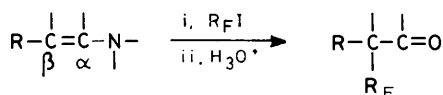


## Condensation of Perfluoroalkyl Iodides with Unsaturated Nitrogen Compounds

By Danièle Cantacuzène,\* Claude Wakselman, and Régine Dorme, C.N.R.S.-C.E.R.C.O.A. 2, rue Henry Dunant, 94320 Thiais, France

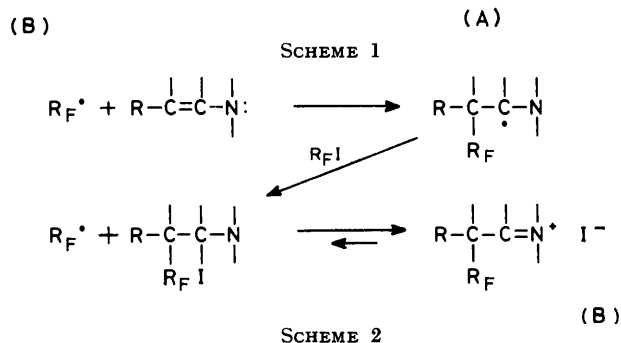
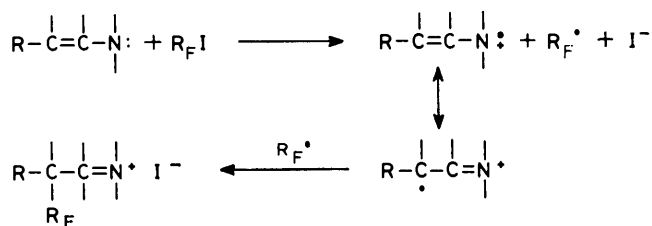
Condensation of enamines with perfluoroalkyl iodides yields  $\alpha$ -perfluoroalkyl ketones. An intermediate charge-transfer complex between an iminium iodide and the perfluoroalkyl iodide has been detected. The reaction has been extended to  $\alpha$ -alkoxy-enamines, ynamines, and pyrroles. It is rapid and uncatalysed for many simple enamines; others require u.v. light.

In a preliminary report<sup>1</sup> we described a simple, general method of introducing a perfluoroalkyl chain  $\alpha$  to a carbonyl group. The reaction involved addition of a perfluoroalkyl iodide ( $R_F I$ ) to an enamine under u.v. irradiation in an inert solvent. In this paper the experimental procedure, the nature of the intermediates, and the extension of the reaction to other unsaturated nitrogen compounds are described. Furthermore we show that, in contrast to other unsaturated systems,<sup>2</sup> enamines react with perfluoroalkyl iodides very rapidly at room temperature, without u.v. irradiation or



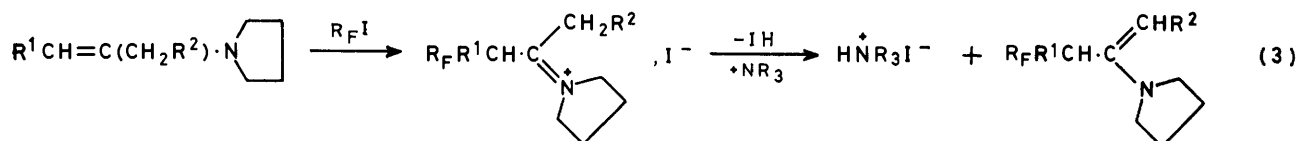
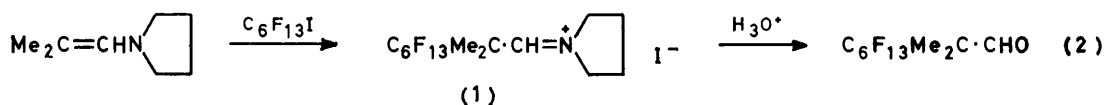
initiator. Photochemical and thermal reactions of carbon tetrachloride with enamines, giving  $\alpha$ -dichloromethylene ketones<sup>3</sup> or aldehydes,<sup>4</sup> have been reported. No precise mechanism for the radical reactions of enamines has been proposed. As suggested for the reaction of methylene iodide with enediamines,<sup>5</sup> it may reasonably be assumed that a radical cation (A) is formed; with perfluoroalkyl iodides a perfluoroalkyl radical  $R_F^\bullet$  is obtained which attacks the  $\beta$ -carbon atom to give the iminium iodide (B) (Scheme 1). However in view of the rapidity of the condensation it is more likely that the reaction proceeds through a conventional chain mechanism (Scheme 2). An experiment described

due to the presence of a charge-transfer complex between the amino-group of the enamine and  $R_F I$ , leading to easier formation of the radical cation (A) and thus of



$R_F^\bullet$ . Such complexes between amines and  $R_F I$  are well known.<sup>6</sup>

Favourable conditions for introducing an  $R_F$  group are specified; enamines in which R is alkyl or H react in high yield without u.v. irradiation or radical initiator



below extending the reaction to ynamines provides support for the chain mechanism.

Perfluoroalkyl iodides condense with enamines more readily than does carbon tetrachloride.<sup>3</sup> This may be

<sup>1</sup> D. Cantacuzène and R. Dorme, *Tetrahedron Letters*, 1975, 2031.

<sup>2</sup> (a) W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969; (b) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1953, 1199; (c) N. O. Brace, *J. Org. Chem.*, 1962, **27**, 3033; 1967, **32**, 430.

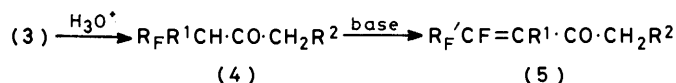
<sup>3</sup> J. Wolinsky and D. Chan, *Chem. Comm.*, 1966, 567.

<sup>4</sup> E. Elkik and P. Vaudescal, *Compt. rend.*, 1967, **264C**, 1779.

<sup>5</sup> C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, 1974, **39**, 918.

<sup>6</sup> (a) R. N. Haszeldine, *J. Chem. Soc.*, 1953, 2622; (b) N. F. Cheetham, I. J. McNaught, A. D. E. Pullin, *Austral. J. Chem.*, 1974, **27**, 987, 1009 and references herein.

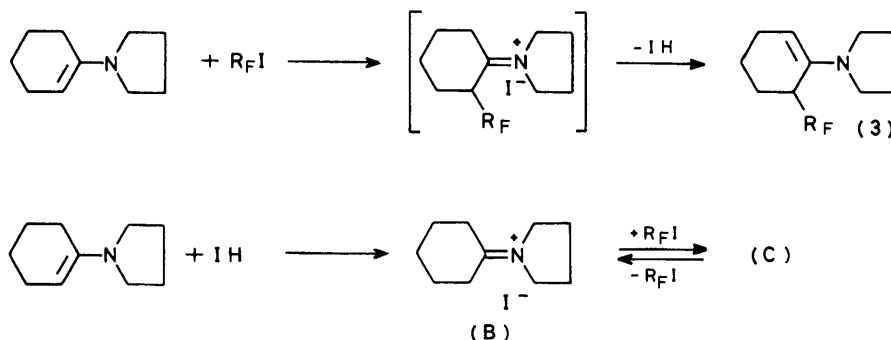
A new type of charge-transfer complex between an iminium iodide and a perfluoroalkyl iodide has been



|  |   |
|--|---|
| a; R <sup>1</sup> = R <sup>2</sup> = Me                            | R <sub>F</sub> = CF <sub>3</sub>                |
| b; R <sup>1</sup> R <sup>2</sup> = [CH <sub>2</sub> ] <sub>3</sub> | R <sub>F</sub> = CF <sub>3</sub>                |
| c; R <sup>1</sup> = R <sup>2</sup> = Me                            | R <sub>F</sub> = C <sub>2</sub> F <sub>5</sub>  |
| d; R <sup>1</sup> R <sup>2</sup> = [CH <sub>2</sub> ] <sub>3</sub> | R <sub>F</sub> = C <sub>2</sub> F <sub>5</sub>  |
| e; R <sup>1</sup> = R <sup>2</sup> = Me                            | R <sub>F</sub> = C <sub>3</sub> F <sub>7</sub>  |
| f; R <sup>1</sup> = R <sup>2</sup> = Me                            | R <sub>F</sub> = C <sub>6</sub> F <sub>13</sub> |
| g; R <sup>1</sup> R <sup>2</sup> = [CH <sub>2</sub> ] <sub>3</sub> | R <sub>F</sub> = C <sub>6</sub> F <sub>13</sub> |

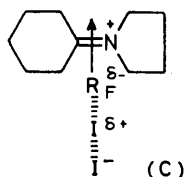
detected. Finally an extension of the above reaction to α-alkoxy-enamines, ynamines, and pyrroles is described.

*Enamines derived from Simple Ketones and Aldehydes;*



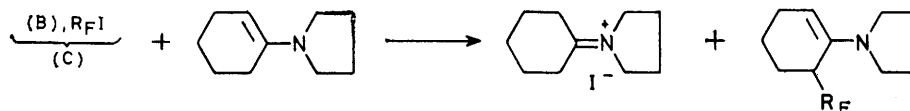
SCHEME 3

*Formation of a Charge-transfer Complex.*—2-Methylpropenylpyrrolidine reacts easily with perfluoroalkyl iodide. In this case the iminium iodide (1) is formed;



hydrolysis affords the α-perfluoroalkyl aldehyde (2) in 60% yield.

Enamines derived from simple enolizable ketones, in



pentane solution, condense rapidly with R<sub>F</sub>I at room temperature, without irradiation or initiator, affording perfluoroalkyl enamines (3a—g); the yields are much higher if an additional tertiary amine is used to trap HI. α-Perfluoroalkyl enamines (3) are hydrolysed, as expected, to α-perfluoroalkyl ketones (4) [the latter contain traces of αβ-unsaturated ketones (5)]. Yields

vary from 45 (CF<sub>3</sub>) to 65% (C<sub>6</sub>F<sub>13</sub>), providing that starting materials are freshly distilled under argon. Traces of oxygen or of a radical inhibitor such as diphenylpicrylhydrazyl slow the reaction and decrease the yields.

During the condensation of the starting enamine with R<sub>F</sub>I in an inert solvent (pentane) and providing that no additional amine is used to trap HI, an abundant precipitate (C) is rapidly formed which is not the iminium iodide of type (B) observed in the case of isobutyraldehyde. The analytical figures for (C) correspond to a stoichiometric mixture of enamine, HI, and R<sub>F</sub>I. Scheme 3 illustrates a typical experiment. The chemical characteristics of (C) are those of the product of a reversible association between one molecule of an iminium iodide (with no perfluoroalkyl group) and one molecule of R<sub>F</sub>I. Heated at 110 °C under vacuum,

(C) yields R<sub>F</sub>I (yield 70%) and the iminium iodide (B), whereas (B), synthesized independently, forms the complex (C) when in suspension in a pentane solution containing R<sub>F</sub>I. Hydrolysis of (C) produces a mixture of cyclohexanone and perfluoroalkyl iodide (yield 80%). The physicochemical data of (C) are in agreement with a charge-transfer complex. The u.v. spectrum displays absorption at 290 nm (*cf. ca.* 220 nm for an enamine or an iminium salt<sup>7</sup>), the position of which depends on the nature of the solvent and of the amino-group (see Experimental section). The n.m.r. spectrum of (C) shows no vinylic proton. The fluorine n.m.r. spectrum shows a signal at 66 p.p.m. (to high field of CFCl<sub>3</sub>) for

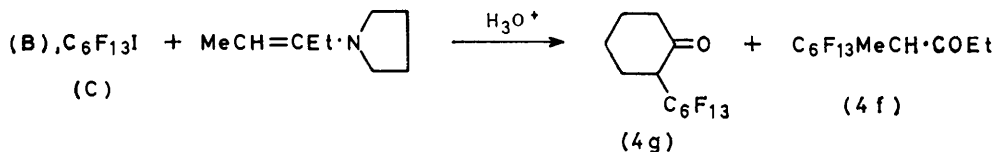
the CF<sub>2</sub>I group, whereas the corresponding signal of R<sub>F</sub>I appears at 59 p.p.m.

It has not been possible to determine the structure of (C) by X-ray crystallography because of the difficulty to obtain a suitable crystal. On the basis of the above experiments it is reasonable to assume a charge-transfer complex between an iminium iodide and R<sub>F</sub>I. The importance of the anion (iodide) and of the iminium structure are clearly demonstrated since neither the iminium perchlorate corresponding to (B) nor the

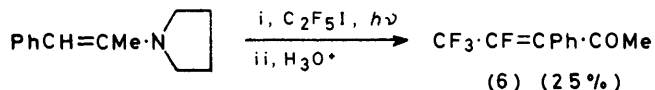
<sup>7</sup> (a) A. G. Cook, 'Enamines: Synthesis, Structure, and Reactions,' Dekker, New York, 1969; (b) G. Opitz, H. Hellman, and H. W. Schubert, *Annalen*, 1959, **623**, 117.

ammonium iodide  $\text{MeEt}_3\text{N}^+\text{I}^-$  show any sign of complexation with  $\text{R}_2\text{I}$ .

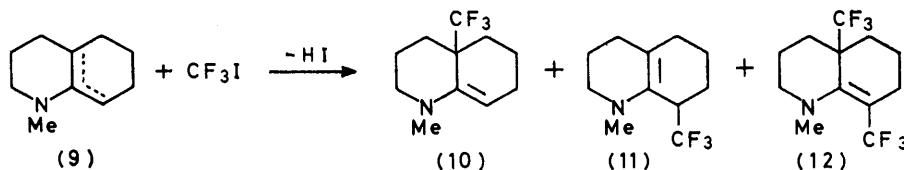
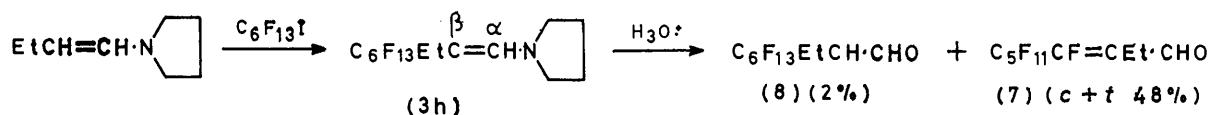
An excess of enamine decreases the yield of complex



(C), which disappears completely when a three-fold excess of enamine is used. Formation of (C) is shown to be reversible as follows. (i) If (C), in suspension in

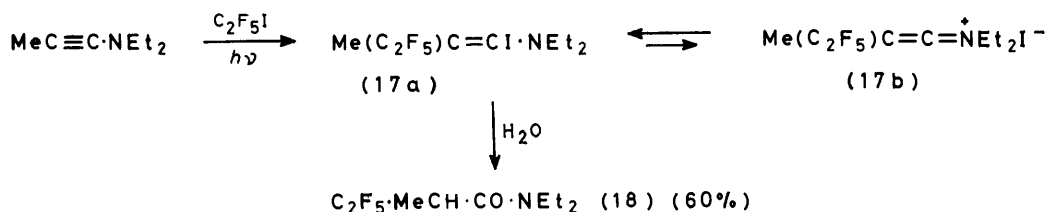
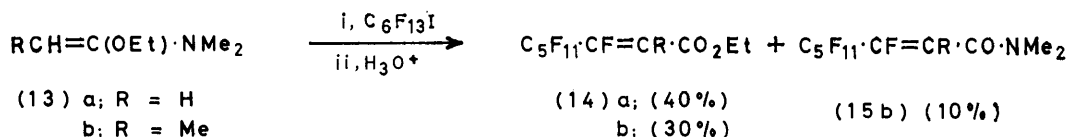


pentane, is mixed with the same enamine as used for its synthesis, it disappears giving the iminium iodide (B) and enamine (3). (ii) If (C) is mixed with an enamine



other than the one used for its formation, the two possible  $\alpha$ -perfluoroalkyl ketones are produced after hydrolysis.

*Extension of the Reaction to Other Unsaturated Nitrogen*



*Compounds.*—An attempted extension of the above reaction to deactivated enamines such as enamino-ketones ( $\text{R} = \text{COR}'$ ) or enamines bearing a  $\beta$ -phenyl substituent ( $\text{R} = \text{Ph}$ ) has met with only little success. Condensation of  $\alpha$ -methylstyrylpyrrolidine with perfluoroethyl iodide requires u.v. light, and hydrolysis yields only 25% of the unsaturated ketone (6).

(*N*-Methyltetrahydro-4-pyridyl)pyrrolidine reacts

with  $\text{C}_6\text{F}_{13}\text{I}$  without irradiation. However the yield of 2-perfluoroethyl-*N*-methyl-4-piperidone is only 20%.

Attempts to introduce a perfluoroalkyl chain into

3-dimethylaminopropanal have not been successful. Likewise conjugated dienamines give only small yields of condensation products.

U.v. irradiation is necessary to effect the reaction between but-1-enylpyrrolidine and perfluoroethyl iodide. Hydrolysis affords a *cis-trans*-mixture (7 : 9) of isomeric ketones (7) in 50% yield. Traces of the saturated aldehyde (8) were also isolated (2%). A difference in reactivity between 2-methylpropenylpyrrolidine and its straight-chain isomer in condensations with  $\text{CCl}_4$ <sup>3</sup> has

been reported. The proportion of the saturated aldehyde (8) can be increased to 15% if no amine is used during irradiation (the total yield is then only 33%). The intermediate enamine (3h) does not yield an enamino-

ketone after hydrolysis, such as observed with cyclic compounds<sup>8</sup> or when the  $\beta$ -carbon bears a hydrogen atom.<sup>9</sup>

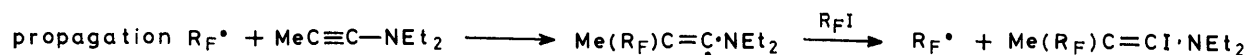
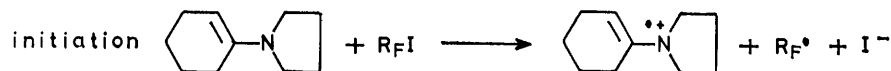
The heterocyclic amine (9) condenses easily with  $\text{CF}_3\text{I}$ . The reaction affords, as expected, a mixture of enamines (10) and (11) in the ratio 2 : 1, identified after reduction of the double bonds ( $\text{NaBH}_4$ ). The resulting amines were obtained in the same ratio. When  $\text{CF}_3\text{I}$

<sup>8</sup> J. C. Blazewski, D. Cantacuzène, and C. Wakselman, *Tetrahedron Letters*, 1974, 2055.

<sup>9</sup> M. Leblanc, G. Santini, and J. C. Riess, *Tetrahedron Letters*, 1975, 4151.

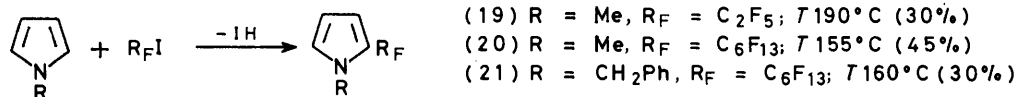
was used in excess, compound (12) was isolated; it was also reduced ( $\text{NaBH}_4$ ) for identification.

The  $\alpha$ -alkoxy-enamine (13a) reacts with  $\text{C}_6\text{F}_{13}\text{I}$  under irradiation: here also an amine was used to trap HI. After hydrolysis the  $\alpha\beta$ -unsaturated ester (14a) was obtained in 40% yield (without u.v. irradiation the yield



was only 7%). With compound (13b) the condensation was easily performed at room temperature without irradiation. Hydrolysis yielded a mixture of  $\alpha\beta$ -unsaturated ester and amide [(14b) and (15b), respectively<sup>10</sup>] in the ratio 3 : 1. Attempts to avoid loss of HF were not successful.

Condensation of the ynamine (16) with  $\text{C}_2\text{F}_5\text{I}$  under u.v. light for 2 h produced, after hydrolysis, the amide (18) in 60% yield. The thermally initiated addition of  $\text{CF}_3\text{I}$  to



*NN*-bistrifluoromethylethynylamine [ $(\text{CF}_3)_2\text{N-C}\equiv\text{CH}$ ] has been reported<sup>11</sup> (215 °C; 22 h;  $\text{CF}_3\text{I}$  in excess). Surprisingly, the intermediate (17) does not display the iminium structure (17b) as evidenced by n.m.r. spectroscopy. The enamine (17a) can even be distilled without alteration. In the case of ynamines the need of irradiation for the reaction to take place can be explained by the fact that the nitrogen lone pair is not available enough to give a charge-transfer complex and thus to induce rupture of the  $\text{R}_\text{F}\text{-I}$  bond. However, when a small amount of cyclohexenylpyrrolidine is added to the solution containing the ynamine and  $\text{R}_\text{F}\text{I}$ , the reaction proceeds and the amide (18) is obtained in 10% yield after hydrolysis. In this case the enamine has initiated the formation of the perfluoroalkyl radical, which then reacts with the electron-rich ynamine in a normal short chain reaction.

Of the two mechanisms suggested in the Introduction the chain mechanism (Scheme 2) appears more likely; indeed its existence has been proved in the case of ynamines. It has not been possible, however, to initiate the condensation of but-1-enylpyrrolidine with cyclohexenylpyrrolidine; therefore competition of the coupling of the two radicals  $\text{R}_\text{F}^\bullet$  and (A) (Scheme 1) with the

chain-mechanism in the cases where irradiation is necessary cannot be excluded.

In summary, two conditions are necessary for the reactions described here to take place without u.v. or radical initiator: the lone pair on the nitrogen must be available to give a charge-transfer complex, and the

double bond must be rich enough in electrons to add the  $\text{R}_\text{F}^\bullet$  radical.

The condensation of pyrroles with perfluoroalkyl iodides does not take place under the conditions described for the enamines. As with arene derivatives<sup>12</sup> or with pyridine,<sup>13</sup> condensation is achieved by heating the mixture. The reaction temperature depends on the perfluoroalkyl iodide used. Yields are 30–45%. As usually observed,<sup>14</sup> condensations with *N*-methylpyrrole

afford specific substitution at the 2-position. Products were identified by n.m.r. (250 MHz spectrometer). When heated at 160 °C with  $\text{C}_6\text{F}_{13}\text{I}$ , pyrrole only produces tar. We hoped to be able to protect the NH function with a benzyl group: in this case the expected *N*-benzyl-2-perfluoroalkylpyrrole (21) was obtained in 30% yield. However attempts to remove the benzyl group with sodium in liquid ammonia<sup>15</sup> or by catalytic reduction<sup>16</sup> were not successful.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were recorded with a Hitachi-Perkin-Elmer R24 spectrometer ( $\text{Me}_4\text{Si}$  as internal standard). <sup>19</sup>F N.m.r. spectra were run at 56.4 MHz with a JEOL 60 HL instrument (positive values to high field of internal  $\text{CFCl}_3$ ). Spectra at 250 MHz were obtained with a CAMECA instrument. I.r. spectra were measured with a Perkin-Elmer 457 spectrometer, and u.v. spectra with a Varian-Techtron 635 instrument. U.v. irradiation was performed with a high-pressure mercury lamp (TQ Hanau) in a silica vessel. Spinning-band distillations were carried out with a Nester Faust NFT 51 column.

Perfluoroalkyl iodides ( $\text{R}_\text{F} = \text{C}_2\text{F}_5$ ,  $\text{C}_6\text{F}_{13}$ , or  $\text{C}_8\text{F}_{17}$ ) were a gift from PCUK.  $\text{CF}_3\text{I}$  and  $\text{C}_3\text{F}_7\text{I}$  are commercial products (PCR, U.S.A.). All unsaturated amines were carefully distilled under nitrogen before use.

$\alpha$ -Perfluoroalkyl Ketones and Aldehydes.—Procedure A:

<sup>10</sup> P. Deslongchamps, S. Dubé, C. Lebreux, D. Patterson, and R. Taillefer, *Canad. J. Chem.*, 1975, **53**, 2791.

<sup>11</sup> J. Freear and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 1096.

<sup>12</sup> M. Birchall, G. Irvin, and R. A. Boysson, *J.C.S. Perkin II*, 1975, 435.

<sup>13</sup> (a) L. M. Yagupolski, A. G. Galushko, and M. A. Rzhavinskaya, *Zhur. obshchei Khim.*, 1968, **38**, 668 (*Chem. Abs.*, 1968, **69**, 59064b); (b) L. M. Yagupolski, A. G. Galusko, and V. I. Troitskaya, *ibid.*, p. 1736 (*Chem. Abs.*, 1969, **70**, 5213b).

<sup>14</sup> (a) H. J. Anderson and H. Nagy, *Canad. J. Chem.*, 1972, 1961; (b) T. S. Croft and J. J. Brady, *J. Heterocyclic Chem.*, 1975, 845.

<sup>15</sup> M. Julia, P. Manoury, and I. Igolen, *Compt. rend.*, 1960, **251**, 394.

<sup>16</sup> J. S. Buck and R. Baltzgly, *J. Amer. Chem. Soc.*, 1941, **63**, 1964.

2-(perfluoroethyl)cyclohexanone (4d). *N*-Cyclohex-1-enylpyrrolidine (9 g, 0.06 mol) was dissolved in pentane (150 ml) with *N*-ethyl-di-isopropylamine (EDPA) (7.8 g, 0.06 mol). Perfluoroethyl iodide (7.4 g, 0.03 mol) was added to the solution. A solid CO<sub>2</sub>-acetone condenser was used to avoid evaporation of the iodide. A precipitate of EDPA hydroiodide was formed instantaneously. After 3 h the precipitate was filtered off and the solution evaporated. [If the enamine (3d) is distilled, loss of HF is observed.] The crude liquid was hydrolysed with 40% H<sub>2</sub>SO<sub>4</sub> (6 ml: the minimum quantity to give an acidic medium). The mixture is stirred for 3 h and extracted with ether. The ether layer was neutralized with aqueous sodium hydrogen carbonate, washed with water, and dried (MgSO<sub>4</sub>). Distillation of the crude liquid afforded a mixture (3.4 g) shown by <sup>19</sup>F n.m.r. to consist of 2-(perfluoroethyl)cyclohexanone (4d) and the corresponding unsaturated ketone (5d) in the ratio 93 : 7. The ketone (4d) was purified by spinning-band distillation; b.p. 90—92° at 20 mmHg (3.1 g, 48%);  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 738 cm<sup>-1</sup>; <sup>19</sup>F n.m.r. (CDCl<sub>3</sub>) 83.3 (s) and 118.7 p.p.m. (*J*<sub>FF</sub> 276.7, *J*<sub>HF</sub> 15.2 Hz) (Found: C, 44.4; H, 4.2; F, 44.15). C<sub>8</sub>H<sub>9</sub>F<sub>5</sub>O requires C, 44.45; H, 4.2; F, 43.95%.

*Procedure B: 2-(perfluorohexyl)butyraldehyde (8).* (a) *N*-But-1-enylpyrrolidine (5 g, 0.04 mol) was dissolved in pentane (250 ml) containing EDPA (5.2 g, 0.04 mol). Perfluorohexyl iodide (9 g, 0.02 mol) was added. Irradiation was carried out at 0—10 °C for 3 h. The precipitate of EDPA hydroiodide was filtered off and the solution evaporated. Hydrolysis of the liquid with 40% H<sub>2</sub>SO<sub>4</sub> (5 ml) and work-up as above produced after distillation (b.p. 30—35° at 0.5 mmHg) 3.9 g (48%) of a mixture shown by <sup>1</sup>H n.m.r. to consist of the isomeric aldehydes (7) and traces (2%) of the saturated aldehyde (8). The aldehydes (7) and (8) were purified by g.l.c. on FFAP; 2-ethylperfluoro-oct-2-enal (7) (*c:t* 35:45) showed  $\nu_{\max}$  (CCl<sub>4</sub>) 1 658—1 690 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.93 (t), 7.55 (m), 0.1, and -0.1; <sup>19</sup>F n.m.r. 81 p.p.m. (CF<sub>3</sub>) (Found: C, 32.35; H, 1.55; F, 61.0). C<sub>10</sub>H<sub>8</sub>F<sub>12</sub>O requires C, 32.45; H, 1.65; F, 61.6%. 2-(Perfluorohexyl)butyraldehyde (8) had  $\nu_{\max}$  (CCl<sub>4</sub>) 1 728—1 735 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 9.00 (t), 8.08 (q), 7.1, and 0.48 (m); <sup>19</sup>F n.m.r. 80.5 p.p.m. (CF<sub>3</sub>) (Found: C, 30.8; H, 1.75; F, 63.2). C<sub>10</sub>H<sub>7</sub>F<sub>13</sub>O requires C, 30.8; H, 1.8; F, 63.1%.

(b) Irradiation at 0—10 °C of *N*-but-1-enylpyrrolidine (0.04 mol), in pentane (250 ml), with perfluorohexyl iodide (0.02 mol) produced after the usual work-up and distillation (b.p. 30—35° at 0.5 mmHg) a mixture shown by <sup>1</sup>H n.m.r. to consist of the aldehydes (7) and (8) in the ratio 60 : 40 (2.6 g; total yield 33%).

2-Trifluoromethylpentan-3-one (4a). Condensations with trifluoromethyl iodide do not require the use of a tertiary amine. The best yields are obtained when a two-fold excess of enamine is used. Thus *N*-(1-ethylprop-1-enyl)pyrrolidine (8.4 g, 0.06 mol) and trifluoromethyl iodide (6 g, 0.03 mol) were dissolved in pentane (150 ml). Procedure A was followed. Distillation (spinning-band column) yielded 2-trifluoromethylpentan-3-one (2 g, 45%), b.p. 68—70° at 134 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 735 cm<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 8.95 (t), 8.69 (d), 7.42 (q), and 6.62 (m); <sup>19</sup>F n.m.r. 69.5 p.p.m. (*J*<sub>HF</sub> 8.5 Hz) (Found: C, 46.8; H, 5.8; F, 36.35). C<sub>6</sub>H<sub>9</sub>F<sub>3</sub>O requires C, 46.75; H, 5.9; F, 36.95%.

2-Trifluoromethylcyclohexanone (4b). The same procedure as for (4a) gave 2-trifluoromethylcyclohexanone, purified from cyclohexanone by spinning-band distillation (yield 45%); b.p. 90—92° at 30 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 735 cm<sup>-1</sup>; <sup>19</sup>F

n.m.r. 69.5 p.p.m. (*J*<sub>HF</sub> 8.2 Hz) (Found: C, 50.6; H, 5.4; F, 34.0). C<sub>7</sub>H<sub>9</sub>F<sub>3</sub>O requires C, 50.6; H, 5.45; F, 34.3%.

The intermediate enamine, *N*-(6-trifluoromethylcyclohex-1-enyl)pyrrolidine (3b), can be distilled without loss of HF but cannot be separated from *N*-cyclohex-1-enylpyrrolidine; (3b) is obtained pure by the TiCl<sub>4</sub> method of Weingarten;<sup>17</sup> condensation is carried out at room temperature; b.p. 85—90° at 30 mmHg;  $\nu_{\max}$  (liquid) 1 645 cm<sup>-1</sup> (C=C str.);  $\tau$  (CDCl<sub>3</sub>) 5.37 (C=CH); <sup>19</sup>F n.m.r. 68 p.p.m. (CF<sub>3</sub>, d, *J* 7.9 Hz).

2-Perfluoroethylpentan-3-one (4c). Procedure A: a first distillation yielded a mixture shown by <sup>19</sup>F n.m.r. to consist of 2-perfluoroethylpentan-3-one (4c) and the corresponding unsaturated ketone (5c) in the ratio 95 : 5. The ketone (4c) was purified by spinning-band distillation (yield 48%); b.p. 53—55° at 55 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 735 cm<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 8.95 (t), 8.69 (d), 7.44 (q), and 6.62 (m); <sup>19</sup>F n.m.r. 83.7 (s) and 119.5 p.p.m. (*J*<sub>FF</sub> 279, *J*<sub>HF</sub> 19.4—10.2 Hz) (Found: C, 44.5; H, 4.0; F, 43.8). C<sub>8</sub>H<sub>9</sub>F<sub>5</sub>O requires C, 44.45; H, 4.2; F, 43.95%.

2-Perfluoropropylpentan-3-one (4e). Procedure A: distillation of the products obtained after hydrolysis yielded a mixture shown by <sup>19</sup>F n.m.r. to consist of 2-perfluoropropylpentan-3-one (4e) and the corresponding unsaturated ketone (5e) (15%). The ketone (4e) was purified by spinning-band distillation (yield 43%); b.p. 76—78° at 80 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 735 cm<sup>-1</sup>;  $\tau$  (CCl<sub>4</sub>) 8.93 (t), 8.63 (d), 7.6 (q), and 6.6 (m); <sup>19</sup>F n.m.r. 81.5 (t, *J*<sub>FF</sub> 9.8 Hz), 114 (m), and 124 p.p.m. (m) (Found: C, 37.8; H, 3.5; F, 52.0). C<sub>9</sub>H<sub>9</sub>F<sub>7</sub>O requires C, 37.8; H, 3.55; F, 52.3%.

2-(Perfluorohexyl)pentan-3-one (4f). Distillation of the products obtained after hydrolysis (procedure A) gave a mixture shown by <sup>1</sup>H n.m.r. to consist of 2-(perfluorohexyl)pentan-3-one (4f) and the unsaturated ketone (5f) in the ratio 93 : 7. The ketone (4f) was purified by spinning band distillation (yield 63%); b.p. 86—87° at 18 mmHg;  $\nu_{\max}$  1 720—1 735 cm<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 8.95 (t), 8.68 (d), 7.42 (q), and 6.62 (m); <sup>19</sup>F n.m.r. 81.6 (CF<sub>3</sub>), 115.2, 121.2, 123.3, and 126.6 p.p.m. (CF<sub>2</sub>) (Found: C, 32.65; H, 2.3; F, 61.0). C<sub>11</sub>H<sub>9</sub>F<sub>13</sub>O requires C, 32.7; H, 2.25; F, 61.1%.

2-(Perfluorohexyl)cyclohexanone (4g). Procedure A: because of the complexity of the n.m.r. signals, it is not possible to give a value for the percentage of the unsaturated ketone (5g), which was characterized by its i.r. C=C band at 1 680 cm<sup>-1</sup>. 2-(Perfluorohexyl)cyclohexanone (4g) was purified by spinning-band distillation (yield 63%); b.p. 71—73° at 0.4 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 735 cm<sup>-1</sup>; <sup>19</sup>F n.m.r. (CCl<sub>4</sub>) 80.4 (CF<sub>3</sub>), 111.6, 118.2, 120.7, and 124.9 p.p.m. (CF<sub>2</sub>) (Found: C, 34.6; H, 2.35; F, 59.1). C<sub>12</sub>H<sub>9</sub>F<sub>13</sub>O requires C, 34.65; H, 2.2; F, 59.35%.

1-Methyl-3-(perfluorohexyl)-4-piperidone. Procedure A: a first distillation of the crude liquid yielded a mixture of 1-methyl-3-perfluorohexyl-4-piperidone and the corresponding unsaturated ketone (characterized by its i.r. C=C band at 1 680 cm<sup>-1</sup>) (total yield 20%). However it was not possible to purify the saturated ketone which decomposed during spinning-band distillation; the mixture had b.p. 85—90° at 1 mmHg;  $\nu_{\max}$  (CCl<sub>4</sub>) 1 725—1 680 cm<sup>-1</sup>; <sup>19</sup>F n.m.r. (CCl<sub>4</sub>) 81 (CF<sub>3</sub>), 114, 119, and 123 p.p.m. (CF<sub>2</sub>).

2-Dimethylperfluoro-octanal (2). Condensation of perfluorohexyl iodide with *N*-(2-methylprop-1-enyl)pyrrolidine does not require the use of a tertiary amine. A two-fold excess of enamine is used. Thus the enamine (7.5 g,

<sup>17</sup> W. A. White and H. Weingarten, *J. Org. Chem.*, 1967, **32**, 213.

0.06 mol) and perfluorohexyl iodide (13.4 g, 0.03 mol) were dissolved in pentane (150 ml). A precipitate appeared. After 3 h pentane was evaporated off. The remaining solid-liquid mixture was shown by  $^1\text{H}$  n.m.r. to consist of the iminium iodide (1),  $\tau$  ( $\text{CDCl}_3$ ) 0.25 ( $\text{CH}=\text{N}$ ) and 6.6 ( $\text{N}\cdot\text{CH}_2$ );  $^{19}\text{F}$  n.m.r. 81 p.p.m. ( $\text{CF}_3$ ); which is air sensitive. The mixture was hydrolysed and after usual work-up and distillation gave the aldehyde (2) (7 g, 60%); b.p. 65–67° at 15 mmHg;  $\nu_{\text{max}}$  2700–1715  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 8.67 and 0.5;  $^{19}\text{F}$  n.m.r. 80.1 ( $\text{CF}_3$ ), 117, 119, 122.8, and 126.6 p.p.m. ( $\text{CF}_2$ ) (Found: C, 30.9; H, 1.7; F, 63.15.  $\text{C}_{10}\text{H}_7\text{F}_{13}\text{O}$  requires C, 30.8; H, 1.75; F, 63.2%).

**4,5,5,5-Tetrafluoro-3-phenylpent-3-en-2-one** (6).—*N*-( $\alpha$ -Methylstyryl)pyrrolidine (11.2 g, 0.06 mol) was mixed with pentafluoroethyl iodide (7.4 g, 0.03 mol) and EDPA (7.8 g, 0.06 mol) in pentane (250 ml). Procedure B was followed. After the usual work-up, and spinning-band distillation, the pentenone (6) was obtained (1.7 g, 25%); b.p. 90–91° at 20 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1722–1700  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 7.7 (d,  $J$  2 Hz);  $^{19}\text{F}$  n.m.r. 53.5 (d,  $J_{\text{FF}}$  9.15 Hz) and 100 p.p.m. (m) (Found: C, 56.5; H, 3.7; F, 32.25.  $\text{C}_{11}\text{H}_9\text{O}$  requires C, 56.9; H, 3.45; F, 32.75%).

**Unsaturated Ketones** (5).—The ketone (4) (0.015 mol) was stirred with aqueous 15% sodium hydroxide (2 ml) [2.5 h for (4c, d, and f)] or with aqueous 40% sodium hydroxide [0.5 h for (4e)]. Completion of the reaction was determined by n.m.r. so as not to leave the ketone (4) too long in the basic medium. The aqueous phase was then extracted with ether; the ether layer was neutralised with 10% hydrochloric acid, washed with water, and dried ( $\text{MgSO}_4$ ). The ketones (5) were purified by spinning-band distillation (yield 60%). **2-(Perfluoroethylidene)pentan-3-one** (5c) had b.p. 40° at 40 mmHg;  $\nu_{\text{max}}$  1725–1700–1675  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (cyclohexane) 216 nm ( $\epsilon$  6030);  $\tau$  ( $\text{CCl}_4$ ) 8.9 (t), 8.07 (q,  $J$  2.3 Hz), and 7.34;  $^{19}\text{F}$  n.m.r. 68.4 (d of d,  $J$  7 and 2.5 Hz) and 122 p.p.m. (only one isomer) (Found: C, 45.25; H, 4.2; F, 40.8.  $\text{C}_8\text{H}_8\text{F}_4\text{O}$  requires C, 45.65; H, 4.4; F, 41.25%). **2-(Perfluoroethylidene)cyclohexanone** (5d) (*c* + *t*) had b.p. 60° at 15 mmHg;  $\nu_{\text{max}}$  1725–1700–1680  $\text{cm}^{-1}$ ;  $^{19}\text{F}$  n.m.r. ( $\text{CDCl}_3$ ) 67.4–68.7 ( $\text{CF}_3$ ,  $J_{\text{FF}}$  6.3 and 8.5,  $J_{\text{FH}}$  0.7 Hz), 125.3, and 129.9 p.p.m. (CF) (Found: C, 48.95; H, 4.19; F, 38.45.  $\text{C}_8\text{H}_8\text{F}_4\text{O}$  requires C, 49.0; H, 4.1; F, 38.75%). **2-(Perfluoropropylidene)pentan-3-one** (5e) had b.p. 35° at 30 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1722–1700–1670  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (cyclohexane) 218 nm ( $\epsilon$  6072);  $\tau$  ( $\text{CCl}_4$ ) 8.9 (t), 8.09 (q,  $J$  2.3 Hz), and 7.3 (m);  $^{19}\text{F}$  n.m.r. 83 and 84 (d of t,  $J_1$  2.3,  $J_2$  8.5;  $J'_1$  2.3,  $J'_2$  7 Hz), 116 (m), and 117 p.p.m. (two isomers in 90:10 ratio) (Found: C, 41.25; H, 3.4; F, 47.85.  $\text{C}_8\text{H}_8\text{F}_6\text{O}$  requires C, 41.05; H, 3.45; F, 48.7%). **2-(Perfluorohexylidene)pentan-3-one** (5f) had b.p. 77–80° at 30 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1722–1700–1670  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (cyclohexane) 218 nm ( $\epsilon$  6100);  $\tau$  ( $\text{CCl}_4$ ) 8.9 (t), 8.1 (q,  $J$  2.3 Hz), and 2.66;  $^{19}\text{F}$  n.m.r. 81.5 p.p.m. ( $\text{CF}_3$ ) (Found: C, 36.1; H, 2.25; F, 61.45.  $\text{C}_{11}\text{H}_8\text{F}_{12}\text{O}$  requires C, 35.9; H, 2.2; F, 61.9%).

**Heterocyclic Enamines** (10)–(12).—(a) A mixture of  $\Delta^{4a(8a)}$ - and  $\Delta^8$ -1-methyloctahydroquinoline (9)<sup>18</sup> (3.4 g, 0.02 mol) was added to a solution of trifluoromethyl iodide (4 g, 0.02 mol) in pentane (150 ml). After 3 h the precipitate was filtered off and pentane was removed under reduced pressure. A first distillation yielded a mixture (3 g) shown by g.l.c. to consist of unchanged enamine (9) (50%), 35% of (10), and 15% of (11). 1-Methyl-4a-trifluoromethyl- $\Delta^8$ -octahydroquinoline (10) was purified by

t.l.c. on silica gel 60 FP (benzene as eluant);  $\nu_{\text{max}}$  (liquid) 1643  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CDCl}_3$ ) 7.6 and 5.2 ( $\text{C}=\text{CH}$ );  $^{19}\text{F}$  n.m.r. 67.1 p.p.m. (s);  $m/e$  219 ( $M^+$ ), 204, 190, and 189. Compound (11) displays a  $^{19}\text{F}$  n.m.r. signal at 66.3 p.p.m. (d,  $J$  8.5 Hz); it was not purified.

(b) The distilled mixture (3 g) was introduced into a flask with tetrahydrofuran (250 ml) and sodium borohydride (3 g). Glacial acetic acid (75 ml) was added dropwise. The mixture was refluxed for 2 h. Tetrahydrofuran was removed under reduced pressure, and the residual liquid was neutralized with 10% sodium hydroxide and extracted with ether; the ether layer was washed with water, dried ( $\text{MgSO}_4$ ), and evaporated. Distillation of the crude product (2.9 g) (b.p. 68–75° at 1 mmHg) gave a mixture (2.7 g) shown by g.l.c. to consist of 1-methyldecahydroquinoline (50%), 1-methyl-4a-trifluoromethyldecahydroquinoline (35%), and 1-methyl-8-trifluoromethyl decahydroquinoline (15%). The 4a-trifluoromethyl derivative was purified by preparative g.l.c. on an SE 30 column (yield 0.7 g, 15%);  $\tau$  ( $\text{CDCl}_3$ ) 7.82 ( $\text{N}\cdot\text{CH}_3$ );  $^{19}\text{F}$  n.m.r. 58.8 p.p.m. (s) (Found: C, 60.1; H, 8.35; F, 25.15.  $\text{C}_{11}\text{H}_{18}\text{F}_3\text{N}$  requires C, 59.7; H, 8.2; F, 25.75%). It was not possible to purify the 8-trifluoromethyl derivative by g.l.c.: 10% of the 4a-isomer is always present. The  $^{19}\text{F}$  n.m.r. spectrum of the former displays a signal at 64.6 p.p.m. (d,  $J$  9.5 Hz). Its analytical figures (with 10% of the 4a-isomer) are correct (Found: C, 59.1; H, 8.55; F, 24.75%).

(c) The enamine (9) (5.5 g, 0.036 mol) was dissolved in pentane with an excess of trifluoromethyl iodide (9 g, 0.046 mol). Usual work-up and distillation afforded a mixture (6 g) shown by g.l.c. and  $^{19}\text{F}$  n.m.r. to consist of the enamines (9)–(12); ratio (10):(11):(12) 6:2:1. The  $^{19}\text{F}$  n.m.r. spectrum of 1-methyl-4a,8-bistrifluoromethyl- $\Delta^8$ -octahydroquinoline (12) displays signals at 62.5 and 68.4 p.p.m. Compound (12) was identified after reduction of the distilled mixture (6 g) by sodium borohydride as above. 1-Methyl-4a,8-bistrifluoromethyldecahydroquinoline was purified by g.l.c. on an SE 30 column (yield 0.3 g);  $\tau$  ( $\text{CDCl}_3$ ) 7.72 ( $\text{N}\cdot\text{CH}_3$ );  $^{19}\text{F}$  n.m.r. 60.4 (quint.,  $J_{\text{HF}} = J_{\text{FF}} = 11$  Hz) and 61.7 p.p.m. (q,  $J_{\text{FF}} = 11$  Hz). Identification was performed after fluorine spin-spin decoupling (Found: C, 50.15; H, 5.85; F, 38.85.  $\text{C}_{12}\text{H}_{17}\text{F}_6\text{N}$  requires C, 49.8; H, 5.95; F, 39.4%).

**$\alpha$ -Alkoxy-enamines.**—(a) Procedure B: from 1-ethoxy-*NN*-dimethylvinylamine (13a) (2.3 g, 0.02 mol), perfluorohexyl iodide (4.5 g, 0.01 mol), and EDPA (2.6 g, 0.02 mol), ethyl 2H-dodecafluoro-oct-2-enoate (14a) (1.5 g, 40%) was obtained after distillation; b.p. 73–75° at 18 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1702–1740–1750  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 4.1 ( $J_{\text{HF}} = 30$  Hz), 5.75 (q), and 8.7 (t);  $^{19}\text{F}$  n.m.r. 81 p.p.m. ( $\text{CF}_3$ ) (Found: C, 31.25; H, 1.55; F, 58.75.  $\text{C}_{10}\text{H}_6\text{F}_{12}\text{O}_2$  requires C, 31.1; H, 1.55; F, 59.05%).

(b) Procedure A: from 1-ethoxy-*NN*-dimethylprop-1-enylamine (13b)<sup>19</sup> (7.8 g, 0.06 mol), perfluorohexyl iodide (13.5 g, 0.03 mol), and EDPA (7.8 g, 0.06 mol), 3.6 g (30%) of ethyl dodecafluoro-2-methyloct-2-enoate (14b) (3.6 g, 30%) and dodecafluoro-2,NN-trimethyloct-2-enamide (15b) (1.2 g, 10%) were obtained after the usual work-up and distillation: (14b), b.p. 53–55° at 2 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1725  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 5.73 (q), 8.0 (m), and 8.7 (t);  $^{19}\text{F}$  n.m.r. 82.5 p.p.m. ( $\text{CF}_3$ ) (Found: C, 32.85; H, 2.15; F, 56.35.  $\text{C}_{11}\text{H}_8\text{F}_{12}\text{O}_2$  requires C, 33.0; H, 2.0; F, 56.9%); (15b), b.p. 70–72° at 2 mmHg;  $\nu_{\text{max}}$  1662  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 7.92 (m)

<sup>19</sup> H. Bredereck, F. Eggenberger, and H. P. Beyerlin, *Chem. Ber.*, 1964, **97**, 3081.

<sup>18</sup> D. A. Evans, *J. Amer. Chem. Soc.*, 1970, **92**, 7593.

and 7 (m);  $^{19}\text{F}$  n.m.r. 82 p.p.m. ( $\text{CF}_3$ ) (Found: C, 33.25; H, 2.25; F, 56.75.  $\text{C}_{11}\text{H}_9\text{F}_{12}\text{NO}$  requires C, 33.1; H, 2.25; F, 57.1%).

**Ynamine.**—(a) 1-Diethylaminopropyne (16) (4.8 g, 0.04 mol) was dissolved in pentane (250 ml) with perfluoroethyl iodide (10 g, 0.04 mol). Irradiation was carried out for 3 h. A small amount of viscous precipitate was removed and the solution was evaporated. The remaining liquid 1-diethylaminopentafluoro-1-iodo-2-methylbut-1-ene (17a) (13 g) showed  $\tau$  8.15 (s,  $\text{CH}_3$ ), 0.02 (t), and 7.9 (m) (NET);  $^{19}\text{F}$  n.m.r. 83.3 (s) and 110 (s) p.p.m. The chemical shift for  $\text{N}\cdot\text{CH}_2$  is as expected: no trace of an iminium structure was detected. Compound (17a) can be distilled (b.p. 95–100° at 15 mmHg); the product (11 g) displayed the same n.m.r. spectra as above, with an extra  $\text{N}\cdot\text{CH}_2$  signal at  $\delta$  7.28 (m) (10%); this chemical shift does not correspond to an iminium structure. The crude mixture (13 g) was cooled (ice-bath) and hydrolysed with 15% sulphuric acid; the aqueous phase was extracted with ether. The ether layers were washed with sodium hydrogen sulphite solution, neutralized with sodium hydrogen carbonate, then washed with water, dried ( $\text{MgSO}_4$ ), and evaporated. Distillation gave NN-diethyl-2H-pentafluoro-2-methylbutyramide (18) (6 g, 60%), b.p. 110° at 15 mmHg;  $\nu_{\text{max}}$  ( $\text{CCl}_4$ ) 1 655br  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 8.72 (d of t), 8.6 (d), and 6.7 (m);  $^{19}\text{F}$  n.m.r. 83.4 (s,  $\text{CF}_3$ ) and 119 p.p.m. ( $\text{CF}_2$ ,  $J_{\text{HF}}$  4.9 Hz) (Found: C, 43.6; H, 5.6; F, 38.05.  $\text{C}_9\text{H}_{14}\text{F}_5\text{NO}$  requires C, 43.75; H, 5.7; F, 38.45%).

When the ynamine and perfluoroethyl iodide were mixed in pentane and left without irradiation, an abundant viscous product was formed but no condensation to give (17) appeared to occur.

(b) 1-Diethylaminopropyne (6 g, 0.06 mol) was mixed with perfluoroethyl iodide (8 g, 0.03 mol) in pentane solution. *N*-(Cyclohex-1-enyl)pyrrolidine (40 mg) was added. Formation of compound (17) was determined by  $^{19}\text{F}$  n.m.r. analysis; a viscous product also appeared which did not contain the expected (17). After 1.5 h the solution was evaporated and the products were hydrolysed as above. Distillation gave a mixture (0.7 g, 10%) of the amide (18) and the corresponding  $\alpha\beta$ -unsaturated amide. A parallel experiment was carried out without added enamine: in this case no (17) appeared in the solution; only the viscous product was formed.

**Pyrroles.**—1-Methyl-2-perfluoroethylpyrrole (19). *N*-Methylpyrrole (2.5 g, 0.03 mol) was introduced with perfluoroethyl iodide (4 g, 0.015 mol) and EDPA (3.9 g, 0.03 mol) into an autoclave. The mixture was heated at 190 °C for 3 h. Cooling, filtration, and column chromatography of the remaining liquid on silica gel 60 (pentane as an eluant) gave 1-methyl-2-perfluoroethylpyrrole (19) in the first fraction (0.9 g, 30%);  $\tau$  ( $\text{CCl}_4$ ) (250 MHz) 6.28 ( $\text{CH}_3$ ), and 3.4, 3.56, and 3.99 (1 H) ( $J_1$  3.75,  $J_2$  2.25,  $J_3$  1.25 Hz);  $^{19}\text{F}$  n.m.r. 83.4 (t,  $J$  2.8 Hz) and 106 p.p.m. (Found: C, 42.55; H, 3.1; F, 47.35.  $\text{C}_7\text{H}_6\text{F}_5\text{N}$  requires C, 42.2; H, 3.05; F, 47.7%).

1-Methyl-2-perfluorohexylpyrrole (20). The same procedure as above was used: the mixture was heated at

155 °C. *N*-Methylpyrrole (2.5 g), perfluorohexyl iodide (6.7 g), and EDPA (3.9 g) gave the 2-perfluorohexylpyrrole (20) (2.7 g, 45%); b.p. 50–53° at 0.5 mmHg;  $\tau$  ( $\text{CCl}_4$ ) (250 MHz) 6.32 ( $\text{CH}_3$ ), and 3.3, 3.45, and 3.9 (1 H) ( $J_1$  3.75,  $J_2$  2.25,  $J_3$  1.3 Hz);  $^{19}\text{F}$  n.m.r. 80.5 p.p.m. ( $\text{CF}_3$ ) (Found: C, 32.85; H, 1.7; F, 61.65.  $\text{C}_{11}\text{H}_8\text{F}_{13}\text{N}$  requires C, 33.1; H, 1.5; F, 61.9%).

*N*-Benzyl-2-perfluorohexylpyrrole (21). A mixture of *N*-benzylpyrrole (3.2 g, 0.02 mol), perfluorohexyl iodide (4.5 g, 0.01 mol), and EDPA (2.6 g, 0.02 mol) was heated at 155 °C for 3 h. The usual work-up gave the 2-perfluorohexylpyrrole (21) (1.4 g); m.p. 36–38°;  $\tau$  ( $\text{CCl}_4$ ) 4.95 ( $\text{CH}_2\text{Ph}$ ), and 3, 3.45, and 3.9;  $^{19}\text{F}$  n.m.r. 82.2 p.p.m. ( $\text{CF}_3$ ) (Found: C, 42.6; H, 2.25; F, 51.1.  $\text{C}_{17}\text{H}_{10}\text{F}_{13}\text{N}$  requires C, 42.95; H, 2.1; F, 51.95%).

**Charge-transfer Complex between the Iminium Iodide (B) and Perfluoro-octyl Iodide.**—**Formation.** *N*-(Cyclohex-1-enyl)pyrrolidine (4.5 g, 0.03 mol) was dissolved in pentane (150 ml) with perfluoro-octyl iodide (16.9 g, 0.03 mol). After 2 h the precipitate was carefully filtered off under argon and dried at atmospheric pressure in a desiccator filled with argon and containing  $\text{P}_2\text{O}_5$  to give 9.5 g of solid complex;  $\lambda_{\text{max}}$  (dioxan) 292 nm,  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 286 nm (Found: C, 26.3; H, 2.2; F, 38.55; I, 29.95; N, 1.55.  $\text{C}_{18}\text{H}_{18}\text{F}_{17}\text{I}_2$  requires C, 26.2; H, 2.2; F, 39.15; I, 30.7; N, 1.7%). The complex obtained from cyclohexenylmorpholine displays u.v. absorption at 268 nm (dioxan).

**Stability.** Heated at 110 °C and 15 mmHg, the precipitate (9.5 g) decomposed to give perfluoro-octyl iodide (4.2 g). Hydrolysis of the remaining iminium iodide (B) in basic medium yielded cyclohexanone (0.9 g) and perfluoro-octyl iodide (0.8 g). Hydrolysis of the precipitate (9.5 g) in an acidic medium gives perfluoro-octyl iodide (5 g) (from an extraction in acidic medium) and cyclohexanone (0.9 g) (from an extraction in basic medium).

**Exchange.** *N*-(Cyclohex-1-enyl)pyrrolidine (4.5 g, 0.03 mol) was dissolved in pentane (150 ml) with perfluorohexyl iodide (13 g, 0.03 mol). The precipitate was filtered off after 2 h, dried as above [6.8 g of (C) were obtained], and introduced into a pentane solution containing *N*-(1-ethyl-prop-1-enyl)pyrrolidine (2 g). After 4 h the precipitate was filtered off and the solution evaporated. The liquid obtained was hydrolysed as usual. Distillation gave two ketones: b.p. 55 °C at 15 mmHg, 0.4 g [ketone (4f)]; b.p. 80 °C at 15 mmHg, 0.9 g [ketone (4g)].

**Independent synthesis.** The iminium iodide (B) was synthesized by addition of a solution of hydrogen iodide in pentane to *N*-(cyclohex-1-enyl)pyrrolidine in the same solvent. The iminium salt (5.6 g, 0.02 mol) was washed several times with pentane and finally added to a solution of perfluoro-2-octyl iodide (12.5 g, 0.023 mol) in pentane. After 3 h the new precipitate was filtered off: its  $^{19}\text{F}$  n.m.r. spectrum displayed the same signals as (C) and its u.v. spectrum showed the same absorption maximum.

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