Fluorocarbon Derivatives of Nitrogen. Part 8. Reactions Between Heteroaromatic *N*-Imines (*N*-Iminopyridinium and *N*-Iminoquinolinium Ylide) and Perfluoropropene, 2*H*-Pentafluoropropene, Perfluorobut-2-ene, Perfluoro-(2-methylpent-2-ene), Perfluorobut-2-yne, and Perfluoropyridine: Synthesis of Fluorinated 3-Azaindolizines (Pyrazolo[1,5-*a*]-pyridines) [1]

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N-Iminopyridinium ylide reacts with perfluoropropene (or 2*H*-pentafluoropropene) and perfluorobut-2-ene (or perfluorobut-2-yne) to provide 2-fluoro-3-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine and 2,3-bis(trifluoromethyl)-pyrazolo[1,5-*a*]pyridine, respectively; oxidation of these products with aqueous potassium permanganate gives the corresponding pyrazolecarboxylic acids. Perfluoro-(2-methylpent-2-ene) is attacked by *N*-iminopyridinium ylide to produce 2-(pentafluoroethyl)-3,3-bis(trifluoromethyl)-3,3*a*-dihydropyrazolo[1,5-*a*]pyridine, which can be converted *via* thermal treatment with tetracyanoethylene into a mixture of 2-(pentafluoroethyl)-3-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine and 5-(dicyanomethylene)-2-(pentafluoroethyl)-3,3-bis(trifluoromethyl)-3,5-dihydropyrazolo[1,5-*a*]pyridine. *N*-Iminoquinolinium ylide reacts with perfluoropropene, perfluorobut-2-ene, and perfluoropyridine in hot dimethylformamide in the presence of potassium carbonate to yield 2-fluoro-3-(trifluoromethyl)pyrazolo[1,5-*a*]quinoline, 2,3-bis(trifluoromethyl)pyrazolo[1,5-*a*]quinoline, and *N*-(tetrafluoro-4-pyridyl)iminoquinolinium ylide, respectively.

SOMEWHAT surprisingly, the trio of isoelectronic chemical classes comprising the heteroaromatic *N*-oxides, -imines and -ylides has scarcely featured in the abundance of chemistry—synthetic, mechanistic, and commercial—that is centred on the susceptibility of unsaturated fluorocarbon systems to nucleophilic attack. Our involvement with this set of reagents began in 1966 with work on the reaction between pyridine *N*-oxide and perfluoropropene, the final outcome [2] of which prompted us to embark in 1976 [3] (when still no report connecting an *N*-imine with organofluorine chemistry could be found) on an investigation of the interaction of *N*-imino-pyridinium ylide (1) with perfluoropropene and related substrates. Here we report in detail [1] on results achieved with the compounds CF₃CF=CF₂, CF₃CH=CF₂, CF₃CF=CFCF₃ (*E* and *Z*), (CF₃)₂C=CFC₂F₅, and CF₃C≡CCF₃; full information regarding attack by the ylide (1) on perfluoro-2-azapropene, perfluoro-1-azacyclohexene, trifluoroacetonitrile, and fluoroaromatics can be found elsewhere.[4,5] Like *N*-iminopyridinium ylide, *N*-imino-quinolinium ylide (2)—reactions of which with perfluoropropene and perfluorobut-2-ene also feature in the present report—smoothly effects nucleophilic displacement of fluorine from pentafluoropyridine (see Scheme 1); † this is true also for pyridinium t-butoxycarbonylmethylide, the heteroaromatic *N*-ylide we have chosen recently to treat with fluorocarbon substrates.[6]

Synthetic Aspects of Reactions between Fluoro-olefins and N-Iminopyridinium or N-Iminoquinolinium Ylide.—It has long been appreciated [7] that *N*-iminopyridinium ylide and related heteroaromatic *N*-imines possess 1,3-

dipolar character of the azomethine imine type [*e.g.* (1) ◄─► (1′) ◄─► (1″) (Scheme 2)], so it is not surprising that the hydrocarbon literature abounds with examples of their use in the synthesis of nitrogen-bridged bicyclic heterocycles. Access to 3-azaindolizines (pyrazolo[1,5-*a*]pyridines) can be gained by employing activated
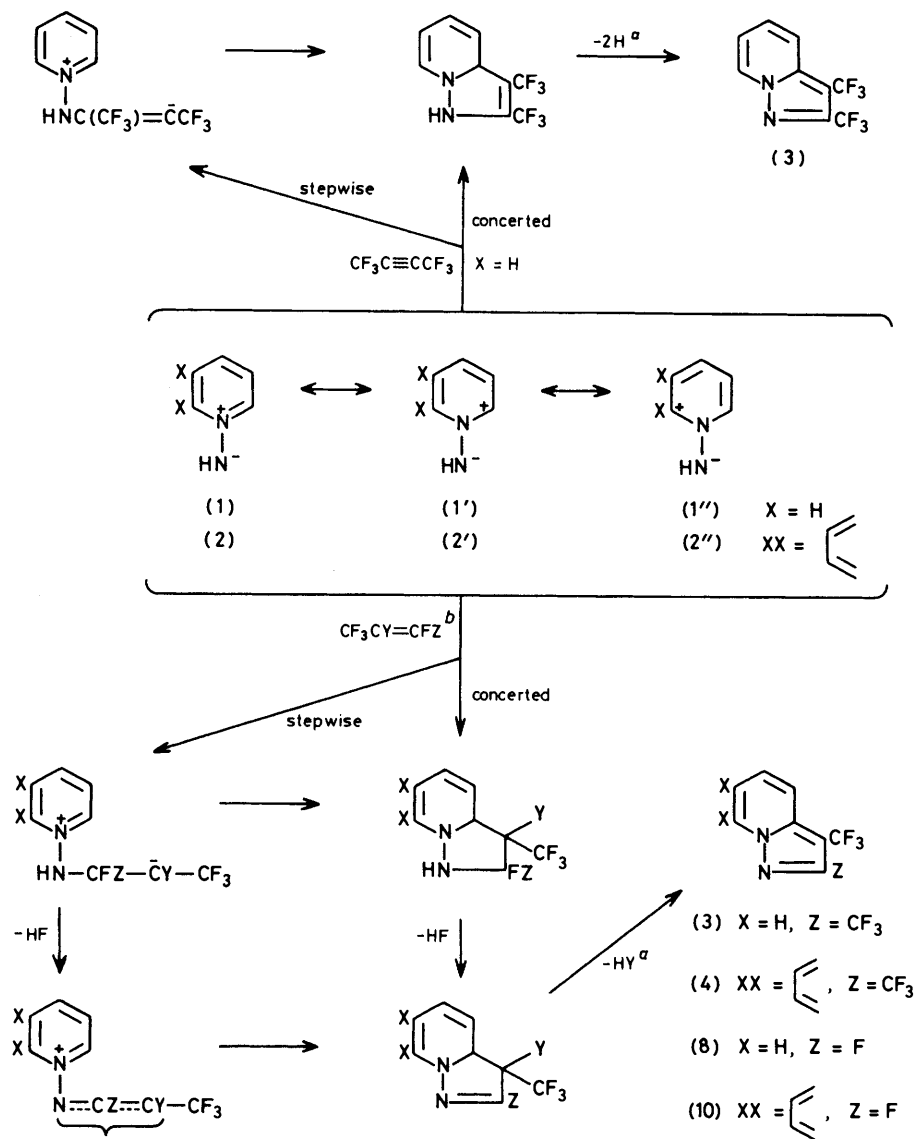

(1) X = H[a]

(2) XX = [b]
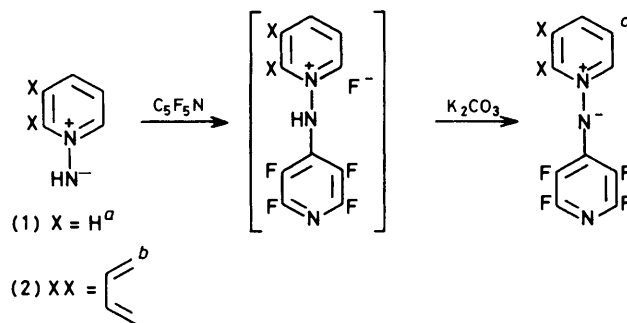
SCHEME 1

a Generated from C₅H₅N⁺NH₂ I⁻ + K₂CO₃ in EtOH at 20 °C, the temperature at which the S_NAr reaction was then carried out (ref. 5); *b* Generated *in situ* by heating (80 °C) a mixture of the dimer of (2), C₅F₅N, and K₂CO₃ in dimethylformamide (DMF); *c* Yields: X = H, 72% (ref. 5); XX = —CH=CH·CH=CH—, 65%.

alkenes (*e.g.* MeCCl=CHCO₂Et) or alkynes [*e.g.* DMAD (dimethyl acetylenedicarboxylate)] as dipolarophiles,‡ the reactions proceeding *via* aromatization of initial 1 : 1 adducts; hence, production of the 2,3-bis(trifluoro-

† Except in the case of compound (15), yields quoted throughout this paper refer to purified materials.

‡ Some typical examples are quoted in a recent review of methods for the construction of the indolizine nucleus: T. Uchida and K. Matsumoto, *Synthesis*, 1976, 209.

HNC(CF₃)=C̄CF₃

−2H[a]

(3)

stepwise   concerted

CF₃C≡CCF₃   X = H

(1)   (1′)   (1″)   X = H
(2)   (2′)   (2″)   XX =

CF₃CY=CFZ[b]

stepwise   concerted

HN—CFZ—C̄Y—CF₃

−HF

N=CZ=CY—CF₃

−HF

−HY[a]

(3) X = H, Z = CF₃

(4) XX = , Z = CF₃

(8) X = H, Z = F

(10) XX = , Z = F

SCHEME 2

[a] The hydrogen (Y = H) acceptor(s) was (were) not identified. See refs. 4 and 9 for a discussion of related cases; [b] When Y = F and Z = CF₃ or F, X = H or XX = —CH=CH·CH=CH—; when Y = H and Z = F, X = H.

methyl)compound (3) (Scheme 2) when we used per-fluorobut-2-yne as a substrate for N-iminopyridinium ylide complied with expectation. A much better yield of the same fluorinated 3-azaindolizine (77 vs. 18%) was achieved when a 1 : 3 mixture of cis- and trans-perfluoro-but-2-ene was used in place of its alkyne equivalent, a switch which demanded that dehydrofluorination must feature successfully in the aromatization stage; the corresponding reaction involving N-iminoquinolinium ylide gave the expected pyrazoloquinoline (4) (31%). Perfluorobut-2-yne has featured previously as a di-polarophile in a synthetic route to the 2,3-bis(trifluoro-methyl)pyrazolo[1,5-a]pyridines (5)—(7) based on the 1,3-dipolar nature of substituted diazocyclopentadienes.[8]

Both perfluorobut-2-yne and perfluorobut-2-ene are

gaseous at room temperature, so the technique used to procure the bis(trifluoromethyl)azaindolizine (3) in either case involved vacuum transfer of the dipolarophile
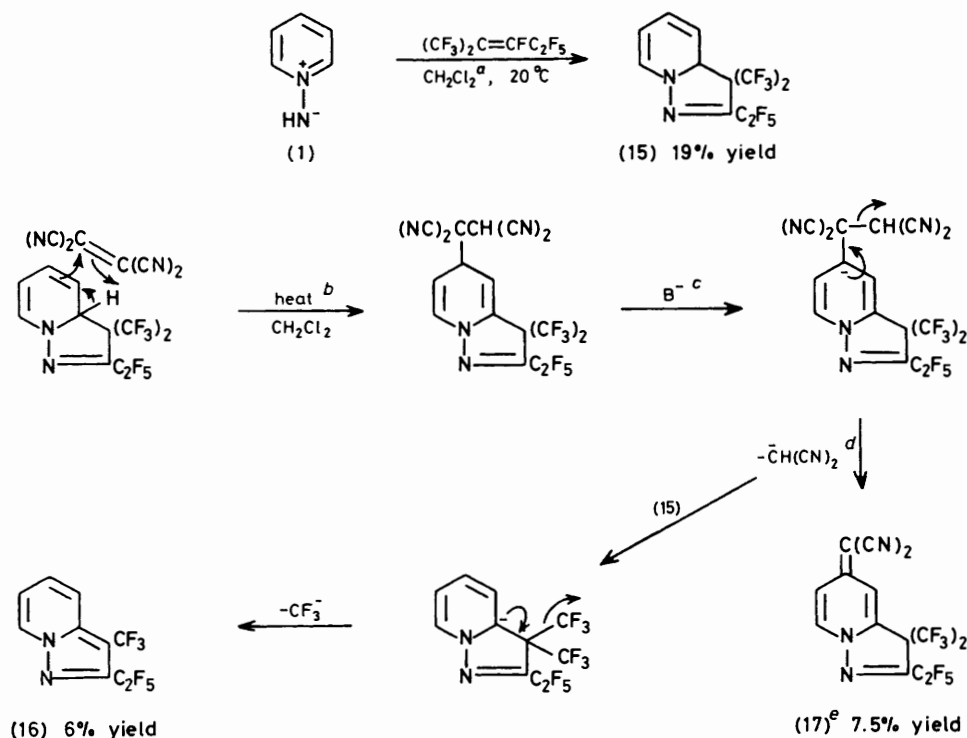
(5) Y = Z = Ph

(6) YY = , Z = Ph
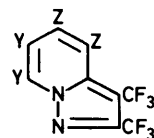
(7) YY = ZZ =

to a cold (−196 °C) Pyrex tube containing dichloro-methane (solvent) and a conventional in situ source of N-iminopyridinium ylide, viz. N-aminopyridinium iodide plus anhydrous potassium carbonate.[10] The product
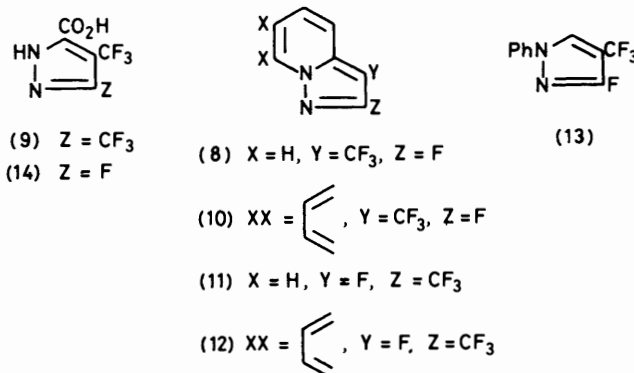
SCHEME 3

[a] Use of methanol or DMF as solvent led to the production of much tar and very little of the desired product (15); [b] TCNE has been noted to act as an enophile towards *cis*-1,3-dienes (ref. 16); [c] B⁻ = Base (obvious candidates are F⁻, CF₃⁻ and, from attack of the latter on the solvent, HCl₂C⁻); [d] Or other basic species (*cf.* footnote c); [e] For related examples of the use of TCNE for the introduction of a dicyanomethylene group, see ref. 17.

(3) was identified by elemental and spectroscopic * analysis and conventional oxidation (aqueous KMnO₄) [11] to the corresponding pyrazolecarboxylic acid (9). In the same manner, except that the ylide required was generated *in situ* by heating its dimer in DMF at *ca.* 80 °C,[12] 2,3-bis(trifluoromethyl)pyrazolo[1,5-*a*]quinoline (4) was synthesized from perfluorobut-2-ene and *N*-iminoquinolinium ylide (2) in 31% yield; potassium carbonate, which was used in excess to liberate *N*-iminopyridinium ylide (1) from *N*-aminopyridinium iodide, was added to the reaction mixture at the outset to aid dehydrofluorination of intermediates (Scheme 2).

Using the procedure outlined above, perfluoropropene was treated with *N*-iminopyridinium ylide and with *N*-iminoquinolinium ylide to provide two more new fluorinated 3-azaindolizines, 2-fluoro-3-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine (8) and its quinoline analogue (10), respectively, in yields of 65 and 31%. The pyrazolopyridine (8) was also obtained, though in much lower yield (15%), from 2*H*-pentafluoropropene and *N*-iminopyridinium ylide; clearly, with this olefin as substrate, dehydrogenation as well as dehydrofluorin-

* See H. Dürr, H. Kober, R. Sergio, and V. Formacek, *Chem. Ber.*, 1974, **107**, 2037, for spectroscopic data (¹⁹F and ¹³C n.m.r., mass spectra) of substituted 2,3-bis(trifluoromethyl)pyrazolo-[1,5-*a*]pyridines. The literature concerning 3-azaindolizines is replete with ¹H n.m.r. parameters relevant to our compounds (see, for example, ref. 14).

ation is required in the reaction mechanism (Scheme 2). Product identification in these cases demanded that a distinction be made *either* between regioisomers (8) and (11) *or* between (10) and (12) since ¹⁹F n.m.r. data revealed that the pyrazole moieties were the same in

(9) Z = CF₃
(14) Z = F

(8) X = H, Y = CF₃, Z = F

(10) XX = ⟨benzo⟩, Y = CF₃, Z = F

(11) X = H, Y = F, Z = CF₃

(12) XX = ⟨benzo⟩, Y = F, Z = CF₃

(13)

each instance (as expected from the method of synthesis); thus, only the pyridine derivative was chosen for close scrutiny. The ¹³C n.m.r. spectrum of the 3-azaindolizine from CF₃CF=CF₂, which was compared with spectra for other heterocycles of its class,* including the bis(trifluoromethyl)compound (3), immediately provided a strong motive for adoption of structure (8) rather than (11): the bridgehead carbon (C-3*a*) was

coupled only to fluorines of the CF_3 group present (q, $^3J_{CF}$ 2.5 Hz), while the signal assigned to C-2 appeared as a widely spaced doublet ($^1J_{CF}$ 250.4 Hz) of quartets ($^3J_{CF}$ 2.2 Hz). A fully consistent ^{15}N n.m.r. spectrum [$^2J_{N(1)F}$ 37.4, $^3J_{N(8)F}$ 5.1 Hz], together with an excellent correlation between ^{19}F n.m.r. data for the fluoro-pyrazole (13) [13] and that of the pyrazolecarboxylic acid which the pyrazolopyridine [either (8) or (11)] gave on oxidation with aqueous potassium permanganate, completed the evidence which led to rejection of structure (11) [and hence also of (12)]. On this basis, the new pyrazolecarboxylic acid provided by this work was 3(5)-fluoro-4-(trifluoromethyl)pyrazole-5(3)-carboxylic acid (14) (*ca.* 75% yield).

Clearly, the results discussed above lead one to predict that treatment of a perfluoroalkene carrying only one vinylic fluorine should react with *N*-iminopyridinium ylide to give a dihydro-3-azaindolizine. This is indeed so when perfluoro-(2-methylpent-2-ene) is employed as substrate, and the product (15) can be aromatized to 2-(pentafluoroethyl)-3-(trifluoromethyl)pyrazolo[1,5-*a*]pyridine (16) by heating it (without isolation) with tetracyanoethylene (TCNE) in boiling dichloromethane; this technique, use of which is an extension of similar work with dihydropyrazolo[1,5-*a*]pyridines derived from *N*-alkoxycarbonyliminopyridinium ylides and DMAD,[14] also provides the dicyanomethylene-compound (17). Possible reaction mechanisms are shown in Scheme 3.

Our work on reactions between *N*-iminopyridinium ylide and cyclic fluoro-olefins is not yet complete.[3] Others have reported that the 1 : 1 cycloadducts (18) and (19) can be obtained by treating 1,2-dibromodi-fluorocyclopropene and 1,2-dichlorotetrafluorocyclo-butene, respectively, with *N*-substituted iminopyrid-azinium ylides.[15]
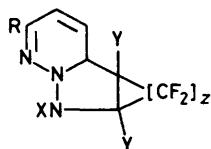

(18) *z* = 1; R = H or Ph; X = COMe ; Y = Br
(19) *z* = 2; R = H or Ph; X = COMe or CO₂Et ; Y = Cl

Mechanisms.—Reaching a decision regarding how an incipient 3-azaindolizine forms during a reaction between a fluorinated olefin or acetylene and *N*-iminopyridinium ylide or its quinoline counterpart involves distinguishing between a concerted mechanism and a stepwise one (choice of two) initiated by nucleophilic attack (see Scheme 2). No guidance is provided by the orientations of the products isolated in the present study: the regio-specificities observed follow whether one considers a concerted process with dipole HOMO–dipolarophile LUMO control or the known orientations of nucleophilic attack on the unsymmetrically substituted substrates $CF_3CF=CF_2$,[18] $CF_3CH=CF_2$,[19] and $(CF_3)_2C=CFC_2F_5$.[20] Nor

do the results of work on reactions between pyridine *N*-oxide and the first and last of these fluoro-olefins help, though one should note that the products [(20) and (21), respectively] possess identities consistent with the intermediacy of isoxazolidines [(22) and (23)] correspond-ing, respectively, with the two possible hydroaromatic precursors of the 3-azaindolizine (8), *viz.* compounds (24) and (25), and with the dihydro-compound (15) and its precursor (26) should a concerted cycloaddition be involved.

Consideration of the magnitudes of yields, coupled with knowledge of S_NAr reactions between the ylides and aromatic substrates of the fluorocarbon class (see above and ref. 5), prompts us to favour a stepwise mechanism

(20) R = F, R' = CF₃   (22)   (23)
(21) R = R' = CF₃

(24)   (25)   (26)
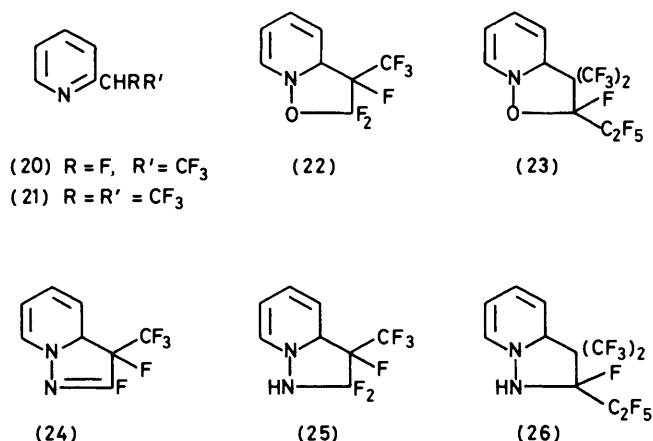
for the cycloaddition involved in azaindolizine formation *via* attack of *N*-iminopyridinium ylide or its quinoline counterpart on the electrophilic acyclic substrates studied here. Tarry material was formed in every reaction studied, and even with perfluoropropene, for which some optimization of conditions was achieved owing to the need to build up stocks of compound (8) for an investigation of its chemistry, the best yield was only 70%; while appreciable reductions in yields may well result from the need for aromatization processes to follow both concerted and stepwise construction of hydroaromatic azaindolizines, they can more readily be visualized as resulting from side reactions * inherent in a stepwise anionic mechanism, *e.g.*, oligomerization of fluorinated starting materials, interception of transient intermediates by water, and nucleophilic displacement of imidoyl fluorine from the dihydro-aromatic (24). Water, of course, could not be excluded from reaction systems involving *N*-iminopyridinium ylide owing to the method of generation employed for this species ($C_5H_5\overset{+}{N}NH_2$ I⁻ + K_2CO_3), and can also be produced in aromatization steps requiring elimination of hydrogen fluoride with either this ylide or its quinolinium counterpart (see Scheme 2); thus, undisturbed operation of a stepwise dipolar mechanism is surely too much to expect. This line of

* Note that a relatively complex situation could easily develop in the case of the olefin ($CF_3)_2C=CFC_2F_5$ (' perfluoropropene dimer ') (ref. 20).

argument can be used [4] to explain the production of N-cyanoiminopyridinium ylide (27) and N-(perfluoro-6-oxo-3,4,5,6-tetrahydropyridin-2-yl)iminopyridinium ylide (28) when perfluoro-2-azapropene and perfluoro-1-azacyclohexene, respectively, are treated with N-iminopyridinium ylide generated *in situ* from N-amino-pyridinium iodide and potassium carbonate; hydrolysis of N-(perfluoro-2-azaprop-1-enyl)iminopyridinium ylide (29) formed first is presumed to lead to the cyano-ylide (27), and material believed to be this ylide can be isolated


(27) X = CN

(28) X =

(29) X = CF=NCF₃
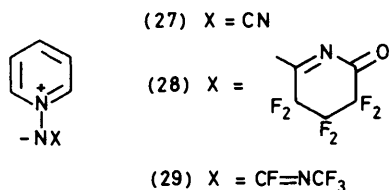
in 34% yield from the tarry reaction product.[4] Following this lead, painstaking work on the product derived from perfluoropropene provided a small sample (130 mg from *ca.* 30 g of C_3F_6) of a red oil that possessed n.m.r. (^{1}H and ^{19}F) characteristics not inconsistent with N-(2,3,3,3-tetrafluoropropionyl)iminopyridinium ylide (30), *i.e.* a compound which can plausibly arise *via* interception by water of a simple 1 : 1 adduct (31) from N-iminopyridinium ylide and perfluoropropene or of the related N-(perfluoroprop-1-enyl)iminopyridinium ylide (32), as demonstrated in Scheme 4 (see also Scheme 2).

photometers and AEI MS902 or Kratos MS45 spectrometers (electron beam energies 70 eV), respectively. N.m.r. analyses were carried out with Perkin-Elmer R32 (^{1}H at 90 and ^{19}F at 84.6 MHz) and Bruker WP80 (^{13}C at 20.1 MHz) and WH180 (^{15}N at 18.24 MHz) instruments; unless stated otherwise, 1,4-$Cl_2C_6H_4$ (external, ^{1}H), CF_3CO_2H (external, ^{19}F), $CDCl_3$ [internal (solvent and 'lock'), ^{13}C], and CD_3NO_2 [external, ^{15}N; $Cr(acac)_3$ as relaxation agent] [21] were used as references. Chemical shifts to low field of reference signals have been assigned positive values, and data for ^{13}C nuclei have been converted to the Me_4Si scale using the conversion factor δ_C([13]CD-Cl_3) = +76.9 p.p.m. Light petroleum refers to that fraction boiling in the range 40—60 °C.

Starting Materials.—Commercial samples of perfluoropropene and perfluorobut-2-yne were used. Other reagents were synthesized by methods indicated in the text.

Reactions of N-*Iminopyridinium Ylide* (1).—(a) *With perfluoropropene.* An excess of perfluoropropene (3.75 g, 25.0 mmol) was condensed, *in vacuo*, into a cold (−196 °C) Pyrex tube (450 cm³) equipped with a Rotaflo glass–PTFE valve and containing a PTFE-encapsulated magnetic stirrer follower and a degassed mixture of dichloromethane (100 cm³), finely powdered anhydrous potassium carbonate (8.0 g, 58 mmol), and N-aminopyridinium iodide (4.44 g, 20.0 mmol).[22] The tube was sealed, allowed to warm to room temperature, then left in an explosion-proof steel cabinet for five days with the stirrer in motion; during this period the liquid phase (viewed through a Cobex window) changed from purple, through yellow, to greenish brown. After removal of the unchanged perfluoropropene plus carbon dioxide which had been produced (detected by i.r. spectroscopy), the liquid phase was filtered to remove the
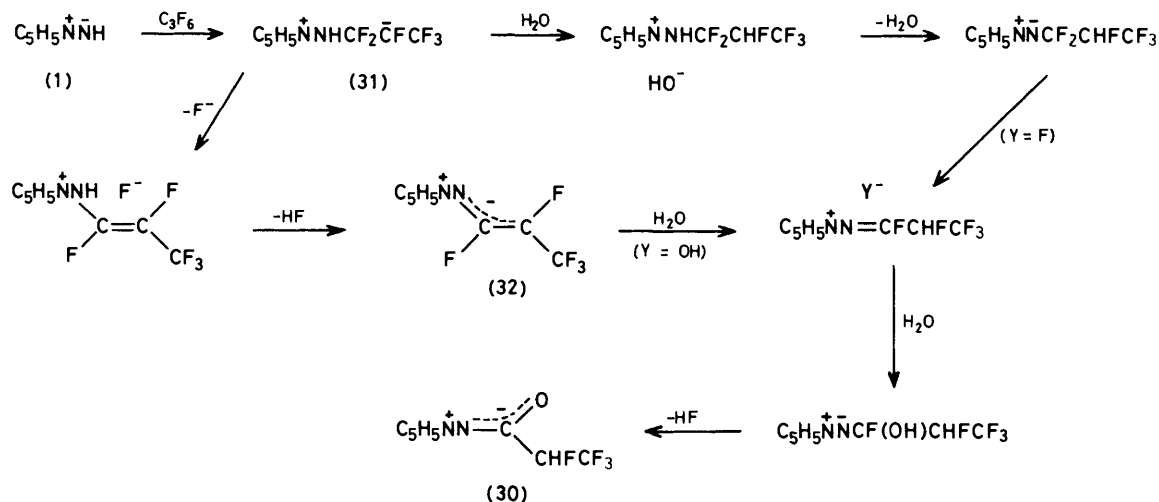
SCHEME 4

In conclusion, circumstantial evidence points to ring-closure *via* a stepwise mechanism in the reactions reported here. A search for corroborative evidence (or otherwise) has been initiated.[3]

EXPERIMENTAL

Spectroscopic Analyses.—I.r. and mass spectra were obtained with the aid of Perkin-Elmer 197 or 720 spectro-

inorganic salts and any other insoluble material, and the residue was washed with dichloromethane (3 × 20 cm³). The filtrate and washings were evaporated under reduced pressure; the brown crystalline residue was purified by column chromatography [alumina (40 × 3.5 cm), with dichloromethane as eluant], followed by vacuum sublimation (bath temperature 40 °C), to provide 2-*fluoro*-3-(*trifluoromethyl*)*pyrazolo*[1,5-a]*pyridine* (8) (2.65 g, 65%) as needles, m.p. 62—63 °C (sealed tube) [Found: C, 47.1;

H, 1.7; F, 37.4; N, 13.7%; M^+, 204 (base peak). $C_8H_4F_4N_2$ requires C, 47.1; H, 2.0; F, 37.25; N, 13.7%; M, 204]; δ_F (35% soln. in $CDCl_3$) 23.2 (d, $J_{(CF_3,F)}$, 8 Hz, CF_3) and −45.7 br. p.p.m. (q, CF) (relative intensity 3 : 1); δ_H (35% soln. in $CDCl_3$) 1.16 (dt, 7-H), 0.45br. (d, 4-H), 0.2br. (dd, 5-H), and −0.19 (td, 6-H) (rel. int. 1 : 1 : 1 : 1; $J_{4-H,5-H}$ 9, $J_{4-H,6-H}$ 2, $J_{5-H,6-H}$ 7, $J_{5-H,7-H} \approx J_{4-H,7-H}$ ca. 1, $J_{6-H,7-H}$ 7 Hz); δ_C (35% soln. in $CDCl_3$; broadband decoupled) 162.0 (dq, $^1J_{CF}$ 250.4, $^3J_{CF}$ 2.2 Hz, C-2), 139.3 (q, $^3J_{CF}$ 2.5 Hz, C-3a), 129.0 (s, C-7), 127.4 (s, C-6), 122.2 (qd, $^1J(CF_3)$ 265.4, $^3J_{CF}$ 5.1 Hz, CF_3), 116.2 (q, $^4J_{CF}$ 1.5 Hz, C-4), 113.4 (d, $^5J_{CF}$ 2.2 Hz, C-5), and 84.8 p.p.m. (6 lines, $^2J_{COF}$ 40.4, $^2J(CCF_3)$ 22.1 Hz, C-3); δ_N (40% soln. in $CDCl_3$) −130.8 (d, $^2J_{NCF}$ 37.4 Hz, N-1) and −168.0 p.p.m. (d, $^3J_{NCF}$ 5.1 Hz, N-8). Further elution of the alumina column with dichloromethane provided a red oil (9 mg); n.m.r. analysis of a larger (130 mg) sample procured by carrying out several large scale (3 times the above scale, using 1 200 cm³ tubes) reactions between perfluoropropene and N-iminopyridinium ylide [the yield of the pyrazolopyridine (8) always fell within the range 60—70%] showed it to comprise mainly a compound thought to be N-(2,3,3,3-tetrafluoropropionyl)-iminopyridinium ylide (30) [δ_F 4.5 (dd, $^3J_{HF}$ 6.3 Hz, CF_3) and −121.7 p.p.m. (dq, $^2J_{HF}$ 46.5, $^3J_{FF}$ 12.7 Hz, CHF) (rel. int. 3 : 1); δ_H 1.57br. (d, J 6.5 Hz, 2- and 6-H), 0.86 (t, 4-H), 0.6 (m, 3- and 5-H), and −1.88 (dq, CHF)].

(b) *With* 2H-*pentafluoropropene.* Using the same procedure, 2H-pentafluoropropene [19] (3.96 g, 30.0 mmol) was treated with N-iminopyridinium ylide to yield, after flash chromatography [23] [silica (15 × 4.0 cm); CH_2Cl_2 as eluant], spectroscopically (i.r., n.m.r.) pure compound (8) [0.46 g, 15% based on $CF_3CH=CF_2$ consumed (15 mmol were recovered)].

(c) *With perfluorobut-2-ene.* Experiment (a) was repeated with a 1 : 3 mixture (by ^{19}F n.m.r. spectroscopy) of *cis*- and *trans*-perfluorobut-2-ene [24] (5.0 g, 25 mmol). Subjection of the tarry brown product (after removal of CH_2Cl_2) to flash chromatography [silica (15 × 6 cm); dichloromethane–light petroleum (1 : 1 v/v) as eluant], followed by vacuum sublimation (bath temp. 40 °C) of the white solid thus isolated, provided crystalline 2,3-*bis*-(*trifluoromethyl*)*pyrazolo*[1,5-a]*pyridine* (3) (3.92 g, 77%), m.p. 35—37 °C [Found: C, 42.4; H, 1.4; F, 45.2; N, 11.1%; M^+ 254 (base peak). $C_9H_4F_6N_2$ requires C, 42.5; H, 1.6; F, 44.9; N, 11.0%; M, 254]; δ_F (35% soln. in $CDCl_3$) 24.2 (q, $J(CF_3,CF_3)$ 7 Hz, 3-CF_3) and 17.2 p.p.m. (q, 2-CF_3), (rel. int. 1 : 1); δ_H (35% soln. in $CDCl_3$; ext Me_4Si) 8.53 (dt, 7-H), 7.8br. (d, 4-H), 7.45 (ddd, 5-H), and 7.08, (td, 6-H) (rel. int. 1 : 1 : 1 : 1; $J_{4-H,5-H}$ 9, $J_{4-H,6-H}$ 1.5, $J_{5-H,6-H}$ 7, $J_{5-H,7-H} \approx J_{4-H,7-H}$ ca. 1, $J_{6-H,7-H}$ 7 Hz); δ_C (50% soln. in $CDCl_3$) 141.8 (qq, C-2), 139.9 (q, $^3J_{CF}$ 2.2 Hz, C-3a), 129.4 (s, C-7), 127.8 (s, C-6), 122.5 (q, $^1J(CF_3)$ 267 Hz, 3- or 2-CF_3), 120.6 (q, $^1J(CF_3)$ 270.5 Hz, 2- or 3-CF_3), 118.1 (q, C-4), 115.4 (s, C-5), and 101.2 p.p.m. (qq, C-3).

(d) *With perfluorobut-2-yne.* Experiment (c) above was repeated with an excess of perfluorobut-2-yne (4.86 g, 30.0 mmol) as the substrate. Identical work-up gave compound (3) (0.915 g, 18%), identical with an authentic specimen (i.r.).

(e) *With perfluoro-*(2-*methylpent-2-ene*). The olefin [25] (6.25 g, 20.8 mmol) was added in one portion to a vigorously stirred purplish blue solution of N-iminopyridinium ylide in dichloromethane [prepared by mixing N-aminopyridinium iodide (4.44 g, 20.0 mmol) in dichloromethane (100 cm³) with anhydrous potassium carbonate (8.0 g, 58 mmol) at

room temperature under nitrogen]. Immediately, the mixture turned yellow. The mixture was stirred for 24 h under nitrogen then filtered and the filtrate was worked up by standard techniques [evaporation then chromatography of the residue on silica gel (40 × 3.5 cm; dichloromethane as eluant)] to afford a deep yellow oil possessing spectroscopic properties consistent with those of 2-(pentafluoroethyl)-3,3-bis(trifluoromethyl)-3,3a-dihydropyrazolo-[1,5-a]pyridine (15) (1.42 g, 19%) [$\nu_{max.}$ (neat) 1 630 cm⁻¹ (C=N); δ_F (neat) 11.9br. (m, CF_3), 10.1v.br. (m, CF_3), −5.8 (s, CF_3CF_2), and −31.0br. p.p.m. (m, CF_2), (rel. int. 3 : 3 : 3 : 2); δ_H (neat) −0.77br. (d, $J_{6-H,7-H}$ 7.5 Hz, 7-H), −1.36 (m, 5-H), −1.68br. (d, $J_{4-H,5-H}$ 10 Hz, 4-H), −2.06v.br. (s, 3a-H), and −2.22br. (t, $J_{5-H,6-H}$ ca. 7 Hz, 6-H) (rel. int. 1 : 1 : 1 : 1 : 1)].

The experiment was repeated but, after the crude mixture had been filtered to remove K_2CO_3, KF, etc., tetracyanoethylene (2.46 g, 19.2 mmol) was added to the filtrate and the resulting solution was heated under reflux with stirring until no further change could be detected by t.l.c. (4 h). Work-up of the product by standard procedures, followed by flash chromatography [23] [silica (15 × 6 cm); CH_2Cl_2 as eluant] and vacuum sublimation at 80—90 °C, provided 2-(*pentafluoroethyl*)-3-(*trifluoromethyl*)*pyrazolo*[1,5-a]*pyridine* (16) (0.36 g, 6%), m.p. 59.5—60.5 °C (Found: C, 39.7; H, 1.0; F, 49.7; N, 9.5. $C_{10}H_4F_8N_2$ requires C, 39.5; H, 1.3; F, 50.0; N, 9.2%); δ_F (25% soln. in $CDCl_3$) 25.0br. (t, $J(CF_3,CF_2)$ 12 Hz, 3-CF_3), −4.6br. (m, CF_3CF_2), and −31.8br. p.p.m. (q, CF_2) (rel. int. 3 : 3 : 2); δ_H (25% soln. in $CDCl_3$; int. Me_4Si) 8.54 (dt, 7-H), 7.82br. (d, 4-H), 7.42 (ddd, 5-H) and 7.05 (td, 6-H) (rel. int. 1 : 1 : 1 : 1; $J_{4-H,5-H}$ 10, $J_{4-H,6-H}$ 1.3, $J_{5-H,6-H}$ 7, $J_{5-H,7-H} \approx J_{4-H,7-H}$ ca. 1, $J_{6-H,7-H}$ 7 Hz); m/z 304 ($M^{+\cdot}$, 79%), 235 ($M^{+\cdot}$ − CF_3, 100), and 78 ($C_5H_4N^+$, 21); further elution gave bright orange crystals of 5-(*dicyanomethylene*)-2-(*pentafluoroethyl*)-3,3-*bis*(*trifluoromethyl*)-3,5-*dihydropyrazolo*[1,5-a]*pyridine* (17) (0.65 g, 7.5%), m.p. 199—201 °C (Found: C, 38.8; H, 0.4; F, 47.5; N, 12.9. $C_{14}H_3F_{11}N_4$ requires C, 38.5; H, 0.7; F, 47.9; N, 12.8%); $\nu_{max.}$ (mull) 2210 (C≡N) and 1 625 (C=N) cm⁻¹; δ_F [20% soln. in $(CD_3)_2CO$] 11.0 [t, $^5J_{FF}$ 11 Hz, $C(CF_3)_2$], −4.8 (s, CF_3CF_2), and −32.5 p.p.m. (sept., CF_2) (rel. int. 6 : 3 : 2); δ_H [20% soln. in $(CD_3)_2CO$] 0.61 (d, $J_{6-H,7-H}$ 9 Hz, 7-H), −0.56br. (s, 4-H), and −0.80 (dd, $J_{4-H,6-H}$ 2 Hz, 6-H); m/z 436 ($M^{+\cdot}$, 77), 367 ($M^{+\cdot}$ − CF_3, 100), 298 ($M^{+\cdot}$ − 2 CF_3, 74), and 69 (CF_3^+, 66).

Reactions of N-*Iminoquinolinium Ylide* (2).—(a) *With perfluoropyridine.* A stirred mixture of N-iminoquinolinium ylide dimer [26] (1.44 g, 5.00 mmol), perfluoropyridine (1.80 g, 10.7 mmol), and anhydrous potassium carbonate (2.0 g, 14.5 mmol) in DMF (20 cm³) turned red when heated at 75—80 °C under reflux. After 2 h, the mixture was stirred overnight at room temperature (throughout, moisture was rigorously excluded from the apparatus), then re-heated at 80 °C for 1 h, cooled to 18 °C, and treated dropwise with water (50 cm³). The mixture was filtered and the precipitate was washed with cold water (3 × 10 cm³), dried *in vacuo* (P_2O_5), then slowly re-precipitated from a solution in DMF with the minimum quantity of cold water. The brick red solid thus obtained was thoroughly dried (*in vacuo*; P_2O_5) and was shown to be N-(2,3,5,6-*tetrafluoro-4-pyridyl*)*iminoquinolinium ylide* (1.91 g, 65%), m.p. 140—141 °C (Found: C, 57.6; H, 2.4; F, 25.5; N, 14.4. $C_{14}H_7F_4N_3$ requires C, 57.3; H, 2.4; F, 25.9; N, 14.3%); δ_F [25% soln. in $(CD_3)_2CO$] −21.0 (2- and 6-F) and −86.6 p.p.m. (3- and 5-F) (rel. int. 1 : 1); δ_H (25% soln. in $(CD_3)_2$-

CO) 2.04br. (d, 2-H), 1.51 (m), 1.16 (m), 0.98 (m), and 0.87—0.39 (rel. int. 1 : 1 : 1 : 1 : 3); m/z 293 ($M^{+•}$, 19) and 129 ($C_9H_7N^{+•}$, 100).

(b) *With perfluoropropene.* A stirred mixture of per-fluoropropene (2.25 g, 15.0 mmol), N-iminoquinolinium ylide dimer (1.44 g, 5.00 mmol), and anhydrous potassium carbonate (3.0 g, 22 mmol) in DMF (25 cm³) was heated at 75 °C for 2.5 h under anaerobic conditions in a Rotaflo tube (300 cm³). After being left at room temperature overnight, the mixture was heated at 80 °C for 5 h then cooled to −196 °C to allow gaseous products [shown (i.r.) to comprise $CF_3CF=CF_2$, $CF_3CHFCHF_2$, and CO_2] to be transferred to a vacuum system by standard techniques. The dark reddish brown liquid product containing an insoluble solid was poured into water (250 cm³) and the aqueous mixture was worked up *via* extraction with chloro-form (2 × 25 cm³) to provide a brown oil which was chro-matographed on alumina [40 × 3.5 cm; dichloromethane–light petroleum (1 : 1 v/v) as eluant] to give a pale reddish brown solid (1.3 g), recrystallization of which from ethanol (with charcoal) provided 2-*fluoro*-3-*(trifluoromethyl)pyr-azolo*[1,5-a]*quinoline* (10) (0.98 g, 39%) as cream crystals, m.p. 129—130 °C [Found: C, 57.0; H, 2.4; F, 30.2; N, 10.7%; M^+, 254 (base peak). $C_{12}H_6F_4N_2$ requires C, 56.7; H, 2.4; F, 29.9; N, 11.0%; M, 254]; δ_F (20% soln. in CDCl₃) 23.2 (dd, J(CF₃,F) 8 Hz, CF₃) and −46.1br. p.p.m. (q, CF) (rel. int. 3 : 1).

(c) *With perfluorobut-2-ene.* A mixture of perfluorobut-2-ene (1 : 3 mixture of *cis* and *trans* isomers; 3.0 g, 15 mmol), N-iminoquinolinium ylide dimer (1.22 g, 4.24 mmol), and anhydrous potassium carbonate (3.0 g, 22 mmol) in DMF (25 cm³) was heated at 85 °C with stirring for 24 h under anaerobic conditions in a Rotaflo Pyrex tube (300 cm³) equipped with a PTFE-coated stirrer bar. The deep red mixture was poured into water (200 cm³) and extracted with CH₂Cl₂ (2 × 30 cm³); the extracts were dried (MgSO₄) then evaporated; the residue was flash chromatographed [silica (15 × 6 cm); CH₂Cl₂ as eluant]; and the crude product sublimed *in vacuo* at 80 °C to give crystals of 2,3-*bis(trifluoromethyl)pyrazolo*[1,5-a]*quinoline* (4) (0.80 g, 31%), m.p. 80—81 °C [Found: C, 51.5; H, 1.6; F, 38.0; N, 9.4%; M^+, 304 (base peak). $C_{13}H_6F_6N_2$ re-quires C, 51.3; H, 2.0; F, 37.5; N, 9.2%; M, 304]; δ_F (20% soln. in CDCl₃) 24.2 (q, J(CF₃,CF₃) 7 Hz, CF₃) and 17.4 p.p.m. (q, CF₃); δ_H (20% soln. in CDCl₃; ext. Me₄Si) 8.42br. (dd, 9-H), and 7.42—7.81 (rel. int. 1 : 5).

Oxidation of Fluorinated Pyrazolopyridines.—(a) 2-*Fluoro-*3-*(trifluoromethyl)pyrazolo*[1,5-a]*pyridine* (8). A mixture of compound (8) (2.04 g, 10.0 mmol) and potassium perman-ganate (8.0 g) in water (150 cm³) was stirred at room temperature for 2 days then filtered to remove manganese dioxide which was washed with water (3 × 20 cm³). The filtrate and washings were shaken with dichloromethane (2 × 50 cm³), then strongly acidified with concentrated hydrochloric acid (to pH 1) before being evaporated to dryness. The residue was shaken with dry acetone until no more material dissolved, and the mixture was filtered and the filtrate evaporated under reduced pressure to provide off-white crystals, m.p. 176—178 °C, of 3(5)-*fluoro*-4-*(trifluoromethyl)pyrazole*-5(3)-*carboxylic acid* (14) (1.48 g, 75%) which did not give satisfactory analyses (Found: C, 29.7; H, 1.2; F, 30.6; N, 13.3. $C_5H_2F_4N_2O_2$ requires C, 30.3; H, 1.0; F, 38.4; N, 14.1%) yet possessed spectroscopic properties consistent with the structure assigned {$\nu_{max.}$ (mull) 3 635—2 085 v.br. (O–H and N–H)

and 1 720 cm⁻¹ (C=O); δ_F [30% soln. in (CD₃)₂SO] 23.5 (d, J(CF₃,F) 14 Hz, CF₃) and −49.1 p.p.m. (q, CF) (rel. int. 3 : 1); m/z 198 ($M^{+•}$, 100), 180 ($M^{+•}$ − OH, 82), 69 (CF₃⁺, 10), and 45 (CO₂H⁺, 11)}.

(b) 2,3-*Bis(trifluoromethyl)pyrazolo*[1,5-a]*pyridine* (3). This pyrazolopyridine (2.54 g, 10.0 mmol) was oxidized exactly as described above for its 2-fluoro-analogue. After the aqueous filtrate and washings had been acidified, the solution was evaporated to *ca.* 60 cm³ volume then kept at room temperature overnight. The crystals which deposited were filtered off and were shown to be 3(5),4-*bis(trifluoro-methyl)pyrazole*-5(3)-*carboxylic acid* (9) *monohydrate* (0.70 g, 26%) (Found: C, 27.2; H, 1.4; F, 42.9; N, 10.7. $C_6H_4F_6N_2O_3$ requires C, 27.1; H, 1.5; F, 42.9; N, 10.5%) (crystals dried in air prior to analysis); the filtrate was evaporated to dryness to provide a further crop (1.03 g; total yield 65%) of the monohydrate. Storage of the monohydrate over P₂O₅ *in vacuo* afforded the *anhydrous acid* (9), m.p. 160—161 °C (Found: C, 29.3; H, 0.4; F, 46.2; N, 11.6. $C_6H_2F_6N_2O_2$ requires C, 29.0; H, 0.8; F, 46.0; N, 11.3%); $\nu_{max.}$ (mull) 3 450—2 500 v.br. (O–H and N–H) and 1 715 cm⁻¹ (C=O); δ_F [30% soln. in (CD₃)₂SO] 17.2 (q, J(CF₃,CF₃) 9 Hz, CF₃) and 23.7 p.p.m. (q, CF₃) (rel. int. 1 : 1); m/z 248 ($M^{+•}$, 100), 231 ($M^{+•}$ − OH, 11), 69 (CF₃⁺, 51), and 45 (CO₂H⁺, 17).

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