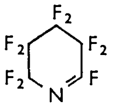
672. *Heterocyclic Polyfluoro-compounds. Part II.*[1] *Some Reactions of Undecafluoropiperidine: The Preparation of Perfluoro-*2,3,4,5-*tetrahydropyridine and Perfluoro-*(1-*methylpyrrolidine*).

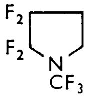
By R. E. BANKS, W. M. CHENG, and R. N. HASZELDINE.

Pyrolysis of undecafluoropiperidine over mild steel at 400—600°/~1 atm. yields a mixture of perfluoro-2,3,4,5-tetrahydropyridine (I), perfluoro-(1-methylpyrrolidine) (II), a compound believed to be perfluoro-(*N*-butylidenemethylamine) (III), and small amounts of pentafluoropyridine. Compounds (II) and (III) can be obtained almost exclusively by thermal rearrangement of the piperidine in platinum apparatus at 550°/1 atm. The N–F bond in undecafluoropiperidine liberates iodine almost quantitatively from aqueous iodide solutions, and the piperidine is thus converted into hexafluoroglutaric acid. Diethyl hexafluoroglutarate is obtained by ethanolysis of undecafluoropiperidine. The nuclear magnetic resonance spectra of some of these compounds are discussed.

IN Part I[1] was described the preparation of pentafluoropyridine by the passage of undecafluoropiperidine over mild steel at 580—610°/<1 mm. with a contact time of *ca.* 1 sec. Perfluoroalicyclic compounds cannot normally be aromatised under these conditions, and it was suggested that the N–F bond in undecafluoropiperidine facilitates defluorination. Evidence for this has now been obtained by effecting the ready defluorination of the piperidine to perfluoro-2,3,4,5-tetrahydropyridine (I), a reaction which is accompanied, to an extent dependent upon the conditions, by thermal rearrangement of the piperidine to a mixture of perfluoro-(1-methylpyrrolidine) (II) and a compound believed to be perfluoro-(*N*-butylidenemethylamine) (III). Only small amounts of pentafluoropyridine, and no compounds containing C⁚C bonds, *e.g.*, (IV)—(VI), were isolated. The reactivity of the N–F group of undecafluoropiperidine has been further demonstrated by its ability to oxidise iodide ion and ethanol.

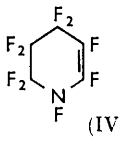


(I)

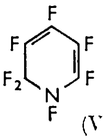


(II)

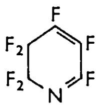
$CF_3{\cdot}[CF_2]_2{\cdot}CF{:}N{\cdot}CF_3$
(III)



(IV)



(V)



(VI)

Preparation, Hydrolysis, and Ethanolysis of Undecafluoropiperidine.—Undecafluoropiperidine was prepared by the electrochemical fluorination of pyridine and of 2-fluoropyridine. The latter substrate was investigated since it appeared that fission of the C–N bonds in pyridine might be reduced by replacement of an α-hydrogen atom by fluorine before fluorination. This proved to be the case: the yield of undecafluoropiperidine (13%) from 2-fluoropyridine, which is readily prepared in 37% yield from commercially available 2-aminopyridine by a Balz–Schiemann reaction,[2] was nearly twice that obtained from pyridine (7·5%). Thus, when only small cells (<2-l. capacity) are available for electrochemical fluorination it is more convenient to use 2-fluoropyridine; when larger cells are available, use of pyridine itself is more economical and is preferred.

Undecafluoropiperidine is unaffected by aqueous sodium hydroxide or hydrochloric acid at 70°, but it reacts fairly rapidly with an excess of warm hydriodic acid or aqueous potassium iodide, to liberate iodine almost quantitatively (95%) according to the equation:

$$C_5F_{10}NF + 2I^- + 4H_2O \longrightarrow [CF_2]_3(CO_2H)_2 + I_2 + NH_4F + 2HF + 2F^-$$

In this respect, the oxidising power of the N–F group resembles that of similar groups in

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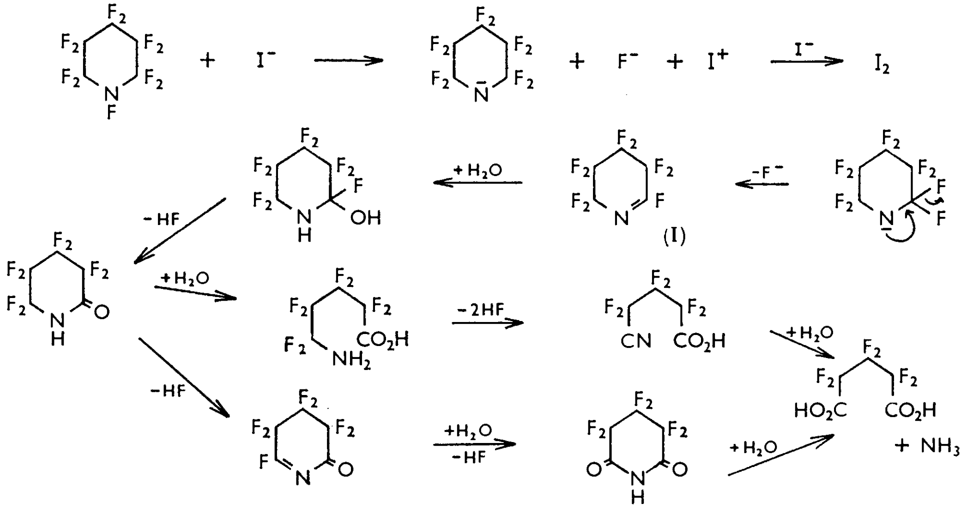
[1] Part I, Banks, Ginsberg, and Haszeldine, *J.*, 1961, 1740.

[2] Roe and Hawkins, *J. Amer. Chem. Soc.*, 1947, **69**, 2443.

the compounds NHF_2,[3] N_2F_2,[4] and $(CF_3)_2NF$.[5] The annexed reaction scheme is suggested. Compound (I), postulated here as an intermediate, has been prepared as described below; it undergoes rapid aqueous hydrolysis to hexafluoroglutaric acid with the quantitative liberation of three fluorine atoms as fluoride per molecule.

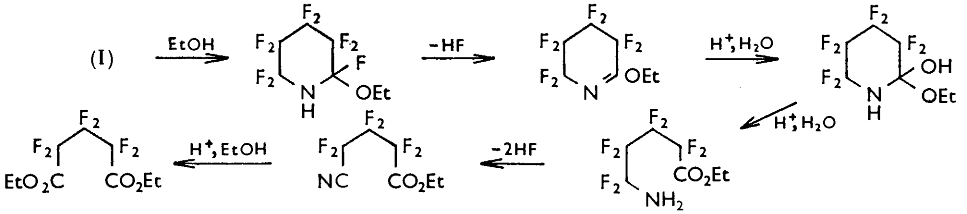


Undecafluoropiperidine reacted smoothly with ethanol at 100° in a sealed tube. Diethyl hexafluoroglutarate was the main product (46% yield), but also identified were acetaldehyde, diethyl ether, and ethyl fluoride. Compound (I), prepared as described below, was shown by a separate experiment to react with ethanol to give diethyl hexa-

$$C_5F_{10}NF + EtOH \longrightarrow C_5F_{10}NH + MeCHO + HF$$

$$Et_2O \overset{H^+}{\rightleftharpoons} EtOH \overset{HF}{\rightleftharpoons} EtF + H_2O$$

$$C_5F_{10}NH \xrightarrow{-HF} (I)$$



fluoroglutarate in 91% yield. Methanolysis of the simpler compound $CF_3{\cdot}N{:}CF_2$ follows a somewhat similar course,[6] so that alcoholysis of the $R_FCF{:}NR_F$ system appears to be a general reaction.

Recently, Russian workers [7] have claimed that a compound said to have the structure $\overline{\mathrm{CF_2{\cdot}CF{:}CF{\cdot}N}}\mathrm{F}$ forms an ethoxy-derivative $\overline{\mathrm{CF_2{\cdot}CF{:}CF{\cdot}N}}\mathrm{{\cdot}OEt}$ on treatment with ethanol; if this is the case, the reaction must follow quite a different course from that postulated above.

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[3] Lawton and Weber, *J. Amer. Chem. Soc.*, 1959, **81**, 4755.
[4] Schmeisser and Sartori, *Angew. Chem.*, 1959, **71**, 523.
[5] Young, Durrell, and Dresdner, *J. Amer. Chem. Soc.*, 1959, **81**, 1587.
[6] Barr and Haszeldine, *J.*, 1955, 1881.
[7] Knunyants and Bykhovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1960, **131**, 1338.

Pyrolytic Defluorination of Undecafluoropiperidine.—Pyrolysis of undecafluoropiperidine at 500°/~1 atm. during 2 hr. in a mild-steel autoclave packed with mild-steel wool gave pentafluoropyridine (*ca.* 6% yield) and a more volatile material, distillation range 37—41·5°, which gave two peaks on a gas chromatogram. Chromatographic separation of the latter material yielded perfluoro-2,3,4,5-tetrahydropyridine (I) (40% yield) and an inseparable, approximately equimolar mixture (20% yield) of perfluoro-(1-methylpyrrolidine) (II) and perfluoro-(*N*-butylidenemethylamine) (III). These last two compounds arise by thermal rearrangement of undecafluoropiperidine as discussed in the next section.

Perfluoro-2,3,4,5-tetrahydropyridine, the first compound of its class to be described, is a colourless, volatile liquid (b. p. 40·7°). Its infrared spectrum shows a strong band at 5·70 μ assigned to the N:C stretching vibration, and it appears that replacement of a =CF– group by =N– in a fluorocarbon causes only a small shift of the double-bond vibration to shorter wavelength (see Table 1). It was noted earlier[6] that replacement of a =CF– group in a fluorocarbon by a nitrogen atom scarcely affects the boiling point [*e.g.*, C_3F_8, b. p. –39°; $(CF_3)_2NF$, b. p. –37°]. This applies also to terminal perfluoro-olefin systems and to perfluoro-aromatic compounds, but not to the internal olefin systems

$$CF_3\cdot CF{:}CF\cdot CF_3/CF_3\cdot N{:}CF\cdot CF_3 \text{ and } CF_2\cdot(CF_2)_3\cdot CF{:}CF/CF_2\cdot(CF_2)_3\cdot N{:}CF$$

where replacement of =CF– by =N– causes an appreciable decrease in b. p. (see Table 1).

TABLE 1.

Infrared and b. p. data.[1,6,8,9]

	C:C vibration (μ)	B. p.		N:C vibration (μ)	B. p.
$CF_3\cdot CF{:}CF_2$	5·56	–29°	$CF_3\cdot N{:}CF_2$	5·53	–33·7°
$C_2F_5\cdot CF{:}CF_2$	5·58	1	$C_2F_5\cdot N{:}CF_2$............	5·52	–6
$C_3F_7\cdot CF{:}CF_2$	5·57	29	$C_3F_7\cdot N{:}CF_2$............	5·51	25·6
$CF_3\cdot CF{:}CF\cdot CF_3$	5·77	0	$CF_3\cdot N{:}CF\cdot CF_3$	5·60	–15
$CF_2\cdot[CF_2]_3\cdot CF{:}CF$ ...	5·74	53	$CF_2\cdot[CF_2]_3\cdot N{:}CF$ ...	5·70	40·7
Perfluorobenzene ...	6·51 *	81	Perfluoropyridine ...	6·68 *	83·3

* Characteristic ring vibrations.

When the mixture of perfluoro-compounds (II) and (III), isolated in 20% yield from the products of defluorination of undecafluoropiperidine, was shaken with aqueous sodium hydroxide at room temperature, approximately half of it was hydrolysed to heptafluorobutyric acid and ammonium fluoride, and the residue still had the molecular formula $C_5F_{11}N$. Comparison of the infrared spectrum of this residue, which showed only features typical of a saturated fluorocarbon, with that of the mixture before hydrolysis revealed the disappearance of the 1773 cm.$^{-1}$ band and of other bands present in the spectrum[10,11] of an authentic specimen (structure based on nuclear magnetic resonance spectroscopy[12]) of perfluoro-(*N*-butylidenemethylamine) (III) ($C_5F_{11}N$; b. p. 39°). The above hydrolysis supported the presence of this compound in the material:

$$\underset{\text{(III)}}{CF_3\cdot[CF_2]_2\cdot CF{:}N\cdot CF_3} \longrightarrow C_3F_7\cdot CO\cdot NH\cdot CF_3 \longrightarrow C_3F_7\cdot CO_2H$$

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[8] Barr and Haszeldine, *J.*, 1956, 3416; Weiblen, " Fluorine Chemistry," ed. Simons, Academic Press Inc., New York, 1954, Vol. II, p. 453; Lovelace, Rausch, and Postelnek, " Aliphatic Fluorine Compounds," Amer. Chem. Soc. Monograph No. 138, Reinhold Publ. Inc., New York, 1958; Birchall and Haszeldine, *J.*, 1959, 13.

[9] Barr, Haszeldine, and Willis, *J.*, 1961, 1351.

[10] Halpern and Goldenson, *Appl. Spectroscopy*, 1957, **11**, 173.

[11] A personal communication from Dr. F. W. Hoffman is gratefully acknowledged.

[12] Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

However, since the isomeric compound (VII) would also yield heptafluorobutyric acid on hydrolysis:

$$\underset{\text{(VII)}}{CF_3{\cdot}[CF_2]_2{\cdot}CF_2{\cdot}N{:}CF_2} \longrightarrow C_4F_9{\cdot}NCO \longrightarrow C_4F_9{\cdot}NH{\cdot}CO_2H \longrightarrow C_4F_9{\cdot}NH_2 \longrightarrow C_3F_7{\cdot}CN \longrightarrow C_3F_7{\cdot}CO_2H$$

it could be argued that a small amount, say 5%, of this compound might also be present in (III) and remain undetected by nuclear magnetic resonance or infrared spectroscopy. This possibility is considered unlikely since gas chromatography did not reveal the presence of (VII), which, according to the known physical properties [9] of isomeric compounds of the type $R_FN{:}CF_2$ and $R_F'N{:}CFR_F''$, should boil at *ca.* 54°, some 15° higher than (III). An approximately equimolar mixture of compound (III) and the hydrolysis residue $C_5F_{11}N$ boiled at 39°.

The authentic specimen of perfluoro-(*N*-butylidenemethylamine), b. p. 39°, referred to above was prepared by the pyrolysis of the tertiary amine $(n\text{-}C_4F_9)_3N$,[11] despite the claim in the literature [13] that pyrolysis of this amine at 650° in a carbon tube yields the isomer $CF_3{\cdot}[CF_2]_3{\cdot}N{:}CF_2$ (77% yield), the boiling point of which is also given as 39°. In our hands, pyrolysis of the tertiary amine in a platinum tube at 650° gave, as major product (43% yield), a compound, b. p. 39°, spectroscopically (infrared and nuclear magnetic resonance) identical with the perfluoro-(*N*-butylidenemethylamine) obtained by thermal rearrangement of undecafluoropiperidine. The pyrolysate, b. p. >39°, was a complex mixture, and an unsuccessful attempt was made to separate it to determine whether it contained some of the isomer $CF_3{\cdot}[CF_2]_3{\cdot}N{:}CF_2$. The pyrolysate did not contain perfluoro-(1-methylpyrrolidine), which could conceivably be formed by cyclisation of the perfluorobutylideneamine under the pyrolysis conditions.

The residue, b. p. 36·4°, from the alkaline hydrolysis of the mixture of the perfluorobutylideneamine and -pyrrolidine contained no N–F group since (i) it did not liberate iodine from warm aqueous potassium iodide and (ii) it was not defluorinated by mild steel at 500°/1 atm. to yield material containing C:N or C⋮N groups [cf.[14] $(CF_3)_2NF \xrightarrow[515°]{Cu} CF_3{\cdot}N{:}CF_2$; $C_2F_5{\cdot}NF_2 \xrightarrow[515°]{Cu} CF_3{\cdot}C{⋮}N$]. It was not affected by hot concentrated acid or alkali. On the basis of this evidence and the isolation of the same compound after electrochemical fluorination of 1-methylpyrrolidine, the hydrolysis residue was identified as perfluoro-(1-methylpyrrolidine), a new perfluorinated heterocyclic compound. This assignment of structure was supported by nuclear magnetic resonance results.

Thermal Rearrangement of Undecafluoropiperidine.—Studies of the defluorination of undecafluoropiperidine at 1—2 atm. in a nickel autoclave packed with mild steel revealed that the amount of the mixture (II + III) in the product increased at the expense of the perfluoro-2,3,4,5-tetrahydropyridine (I) as the defluorination temperature was increased, in stages, from 400° to 600°.

To throw further light on this, the piperidine was pyrolysed at 550°/1 atm. in a platinum flow apparatus with a contact time of *ca.* 15 min.; this yielded a product (45% yield) which contained (II + III) and (I) in the ratio 9 : 1. The formation of (II) and (III) thus involves a purely thermal rearrangement, and defluorination to yield (I) proceeds only slowly in the absence of a defluorinating agent. Competition occurs between these two processes in the presence of a defluorinating agent (*e.g.*, iron). Thus, when undecafluoropiperidine was passed through a mild steel tube at 500°/1 atm. with a contact time of *ca.* 13 min. the above ratio was 1 : 2 (product yield *ca.* 90%). Pyrolysis of undecafluoropiperidine over mild steel at 600°/1 mm. with a contact time of *ca.* 1 sec.[1,15] gives pentafluoropyridine (26%) and (II + III) and (I) in the ratio 1 : 5, *i.e.*, defluorination

[13] Pearlson and Hals, U.S.P. 2,643,267/1953.

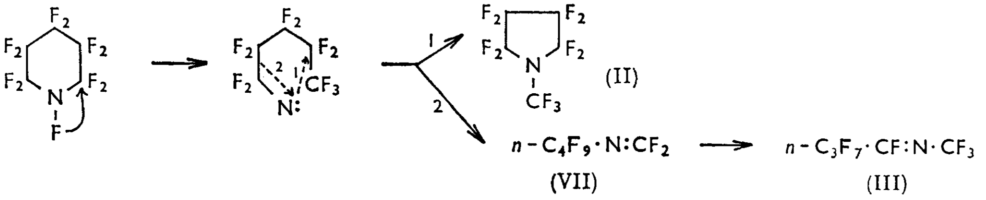
[14] Attaway, Groth, and Bigelow, *J. Amer. Chem. Soc.*, 1959, **81**, 3599.

[15] Banks, Burgess, and Haszeldine, unpublished results.

predominates and is more extensive than in reactions at atmospheric pressure. This result can be attributed to the increase in the mean free path of the undecafluoropiperidine molecules at lower pressures, which leads to an increase in the ratio of the number of collisions with wall or defluorinating agent (leading mainly to defluorination) to the number of molecule–molecule collisions.

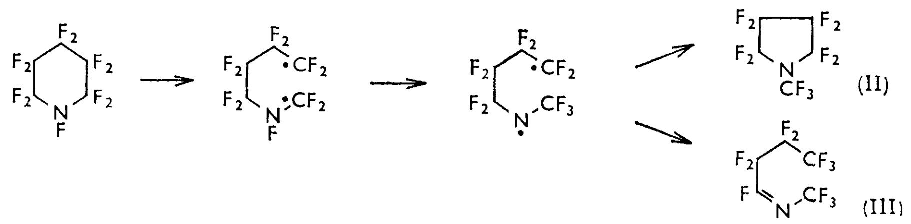
Defluorination experiments at 1 atm. confirmed that the use of sub-atmospheric pressure is important in order to obtain satisfactory yields of pentafluoropyridine. Thus the yields obtained at temperatures and contact times of 500°/13 min., 500°/120 min., 550°/40 min., 570°/26 min., and 600°/95 min. are 0, 6, 19, 3, and 18%, respectively, and these are to be compared with the 26% yield obtained at 600° with only a *ca.* 1 sec. contact time.[1,15]

The thermal ring-contraction of undecafluoropiperidine to perfluoro-(1-methylpyrrolidine) may occur by shift of the fluorine of the N–F group to the α-carbon atom, either intramolecularly or *via* formation of a fluorine atom, followed by rearrangement of the electron-deficient species formed. Since the butylidenemethylamine (III) was not obtained by pyrolysis of the pyrrolidine (II), it is suggested that the intermediate illustrated could also be the precursor of this product, and that the isomer (VII) formed first then isomerises.



Proof that such an isomerisation can occur on pyrolysis must await the synthesis of compounds (III) and (VII) by unambiguous routes.

Alternatively the rearrangement could involve carbon–carbon fission as follows:



There is no simple way of distinguishing between these alternatives at present.

EXPERIMENTAL

Undecafluoropiperidine and its defluorination products are volatile and were manipulated in a conventional vacuum system to avoid handling losses and attack by moisture. The identity of products was confirmed by molecular-weight determination (Regnault's method), elemental analysis, physical properties, infrared spectroscopy (Perkin–Elmer spectrophotometer model 21 with sodium chloride optics), ^{19}F nuclear magnetic resonance spectroscopy (A.E.I. RS2 spectrometer operating at 60 Mc./sec.), and gas–liquid chromatography (GLC) (Perkin–Elmer "Vapor Fraktometer," model 116). GLC analysis was effected with a 4 m. × 5 mm. coiled aluminium column packed with 30% w/w of "dinonyl" phthalate on Celite. Large-scale separations were achieved with a 3 m. × 2·2 cm. column containing the same packing.

All chromatographic-peak area ratios quoted have been found by calibration to correspond approximately to molar ratios.

Preparation of Undecafluoropiperidine.—All the undecafluoropiperidine had a GLC purity >99% (b. p. 49°) and was prepared by the electrochemical fluorination of pyridine, as described previously [1] (yield 7·5%) and of 2-fluoropyridine (yield 13%). In the latter case, 2-fluoropyridine (50 g.), prepared in 37% yield by diazotisation of 2-aminopyridine in fluoroboric acid,[2] was dissolved in anhydrous hydrogen fluoride (580 g.) contained in a small laboratory cell [16] and the solution (1·75 mole%) was electrolysed at 4·5 v (initial current 6·0 amp.). After the passage of 8·86 faradays, product ceased to be condensed in the traps at −72°. Distillation of the product (101 g.) through a 2-ft. vacuum-jacketed Vigreux column yielded crude undecafluoropiperidine (18·8 g.), b. p. 46—55°, with a GLC purity of >95%. Final purification of this material and the crude undecafluoropiperidine prepared by electrochemical fluorination of pyridine was effected by distillation through a 30 cm. × 8 mm. Podbielniak column with a " heli-grid " nichrome packing.

Reactions of Undecafluoropiperidine.—(*a*) *With iodide ion.* Undecafluoropiperidine (0·49 g., 1·73 mmoles) and an excess of 2N-potassium iodide (5 ml.) were vigorously shaken in a sealed 20-ml. Pyrex ampoule at 50° for 2 days. After neutralisation by sodium hydrogen carbonate, the solution was made up to 100 ml. and titrated against 0·1N-sodium arsenite (free iodine 0·419 g., 1·65 mmoles, 95·4%). The solution, free from iodine, was then evaporated to dryness *in vacuo* and the white residue extracted with absolute ethanol (50 ml.). Evaporation of the extract gave the alkali-metal salts of hexafluoroglutaric acid. These were dissolved in water (10 ml.), and the solution (pH adjusted to 4) was added to a solution of *S*-benzylthiouronium chloride, to give di-(*S*-benzylthiouronium) hexafluoroglutarate (0·39 g.; 31·2%), m. p. 190° (lit.,[17] 190°) (Found: C, 44·3; H, 3·5; N, 9·9. Calc. for $C_{21}H_{22}F_6N_4O_4S_2$: C, 44·1; H, 3·9; N, 9·8%).

In a similar experiment, undecafluoropiperidine (0·50 g., 1·76 mmoles) and N-hydriodic acid (7·5 ml.) were shaken in a 20-ml. tube at 50°. The organic layer had disappeared after 12 days and the solution was strongly coloured by free iodine. After neutralisation by sodium hydrogen carbonate, the solution was extracted with carbon tetrachloride to remove the iodine, acidified by sulphuric acid, and further extracted continuously with ether overnight. Treatment of the ethereal extract with aniline gave dianilinium hexafluoroglutarate (0·30 g., 40%), m. p. >220° (decomp.) (Found: C, 48·0; H, 3·7; N, 6·7%; equiv., 211. Calc. for $C_{17}H_{16}F_6N_2O_4$: C, 47·9; H, 3·8; N, 6·6%; equiv., 213). The iodine (0·422 g., 1·66 mmoles, 94·3%) in the carbon tetrachloride extract was estimated with 0·1N-sodium arsenite.

Reaction between undecafluoropiperidine and hydriodic acid at room temperature was incomplete after 12 days, since only 70% of the theoretical amount of iodine was liberated.

(*b*) *With absolute ethanol.* Undecafluoropiperidine (8·55 g., 30·2 mmoles) and absolute ethanol (25 ml.) were heated together in a 114-ml. nickel autoclave at 100° for 4 weeks. A volatile product (0·2 g.) was identified as ethyl fluoride by infrared spectroscopy. The liquid product (22·6 g.) was distilled to yield (i) a fraction (14·0 g.), b. p. 30—78°, which was shown by GLC analysis to be ethanol containing traces of diethyl ether (0·56 g.) and acetaldehyde (0·1 g.), and (ii) diethyl hexafluoroglutarate (4·1 g., 46% based on $C_5F_{11}N$), b. p. 83—84°/7 mm. (Found: C, 36·5; H, 3·3%; equiv., 146. Calc. for $C_9H_{10}F_6O_4$: C, 36·5; H, 3·4%; equiv., 148). The infrared spectrum of this ester was identical with that of an authentic specimen of diethyl hexafluoroglutarate.

(*c*) *Attempted hydrolysis.* Undecafluoropiperidine was recovered unchanged after treatment with (i) 8% aqueous sodium hydroxide at 70° for 6 weeks and (ii) 18% aqueous hydrochloric acid at 70° for 4 days.

(*d*) *Static pyrolysis in the presence of mild steel.* Preliminary experiments were carried out by heating undecafluoropiperidine (1·0 g.) at 200°, 300°, 400°, 500°, and 600° at *ca.* 2 atm. in a sealed nickel tube (16″ × 0·75″) packed tightly with mild-steel wool. At each temperature, the cold tube was placed in a preheated electric furnace, left for 2 hr., and cooled, and the volatile products were examined by molecular-weight measurement and GLC and infrared analysis. Little defluorination occurred at 300°, but at 400° no undecafluoropiperidine remained, and a volatile liquid (0·7 g.; *M*, 254) was recovered which gave two peaks on a gas chromatogram (retention times relative to undecafluoropiperidine: peak 1, 0·78; peak 2, 1·32) and showed strong absorption bands at 1754 and 1773 cm.$^{-1}$ indicating the presence of C:N

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[16] Gramstad and Haszeldine, *J.*, 1956, 173.

[17] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

and/or C:C groups. The products of defluorination at 500° and 600° were the same, except for traces of pentafluoropyridine detected by infrared spectroscopy (band at 1497 cm.$^{-1}$). The area ratio of chromatogram peak 1 : peak 2 increased with the defluorination temperature, thus: 400°, 0·75; 500°, 0·86; 600°, 0·90.

To obtain sufficient product for study, a series of defluorinations was carried out at 500° (contact time 2 hr.) in a sealed mild-steel tube (22″ × 1·6″) packed with mild-steel wool (250 g.). Distillation, through a Podbielniak column, of the product (20 g.) obtained from the defluorination of 28 g. of undecafluoropiperidine (~3 g. per experiment) yielded a fraction (15 g.), b. p. 37—41·5°, which showed the same two GLC peaks as observed previously, but with area ratio 0·62. The distillation residue (1·8 g.) was refractionated in a small Vigreux still, yielding pentafluoropyridine (1 g., 6%), b. p. 83·5° (Found: C, 35·2; N, 8·1%; *M*, 173. Calc. for C_5F_5N: C, 35·5; N, 8·3%; *M*, 169). Separation of part of the fraction of b. p. 37—41·5° by large-scale chromatography yielded a volatile, colourless liquid (peak 1, 2·2 g.), b. p. 39°/760 mm. (Found: C, 21·9%; *M*, 280. Calc. for $C_5F_{11}N$: C, 21·2%; *M*, 283), infrared band at 1773s cm.$^{-1}$, and *perfluoro*-2,3,4,5-*tetrahydropyridine* (peak 2, 4·2 g.) (Found: C, 24·5; N, 5·7%; *M*, 245. C_5F_9N requires C, 24·5; N, 5·7%; *M*, 245), infrared band at 1754 cm.$^{-1}$.

The vapour pressure of perfluoro-2,3,4,5-tetrahydropyridine, measured over the range −24° to 37°, is given by the equation $\log_{10} p$ (cm.) = 6·764 − 1532/*T*. The calculated b. p. is 40·7°, Trouton's constant is 22·4, and the latent heat of vaporisation is 7010 cal. mole^{-1}.

Material (0·5 g.) yielding chromatogram peak 1 was shaken with N-hydriodic acid (6 ml.) in a 20-ml. Pyrex ampoule at 25° for 12 days. No iodine was liberated but visual examination indicated that part of the sample had been destroyed. In a further experiment, the same material (0·46 g.) was shaken (30 min.) with 2N-sodium hydroxide (4 ml.); the organic residue (0·23 g.) recovered by distillation *in vacuo* and dried (P_2O_5) was *perfluoro*-(1-*methylpyrrolidine*) (Found: C, 21·4; N, 5·2%; *M*, 280. $C_5F_{11}N$ requires C, 21·2; N, 4·95%; *M*, 283). Comparison of the infrared spectra of this product and of the material of peak 1 showed that the 1773 cm.$^{-1}$ band and others (1101, 1071, 942, 855, 823, 750 cm.$^{-1}$) characteristic of the compound $CF_3\cdot[CF_2]_2\cdot CF{:}N\cdot CF_3$ had disappeared. The hydrolysate from the material of peak 1 gave positive tests for ammonium and fluoride ion, and heptafluorobutyric acid was isolated as its *S*-benzylthiouronium salt (Found: C, 38·4; H, 2·4; N, 7·4. Calc. for $C_{12}H_{11}F_7N_2O_2S$: C, 37·9; H, 2·9; N, 7·4%), m. p. 187°, by standard techniques.

The vapour pressure of perfluoro-(1-methylpyrrolidine), measured over the range −24° to 33°, is given by the equation $\log_{10} p$ (cm.) = 6·843 − 1535/*T*. The calculated b. p. is 36·4°, Trouton's constant is 22·7, and the latent heat of vaporisation is 7030 cal. mole^{-1}.

(*e*) *Flow pyrolysis in platinum.* At atmospheric pressure, undecafluoropiperidine (12·0 g.) was passed (0·75 g./hr.) in a slow stream of nitrogen through an empty platinum tube (100 × 1 cm.) held at 550° over 56 cm. of its length. The pyrolysate (10·1 g.) was separated by trap-to-trap fractional condensation *in vacuo* into a gaseous fraction (1·5 g.) containing the compounds CF_4, C_2F_6, $CF_3\cdot N{:}CF_2$, COF_2, and SiF_4 (the last two arising by attack of the hot pyrolysate on the glass trap at the exit to the platinum tube), and a liquid fraction (8·5 g.) which was separated by distillation through a Podbielniak column into a mixture (4·3 g., 45% based on undecafluoropiperidine converted; b. p. 37—40°) of perfluoro-(1-methylpyrrolidine), perfluoro-(*N*-butylidenemethylamine) (which together make up the GLC peak 1 referred to earlier), perfluoro-2,3,4,5-tetrahydropyridine (GLC peak 2, referred to earlier) (GLC peak 1 : peak 2 ratio, 9), and unchanged undecafluoropiperidine (2·4 g.), b. p. 49°.

(*f*) *Flow pyrolysis in mild steel.* At atmospheric pressure, undecafluoropiperidine (3·0 g.) was passed (0·5 g./hr.) in a slow stream of nitrogen through an unpacked mild-steel tube (100 × 0·75 cm.) held at 500° over 56 cm. of its length. The pyrolysate (2·74 g.) was collected in traps cooled to −72° and −196°. The first trap contained a mixture (2·65 g.) of the perfluoro-pyrrolidine and -*N*-butylidenemethylamine, and perfluoro-2,3,4,5-tetrahydropyridine (GLC peak 1 : peak 2 ratio, 0·52), but no undecafluoropiperidine. The −196° trap contained a mixture (0·09 g.) of the compounds CF_4, C_2F_6, C_2F_4, C_3F_8, and, from attack on glass, CO_2, COF_2, and SiF_4.

In a similar experiment in which the mild-steel tube was packed with steel wool, undecafluoropiperidine (3·0 g.) at 500° gave a product (2·5 g.), collected at −72°, for which the GLC peak 1 : peak 2 ratio was 0·47.

Effect of Temperature, Pressure, and Contact Time on Yield of Pentafluoropyridine.—A series of defluorinations carried out at 1 atm. in mild steel tubes packed with steel wool (heated length, 54—56 cm.) showed that pentafluoropyridine is obtained in reasonable yield only by use of prolonged contact times:

Undecafluoropiperidine (g.)	Temp.	Tube (cm.)	Contact time (min.)	Pentafluoropyridine (yield %)
3·0	500°	100 × 0·75	13	0
28·0	500	56 × 4·1	120	6
2·0	550	95 × 1·95	40	19
9·0	570	,,	26	3
2·0	600	,,	95	18

Burdon *et al.*[18] synthesised pentafluoropyridine by using nickel gauze to defluorinate undecafluoropiperidine at 560°/1 atm. They did not state the contact time, but from their data we calculate [1] that the yield of pentafluoropyridine was *ca.* 12%, on the assumption that no handling losses occurred during GLC separation. This result is thus consistent with the interrelations of temperature, pressure and contact time given earlier,[1] and suggests that the contact time must have been at least 30 min.

*Reactions of Perfluoro-*2,3,4,5-*tetrahydropyridine.*—(*a*) *Hydrolysis.* A thin-walled glass ampoule containing perfluoro-2,3,4,5-tetrahydropyridine (0·06131 g., 0·2503 mmole) was crushed under the surface of N-sodium hydroxide (30 ml.). After being shaken for 2 hr. the solution contained free fluoride (0·01417 g., 0·7457 mmole; 99·3% of 3F).

When 0·20 g. of perfluoro-2,3,4,5-tetrahydropyridine was shaken with 2N-sodium hydroxide (4 ml.) for 30 min., the hydrolysate, after adjustment of the pH to 4, afforded di-(*S*-benzylthiouronium) hexafluoroglutarate (0·30 g., 64%) (Found: C, 44·2; H, 4·2; N, 9·6. Calc. for $C_{21}H_{22}F_6N_4O_4S_2$: C, 44·1; H, 3·9; N, 9·8%), m. p. 190°.

(*b*) *Ethanolysis.* Perfluoro-2,3,4,5-tetrahydropyridine (0·81 g.) and ethanol (7 ml.) were shaken together in a 20-ml. Pyrex ampoule at 100° for 4 days. Distillation of the products yielded ethyl fluoride (*ca.* 0·01 g.) and chromatographically and spectroscopically pure diethyl hexafluoroglutarate (0·89 g., 91%), b. p. 84°/8 mm.; ammonium fluoride (0·09 g.) was recovered from the ampoule.

Attempted Reactions of Perfluoro-(1-*methylpyrrolidine*).—(*a*) No reaction occurred when the pyrrolidine (0·16 g.) was shaken with 30% aqueous potassium iodide (4 ml.) at 50° for 4 days. (*b*) The pyrrolidine (0·143 g.) was recovered almost quantitatively (96%) after being shaken with concentrated sulphuric acid (3 ml.) or 40% aqueous sodium hydroxide (3 ml.) at 60° for 7 days. (*c*) The pyrrolidine (0·39 g.) was recovered almost quantitatively (95%) after passage (0·26 g./hr.) in a slow stream of nitrogen through a mild-steel tube (100 × 0·75 cm.) packed with mild-steel wool and held at 500° over 56 cm. of its length.

Electrochemical Fluorination of 1-*Methylpyrrolidine.*—A solution of 1-methylpyrrolidine (65 g.) in anhydrous hydrogen fluoride (550 ml.) was electrolysed for 7 days at 4·5 amp. and 5·0 v in a small cell of the type described previously.[16] The product (0·75 g.) collected in a trap cooled to −72° was separated by repeated trap-to-trap fractional condensation, *in vacuo*, into *perfluoro-*(1-*methylpyrrolidine*) (0·30 g., 0·2%) (Found: C, 21·4; N, 5·2%; *M*, 281. $C_5F_{11}N$ requires C, 21·2; N, 4·95%; *M*, 283) and perfluoro-n-butane (0·15 g.; identified spectroscopically).

Pyrolysis of Tris(*nonafluoro-n-butyl*)*amine.*—A commercial sample of tris(nonafluoro-n-butyl)amine (65·2 g.) was purified by distillation and pyrolysed by passage (6·8 g./hr.) in a stream of nitrogen (0·25 l./hr.) through a platinum tube (100 × 1 cm.) held at 650° over 56 cm. of its length. The pyrolysate (53 g.) was distilled, to yield *perfluoro-*(N-*butylidenemethylamine*) (12·0 g., 43%) (Found: C, 21·6; N, 5·0%; *M*, 280. $C_5F_{11}N$ requires C, 21·2; N, 4·95%; *M*, 283), b. p. 39°, which was shown by GLC analysis to be at least 95% pure (two unknown impurities present), and spectroscopically identical with the material obtained by the pyrolysis of undecafluoropiperidine. No other definite distillation fractions were obtained, but only complex mixtures of fluorocarbons. The material boiling in the range 40—53° (5 g.) contained appreciable amounts of the butylideneamine and at least three other (unidentified) compounds; an attempt to effect a separation by large-scale GLC failed.

Nuclear Magnetic Resonance Spectra.—*Perfluoro-*(1-*methylpyrrolidine*). The ^{19}F nuclear magnetic resonance spectrum consists of three regions, apparently corresponding to three chemically distinct types of fluorine atom. The internal chemical shifts (relative to the band at lowest applied field) are 38·2 and 78·3 p.p.m. The lowest-field absorption consists of a

[18] Burdon, Gilman, Patrick, Stacey, and Tatlow, *Nature*, 1960, **186**, 231.

symmetrical 1 : 4 : 6 : 4 : 1 quintet in which the multiplet spacing is 8·4 c./sec. The absorption at 38·2 p.p.m. is a 1 : 3 : 3 : 1 quartet with a spacing of 8·5 c./sec. The highest-field absorption has no multiplet structure but is rather broader than the other bands (*ca.* 4 c./sec. width at half-height). The multiplet structure and the relative integrated absorption intensities agree with the postulated structure. The low-field spectrum is assigned to the $>N{\cdot}CF_3$ group in which the F nuclei are coupled equally by spin–spin interaction to the α(or possibly the β)-fluorine nuclei (J = 8·5 c./sec.). This is confirmed by the 38·2 p.p.m. absorption which must be assigned to the nuclei with the 8·5 c./sec. coupling constant to $>N{\cdot}C\underline{F}_3$. The absence of observable splitting in the third regions is in harmony with the reported near-zero coupling between fluorine atoms on adjacent saturated carbon atoms in certain compounds.[19] The fact that this is at highest field is compatible with its association with the fluorine atoms most distant from the electronegative nitrogen.

Mixture of perfluoro-(1-*methylpyrroldine*) *and perfluoro-*(N-*butylidenemethylamine*). The ^{19}F spectrum of an equimolar mixture of these two compounds consists of eight absorption regions which are analysed in Table 2.

Chemical-shift measurements have been made with trifluoroacetic acid as external reference compound. Bulk-diamagnetic-susceptibility corrections have not been made.

Analysis of the spectrum of the mixture shows the presence of two compounds, of which one is the ring compound (A) and the other is identified as the straight-chain compound (B), both on account of the multiplet splitting of its bands and of their associated chemical-shift values.[12] The bands associated with the various ^{19}F atoms in the compound, in p.p.m. from trifluoroacetic acid are:

	CF_3 —	CF_2 —	CF_2 —	$CF=$	$N{\cdot}CF_3$
	5·2	42·5	50·8	−52·9	−18·3
or, possibly,	5·2	50·8	42·5	−52·9	−18·3

Chemical-shift values are in good agreement with those in the literature,[12] except for the value associated with the $=N{\cdot}CF_3$ group. We incline to the conclusion that the previously quoted value of −36·2 p.p.m. is incorrect.*

TABLE 2.

Nuclear magnetic resonance of (A) $\overline{CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}N}{\cdot}CF_3$ and (B) $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CF{:}N{\cdot}CF_3$.

Chemical shift (p.p.m.)	Multiplet structure	Assignment to compound
−52·9	Broad, structureless (width at half-height ≈50 c./sec.)	B
−21·0	1 : 4 : 6 : 4 : 1 quintet (J = 8·4 c./sec.)	A
−18·3	Doublet (J = 15·3 c./sec.)	B
+5·2	Triplet (J = 8·8 c./sec.) of doublets (J = 1·3 c./sec.)	B
+17·3	1 : 3 : 3 : 1 quartet (J = 8·5 c./sec.)	A
+42·5	1 : 4 : 6 : 4 : 1 quintet (J = 9·7 c./sec.)	B
+50·8	Doublet (J = 6·8 c./sec.)	B
+57·3	Singlet, slightly broadened (width at half-height ≈4 c./sec.)	A

TABLE 3.

Chemical shift (p.p.m.)	Multiplet structure
0	1 : 2 : 1 broadened triplet (J = 24 c./sec.)
40·8	Broad structureless band (width at half-height ≈28 c./sec.)
69·9	9 bands analysing as an overlapping doublet (J = 26 c./sec.) of quintets; (J = 7·6 c./sec.) with possible further splitting into triplets (J ≈0·5 c./sec.)
82·4	Septet of bands (J = 7·5 c./sec.) with further splitting into doublets (J ≈1 c./sec.)
83·6	Very complex group of at least 20 bands with little recognisable symmetry

*Perfluoro-*2,3,4,5-*tetrahydropyridine.* The ^{19}F nuclear magnetic resonance spectrum possesses five absorption systems of which three are distinctly separated and two are at similar magnetic field strengths (cf. Table 3). The chemical shift values were measured relative to the absorption band at lowest applied field.

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* Since this manuscript was submitted Drs. Lauterbur and Klapper have informed us that they agree that the −36·2 p.p.m. is an error, and that a value of about −19 p.p.m. should replace it.

[19] Petrakis and Sederholm, *J. Chem. Phys.*, 1961, **35**, 1243.

The analysis of the spectrum is compatible with the proposed structure of the compound, but absolute confirmation of the position of the double bond in the ring cannot be given at present owing to difficulties in the interpretation of the two complex bands at highest field. However, the band at lowest field can be assigned with some certainty to the 6-fluorine atom which is exhibiting coupling to the two 5-fluorine atoms ($J_{56} = 24$ c./sec.). The single diffuse band at 40·8 p.p.m. is attributed to the 2-fluorine nuclei, on account both of its chemical shift and of the absence of multiplet splitting. The absorption band at 69·9 p.p.m. is rather tentatively assigned to the 5-fluorine nuclei. The multiplet structure can be interpreted as arising from spin–spin coupling with the 6-fluorine nucleus followed by equivalent weaker coupling with the 3- and 4-fluorine nuclei, with the assumption that $J_{35} \approx J_{45}$. On the above argument, the doublet splitting $J_{56} = 24$ c./sec. and $J_{35} \approx J_{45} = 7·6$ c./sec. The remaining two barely separated absorption regions are assigned to the fluorine atoms in the 3- and the 4-position in the heterocyclic ring. More specific assignment of these bands will require a detailed theoretical analysis which has not yet been performed.

Finally, it should be noted that the absorption signal due to the single fluorine nucleus occurs at lowest applied field, supporting a double bond adjacent to the electronegative ^{14}N atom.

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