Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

THE PREPARATION AND REACTIONS OF SOME CARBINOLS CONTAINING THE PENTAFLUOROPROPENYL GROUP

PAUL TARRANT, RALPH W. WHITFIELD, JR. AND RICHARD H. SUMMERVILLE
Department of Chemistry, University of Florida, Gainesville, Fla. 32601 (U.S.A.)

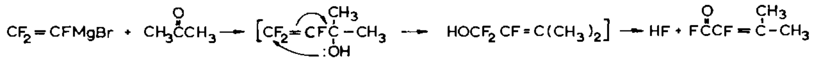
(Received September 8th, 1970)

SUMMARY

1,1,1,2,3,3-Hexafluoropropane was dehydrofluorinated to yield a 1:1 mixture of *(Z)*- and *(E)*-1*H*-pentafluoropropene. This mixture was found to react with butyl-lithium to give pentafluoropropenyl-lithium, which reacted with a series of carbonyl compounds to give exclusively *(Z)*- pentafluoropropenyl carbinols. The yields were greater than 50%, indicating that the lithium reagent does not retain its stereochemical identity at low temperature, contrary to the hydrocarbon analog. Hydrolysis of the $CF_3CF{=}CFLi$ also gives exclusively the *(Z)*-*F*-olefin. Treating *(Z)*-$CF_3CF{=}CFC(CF_3)_2OH$ with SF_4 gave the *(E)* isomer. Some chemical properties of the carbinols are described.

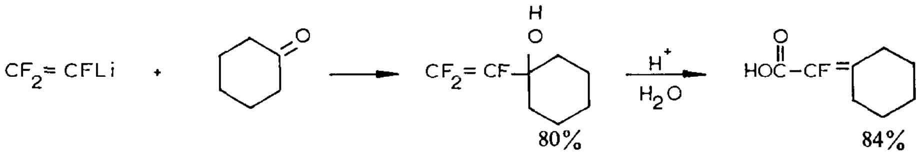
INTRODUCTION

In 1958 Sterlin, Yatsenko and Knunyants[1] reported the formation of α-fluoro-β-methylcrotyl fluoride from the reaction of trifluorovinylmagnesium bromide with acetone. They postulated the following rearrangement to account for the product:



$$CF_2{=}CFMgBr + CH_3\overset{O}{C}CH_3 \rightarrow [CF_2{=}CF\overset{CH_3}{\underset{:OH}{C}}-CH_3 \rightarrow HOCF_2CF{=}C(CH_3)_2] \rightarrow HF + F\overset{O}{C}CF{=}\overset{CH_3}{C}-CH_3$$

In 1963 we reported[2] the isolation of the unsaturated tertiary alcohol from the reaction of trifluorovinyl-lithium and cyclohexanone, and showed that it rearranged to cyclohexylidenefluoroacetic acid in 84% yield when refluxed with hydrochloric acid.



Furthermore, it was shown that the presence of a perfluoroalkyl group on the carbinol carbon retards the rearrangement; when methyl-lithium, trifluorovinyl bromide and pentafluoropropionaldehyde were allowed to react, the chief product (28%) was the tertiary alcohol and only a small amount ($<2\%$) of α-fluoro-β-pentafluoroethylacrylic acid was formed. Trifluoroacetaldehyde gave[3] a 53% yield of $CF_3CH(OH)CF{=}CF_2$ and no $CF_3CH{=}CFCO_2H$. Later experiments[4] were carried out in which $CF_2{=}CFC(CF_3)_2OH$ was recovered unchanged after 40 h at 225° or after reflux with 60% sulfuric acid for 36 h.

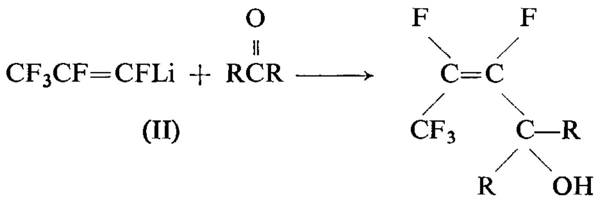
Lithium reagents made from $CF_2{=}CHF$ and $CF_2{=}CHCl$ reacted with acetone to give $(CH_3)_2C{=}CFCO_2H$ and $(CH_3)_2C{=}CClCO_2H$, whereas $CFCl{=}CHCl$ gave a 53% yield of $CFCl{=}CClC(OH)(CH_3)_2$. On the basis of these results[3] it was suggested that a $CF_2{=}$ group was necessary for rearrangement to occur.

Partly to test this concept, and partly to extend the usefulness of unsaturated fluorocarbon lithium reagents, we became interested in $CF_3CF{=}CFLi$ and its reaction products with carbonyl compounds.

RESULTS AND DISCUSSION

Knunyants[5] *et al.* have reported that hexafluoropropylene reacts with hydrogen to give $CF_3CHFCHF_2$ in 96% yield, and that it loses HF to give $CF_3CF{=}CHF$. Campbell, Stephens and Tatlow[6] have shown that 1*H*-nonafluorocyclohexene, 1*H*-heptafluorocyclopentene and 1*H*-pentafluorocyclobutene form lithium reagents which, when treated with acetaldehyde, give the corresponding secondary alcohol in yields of 63%, 42% and 23%, respectively.

We have now found that 1,2,3,3,3-pentafluoropropylene (I) undergoes exchange with butyl-lithium to give pentafluoropropenyl-lithium (II) in at least a 90% yield. Compound (II) was allowed to react with hexafluoroacetone, dichlorotetrafluoroacetone and acetone respectively to give the corresponding pentafluoropropenyl tertiary alcohols (III), (IV) and (V) in yields of 84, 73 and 70%.



(III) $R{=}CF_3$

(IV) $R{=}CF_2Cl$

(V) $R{=}CH_3$

These alcohols showed no inclination to rearrange, thus lending further support to the theory that a $CF_2{=}$ group is needed for this type of reaction to occur.

Compound (II) reacted with acetaldehyde and benzaldehyde to form the secondary alcohols (VI) and (VII) in yields of 63 and 84%, respectively. Tertiary alcohols containing two $CF_3CF=CF$ groups were obtained from (II) and an acid chloride; for example, acetyl chloride and trifluoroacetyl chloride with (II) gave $(CF_3CF=CF)_2C(CH_3)OH$ (VIII) in 85% and $(CF_3CF=CF)_2C(CF_3)OH$ (IX) in 67% yield. Compound (II) also reacted with carbon dioxide to give pentafluorocrotonic acid (X), which could not be purified sufficiently for elemental analysis; however, a pure sample of the ammonium salt (XI) was obtained.

Trimethylchlorosilane reacted with (II) to give $CF_3CF=CFSi(CH_3)_3$ (XII) in 90% yield. Since the yield of the products was based on the two-step reaction (I) → (II) → products, it follows that the hydrogen–lithium exchange occurred to the extent of at least 90%, and was probably close to quantitative.

Surprisingly, the lithium salt of $CF_3CF=CFC(CF_3)_2OH$ failed to react with trimethylchlorosilane, and 90% was recovered; under similar conditions $CF_2=CFC(CF_3)_2OLi$ reacted to give $CF_2=CFC(CF_3)_2OSi(CH_3)_3$ (XIII) in 38% yield.

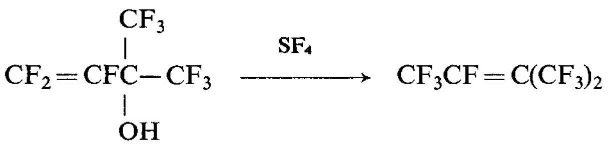
One of the unusual features of the reaction sequence (I) → (II) → products is the formation of *(Z)*-products exclusively. These results were unexpected since Curtin and Crump[7] have shown that *(Z)* and *(E)*-propenyl-lithium were configurationally stable for 1 h in refluxing ether, and Dreiding and Pratt[8] observed a 70–90% preservation of configuration when *(Z)*- and *(E)*-2-bromo-2-butene were transformed into the corresponding acids by carbonation of the lithium reagents.

^{19}F NMR analysis showed the dehydrohalogenation product to be a 1:1 mixture of *(Z)*- and *(E)*-$CF_3CF=CHF$. When this mixture was treated with buthyl-lithium, and the salt hydrolyzed, only the *(Z)* product was formed. This experiment indicates the probable exclusive formation of the *(Z)*-lithium reagent from the mixture.

The formation of *(Z)*-$CF_3CF=CFSi(CH_3)_3$ in 90% yield, and the *(Z)*-carbinols in yields significantly greater than 50%, show that rearrangement of *(E)*-(I) to *(Z)*-lithium reagent is occurring.

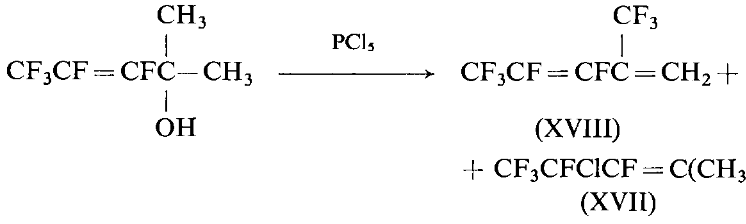
A study is underway in our laboratory to discover the scope of the rearrangement, and the results will be reported later.

Some of the chemical properties of the pentafluoropropenyl carbinols were studied. When *(Z)*-$CF_3CF=CFC(CF_3)_2OH$ (III) was treated with sulfur tetrafluoride at 200° for 36 h, two products were found to be present in a ratio of 3:7. They were separated by preparative gas–liquid phase chromatography and identified by ^{19}F NMR spectroscopy as the *(Z)*-compound (*i.e.*, starting material), with coupling constants about 10–11 Hz for the *(Z)* fluorine atoms, and its *(E)* isomer (XIV), and with coupling constant of 137 Hz for the *(E)* fluorine. These results are in marked contrast to those reported[4] for the reaction of $CF_2=CFC(CF_3)_2OH$ and sulfur tetrafluoride which under milder conditions, at 125° for 20 h, gave the rearranged perfluoro-2-methyl-2-butene in 40% yield.



$$CF_2{=}CF\overset{\displaystyle CF_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}CF_3 \xrightarrow{SF_4} CF_3CF{=}C(CF_3)_2$$

Phosphorus pentachloride also reacts with componds containing the $CF_2{=}CF{-}\overset{|}{\underset{|}{C}}{-}OH$ grouping to give chlorine-containing, rearranged products[4]. For example, $CF_2{=}CFC(CF_2Cl)_2OH$ and PCl_5 gave $CF_2ClCF{=}C(CF_2Cl)_2$ in 58% yield, while the lithium salt of the corresponding perfluoro compound gave $CF_2ClCF{=}C(CF_3)_2$ in 33% yield. When pentafluoropropenyl-bis-trifluoromethyl carbinol (III) was treated with PCl_5, a 40% yield of $CF_3CFCl{-}CF{=}C\genfrac{}{}{0pt}{}{\diagup CF_3}{\diagdown CF_3}$ (XV) was obtained. Similar results were obtained from $CF_3CF{=}CF{-}CHOHCH_3$, which gave $CF_3CFClCF{=}CHCH_3$ (XVI). However, this reaction with $CF_3CF{=}CFC(CH_3)_2OH$ proceeded under very mild conditions to give a butadiene as the preponderant product, along with a minor amount of the chloro-olefin.



$$CF_3CF{=}CF\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}CH_3 \xrightarrow{PCl_5} \underset{\text{(XVIII)}}{CF_3CF{=}CF\overset{\displaystyle CF_3}{\overset{|}{C}}{=}CH_2} + \underset{\text{(XVII)}}{CF_3CFClCF{=}C(CH_3)_2}$$

When a mixture of $CF_3CF{=}C(CF_3)_2OH$ and $CF_2{=}CFCl$ was heated to 200° for 20 h, a quantitative yield of 1,2-dichlorohexafluorocyclobutane was obtained, and the alcohol recovered quantitatively.

It has been found that, whereas $CF_2{=}CFC(CF_3)_2OH$ does not rearrange even at 450°, its acetate apparently rearranges and cleaves to acetyl fluoride and $(CF_3)_2C{=}CFCOF$. The acetate of $CF_3CF{=}CFC(CF_3)_2OH$ (IX) was prepared by reaction with acetyl chloride, and passed through a tube heated to 530°. The products were found to be unreacted starting material, (IX) and acetic acid.

EXPERIMENTAL *

Preparation of unsaturated carbinols

The preparation of perfluoro-2-methyl-3-penten-2-ol (nc) is typical of the method used.

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* Analyses by PCR Inc., Gainesville, Florida.

In a 500 ml 3-necked flask, with argon sweep and magnetic stirrer, butyllithium (0.2 mole) in 130 ml hexane and 130 ml dry ether were cooled to −78° in a Dry Ice–acetone bath. 1-Hydroperfluoropropene (35 g, 0.26 mole) was condensed into the solution. The reaction mixture was stirred for 2 h. Then hexafluoroacetone (45 g, 0.27 mole), previously condensed in a cold trap, was placed in a jacketed addition funnel cooled by Dry Ice–acetone. The hexafluoroacetone was added dropwise over a period of 30 min. The mixture was then allowed to warm up slowly to room temperature. The solvents were removed under an aspirator vacuum under a heat lamp. The residue was hydrolyzed with 25 ml of concentrated hydrochloric acid in 75 ml of water. The organic layer was separated and dried over Drierite. Distillation gave 43.4 g (73%) of $CF_3CF{=}CFC(CF_3)_2OH$, (III), b.p. 85°, n_D^{25} 1.3059. The infrared spectrum had absorption bands at 2.76 (m), 2.9 (s), 5.86 (m), 6.22 (m), 9.75 (vs), 10.45 (vs), 14.76 (vs), and 13.23 (m) μ. The proton nuclear magnetic resonance spectrum had a broad singlet centered at 6.2 τ. The mass spectrum had peaks at 298 [M], and 229 [M−CF_3], $J(CF{=}CF)$ 10.9, 11.2 Hz. Calcd. for $C_6HF_{11}O$: C, 24.16; H, 0.34; Found: C, 23.99; H, 0.46.

1-Chloro-2-(chlorodifluoromethyl)perfluoro-3-penten-2-ol (IV) (nc)

Following the procedure given above, *sym*-dichlorotetrafluoroacetone (20 g, 1 mole) was added to 1-lithioperfluoropropene at −78°. Distillation of the final product gave 23 g (70%) of $CF_3CF{=}CFC(CF_2Cl)_2OH$, (IV), b.p. 135–137°, n_D^{25} 1.3557. The infrared spectrum had absorption bands at 2.81 (s), 3.1 (m), 5.9 (vs), 9.75 (s), 10.4 (vs), 13.86 (m), and 15.2 (m) μ. The proton nuclear magnetic resonance spectrum showed a broad singlet centered at 6.1 τ. The mass spectrum had peaks at 330 [M] (two chlorine atoms), 245 [M−CF_2Cl] (one chlorine atom), and 85 [CF_2Cl] (one chlorine atom), $J(CF{=}CF)$ 12.4 Hz. Calcd. for $C_6HCl_2F_9O$: C, 21.75; H, 0.30; Found: C, 21.45; H, 0.48.

2-Methyl-3,4,5,5,5-Pentafluoro-3-penten-2-ol (V) (nc)

Following the general procedure, acetone (5.8 g, 0.1 mole) was added to 1-lithioperfluoropropene (0.1 mole) at 78°. Distillation of the final product gave 16 g (84%) of $CF_3CF{=}CFC(CH_3)_2OH$, (V), b.p. 114°, n_D^{25} 1.3549. The infrared spectrum had absorption bands at 2.9 (m), 3.4 (m), 5.9 (vs), 7.5 (s), 8.4 (m), 8.8 (m), 9.1 (s), 10.4 (s), and 13.55 (s) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at 6.9 τ and a doublet centered at 8.7 τ. The mass spectrum had peaks at 190 [M], 175 [M−CH_3], 121 [M−CF_3], and 69 [CF_3], $J(CF{=}CF)$ 12.4 Hz. Calcd. for $C_6H_7F_5O$: C, 37.89; H, 3.68; Found: C, 38.12; H, 3.98.

3,4,5,5,5-Pentafluoro-3-penten-2-ol (VI) (nc)

Acetaldehyde (4.4 g, 0.1 mole) was added to 1-lithioperfluoropropene (0.1 mole) at −78°. Distillation of the final product gave 11.0 g (63%) of

$CF_3CF{=}CFCHOHCH_3$, (VI), b.p. 110°, $n_D{}^{25}$ 1.3449. A positive iodoform test was obtained with this alcohol. The proton nuclear magnetic resonance spectrum had a singlet at 5.4 τ, an octet at 5.3 τ, and a doublet at 8.7 τ. The mass spectrum had peaks at 176 [M], 175 [M−H], 161 [$M-CH_3$], 107 [$M-CF_3$], and 69 [CF_3], *J*(CF=CF) 0 Hz. Calcd. for $C_5H_5F_5O$: C, 34.09; H, 2.84; Found: C, 33.87; H, 2.84.

1-Phenyl-2,3,4,4,4-pentafluoro-2-buten-1-ol (VII) (nc)

Freshly distilled benzaldehyde (5.3 g, 0.05 mole) was added to 1-lithioperfluoropropene at −78°. Distillation of the final product gave 10 g (84%) of $CF_3CF{=}CFCHOHC_6H_5$, (VII), b.p. 204°, $n_D{}^{25}$ 1.4509. The infrared spectrum had absorption bands at 2.99 (m), 3.3 (w), 5.85 (vs), 6.7 (s), 6.9 (s), 7.4 (s), 8.4 (m), 8.75 (m), 9.3 (m), 9.65 (m), 9.79 (m), 10.3 (s), 12.0 (m), 12.4 (m), 13.5 (s), 13.9 (m), 14.35 (s), and 15.9 (m) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at 5.8 τ, a doublet centered at 4.77 τ, and a multiplet at 3.1 τ. The mass spectrum had peaks at 238 [M], 219 [M−F], 161 [$M-C_6H_5$], and 131 [C_3F_5], *J*(CF=CF) 8.8, 11.5. Calcd. for $C_{10}H_7F_5O$: C, 50.04; H, 2.94; Found: C, 50.00; H, 2.84.

4-Methylperfluoro-2,5-heptadien-4-ol (VIII) (nc)

Acetyl chloride (3.9 g, 0.05 mole) was added to 1-lithioperfluoropropene at −78°. Distillation of the final product gave 12 g (85%) of $(CF_3CF{=}CF)_2C(CH_3)OH$, (VIII), b.p. 135°, $n_D{}^{25}$ 1.3458. The infrared spectrum had absorption bands at 2.75 (s), 2.9 (m), 3.4 (m), 5.9 (vs), 7.4 (s), 8.3 (m), 8.6 (m), 9.2 (s), 9.4 (s), 10.3 (s), 11.05 (m), 13.5 (s), 14.0 (m), and 14.5 (m) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at 4.6 τ and a multiplet centered at 8.3 τ. The mass spectrum had peaks at 306 [M], 291 [$M-CH_3$], 287 [M−F], 237 [$M-CF_3$], and 69 [CF_3]. Calcd. for $C_8H_4F_{10}O$: C, 31.37; H, 1.31; Found: C, 31.08; H, 1.31.

4-Trifluoromethylperfluoro-2,5-heptadien-4-ol (IX) (nc)

Trifluoroacetyl chloride (7.0 g, 0.053 mole) was added to 1-lithioperfluoropropene (0.05 mole) at −78°. Distillation of the final product gave 12 g (67%) of $(CF_3CF{=}CF)_2C(CF_3)OH$, (IX), b.p. 119°, $n_D{}^{25}$ 1.3235. The infrared absorption spectrum had absorption bands at 2.9 (m), 5.9 (vs), 7.4 (s), 7.8 (m), 8.3 (m), 8.6 (m), 9.75 (m), 9.9 (m), 11.33 (s), 11.7 (m), 12.0 (m), 13.4 (s), and 13.8 (s) μ. The proton nuclear magnetic resonance spectrum had a singlet at 4.5 τ. The mass spectrum had peaks at 360 [M], 341 [M−F], 291 [$M-CF_3$], 272 [$M-CF_4$], 131 [C_3F_5], and 69 [CF_3]. Calcd. for $C_8HF_{13}O$: C, 26.67; H, 0.28; Found: C, 26.69; H, 0.42.

Perfluorocrotonic acid (X) (nc) and the ammonium salt of perfluorocrotonic acid (XI) (nc)

Carbon dioxide was bubbled slowly through a solution of 1-lithioperfluoropropene in hexane–ether at —78°. The bubbling was continued as the reaction mixture was allowed to warm up slowly to room temperature. Distillation of the final product gave 12 g (68%) of $CF_3CF=CFCOOH$, (X), b.p. 143°, n_D^{25} 1.3479. The infrared spectrum had absorption bands at 3.2 (b), 5.8 (s), 6.0 (s), 7.0 (m), 7.5 (s), 8.2 (m), 8.55 (m), 8.7 (m), and 10.3 (m) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at —0.3 τ. The mass spectrum had peaks at 176 [M], 175 [M—H], 132 [M—CO_2] and 69 [CF_3], $J(CF=CF)$ 10.5 Hz.

The ammonium salt of perfluorocrotonic acid was prepared by the reaction of the acid with concentrated ammonia solution. The salt was dried under vacuum and then recrystallized two times from ethyl acetate. Recrystallization gave 400 mg of $CF_3CF=CFCOONH_4$, (XI), m.p. 160°. Calcd. for $C_4H_4F_5NO_2$: C, 24.87; H, 2.07; N, 7.25; Found: C, 24.86; H, 1.84; N, 7.33.

Perfluoropropenyltrimethylsilane (XII) (nc)

Chlorotrimethylsilane (0.1 mole) was added to 1-lithioperfluoropropene (0.1 mole) at —78°. The reaction mixture was allowed to warm up slowly to room temperature. A large quantity of white salt, identified later as LiCl, precipitated during this time. The reaction mixture was filtered. Distillation gave 18 g (90%) of $CF_3CF=CFSi(CH_3)_3$, (XII), b.p. 94°, n_D^{25} 1.3515. The infrared spectrum had absorption bands at 3.4 (s), 6.04 (vs), 7.40 (s), 7.99 (vs), 8.40 (s), 8.80 (s), 9.20 (s), 10.72 (vs), 11.90 (m), 13.10 (m), and 13.65 (vs) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at 9.9 τ. The mass spectrum had peaks at 204 [M], 189 [M—CH_3], 170 [M—CH_3F], 155 [M—CF_3], 131 [M—$(CH_3)_3Si$], 73 [$(CH_3)_3Si$], and 69 [CF_3], $J(CF=CF)$ 10.3 Hz. Calcd. for $C_6H_9F_5Si$: C, 35.29; H, 4.41; Found: C, 35.13; H, 4.62.

Reaction of $CF_2=CFC(CF_3)_2OLi$ with trimethylchlorosilane

In a 500 ml three-necked flask, with argon sweep and magnetic stirrer, butyl-lithium (0.1 mole) in 65 ml hexane and 65 ml dry ether was cooled to —78° in a Dry Ice–acetone bath. Trifluoroethylene (8.2 g, 0.1 mole), previously condensed in a trap, was placed in a jacketed addition funnel cooled by Dry Ice–acetone. The hexafluoroacetone was added dropwise over a period of half an hour. The mixture was then allowed to warm up slowly to room temperature. The solvents were removed under reduced pressure. A dropping funnel and a reflux condenser were attached to the flask. Freshly distilled trimethylchlorosilane (11 g, 0.1 mole) was added to the residue with stirring. An exothermic reaction took place under reduced pressure. Distillation gave 12 g (38%) of $CF_2=CFC(CF_3)_2OSi(CH_3)_3$ (XIII), (nc), b.p. 112°, n_D^{25} 1.3395. The infrared spectrum had absorption bands at 3.38 (m), 5.65 (s), 7.48 (s), 7.79 (s), 7.98 (m), 8.14 (m), 8.6 (m), 8.9 (s), 10.4 (m), 11.0 (s), 11.5 (m), 11.8 (m), 13.15 (m), 13.48 (m), and 13.82 (s) μ. The proton nuclear magnetic resonance spectrum had a sharp singlet at 9.55 τ. The mass spectrum had peaks at 305 [M—CH_3], 251 [M—CF_3], 73 [$(CH_3)_3Si$], and 69 [CF_3]. Calcd. for $C_8H_9F_9OSi$: C, 30.00; H, 2.81; Found: C, 30.04; H, 2.57.

Reaction of $CF_3CF=CFC(CF_3)_2OH$ (III) with sulfur tetrafluoride

$CF_3CF=CFC(CF_3)_2OH$ (0.1 mole) (III) and sulfur tetrafluoride (0.1 mole) were heated together in a stainless steel autoclave at 175° for 24 h. No reaction took place. The reaction mixture was then heated at 200° for 26 h. After cooling, the autoclave was opened to a trap. The condensed gases were identified as unreacted sulfur tetrafluoride and HF. The liquid remaining in the autoclave consisted of unreacted carbinol (30%) and a new compound (70%), as determined by GLPC. The two components were separated by means of preparative gas-liquid phase chromatography. The new compound was identified as the *trans* isomer of $CF_3CF=CFC(CF_3)_2OH$, (XIV) (nc), b.p. 83°, n_D^{25} 1.2929. The infrared spectrum had absorption peaks at 2.78 (m), 2.9 (b), 7.25 (s), 8.4 (s), 8.6 (s), 10.4 (s), 12.3 (s), 13.75 (vs), and 14.7 (s) μ. The double bond was not visible in the infrared spectrum. The proton nuclear magnetic resonance spectrum had a very broad singlet centered at 6.8 τ. The mass spectrum was identical to that of (III), the *cis* isomer. The *trans* structure was confirmed by the ^{19}F nuclear magnetic resonance spectrum with a coupling constant of 137 Hz.

Reaction of $CF_3CF=CFC(CF_3)_2OH$ (III) with phosphorus pentachloride

Compound (III) (12 g, 0.04 mole) and phosphorus pentachloride (15 g, 0.07 mole) were refluxed for 24 h. The solution was hydrolyzed with 50 g ice, the product layer was separated, washed with 20 ml water, 20 ml of 10% K_2CO_3 solution and 20 ml water, and dried over Drierite. Separation on preparative GLPC gave 4-chloro-2-trifluoromethyl-1,1,1,3,4,5,5,5-octafluoropentene-2, (XV), (nc), 0.5 g (40%), b.p. 75°, n_D^{25} 1.3008. The infrared spectrum showed absorptions at 6.00 (s), 7.56 (s), 10.20 (s), 10.72 (s) and 12.45 (m) μ. The mass spectrum had peaks at 316 [M] (1 chlorine atom), 297 [M—CF_3] and 181 [M—C_2F_4Cl]. Calcd. for C_6ClF_{11}: C, 22.73; Found: C, 23.67.

Reaction of $CF_3CF=CFCHOHCH_3$ (VI) with phosphorus pentachloride

$CF_3CF=CFCHOHCH_3$ (4.4 g, 0.025 mole) was refluxed with phosphorus pentachloride (5.4 g, 0.025 mole) for 24 h. The reaction mixture was hydrolyzed by pouring over 100 g of crushed ice. The organic layer was separated and dried over Drierite. Distillation gave 3.5 g (72%) of $CF_3CFClCF=CHCH_3$, (XVI), (nc), b.p. 69°, n_D^{25} 1.3454. The infrared spectrum had absorption peaks at 3.4 (w), 5.95 (m), 7.4 (a), 8.4 (s), 8.75 (s), 9.5 (s), 10.15 (s), 10.5 (s), 13.25 (m), 14.25 (m), and 14.85 (m) μ. The proton nuclear magnetic resonance spectrum had a doublet centered at 8.7 τ (peak area of three protons) and a doublet split into two quartets centered at 5.5 τ (peak area of one proton). The mass spectrum had peaks at 194 [M] (one chlorine atom), 179 [M—CH_3] (one chlorine atom), 159 [M—Cl], 125 [M—CF_3] (one chlorine atom) and 69 [CF_3]. Calcd. for $C_5H_4ClF_5$: C, 30.85; H, 2.06; Found: C, 30.73; H, 2.19.

Reaction of $CF_3CF{=}CFC(CH_3)_2OH$ (V) with phosphorus pentachloride

$CF_3CF{=}CFC(CH_3)_2OH$ (12 g, 0.063 mole) (V) was refluxed with phosphorus pentachloride (13 g, 0.063 mole) for 30 h. The reaction mixture was hydrolyzed by pouring over 100 g of crushed ice. The organic layer was separated, washed with 25 ml of water and dried over Drierite. Distillation gave 3.7 g (18%) of $CF_3CFClCF{=}C(CH_3)_2$, (XVII), (nc), and 13.4 g (72%) of $CF_3CF{=}CFC(CF_3){=}CH_2$, (XVIII), (nc), b.p. 93°. Pure samples of the two compounds could be obtained only by means of preparative gas–liquid chromatography.

The infrared spectrum of $CF_3CFClCF{=}C(CH_3)_2$ had absorption bands at 3.4 (m), 6.1 (s), 7.4 (vs), 8.3 (m), 9.0 (m), and 10.3 (m) μ. The proton nuclear magnetic resonance spectrum had two sharp singlets at 8.10 and 8.14 τ. The mass spectrum had peaks at 208 [M] (one chlorine atom), 195 [M—CH_3] (one chlorine atom), 173 [M—Cl], 139 [M—CF_3], and 69 [CF_3]. Calcd. for $C_6H_6ClF_5$: C, 34.54; H, 2.88; Found: C, 34.63; H, 2.76.

The infrared spectrum of $CF_3CF{=}CFC(CH_3){=}CH_2$ had absorption bands at 5.89 (s), 7.4 (s), 8.3 (s), 8.79 (m), 9.0 (m), 10.4 (m) and 13.4 (m) μ. The proton nuclear magnetic resonance spectrum had a multiplet centered at 5.0 τ (peak area of two protons) and a multiplet centered at 8.5 τ (peak area of three protons). The mass spectrum had peaks at 172 [M], 157 [M—CH_3], 103 [M—CF_3], and 69 [CF_3]. Calcd. for $C_6H_5F_5$: C, 41.86; H, 2.85; Found: C, 41.85; H, 2.80.

Preparation of 2-acetoxy-2-trifluoromethylperfluoropentene-3 (XIX) (nc)

The lithium salt of (III) was prepared from (II) and hexafluoroacetone (0.22 mole) as described above. The solvent was removed to give a solid which was treated with acetyl chloride (0.25 g, 0.32 mole). The vigorously refluxing reaction was left to stir for 6 h. This solution was hydrolyzed with 70 ml water. The product layer was separated, washed with 40 ml water, 50 ml of 10% NaOH solution and 40 ml water, and dried over $CaCl_2$. Acidification of the basic extract gave $CF_3CF{=}C(CF_3)_2OH$ (III) (8.0 g). Distillation through a 10 cm Vigreaux column gave CF_3–$CF{=}CFC(CF_3)_2OAc$, (XIX), 34 g (50%), b.p. 114–116°, n_D^{23} 1.3181. The infrared spectrum had absorption bands at 3.4 (vw), 5.70 (s), 5.92 (m) and 11.70 (s) μ. The proton nuclear magnetic resonance spectrum had only one sharp singlet at 8.16 τ. The mass spectrum had a base peak at 43 [$COCH_3$] and peaks at 340 [M], 321 [M—F], 281 [M—$COCH_3$] and 271 [M—CF_3]. Calcd. for $C_9H_3F_{11}O_2$: C, 28.24; H, 0.88; Found: C, 27.83; H, 0.86.

ACKNOWLEDGEMENT

We are grateful to the National Science Foundation for providing funds for the support of this work under GP-8942. We also acknowledge the aid of Dr. W. S. Brey who interpreted the ^{19}F NMR spectra. Mr. Robert Checkosky prepared the $CF_3CF=CHF$ used in this research.

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