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THE REACTIONS OF CHLORINE MONOFLUORIDE WITH UNSATURATED COM-  
POUNDS AND THE DEHYDROHALOGENATION OF SOME OF THE DERIVATIVES

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SUMMARY

The reactions of chlorine monofluoride with benzene, toluene and nitrobenzene to give monochloro derivatives has been investigated and its addition reactions to various substituted olefins studied. The products from all these reactions are consistent with the participation of a chloronium ion as the reactive species, even in solvents of low dielectric constant. The chlorofluoro addition products formed from the olefins have been dehydrohalogenated and the mechanism of reaction discussed in terms of an E1cb mechanism or paene-carbonium ion extreme.

DISCUSSION

Although the physical and thermodynamic properties of chlorine monofluoride are well known [1], only a few reports [2,3] describe its reactions with organic compounds. We now wish to report some further results we have obtained which may serve to clarify the mechanism of the reactions and the type of products obtained.

For each reaction many experiments were done using various conditions of temperature, solvent and mole ratio of ClF/organic; we are reporting here only the conditions which gave the best yields. Unless otherwise specified, the reactions were usually done using a stoichiometric mixture of ClF and the organic compound. Better yields could probably be obtained, particularly with the more volatile compounds, if it was possible to eliminate loss of reagent in the current of nitrogen used as carrier gas for ClF (see experimental). Since there was a slight excess

of chlorine we also found secondary products arising from this excess.

### 1) Aromatic compounds

From all the substrates monochlorinated products were obtained in high yield, benzene affording chlorobenzene as the sole product and toluene 2- and 4-chlorotoluene in the ratio 66:34. With toluene we found that the rate of reaction and the percentage of the two monosubstituted isomers was practically identical with that obtained using chlorine in the presence of  $\text{FeCl}_3$ . However the rate was much more rapid than that of chlorination in the absence of catalyst. Finally, nitrobenzene formed 3-chloronitrobenzene only.

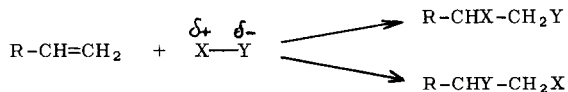
We believe that these results show that the reaction is proceeding via an ionic mechanism, similar to chlorination in the presence of catalysts such as  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ , etc., and that the electrophile attacking the ring is  $\text{Cl}^+$ , in agreement with the likely polarization of the molecule  $\overset{\delta+}{\text{Cl}}-\overset{\delta-}{\text{F}}$ . Even in solvents of low polarity such as  $\text{CCl}_4$  reactive species appear to be generated without the need of catalysts.

### 2) Olefinic compounds

We have also studied the reaction of  $\text{ClF}$  with a series of olefins. They were chosen generally so that the products obtained from the addition would throw some light on the mechanism of reaction. We obtained 1-fluoro-1,2-dichloroethane from monochloroethylene, 1-fluoro-1,2,2-trichloroethane from 1,2-dichloroethylene, 1-fluoro-1-phenyl-2-chloroethane from styrene and 1-fluoro-1,1,2,2-tetrachloroethane from trichloroethylene. Allyl chloride afforded two products, in about equal proportions; these were 1,3-dichloro-2-fluoropropane and 1,2-dichloro-3-fluoropropane. These results also are consistent with the view that the reaction proceeds via an ionic mechanism according the polarity  $\overset{\delta+}{\text{Cl}}-\overset{\delta-}{\text{F}}$ , particularly since we found no evidence for free radical or substitution reactions.

The isomer mixture obtained from allyl chloride may be expected from the inductive effect of the  $-\text{CH}_2\text{Cl}$  group. The inductive effect of a substituent  $-\text{R}$  on the double bond determines the direction of addition provided that there is no superimposed conjugative effect. We have calculated the value of the electronegativity  $\chi$  of the various groups on the basis of the equation

proposed by Kagarise [4], using the electronegativity scale of Gordy for single atoms [5]. These may be related to our experimental results and others reported in the literature with reagents of different dipole moment [6,7,8,9,10] for the general reaction



and in table 1 we give the values of  $\chi$  and the percentage of the various products obtained for different groups -R.

TABLE 1

Electronegativity values of different groups and yields of possible adducts to olefins

group	$\chi$	mole % for R-CHX-CH <sub>2</sub> Y		mole % for R-CHY-CH <sub>2</sub> X	
		our results	literature	our results	literature
-C <sub>6</sub> H <sub>5</sub>	1.78	-	-	100	95-100
-CH <sub>3</sub>	2.34	-	-	-	69-100
-CH <sub>2</sub> Cl	2.48	42.4	-	57.6	31-100
-C-	2.55	-	-	-	-
-CHCl <sub>2</sub>	2.62	-	-	-	2-100
-CH <sub>2</sub> F	2.62	-	-	-	-
-CHF-CH <sub>2</sub> Cl	2.68	59.6	-	40.4	-
-CCl <sub>3</sub>	2.76	-	100	-	-
-CF <sub>3</sub>	3.20	-	100	-	-

If the point of transition from an electron donating to an electron withdrawing effect is taken as the value of  $\chi$  for a single carbon atom, then groups with a value of  $\chi$  less than that of carbon become more electron donating the smaller the value of  $\chi$ , and vice versa. It is important to bear in mind that the values of  $\chi$  calculated from the equation of Kagarise take into account mesomeric and hyperconjugative effects, as well as the inductive properties of the group.

To demonstrate the effect of the  $\chi$  value of the group on the direction of addition it is interesting to observe that the -CH<sub>2</sub>Cl group, with a  $\chi$  value of 2.48, is predicted to be only slightly electron donating. In this case it is not surprising that addition of ClF to allyl chloride gives both possible addition products, with a slight excess of the adduct with chlorine on the =CH<sub>2</sub> group. We also calculate that the CH<sub>2</sub>Cl-CHF-

group is only slightly electron withdrawing, and as we have shown [11,12], in the reaction of ClF with butadiene, the intermediate olefin,  $\text{CH}_2\text{Cl}-\text{CHF}-\text{CH}=\text{CH}_2$ , containing this group, gives again both possible addition products, but now with the adduct containing the terminal  $-\text{CH}_2\text{F}$  group in slight excess.

In the reaction of styrene we found not only addition to the double bond, but also, to a much lesser extent, substitution of chlorine in the ring at the para position. We found no evidence for ortho or meta substitution, or any p-chlorostyrene. In view of the absence of p-chlorostyrene in the products it is possible that substitution in the ring is occurring after addition of ClF to the double bond. However the  $-\text{CH}=\text{CH}_2$  group is known to activate the benzene ring towards electrophilic substitution and we may be observing two competing reactions, one substitution, the other addition, in which the addition reaction is the more rapid. Since we always used only a slight excess of ClF, the absence of p-chlorostyrene might then not be surprising in view of the reactivity of ClF with all types of olefin.

Finally it is interesting to observe that the addition of ClF to trichloroethylene also takes place very easily, in contrast with the difficulty found with the addition of HF. This indicates that the difficulty with HF is not due to steric hindrance but to the low reactivity of  $\text{H}^+$  as an electrophile in contrast with  $\text{Cl}^+$ .

### 3) Dehydrohalogenation reactions

In our earlier study [11,12] of the dehydrohalogenation reactions of 1,3-dichloro-2,4-difluorobutane (A) we showed that the initial product of the reaction was 2,4-dichloro-3-fluoro-1-butene, the proton being lost from the  $-\text{CHCl}-$  group, and fluorine from the terminal carbon atom, the rate being dependent on the concentration of base, thus excluding an E1 process. With 1,4-dichloro-2,3-difluorobutane (B) we observed principally dehydrochlorination to 2,3-difluoro-4-chloro-1-butene, the proton being lost from the  $-\text{CHF}-$  group, comparative experiments showing that the rate of reaction (B) was approximately one quarter that of (A). This result is inconsistent with an E2 concerted elimination since the proton lost from (A) is less acidic than that from (B) and fluorine is a worse leaving group than chlorine. Thus we are led to believe that the reaction proceeds via an E1cb or paene-carbanion extreme mechanism [13].



only one olefin,  $\text{CCl}_2=\text{CHF}$ . Thus the substitution of a second chlorine atom appears to have increased the acidity of the proton lost from carbon atom not bearing fluorine by so great an amount that the elimination goes only one way, and it is possible to write the following order of acidity:



## EXPERIMENTAL.

### Apparatus and experimental conditions

In fig. 1 we show the apparatus for chlorofluorination and in particular the reactor with the thermostatic circuit.

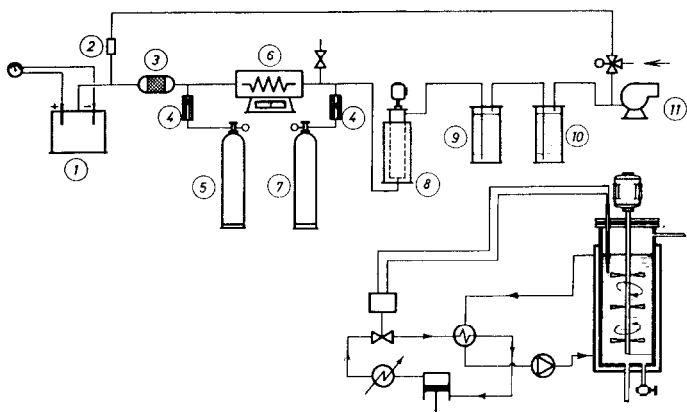


Fig. 1.- 1) Fluorine cell; 2) pressure regulator controlling the valve indicated by the arrow; 3) NaF absorber for HF; 4) rotameters; 5) cylinder of  $\text{Cl}_2$ ; 6) reactor for the synthesis of  $\text{ClF}$ ; 7) cylinder of  $\text{N}_2$ ; 8) reactor for the chlorofluorination of olefins (illustrated in the detailed drawing with the thermoregulating circuit); 9-10) scrubbers containing  $\text{H}_2\text{O}$  and  $\text{NaOH}$  solution; 11) aspirator.

The reaction was conducted by bubbling a mixture of  $\text{ClF}$  and  $\text{N}_2$  into the organic compound dissolved in an inert solvent at a constant temperature. The reactor for the synthesis of  $\text{ClF}$  consists of a nickel tube, internal diameter 25 mm and 100 mm in length, filled with nickel turnings. The reaction is completed at  $250^\circ\text{C}$  with a contact time of 100 seconds, using a 5% excess of  $\text{Cl}_2$ . The chlorofluorination reactor also consists of a nickel vessel, 50 mm internal diameter and 500 mm high, equipped with a stirrer with three Teflon paddles at 50, 150 and 250 mm from the bottom.

The paddles were inclined at an angle to the shaft of the stirrer so as to produce a turbulent motion of the liquid as shown in the figure. The chlorine monofluoride was admitted to the reactor at the bottom through a pipe 1.5 mm internal diameter.

The flow rate of  $F_2$  was calculated from the current flowing through the fluorine cell using the current yield obtained previously by analysis of the anodic gas. The flow rate of chlorine was measured using a flowmeter, and an excess of 5-7 % over stoichiometry was normally employed in order to avoid the presence of  $ClF_3$  or free fluorine, both of which could give rise to radical reactions.

In order to overcome the pressure drop in the reactor and scrubbing towers the apparatus was fitted with an aspirator at the outlet. Nitrogen was added to the chlorine monofluoride so that the pressure in the anode compartment of the cell would not vary from that in the cathode compartment by more than  $\pm 3$  cm of  $H_2O$  as the chlorine monofluoride was absorbed by the organic reagent. The amount of nitrogen added was kept to a minimum so as to avoid loss of the organic by vaporization, especially with the more volatile compounds, and we normally used a mixture containing 30-45 % of  $ClF$ . The reactions were done at  $-30$  to  $+20$  °C with the concentration of organic compound from 5 to 15 %: these conditions were generally a function of the volatility of the compound being reacted. We used a variety of solvents such as  $CHCl_3$ ,  $CCl_4$ , or  $CHCl_2-CHCl_2$ , the choice being made on the basis of ease of separation of the products from solvent, rather than on polarity.

#### Gas-liquid chromatography

For the GLC analysis of reaction mixtures the following units were used: gas-chromatograph C. Erba Fractovap model B (unit I), gas-chromatograph C. Erba Fractovap model P (unit II), gas-chromatograph C. Erba Fractovap model GV (unit III).

#### Spectroscopy

NMR spectra were recorded by a Perkin-Elmer R 20-A spectrometer at 60 MHz for  $^1H$  and 56.4 MHz for  $^{19}F$  spectra: except where otherwise stated the sample was not dissolved in solvents.

Infrared spectra were taken on a Perkin-Elmer 720 spectrophotometer.

Reactions of Chlorine Monofluoride(a) Benzene

The title compound (95 g) in  $\text{CCl}_4$  (850 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (21 l/h, 35 % by vol.  $\text{ClF}$ ) for 3 h at 20 °C. After washing with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (97.8 g) was analysed by GLC (unit I, 2 m x 6 mm i.d., DDP : Chromosorb 80-100 = 20 : 80, 1.5  $\text{kg cm}^{-2}$  He at 150 °C) to give chlorobenzene (90 g) and benzene (7.8 g), both identified by IR spectroscopy.

(b) Toluene

Toluene (95 g) in  $\text{CCl}_4$  (630 g) was treated as before. The reaction product (110.4 g) was analysed by GLC (unit III, 5 m x 2 mm i.d., CW 20 M : Chromosorb 80-100 = 20 : 80, 2  $\text{kg cm}^{-2}$   $\text{H}_2$  and programming the temperature at 100 °C for 3 min. and 3 °C/min to 150 °C) to give 2-chlorotoluene (66.8 g), 4-chlorotoluene (34.4 g) and toluene (11.9 g), all identified by GLC.

(c) Nitrobenzene

Nitrobenzene (61.5 g) in  $\text{CCl}_4$  (350 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (10.5 l/h, 35 % by vol.  $\text{ClF}$ ) for 3 h at 20 °C. After washing with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (65.6 g) was analysed by GLC (unit I, 2 m x 6 mm i.d., DDP : Chromosorb 80-100 = 20 : 80, 1.5  $\text{kg cm}^{-2}$   $\text{H}_2$  at 175 °C) to give 3-chloronitrobenzene (47.2 g) and nitrobenzene (18.4 g), both identified by IR spectroscopy.

(d) Monochloroethylene

Monochloroethylene (65 g) in tetrachloroethane (1230 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (25 l/h, 45 % by vol.  $\text{ClF}$ ) for 2 h at -35 °C. After washing with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (88.8 g) was analysed by GLC (unit I, 4 m x 6 mm i.d., Squalane : Chromosorb 80-100 = 20 : 80, 2  $\text{kg cm}^{-2}$   $\text{H}_2$  at 120 °C) to give 1-fluoro-1,2-dichloroethane (82.7 g) and 1,1,2-trichloroethane (6.1 g), the first identified by NMR spectroscopy (doublet of doublet  $^1\text{H}$ ,  $J(\text{H-F})=18.3$  Hz, at  $\delta$  3.8 from ext. TMS for  $-\text{CH}_2\text{Cl}$  group, doublet of triplets  $^1\text{H}$ ,  $J(\text{H-F})=50.7$  Hz, at  $\delta$  6.1 from ext. TMS for  $-\text{CHClF}$  group) and the second by IR spectroscopy.



(e) 1,2-dichloroethylene

The title compound (97 g) in  $\text{CCl}_4$  (1290 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (25 l/h, 45 % by vol.  $\text{ClF}$ ) for 2 h at 10 °C. After washing with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (119.6 g) was analysed by GLC (unit I, 4 m x 6 mm i.d., Octojl S : Chromosorb 80-100 = 20 : 80,  $2 \text{ kg cm}^{-2} \text{ H}_2$  at 100 °C) to give 1-fluoro-1,2,2-trichloroethane (113.6 g) and 1,1,2,2-tetrachloroethane (6.0 g), both identified by IR spectroscopy.

(f) Allyl chloride

Allyl chloride (78.5 g) in  $\text{CCl}_4$  (900 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (28 l/h, 40 % by vol.  $\text{ClF}$ ) for 2 h at 0 °C. After washing with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (131.8 g) was analysed by GLC (unit II, 4 m x 8 mm i.d., Octojl S : Chromosorb 30-60 = 20 : 80,  $0.5 \text{ kg cm}^{-2} \text{ H}_2$  at 120 °C) to give 1,2-dichloro-3-fluoropropane (40.6 g) identified by NMR spectroscopy (triplet  $^{19}\text{F}$ ,  $J(\text{H-F})=46.7 \text{ Hz}$ , at  $\delta$  141.4 from ext. TFA for  $-\text{CH}_2\text{F}$  group and doublet  $^1\text{H}$  at  $\delta$  3.80 from int. TMS for  $-\text{CH}_2\text{Cl}$  group), 1,3-dichloro-2-fluoropropane (55.1 g) identified by NMR spectroscopy (doublet of pentets  $^{19}\text{F}$ ,  $J(\text{H-F})=45.8 \text{ Hz}$ , at  $\delta$  97.9 from ext. TFA for  $-\text{CHF}-$  group and doublet of doublets  $^1\text{H}$ ,  $J(\text{H-F})=18.7 \text{ Hz}$ , at  $\delta$  3.78 from int. TMS for  $-\text{CH}_2\text{Cl}$  group) and 1,2,3-trichloropropane (5.9 g) identified by IR spectroscopy.

(g) Styrene

Styrene (104 g) in  $\text{CCl}_4$  (590 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (21 l/h, 35 % by vol.  $\text{ClF}$ ) for 3 h at 5 °C. The reaction product (157.6 g) was analysed by GLC (unit II, 2 m x 8 mm i.d., CW 1500 : Chromosorb 30-60 = 20 : 80,  $0.5 \text{ kg cm}^{-2} \text{ H}_2$  at 120 °C) to give 1-fluoro-1-phenyl-2-chloroethane (125.9 g) identified by NMR spectroscopy in  $\text{CCl}_4$  50 % v/v (signal  $^1\text{H}$  at  $\delta$  6.97 from ext. TMS for  $-\text{C}_6\text{H}_5$  group, doublet of triplets  $^1\text{H}$ ,  $J(\text{H-F})=47.9 \text{ Hz}$ , at  $\delta$  5.18 from ext. TMS for  $-\text{CHF}-$  group and doublet of doublets  $^1\text{H}$ ,  $J(\text{H-F})=18.4 \text{ Hz}$ , at  $\delta$  3.37 from ext. TMS for  $-\text{CH}_2\text{Cl}$  group) and other compounds (15.8 g).

(h) 1,3-butadiene

Butadiene (65 g) in  $\text{CCl}_4$  (1230 g) was treated with  $\text{ClF}/\text{N}_2$  mixture (17 l/h, 44 % by vol.  $\text{ClF}$ ) for 3 h at -28 °C. After washing

with a 2 % solution of  $\text{NaHCO}_3$ , drying ( $\text{Na}_2\text{SO}_4$ ) and removal of the solvent, the reaction product (164 g) was analysed by GLC (unit II, 4 m x 8 mm i.d., CW 20 M : Chromosorb 30-60 = 20 : 80,  $0.25 \text{ kg cm}^{-2}$  He at 150 °C) to give 1,3-dichloro-2,4-difluorobutane (55.6 g), 1,4-dichloro-2,3-difluorobutane (31.2 g), 1,2,3-trichloro-4-fluorobutane (15.6 g), 1,3,4-trichloro-2-fluorobutane (47.2 g), 3,4-dichloro-1-butene (5.2 g) and 1,4-dichloro-2-butene (9.2 g), all identified by NMR spectroscopy [11,12].

### Dehydrohalogenation

The chlorofluoroalkanes were dehydrohalogenated by treatment with KOH in ethanol 90 %.

#### (a) 1-fluoro-1,2-dichloroethane

The title compound (58.5 g) was treated with KOH (58 g) in  $\text{C}_2\text{H}_5\text{OH}$  90 % (400 ml) at the reflux temperature. The olefins obtained (36 g) were distilled and analysed by GLC (unit I, 10 m x 6 mm i.d., Octojl S : Chromosorb 80-100 = 20 : 80,  $0.5 \text{ kg cm}^{-2}$   $\text{H}_2$  at 60 °C) to give 1-fluoro-1-chloroethylene (15.2 g) and 1-fluoro-2-chloroethylene (20.8 g), both identified by IR spectroscopy.

#### (b) 1-fluoro-1,2,2-trichloroethane

This compound (75.7 g) was treated as before. The reaction products (44.7 g) were distilled and analysed by GLC (unit I, 8 m x 6 mm i.d., Octojl S : Chromosorb 80-100 = 20 : 80,  $0.5 \text{ kg cm}^{-2}$   $\text{H}_2$  at 60 °C) to give 1-fluoro-2,2-dichloroethylene (43.7 g), identified by IR [15] and NMR spectroscopy (doublet  $^1\text{H}$ ,  $J(\text{H-F}) = 78.5 \text{ Hz}$ , at  $\delta$  7.04 from int. TMS for  $=\text{CHF}$  group), and other products (1 g).

#### (c) 1,2-dichloro-3-fluoropropane

This compound (60.5 g) was treated as before. The reaction product (40.2 g) was distilled, analysed by NMR spectroscopy and identified as 2-chloro-3-fluoro-1-propene (triplet  $^{19}\text{F}$ ,  $J(\text{H-F}) = 47.9 \text{ Hz}$ , at  $\delta$  127.9 from ext. TFA for  $-\text{CH}_2\text{F}$  group and a confused AB quartet  $^1\text{H}$  centred at  $\delta$  5.44 from int. TMS for  $=\text{CH}_2$  group).

#### (d) 1,3-dichloro-2-fluoropropane

The title compound (60.5 g) was treated as before; the olefin obtained after distillation (29.5 g) was analysed by NMR spectroscopy and identified as 2-fluoro-3-chloro-1-propene

(doublet of triplets  $^{19}\text{F}$ ,  $J(\text{H-F})_{\text{trans}}=47.2$  Hz and  $J(\text{H-F})_{\text{cis}}=14.1$  Hz, at  $\delta$  25.5 from ext. TFA for  $-\text{CF}=\text{}$  group, doublet  $^1\text{H}$ ,  $J(\text{H-F})=16.8$  Hz, at  $\delta$  4.06 from int. TMS for  $-\text{CH}_2\text{Cl}$  group and an AB system,  $J(\text{A-B})=3.0$  Hz,  $\text{H}(\text{A})$  at  $\delta$  4.65 and  $\text{H}(\text{B})$  at  $\delta$  4.73 from int. TMS, for  $=\text{CH}_2$  group).

(e) 1,3-dichloro-2,4-difluorobutane

This compound (81.5 g) was treated as before, and the olefin obtained after distillation (47.9 g) was analysed by IR spectroscopy and identified as 2-fluoro-3-chloro-1,3-butadiene ( $2300\text{ cm}^{-1}$  for stretch  $=\text{CH}_2$ ,  $1650\text{ cm}^{-1}$  for stretch  $\text{C}=\text{CF}$ ,  $1590\text{ cm}^{-1}$  for stretch  $\text{C}=\text{CCl}$ ,  $1120\text{ cm}^{-1}$  for stretch  $\text{C-F}$ , 960 and  $880\text{ cm}^{-1}$  for  $=\text{CH}_2$  wag and  $700\text{ cm}^{-1}$  for stretch  $\text{C-Cl}$ ).

(f) 1,4-dichloro-2,3-difluorobutane

This compound (81.5 g) was treated as before. The olefin produced (39.5 g) was distilled, analysed by IR spectroscopy and identified as 2,3-difluoro-1,3-butadiene ( $2320\text{ cm}^{-1}$  for stretch  $=\text{CH}_2$ ,  $1620\text{ cm}^{-1}$  for stretch  $\text{C}=\text{C}$ ,  $1180\text{ cm}^{-1}$  for stretch  $\text{C-F}$ , 950 and  $870\text{ cm}^{-1}$  for  $=\text{CH}_2$  wag).

(g) 1-fluoro-1-phenyl-2-chloroethane

This compound (39.6 g) was treated with  $\text{KOH}$  (29 g) in  $\text{C}_2\text{H}_5\text{OH}$  90 % (200 ml). The olefin produced (31.2 g) was distilled, analysed by NMR spectroscopy (in  $\text{CCl}_4$  50 % v/v) and identified as 1-phenyl-2-chloroethylene (signal  $^1\text{H}$  at  $\delta$  6.83 from ext. TMS for  $-\text{C}_6\text{H}_5$  group and an AB system,  $J(\text{A-B})=13.5$  Hz,  $\text{H}(\text{A})$  at  $\delta$  6.44 and  $\text{H}(\text{B})$  at  $\delta$  6.12 from ext. TMS, for  $-\text{CH}=\text{CHCl}$ ).

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