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REACTIONS OF POLYHALOTERTIARY ALCOHOLS WITH HALOGENATING AGENTS

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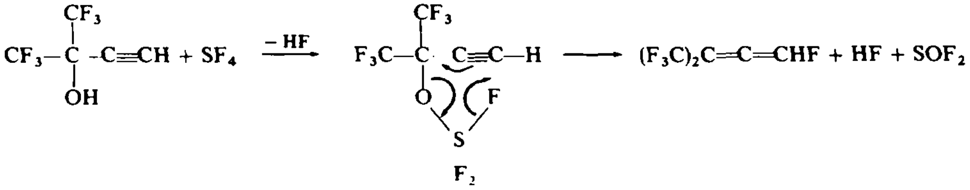
Abstract—Reactions of polyhalotertiary alcohols, $CZ_3C(CF_2X)(CF_2Y)OH$, with a variety of reagents are described. Where Z is H and X and Y are H or F, reaction with SF_4 and PCl_5 leads to olefin formation, $CZ_2{=}C(CF_2X)(CF_2Y)$. If X and/or Y are chlorine, then PCl_5 still gives the corresponding olefin, but SF_4 causes a rapid chlorine migration and the production of saturated compounds. When Z is Cl and both X and Y are F, olefin formation results from reaction with PCl_5, $(C_6H_5)_3PBr_2$ and $(C_6H_5)_3PI_2$. SF_4 and $(C_6H_5)_3PCl_2$ react differently, the former giving a rearranged saturated material and the latter an acid chloride. Related reactions are described and reaction mechanisms are proposed.

IN A previous paper[1] we showed that certain fluorinated acetylenic alcohols reacted in an unusual fashion with sulfur tetrafluoride, giving rearranged products according to the scheme:



In this communication we show that other polyhaloalcohols react anomalously with a variety of reagents which normally effect direct replacement of the OH group.

Sulfur tetrafluoride

Alcohols containing fluorine as the only halogen. In contrast with the unsaturated tertiary alcohols, saturated polyhaloalcohols react very slowly with SF_4 at ambient temperatures. To achieve complete reaction in a reasonable length of time it was found necessary to heat the mixture at 90°, or thereabouts, for several hours. Under these conditions 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (**1a**) was converted to the olefin, 1,1-bis(trifluoromethyl)ethylene, (hexafluoroisobutylene) (**2a**), in 72% yield. No product formed by addition of HF to the olefin was observed.

We feel that the most likely pathway involves an initially formed complex (**3**), similar to that described above for the acetylenic carbinols, which is spatially oriented such that the application of heat will drive the reaction to the more thermodynamically stable products.

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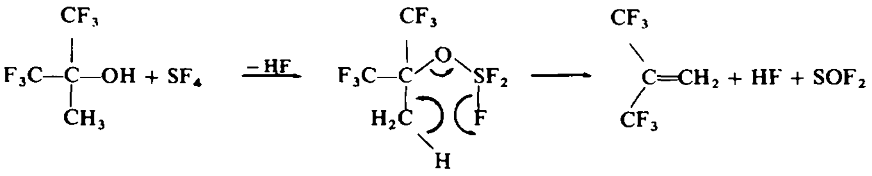
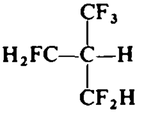


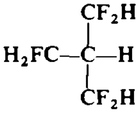
1a **3** **2a**

The less fluorinated alcohols, 1,1,1,3,3-pentafluoro-2-methyl-2-propanol (**1b** and 1,1,3,3-tetrafluoro-2-methyl-2-propanol (**1c**) react similarly, giving olefins **2b** and **2c** respectively. In each of these cases a small amount of by-product, caused by the addition of HF to the double bond, was observed. The structure of the respective products was shown conclusively by NMR spectroscopy, to be **4** and **5**. The observed direction of addition is the one to be expected from electronic considerations.[5] In



$H_2FC{-}C(CF_3)(CF_2H){-}H$

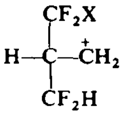
4



$H_2FC{-}C(CF_2H)(CF_2H){-}H$

5

addition, the intermediate positively charged species,

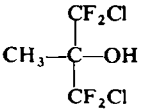


$H{-}C(CF_2X)(CF_2H){-}\overset{+}{C}H_2$

(where X = F or H)

does not possess the destabilizing features that the alternate product would imply.

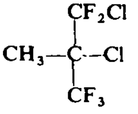
Alcohols containing chlorine and fluorine. When X and/or Y in structure 1 is chlorine, an entirely different reaction arises. It has been reported[6] that 1,3-dichloro-1,1,3,3-tetrafluoro-2-methyl propanol (**6**) reacts with SF_4 at 90° to yield 1,2-dichloro-1,1,3,3,3-



$CH_3{-}C(CF_2Cl)(CF_2Cl){-}OH$

6

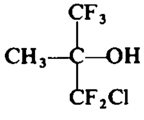
pentafluoro-2-methyl propane (**7**):



$CH_3{-}C(CF_2Cl)(CF_3){-}Cl$

7

Using 1-chloro-1,1,3,3,3-pentafluoro-2-methyl propanol (**8**) we have confirmed that this type of rearranged product is formed and, by carrying out the reaction at 50°, we have shown that the acyl fluoride **9**



$CH_3-\overset{CF_3}{\underset{CF_2Cl}{C}}-OH$

8

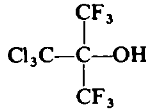
is an intermediate in the reaction. The infrared spectrum of **9** contains a C═O stretching frequency at 1852 cm^{-1}, which is shifted to 1761 cm^{-1} on the addition of MeOH, showing the formation of an ester from the acyl halide. Prolonged reaction of **9** with SF_4 at 50° (about 72 hr) resulted in conversion of most of the acyl fluoride to 1,1,1,3,3,3-hexafluoro-2-methyl-2-chloropropane (**10**). The reaction pathway

$CH_3-\overset{CF_3}{\underset{Cl}{C}}-\underset{O}{\overset{}{C}}-F \xrightarrow{SF_4} CH_3-\overset{CF_3}{\underset{Cl}{C}}-CF_3$

9 **10**

followed by the chlorofluoroalcohols is clearly quite different from that followed by the alcohols of type **1**, and is dependent on the ability of the chlorine atom to migrate. The mechanism for the conversion of **8** to **9** probably is analogous to that described for **11** to **30** later in the text. No trace of any type **2** olefin is apparent from the chlorofluoroalcohols.

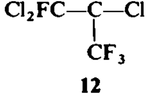
Although alcohols of type **1** react with SF_4 in a very different manner than those exemplified by **6** and **8**, it is clear that in each case the reactions proceed under quite moderate conditions. This is in marked contrast to our observation with the tertiary alcohol 2-trichloromethyl-hexafluoro-2-propanol (**11**)



$Cl_3C-\overset{CF_3}{\underset{CF_3}{C}}-OH$

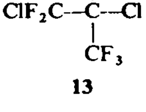
11

which was recovered unchanged after being held at 200° overnight with SF_4. A temperature of 300° was necessary for reaction to occur, when two products were formed. IR spectra showed that O—H, C═O and C═C linkages were not present in either product, and ^{19}F NMR examination indicated the products to be:



$Cl_2FC-\overset{CF_3}{\underset{CF_3}{C}}-Cl$

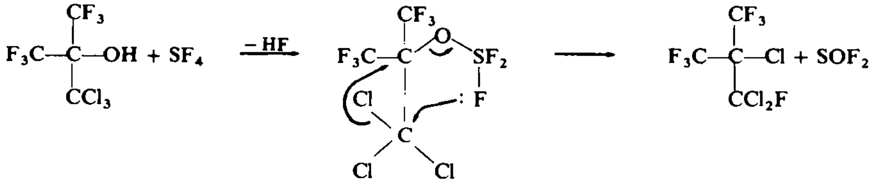
12



$ClF_2C-\overset{CF_3}{\underset{CF_3}{C}}-Cl$

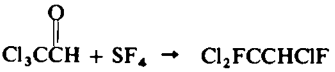
13

The production of **13**, the minor product, probably occurs through simple halogen exchange of Cl for F, caused by the action of SF_4 on **12**.[7] The formation of **12** is more difficult to visualize. A pathway analogous to that already described would involve formation of the olefin 1,1-dichloro-2,2-bis(trifluoromethyl) ethylene $(CF_3)_2C{=}CCl_2$ (**14a**) together with *in situ* or transient formation of ClF, which would immediately add to the olefin to give **12**. Although it has been demonstrated independently[8] that ClF does add to **14a** to give **12**, thermodynamic considerations make the formation of ClF very unlikely in the alcohol-SF_4 reaction. The most reasonable explanation we can find is that in the initially formed complex there is nucleophilic attack by fluorine on the trichloromethyl carbon, with a concerted chlorine migration and thionyl fluoride formation.



11 **12**

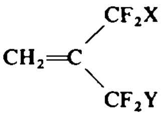
The conversion of **11** to **12** is analogous to a recent report, with no mechanistic interpretation offered, where it was shown that chloral and SF_4 react to form 1,1,2-trichloro-1,2-difluoroethane.[9]



$$Cl_3C\overset{O}{\overset{\|}{C}}H + SF_4 \rightarrow Cl_2FCCHClF$$

Phosphorus pentachloride

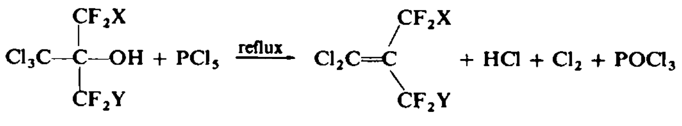
Kaufman and Braun have shown[2] that prolonged reflux (five days) of alcohols **1a**, **6** and **8** with PCl_5 results in good yields of the corresponding olefins **2a**, **15a** and **15b**.



15

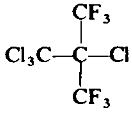
a X = Y = Cl
b X = F; Y = Cl

Rearrangements such as those observed with SF_4 did not occur. We find that the reaction period can be shortened to several hours by judicious use of temperature and pressure, without sacrificing olefin yield, and without addition of by-product HCl to the olefin. Using sealed reactors and temperatures up to 165° alcohols **1a**, **1b**, and **6** were converted to the respective olefins **2a**, **2b** and **15a** in yields up to 86%. In their paper[2] Kaufman and Braun stipulate that there must be hydrogen on the α-carbon atom for olefin production to occur. However, we find that fully halogenated alcohols, such as **11**, will react with PCl_5, under reflux, to yield the corresponding olefins:



11 X = Y = F **14a** X = Y = F
16 X = Y = Cl **14b** X = Y = Cl

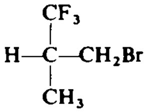
In an attempt to improve the yield of olefin, alcohol **11** was heated under pressure with PCl_5, but this resulted in formation of the tertiary chloride **17**, probably via addition of chlorine to **14a**.



$$\begin{array}{c} CF_3 \\ | \\ Cl_3C{-}C{-}Cl \\ | \\ CF_3 \end{array}$$

17

There is a precedent for this in the observation of Haszeldine[10] that trifluoroisobutylene is not formed from the corresponding alcohol by treatment with PBr_5, but the HBr addition product **18** results.



$$\begin{array}{c} CF_3 \\ | \\ H{-}C{-}CH_2Br \\ | \\ CH_3 \end{array}$$

18

Dibromotriphenylphosphorane

Through the work of Wiley *et al.*[11] dihalotriphenylphosphoranes [$(C_6H_5)_3PX_2$] have become known as reagents for the conversion of alcohols into the corresponding alkyl halides. The ready availability[12] of dibromotriphenylphosphorane [$(C_6H_5)_3PBr_2$] prompted an examination of its reaction with various polyhaloalcohols.

Duncan and Silverstein[13] reported the conversion of the primary fluorinated alcohol, 1,1,7-trihydrododecafluoroheptyl alcohol (**19**) to its bromide (**20**) in 68% yield, using dibromotriphenylphosphorane in MeCN at 50–60° for 1 hr. but were unable to convert the secondary fluorinated alcohol,

$$\underset{\textbf{19}}{H(CF_2)_6CH_2OH} + (C_6H_5)PBr_2 \rightarrow \underset{\textbf{20}}{H(CF_2)_6CH_2Br} + (C_6H_5)_3PO + HBr$$

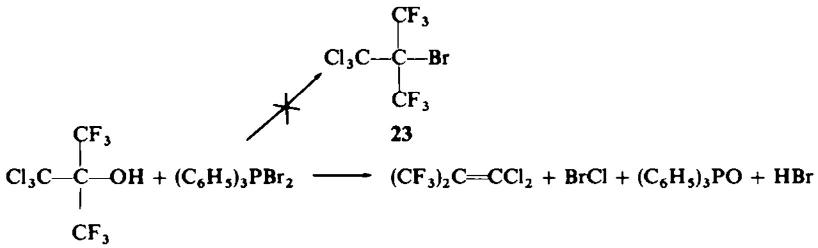
hexafluoroisopropyl alcohol (**21**), into its bromide(**22**).

$$\underset{\textbf{21}}{CF_3CHOHCF_3} + (C_6H_5)_3PBr_2 \rightarrow \underset{\textbf{22}}{CF_3CHBrCF_3} + (C_6H_5)_3PO + HBr$$

We found that by heating the reactants under reflux for 6 hr, in excess hexafluoroisopropyl alcohol, a 54% yield of 2-bromo-1,1,1,3,3,3-hexafluoropropane (**22**) was obtained.[14]

Treatment of the tertiary fluorochloro alcohol (**11**) with dibromotriphenylphosphorane at temperatures to 200° did not result in a similar replacement, but led to a 30% yield of **14**,[15] which was also obtained with PCl_5. There was no evidence of formation of the bromide (**23**). Trace amounts of carbonyl impurities were noted but were not identified.

A plausible reaction mechanism would involve decomposition of the phosphonium bromide intermediate (**24**)[11] via an intramolecular E_2 type of β-elimination reaction leading to bromine monochloride, the olefin, and triphenylphosphine oxide, all of



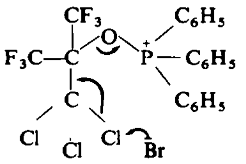
$$\mathrm{Cl_3C{-}C(CF_3)_2{-}OH} + \mathrm{(C_6H_5)_3PBr_2} \longrightarrow \mathrm{(CF_3)_2C{=}CCl_2} + \mathrm{BrCl} + \mathrm{(C_6H_5)_3PO} + \mathrm{HBr}$$

$$\not\longrightarrow \mathrm{Cl_3C{-}C(CF_3)_2{-}Br}$$

23

11 14a

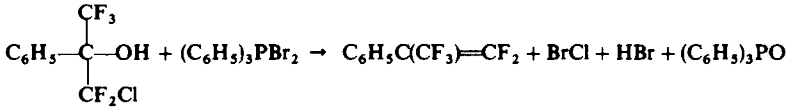
which were isolated from the product mixture. It will be noted that the proposed intermediate is in principle similar to that suggested with SF_4.



24

As an extension of this reaction we examined the possibility of olefin formation from a tertiary fluoroalcohol bearing an α-CF_2Cl group. 1-Chloro-1,1,3,3,3-pentafluoro-2-phenyl-2-propanol (**25**) was chosen as a model compound.[16]

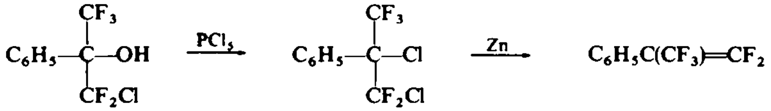
Treatment of **25** with dibromotriphenylphosphorane at 190–200° led to an 82% yield of α-trifluoromethyl-β,β-difluorostyrene (**26**). This compound has been prepared



$$\mathrm{C_6H_5{-}C(CF_3)(CF_2Cl){-}OH} + \mathrm{(C_6H_5)_3PBr_2} \rightarrow \mathrm{C_6H_5C(CF_3){=}CF_2} + \mathrm{BrCl} + \mathrm{HBr} + \mathrm{(C_6H_5)_3PO}$$

25 26

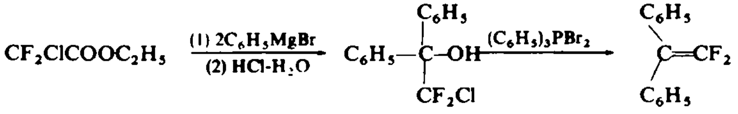
previously in two steps by the chlorination of **25** with PCl_5 to 1,2-dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane (**27**) followed by Zn dechlorination in AcOH.[2]



$$\mathrm{C_6H_5{-}C(CF_3)(CF_2Cl){-}OH} \xrightarrow{PCl_5} \mathrm{C_6H_5{-}C(CF_3)(CF_2Cl){-}Cl} \xrightarrow{Zn} \mathrm{C_6H_5C(CF_3){=}CF_2}$$

25 27 26

Our procedure effectively is a "one-step" halogenation–dehalogenation reaction. A less highly fluorinated tertiary alcohol containing an α-CF_2Cl group, difluorochloromethyldiphenylcarbinol (**28**)[17] also reacted with dibromotriphenylphosphorane at 230–300° and gave a 30% yield of 1,1-diphenyldifluoroethylene (**29**).[18]

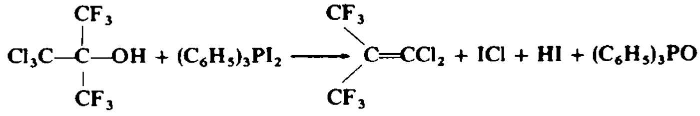


$$\mathrm{CF_2ClCOOC_2H_5} \xrightarrow[\text{(2) HCl-H}_2\text{O}]{\text{(1) 2C}_6\text{H}_5\text{MgBr}} \mathrm{C_6H_5{-}C(C_6H_5)(CF_2Cl){-}OH} \xrightarrow{(C_6H_5)_3PBr_2} \mathrm{(C_6H_5)_2C{=}CF_2}$$

28 29

Diiodotriphenylphosphorane

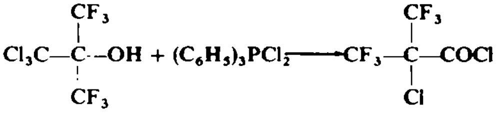
Reaction of **11** with diiodotriphenylphosphorane[19] above 300° similarly led to a 64% yield of dichloroolefin (**14a**) devoid of any carbonyl impurities.



11 **14a**

Dichlorotriphenylphosphorane

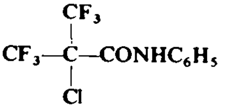
In contrast to the results obtained with the bromo- and iodo-reagents, treatment of **11** with dichlorotriphenylphosphorane led to a 44% yield of a mixture of products in which 2-chlorohexafluoroisobutyryl chloride (**30**)[20] was the major constituent (approximating 85% by gas–liquid chromatography).



$$\mathrm{Cl_3C{-}\underset{CF_3}{\overset{CF_3}{C}}{-}OH} + (\mathrm{C_6H_5})_3\mathrm{PCl_2} \longrightarrow \mathrm{CF_3{-}\underset{Cl}{\overset{CF_3}{C}}{-}COCl}$$

11 **30**

The product was characterized by conversion to its anilide (**31**).[20]

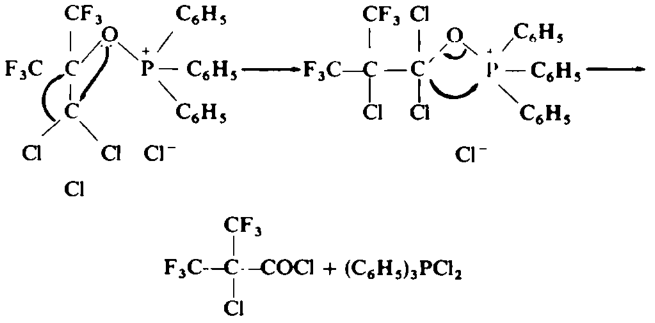


$$\mathrm{CF_3{-}\underset{Cl}{\overset{CF_3}{C}}{-}CONHC_6H_5}$$

31

Among the minor products of the reaction was a small amount of 1,1-dichloro-2,2-bistrifluoromethylethylene (**14a**).

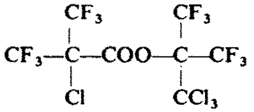
We feel that the formation of **30** may be best represented by the following reaction mechanism:



30

Wiley *et al.*[11] represented the halide ion of the phosphonium halide intermediate as being associated or solvated (hydrogen-bonded) with the HX produced. Therefore, the nucleophilicity of the halide ion must be $I^- > Br^- > Cl^-$ (as in a protic solvent). In the case of the phosphonium halide intermediates derived from **11**, the ability of the chloride ion to attack the CCl_3-group to form olefin (**14a**) would be less than that of bromide and iodide. This reduces the possibility of olefin formation and favors a rearrangement of the phosphonium chloride intermediate.

If the proposed mechanism is correct, then only a catalytic amount of dichlorotriphenylphosphorane should be necessary to effect the reaction. To test this theory, **11** was heated in the presence of a catalytic amount of dichlorotriphenylphosphorane (5%) at 200–210° over a period of 9 hr. In addition to a 16% yield of acid chloride (**30**) (contaminated with a trace amount of olefin), 11% of the ester (**32**) derived from **11** and **30** was obtained. The IR spectrum exhibited a strong carbonyl absorption at 1818 cm^{-1}[21] (identical to that obtained *via* the sodium salt of **11** and **30**).



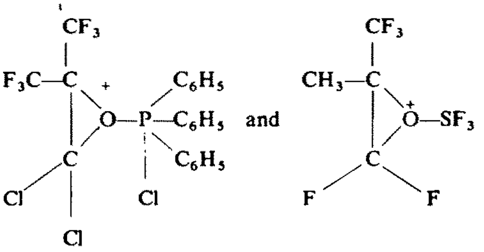
$$CF_3{-}\overset{CF_3}{\underset{Cl}{C}}{-}COO{-}\overset{CF_3}{\underset{CCl_3}{C}}{-}CF_3$$

32

The products isolated correspond to a 27% yield of **30** and support the mechanism postulated.

Footnote:

A referee has suggested an alternate mechanism for the formation of acid halides **9** and **30**, which involves substituted epoxides as intermediates, i.e.



This implies a stepwise rearrangement rather than the concerted mechanism we show and on the basis of available evidence one cannot choose between them.

EXPERIMENTAL

Alcohols **1**, **6** and **8** were made by the addition of MeMgBr to the appropriate halogenated ketones, following established procedures.[2, 22] Alcohol **11** was made by the direct photochemical chlorination of **1a**.[23] NMR spectra were measured on Varian A-60 and Jeolco C60H instruments, using tetramethylsilane and trichlorofluoromethane as internal standards. ^{19}F spectra were calibrated by generating side bands of Cl_3CF. Elemental analyses were made by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. and by Mr. G. E. Mohler of this Corporation.

1,1-*Bis(trifluoromethyl)ethylene*. (**2a**)

(a) *SF_4 reaction.* Hexafluoro-2-methyl-2-propanol (50 g; 0·275 mole) was added to a 300 ml. stainless steel pressure reactor. The reactor was closed, cooled to − 78° and all gaseous matter was evacuated. SF_4 (41 g, commercial material, containing about 0·35 mole SF_4) was condensed into the reactor through a vacuum manifold system. The reactor was heated at 90–95° for 18 hr. At the end of this time the interior pressure had reached 325 psig. The hot vapors were released through (a) an empty trap connected in series with (b) a water scrubber, (c) a caustic soda scrubber, (d) a drying tower ($CaSO_4$) and (e) a trap cooled to − 78° to collect the gaseous product. HF, SOF_2 and excess SF_4 were removed in traps (b) and (c). The product collected in (e) was 1,1-bis(trifluoromethyl)-ethylene, (32·5 g; 72% yield) b.p. 14–15°. IR and NMR spectra of the material were in agreement with those reported previously.[2]

(b) *PCl_5 reaction.* Similarly hexafluoro-2-methyl-2-propanol (50 g; 0·275 mole) was treated with PCl_5 (60 g; 0·289 mole) at 92° for 16 hr. The internal pressure rose to 275 psig. The contents of the reactor were vented as before and 16 g. olefin obtained. In addition, 21·5 g. unreacted alcohol were recovered. The yield of olefin is 62·3% of theoretical based on the alcohol consumed. At 120° a higher conversion is realized.

1.1.1-*Trifluoro-2-difluoromethyl-propene* (**2b**). Reaction of pentafluoro-2-methyl-2-propanol (**1b**) (50 g; 0·305 mole) with SF_4 (40 g; approx. 0·34 mole) at 90–92° for 16 hr. gave 4·8 g. unreacted alcohol and 22 g. 1.1.1-trifluoro-2-difluoromethylpropene (54·7% of theoretical based on alcohol consumed). b.p. 36°. (Calcd. for $C_4H_3F_5$: C. 32·88; H. 2·07. Found: C. 32·86; H. 2·19%). C═C str. 1672 cm^{-1}; δCH_2 6·1 (complex). δCHF_2 6·23 (t. of d.). J_{HCF} 55·0 Hz. J_{HCCCH} 1·0 Hz.

In addition. 2·3 g. 1.1.1.3-tetrafluoro-2-(difluoromethyl) propane (**4**) b.p. 59° were recovered. (Calcd. for $C_4H_4F_6$: C. 28·92; H. 2·43. Found: C. 28·89; H. 2·23%). δCHF_2 6·10 (t. of d.). J_{HCF}, 55 Hz. J_{HCCH} 4·5 Hz. δCH_2F 4·82 (t. of d.). J_{H_2CF} 46·5 Hz, J_{HCCH} 4·5 Hz, δCH 2·9 (complex). Using PCl_5 at 134° for 5¼ hr, the alcohol was converted to the olefin in 60·4% yield.

1.1-*Bis(difluoromethyl)ethylene* (**2c**). Tetrafluoro-2-methyl-2-propanol (**1c**) (35 g; 0·24 mole) was treated with SF_4 (30 g; approx. 0·25 mole) at 95° for 16 hr. to give 1.1-bis(difluoromethyl)ethylene. b.p. 55° (11·8 g: 38·4% yield). (Calcd. for $C_4H_4F_4$: C. 37·50; H. 3·15. Found: C. 37·58; H. 3·30%). C═C str. 1672 cm^{-1}; δCHF_2 6·23. (t. with further splitting). J_{HCF} 54·5 Hz; δCH_2 5·89 (complex).

A high boiling impurity was found to be 1.1.3-trifluoro-2-(difluoromethyl)propane (**5**). b.p. 78° (Calcd. for $C_4H_5F_5$: C. 32·46; H. 3·41. Found: C. 32·46; H. 3·36%). δCFH_2 233. J_{HCF} 46·5 Hz. δCF_2H 124. J_{HCF} 55·5 Hz. J_{FCCCF} 3·5 Hz. δCHF_2 6·04; δCH_2F 4·75. δCH 2·61. J_{HCCF} 30 Hz. J_{HCCH} 13·5 Hz. J_{H_2CCH} 4·5 Hz.

Reaction of chloropentafluoro-2-methyl-2-propanol (**8**) *with* SF_4. SF_4 (17 g; about 0·145 mole) was allowed to react with chloropentafluoro-2-methyl-2-propanol (**8**) (20 g; 0·1 mole) at 50° for 16 hr. Distillation of crude product gave a major fraction b.p. 50–52°. C═C str. 1852 cm^{-1}. believed to be 1-chloro-1-trifluoromethylpropionyl fluoride (**9**) since (a) treatment of a small portion with MeOH caused a shift in the carbonyl absorption in the infrared to 1761 cm^{-1} and (b) prolonged treatment of alcohol (**8**) or acid fluoride (**9**) with SF_4 at 50° gave 1.1.1.3.3.3-hexafluoro-2-methyl-2-chloropropane (**10**) b.p. 43°. δCH 1·89 (septet).

Reaction of 2-trichloromethyl-hexafluoro-2-propanol (**11**) *with* SF_4. At 300° 2-trichloromethyl-hexafluoro-2-propanol (**11**) (30 g; 0·105 mole) reacted with SF_4 (22 g; about 0·19 mole). with shaking for 15 hr. Maximum pressure reached almost 1000 psig. The reactor was cooled. vented and the orange liquid product distilled. The minor product was 2-chloro-2-(chlorodifluoromethyl)-hexafluoropropane (**13**). (3 g) b.p. 58–60°. (Calcd. for $C_4Cl_2F_8$: C. 17·73; Cl. 26·17. Found: C. 17·68; Cl. 25·92%). δCF_3 67·5 (t). δCF_2 55·4 (septet). J_{FCCF} 12·5 Hz. The major product was 2-chloro-2-(dichlorofluoromethyl)-hexafluoropropane (**12**). (16 g) b.p. 95·97°; m.p. 58·5–59°. (Calcd. for $C_4Cl_3F_7$: C. 16·72; Cl. 37·01. Found: C. 16·83; Cl. 36·82%). δCF_3 65·5 (d). δCF 56·5 (septet). J_{FCCCF} 13·5 Hz. The combined products account for 63·8% of the alcohol consumed.

1.1-*Dichloro-2.2-bis(trifluoromethyl)ethylene* (**14a**).

(a) PCl_5 *reaction.* PCl_5 (25 g; 0·12 mole) and 2-trichloromethyl-hexafluoro-2-propanol (**11**) (28 g; 0·098 mole) were heated under reflux. When reflux started gaseous by-products began to be evolved (Cl_2. HCl). Heating was continued for 8 hr.. during which time the reflux temperature fell from 140° to 108°. The mixture was cooled. poured on crushed ice and the organic layer separated. dried and distilled. Unreacted alcohol **11** (16·9 g) was recovered together with 1.1-dichloro-2.2-bis(trifluoromethyl)ethylene (3·8 g). b.p. 66–68°. Yield of olefin was 42% of theoretical based on alcohol consumed. If the reaction is carried out under pressure then the product isolated is 2-chloro-2-(trichloromethyl)hexafluoropropane (**17**). b.p. 132°. m.p. 109–109·5°. (Calcd. for $C_4Cl_4F_6$: C. 15·81; Cl. 46·67. Found: C. 15·66; Cl. 47·05%). δCF_3 64·7 (s).

(b) *Dibromotriphenylphosphorane reaction.* 2-Trichloromethylhexafluoro-2-propanol (**11**) (8·6 g; 0·03 mole) and dibromotriphenylphosphorane (13 g; 0·031 mole) were heated to 200°. for 45 min.. when the reaction mixture became dark red-brown to black and the product formed began to reflux vigorously (accompanied by strong evolution of HBr). Heating was continued at reflux for an additional 4 hr. during which time the temperature fell to 155° and then the mixture was cooled to 25°. Distillation at atmospheric pressure gave 2·1 g (30% yield) of crude 1.1-dichloro-2.2-bistrifluoromethylethylene (**14**) as a light orange-yellow liquid. b.p. 66–68°; lit. b.p. 74·5°.[15] The orange-yellow color was discharged on standing in air to give a pale-yellow to colorless liquid. While the IR spectrum of the crude product showed a trace of carbonyl impurities. it was essentially identical with the product obtained with PCl_5; C═C str. 1613 cm^{-1}; δCF_3 59·3 (s).

Reaction with diiodotriphenylphosphorane. When a mixture of (**11**) (8·6 g; 0·03 mole) and diiodotriphenylphosphorane[19] (18·6 g; 0·036 mole) was heated to 300° no reaction occurred. Above 300° a vigorous reaction occurred with 4 ml. of olefin being formed at once. The product was highly contaminated with I_2 and was treated with Hg to give 4·5 g (64% yield) of crude product as a water-white liquid. Its IR spectrum was devoid of any carbonyl impurities.

1.1-Dichloro-2.2-bis(chlorodifluoromethyl)ethylene (**14b**). 2-Trichloromethyl-tetrafluoro-2-propanol (**16**) (20 g; 0·063 mole) was heated under reflux for 3 hr. with PCl_5 (15 g; 0·072 mole). Reflux temp. decreased from 165° to 141°. After the mixture had been cooled and poured on ice the organic layer was separated and dried. Distillation gave 9·5 g recovered alcohol **16** and 8·6 g (89·5%) 1.1-dichloro-2.2-bis(chlorodifluoromethyl)ethylene (**14b**). b.p. 135°. C=C str. 1585 cm^{-1}. (Calcd. for $C_4Cl_4F_4$: C. 18·07; Cl. 53·34. Found: C. 18·20; Cl. 53·29%). δCF_2 51·5 (s).

1.1-Bis(chlorodifluoromethyl)ethylene (**15a**). This compound was prepared in a similar manner to that used for **2a** using PCl_5 in a pressure reactor at 150–165° for 4½ hr. An 86% yield of 1.1-bis(chlorodifluoromethyl)ethylene (**15a**). b.p. 78° was obtained. Spectral data were in agreement with the literature.[2]

2-Bromo-1,1,1,3,3,3-hexafluoropropane (**22**). A mixture of dibromotriphenylphosphorane (43 g; 0·10 mole) and 32 ml. (0·31 mole) of hexafluoroisopropyl alcohol was heated to reflux. The maximum temp. was controlled at approximately 145–150° initially. After 10 hr. the temp. had dropped to 120°. A dry ice-acetone trap was used to trap any exiting bromide. The reaction mixture was cooled to room temperature. and all volatile material distilled out (alcohol and bromide). and combined with the material in the dry ice-acetone trap. This was decomposed in 250 ml. ice cold 10% NaOH to give 12·5 g (54% yield) of crude product. Pure product (**22**) boils at 32·5–33°; lit.[14] 32·5–33°; δCH 4·45 (septet). J_{HCCF} 6·4 Hz. A similar mixture when heated at 160–170° for 4 hr. in an aerosol compatibility tube (Fischer--Porter) led to a 31% yield of crude product.

1-Chloro-1.1.3.3.3-pentafluoro-2-phenyl-2-propanol (**25**). (**25**) was prepared in 84% yield by the $AlCl_3$ catalyzed addition of monochloropentafluoroacetone to C_6H_6 according to the method of Gilbert *et al.*;[16] b.p. 182–183°. (Calcd. for $C_9H_6ClF_5O$: C. 41·48; H. 2·32. Found: C. 41·6; H. 2·36%).

α-Trifluoromethyl-β.β-difluorostyrene (**26**). A mixture of (**25**) (39·2 g; 0·15 mole) and dibromotriphenylphosphorane (70 g; 0·166 mole) was heated to 200° (30 min). When the temp. reached 190° gaseous evolution became rapid and remained rapid up to 200°. The temp. then fell to 165° over the next 3 hr. due to refluxing product. 14 ml. of product were collected in a Dean–Stark receiver. The mixture was heated for a further 1 hr. and an additional 5 ml. of product were collected. The combined 19 ml. of light orange liquid fumed in air (loss of HBr and BrCl) and left behind 25·4 g (82% yield) of crude product (**26**) as a colorless liquid. GLC showed the product to be pure and the IR spectrum was found to be superimposable with that of an authentic sample prepared according to the method of Kaufman and Braun.[2] (We wish to express our thanks to Dr. E. S. Jones of Specialty Chemicals Division for supplying us with this sample.)

Difluorochloromethyldiphenylcarbinol (**28**). (**28**) was prepared in 85·5% yield by the reaction of ethyl difluorochloroacetate and PhMgBr; m.p. 73–77·5° from petroleum ether (b.p. 30–80°). lit.[17] m.p. 78--79°.

Diphenyldifluoroethylene (**29**). A mixture of (**28**) (13·5 g; 0·05 mole) and dibromotriphenylphosphorane (25·5 g; 0·06 mole) was heated to 260° (15 min) and cooled to 25°. Distillation and redistillation gave 1·6 g (21%) pure product (**29**). b.p. 91–97°/1·5 mm (lit.[18] b.p. 75–85°/0·3 mm); C=C str. 1709 cm^{-1}; δCF_2 88·5 (s).

Reaction of (**11**) *with dichlorotriphenylphosphorane*. To a stirred solution of triphenylphosphine (M & T Chemicals) (13·1 g; 0·05 mole) and 100 ml. of CCl_4 (B & A reagent grade) at 5° (protected from the atmosphere by Drierite) chlorine (4 g; 0·056 mole) was added slowly over a period of 25 min. The temp. was maintained below 10°. The resulting mixture was stirred at room temp. for 20 min and exhaustively evaporated to constant weight to give 16·7 g. of crude dichlorotriphenylphosphorane as a white solid.[11] 2-Trichloromethyl-hexafluoro-2-propanol (**11**) (8·6 g; 0·03 mole) was added and the mixture heated at 160–185° for 20 min. 3·3 g. (44% yield) of crude 2-chlorohexafluoroisobutyryl chloride (**30**)[11] distilled as a water-white liquid. It was shown to be about 85% pure by GLC. The pure compound boiled at 65–67° (lit.[19] b.p. 68–80°). The IR spectrum was consistent with an acid chloride. since it showed a strong carbonyl absorption at 1802 cm^{-1}. and strong C-F absorption at 1280–1190 cm^{-1}. The compound was further identified by conversion to the anilide (**31**). m.p. 72–75° (from 50% EtOH); (lit.[20] m.p. 77–78°). (Calcd for $C_{10}H_6ClF_6NO$: C. 39·3; H. 1·9; N. 4·6; Cl. 11·6. Found: C. 39·8; H. 1·9; N. 4·4; Cl. 11·5%).

Catalytic example. A mixture of (**11**) 8·6 g; 0·03 mole) and dichlorotriphenylphosphorane (0·50 g; 0·0015 mole) in a pressure vessel (Fischer–Porter "Aerosol Compatibility Tube") was heated to 205° over 2 hr. and held at 205–210° for 5 hr. (pressure at 125 psig). The mixture was cooled to 25° (40 psig) and vented. The pressure vessel was resealed and heated at 200–205° for 2 hr. (70 psig). after which it was cooled and vented. Two layers were obtained. The lower layer was distilled to give 1·2 g. (16%) of (**30**). The residue amounted to 1·6 g (11%) of crude ester (**32**). b.p. 136–38°; C=O str. 1802 cm^{-1}. (Calcd. for $C_8Cl_4F_{12}O_2$:

C. 19·28; Cl. 28·5. Found: C. 19·56; Cl. 28·4%).

While the upper layer was not totally investigated. its IR exhibited the characteristic peaks of the olefin (**14**). acid chloride (**30**). and ester (**32**).

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