and 9.72 g (60.0 mmol) of perfluorobut-2-yne. After 2 days at room temperature, the non-volatile reaction product was evaporated in vacuo, leaving a viscous red oil containing a white solid. The latter was removed by dissolving the residue in dichloromethane and filtering the resulting solution. The filtrate showed only one major component when analysed by t.l.c.; this component was isolated by DCFC (silica, 5 x 5 cm eluted with petroleum ether, b.p. 40-60 °C) and found to be 3-ethoxycarbonyl-1,2-bis(trifluoromethyl)indolizine (**8**) (n.c.) (2.33 g, 7.17 mmol, 24%) (Found: C, 47.8; H, 2.6; N, 4.4. $C_{13}H_9F_6NO_2$ requires C, 48.0; H, 2.8; N, 4.3%), m.p. 43-44 °C (orange needles), λ_{max} (mull) 1705 cm^{-1} (C=O str.), m/z 325 (M^+, 100%), 306 [$(M-F)^+$, 7%], 297 [$(M-C_2H_4)^+$, 26%], 280 [$(M-C_2H_5O)^+$, 24%], δ_F (in $CDCl_3$) 24.5 [q, ^5J (FF) 6.7 Hz; CF_3], 26.35 (q; CF_3) p.p.m., δ_H (same soln.) 1.41 (t; CH_3), 4.48 (q; CH_2), 6.98 (t; H-6), 7.26 (t; H-7), 7.88 (d, H-8), 9.36 (d; H-5) p.p.m., δ_C (50% soln. in $CDCl_3$; broadband decoupled) 13.57 (s; CH_3), 61.67 (s; CH_2), 102.4 (q; C-1), 114.5 (q; C-3), 115.0 (s; C-6), 118.3 (q; C-8), 121.0 (q; C-2), 121.6 (q; CF_3-1), 123.1 (q; CF_3-2), 125.2 (s; C-7), 126.7 (s; C-5), 133.4 (q; C-8a), 159.9 (s; C=O) p.p.m. [^1J(1-CF_3) 269.5, ^1J(2-CF_3) 267.4, ^2J(C1-CF_3) 38.1, ^2J(C2-CF_3) 41.8, ^3J(C3-CF_3) 4.7, ^4J(C8-CF_3) 5.3, ^3J(C8a-CF_3) 3.7 Hz].

(c) With 3,3,3-trifluoropropyne

Reaction (b) above was repeated exactly, except that 37.3 mmol (3.51 g) of the acetylenic reactant (3,3,3-trifluoropropyne) were used. The same work-up technique was employed, to give 3-ethoxycarbonyl-1-trifluoromethylindolizine (**10**) (n.c.) (1.67 g, 6.5 mmol, 22%; eluted from silica with a 1:9 v/v mixture of dichloromethane and 40-60 °C petroleum ether) (Found: C, 56.3; H, 3.9; N, 5.2. $C_{12}H_{10}F_3NO_2$ requires C, 56.0; H, 3.9; N, 5.4%), m.p. 54-56 °C (creamy-white needles), λ_{max} (mull) 1700 cm^{-1} (C=O str), m/z 257 (M^+, 100%), 229 [$(M-C_2H_4)^+$, 88%], 212 [$(M-C_2H_5O)^+$, 59%], δ_F (in $CDCl_3$) 22.5 (s) p.p.m., δ_H (same soln.) 1.40 (t; CH_3), 4.40 (q; CH_2), 6.92 (t; H-6), 7.2 (t; H-7), 7.68 (d; H-8), 7.70 (s; H-2), 9.48 (d; H-5), p.p.m., λ_{max} (EtOH) 241 (ε 30364), 247 (ε 34985), 323 (ε 12982) μm. Final elution of the DCFC column with ethanol provided a viscous red oil, possessing highly complex ^1H and ^{19}F n.m.r. spectra which defied analysis.

(d) With Perfluoro-octanenitrile

The nitrile (3.95 g, 10.0 mmol) was added dropwise to a cold (ca. 5 °C) stirred orange solution of the ylide (**3**) [generated under dry nitrogen in DMF (25 cm^3) from equimolar amounts (5 mmol) of NaH and N-ethoxycarbonylmethylpyridinium bromide]. Within 10 minutes of completion of the addition, a cream-coloured solid precipitated. After the reaction mixture had been stirred under nitrogen at 5 °C for 30 minutes and then at ambient temperature for 20 hours, it was filtered. The precipitate thus recovered was recrystallised from 50% aqueous ethanol then dried in vacuo over P_2O_5 and shown to be 3-ethoxycarbonyl-2-(perfluoroheptyl)imidazo[1,2-a]pyridine (**12**) (n.c.) (0.28 g, 0.5 mmol, 10%) (Found: C, 36.6; H, 1.7; N, 5.2. $C_{17}H_9F_{15}N_2O_2$ requires C, 36.6; H, 1.6; N, 5.0%), m.p. 97-98 °C (creamy-white crystals), λ_{max} (mull) 1640 cm^{-1} (C=O str.), m/z 558 (M^+, 100%), 513 [$(M-C_2H_5O)^+$, 27%], 486 ($C_{14}H_5N_2^+$, 42%), 191 ($C_{10}H_{11}N_2O_2^+$, 97%), 167 ($C_8H_{11}N_2O_2^+$, 39.5%), 78 ($C_5H_4N^+$, 22%), 69 (CF_3 21%), δ_F (in $CDCl_3$) - 2.2 (tt; CF_3) and CF_2 multiplets at -27.5, -41.2, -42.0 to -44.5 (three), and -47.5 p.p.m., δ_H (same soln.) 1.41 (t; CH_3), 4.48 (q; CH_2), 7.15 (t; H-6), 7.53 (t; H-7), 7.86 (d; H-8), 9.45 (d; H-5) p.p.m.

The orange filtrate was evaporated *in vacuo* leaving a 3-spot (t.l.c.) viscous orange residue which was chromatographed [DCFC; silica eluted with dichloromethane-light petroleum (b.p. 40-60 °C) (1:9 v/v)] to provide a further sample (0.27 g, 0.48 mmol after recrystallisation; total yield 20%) of the imidazopyridine (**12**), m.p. 97-99 °C, and 0.17 g of a 2:1 (molar) mixture (according to n.m.r. analysis; eluted with 1:4 CH_2Cl_2-pet. ether) of the same imidazopyridine (**12**) and the unreacted ylide precursor, *N*-ethoxycarbonylmethylpyridinium bromide.

*Conversion of 3-Ethoxycarbonyl-1,2-bis(trifluoromethyl)indolizine (**8**) to 1,2-Bis(trifluoromethyl)indolizine (**15**)*

A solution of 3-ethoxycarbonyl-1,2-bis(trifluoromethyl)-indolizine (**8**) (0.60 g, 1.85 mmol) in a mixture of methanol (50 cm^3) and 10% aqueous potassium hydroxide (15 cm^3) was boiled gently under reflux for 6 hours. Evaporation of the product at water pump pressure to remove methanol, followed by dilution (H_2O, 20 cm^3) and acidification (2M-HCl aq.) of the residue caused a white solid to precipitate. This was recovered by filtration, air dried, and found to be 1,2-bis(trifluoromethyl)indolizine-3-carboxylic acid (**16**) (*n.c.*) (0.50 g, 1.68 mmol, 91%) (Found: C, 44.3; H, 1.7; N, 4.4. $C_{11}H_5F_6NO_2$ requires C, 44.4; H, 1.7, N, 4.7%), m.p. 121-123 °C, λ_{max} (mull) 3200-3500 (dimer, O-H str.), 1675 (dimer, C=O str.) cm^{-1}, *m/z* 297 (M^+, 44%), 280 [$(M\text{-}OH)^+$, 19%], 253 [$(M\text{-}CO_2)^+$, 100%], δ_F (30% soln. in $CDCl_3$) 23.7 [q, ^5J(F,F) 11 Hz; CF_3], 25.4 (q; CF_3) p.p.m., δ_H (same soln.) 7.23 (t; H-6), 7.50 (t; H-7), 7.97 (d; H-8), 9.47 (d; H-5), 10.55 (br.s; CO_2H) p.p.m., δ_C (70% soln. in $CDCl_3$; broadband decoupled) 101.0 (q; C-1), 115.8 (s; C-6), 118.2 (q; C-3), 119.8 (q; C-8), 122.2 (q; 1-CF_3), 123.8 (q; 2-CF_3), 126.5 (s; C-7), 127.7 (q; C-2), 133.8 (q; C-8*a*), 160.7 (s; C-5), 205.5 (s; C=O) p.p.m. [^1J(1-CF_3) 274.5, ^1J(2-CF_3) 266.3, ^2J(C1-CF_3) 40.3, ^2J(C2-CF_3) 34.1, ^3J(C3-CF_3) 5.3, ^4J(C8-CF_3) 3.7, ^3J(C8*a*-CF_3) 3.4 Hz].

A sample of 1,2-bis(trifluoromethyl)indolizine-3-carboxylic acid (**16**) (0.25 g, 0.84 mmol) was heated in a small Pyrex tube until gas evolution from the melt ceased (this took 10 minutes as the

temperature was increased from 150 to 180 °C). The product was cooled to room temperature, dissolved in benzene and the solution chromatographed on alumina. Use of dichloromethane as eluant provided a pale brownish-orange solid (0.11 g, 0.43 mmol, 51%), m.p. 42-43 °C, shown to be 1,2-bis(trifluoromethyl)indolizine (**15**) by comparison of its ^{1}H and ^{19}F n.m.r. spectra with those of an authentic sample [12].

Reactions of Pyridinium Phenacylide (**4**)

(a) With perfluoropropene

Pyridinium phenacylide was generated by stirring a solution of N-phenacylpyridinium iodide (3.25 g, 10.0 mmol) in dry DMF (25 cm^3) with sodium hydride (0.48 g, 20 mmol) at 0 °C under nitrogen. The reaction mixture, which turned yellow then brownish orange, was stirred at 0 °C for 20 minutes then transferred to a Pyrex Rotaflo tube (800 cm^3) which was cooled (-196 °C), evacuated and its contents degassed (3 freeze-pump-thaw cycles) before perfluoropropene (1.87 g, 12.5 mmol) was admitted. The tube was sealed, placed in a blast-proof cabinet whilst it warmed to room temperature, then shaken mechanically behind a blast screen for 50 hours. Some non-condensible material and unreacted perfluoropropene (3.3 mmol) were pumped out of the tube before the non-volatile product was filtered [to remove solid material (discarded)] then evaporated *in vacuo*. The highly viscous, brown, liquid residue (one component by t.l.c.) was subjected to DCFC (silica eluted with a 9:1 v/v mixture of 40-60 °C petroleum ether and dichloromethane) to provide 2-fluoro-3-phenacyl-1-(trifluoromethyl)indolizine (**7**) (*n.c.*) (0.36 g, 1.17 mmol, 12%) (Found: C, 62.2; H, 3.0; F, 25.1; N, 4.4. $C_{16}H_9F_4NO$ requires C, 62.5; H, 2.9; F, 24.75; N, 4.6%), m.p. 98-100 °C (pale yellow crystals), λ_{max} (mull) 1620 (C=O str.) cm^{-1}, *m/z* 307 (M^+, 100%), 288 [$(M-F)^+$, 13%], 230 [$(M - C_6H_5)^+$, 30%], 105 ($C_6H_5CO^+$, 45%), δ_F (in $CDCl_3$) 23.9 (d, $^4J_{FF}$ 10 Hz; CF_3), -56.0 (q with further splitting; CF), δ_H (same soln.) 7.12 (t; H-6), 7.2-7.9 (overlapping absorptions; H-7, H-8, C_6H_5), 9.83 (d; H-5) p.p.m.

(b) With perfluorobut-2-yne

The experiment with perfluoropropene [(a) above] was repeated exactly using perfluorobut-2-yne as the dipolarophile. After recovering unchanged perfluorobut-2-yne (3.7 mmol), the involatile product was worked up in the same manner as before to give yellow crystals of 3-phenacyl-1,2-bis(trifluoromethyl)indolizine (**9**) (n.c.) (0.47 g, 1.32 mmol, 13%) (Found: C, 56.8; H, 2.3; F, 32.3; N, 3.7. $C_{17}H_9F_6NO$ requires C, 57.1; H, 2.5; F, 31.9; N, 3.9%), m.p. 69-71 °C, λ_{max} (mull) 1650 cm^{-1} (C=O str.), m/z 358 [$(M + 1)^+$, 100%], 357 (M^+, 50%), 280 [$(M-C_6H_5)^+$, 4%], 105 ($C_6H_5CO^+$, 26.5%), δ_F (in $CDCl_3$) 25.0 (q; CF_3), 26.0 (q; CF_3) p.p.m. [^5J(F,F) 8 Hz].

(c) With 3,3,3-trifluoropropyne

Again, the experiment involving perfluoropropene was repeated but using 3,3,3-trifluoropropyne (1.17 g, 12.5 mmol) to trap the methylide. After evaporation of the solvent (DMF) from the non-volatile product, the viscous red residue was chromatographed (DCFC; silica eluted with 5:95 v/v CH_2Cl_2-petroleum ether) to give pale yellow needles of 3-phenacyl-1-(trifluoromethyl)indolizine (11) (n.c.) (0.41 g, 1.42 mmol, 14%) (Found: C, 66.7; H, 3.3; N, 4.6. $C_{16}H_{10}F_3NO$ requires C, 66.4; H, 3.4; N, 4.8%), m.p. 89-91 °C, λ_{max} (mull) 1615 cm^{-1} (C=O str.), m/z 289 (M^+, 100%), 212 [$(M-C_6H_5)^+$, 30%], 105 ($C_6H_5CO^+$, 9%), δ_F (in $CDCl_3$) 22.2 (s) p.p.m., δ_H (same soln.) 7.03 (t; H-6), 7.2 - 7.8 (overlapping band systems; C_6H_5, H-2, H-7, H-8), 9.95 (d; H-5) p.p.m. A second major component, detected by t.l.c. analysis of the crude product, was not isolated.

REFERENCES

1 Part 19, R.E. Banks, W.T. Flowers, and S. N. Khaffaf, to be submitted to J.Fluorine Chem.

2 R.E. Banks, S.M. Hitchen and J. Thomson, J.Fluorine Chem., **20**, (1982) 127; R.E. Banks and J. Thomson, J.Chem.Res.(S) (1985) 33; (M) (1985) 0671-0689.

3 R.E. Banks and S.N. Mohialdin, J.Fluorine Chem., **34** (1986) 275 (R = $COCF_3$); **38** (1988) 289 (R = CF_3).

4 R.E. Banks, R.G. Pritchard, and J. Thomson, J.Chem.Soc., Perkin Trans. 1, (1986) 1769.

5 R.G.Pritchard, Acta Cryst., C44 (1988) 1150.

6 R.E. Banks and S.M. Hitchen, J.Chem.Soc.,Perkin Trans. 1, (1982) 1593.

7 R.E. Banks and S.M. Hitchen, J.Fluorine Chem., **20** (1982) 373.

8 O. Tsuge, S. Kanemasa, S. Kuraoka, and S. Takenaka, Chem.Lett., (1984) 279 and 281.

9 H.Gilman and R.G.Jones, J.Am.Chem.Soc., **65** (1943) 1458.

10 F. Kröhnke, Ber., **90** (1939) 543.

11 L.C.King, M. McWhirter and K.L. Rowland, J.Am.Chem.Soc., **70** (1948) 241.

12 R.E. Banks and S.N. Mohialdin, J.Fluorine Chem., **34** (1986) 275; full paper in preparation.