Preparation and Reactions of Some Trifluorovinylcarbinols Containing Perhalomethyl Groups[1]

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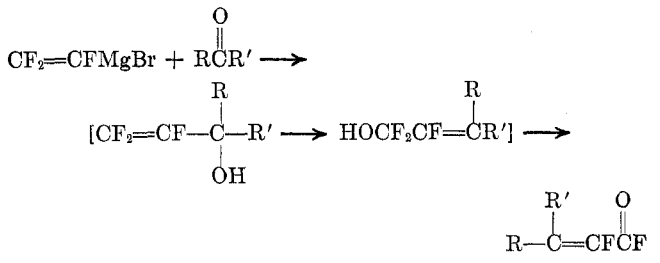
The reaction of trifluorovinyllithium with hexafluoro- and *sym*-dichlorotetrafluoroacetone and trifluoroacetyl chloride has given the corresponding tertiary alcohols. The trifluorovinyl carbinols are thermally stable and do not rearrange under acid or basic conditions; their acetates rearrange. They react with SF_4 and PCl_5 to give rearranged products. Methanol adds across the carbon–carbon double bond to give the corresponding ether.

Knunyants[2] and his associates have reported that the reaction of trifluorovinylmagnesium bromide with acetaldehyde, acetone, and benzaldehyde leads to α-fluoro-α,β-unsaturated acid fluorides; they postulated a mechanism for this reaction as follows.



Subsequent reports[3] from our laboratory have shown that these rearrangements usually occur during the purification step and that it is possible to trap the carbinol. Thus, the reaction product of trifluorovinyllithium and benzaldehyde when treated with 2-naphthyl isocyanate gave the corresponding urethan in 53% yield. Some carbinols can be isolated in the pure state and caused to rearrange in the presence of acids; trifluoromethylcyclohexanol has been found to fall into this category.

We now wish to report that the carbinols I and II

are extremely resistant to either thermal or acid-catalyzed rearrangement. When I and II were passed through a tube heated to 500°, they were recovered unchanged, and even when I was heated to 225° for 40 hr it was recovered unchanged. In addition to demonstrating that $CF_2{=}CFC(CF_3)_2OH$ does not rearrange as does $CF_2{=}CFC(CH_3)_2OH$, this latter experiment also shows that the compound does not dimerize, a reaction characteristic of many compounds containing the $CF_2{=}CF$ group. Similarly, no cyclobutane other than the dimer of $CF_2{=}CFCl$ was obtained when I was heated with $CF_2{=}CFCl$ for 18 hr at 175°; I was recovered quantitatively.

Attempts were made to cause the rearrangement of II by refluxing in 60% aqueous sulfuric for 36 hr and by subjection to 95% sulfuric acid for 2 weeks but only starting material was recovered. It might be presumed that, since the oxygen atom of the carbinol furnishes electrons to the difluoromethylene moiety of the trifluorovinyl group, rearrangement would be favored by converting the alcohol to its sodium salt. However, this was not the case since no reaction occurred when II was refluxed with 20% aqueous sodium hydroxide.

These unusual thermal stabilities and resistance to rearrangement led us to study other chemical properties of I and II.

These carbinols, along with $(CF_2{=}CF)_2C(OH)CF_3$ (III), were made by the reaction of trifluorovinyllithium with CF_2COCF_3, $CF_2ClCOCF_2Cl$, and CF_3COCl in yields of 75%, 65%, and 85%, respectively. Unsuccessful attempts were made to produce the trifluorovinyllithium reagent by the reaction of trifluoroethylene with butyllithium in hexane as ether, which is usually used, is difficult to remove. The failure of this proton exchange reaction suggests that the butyllithium hexamers which are known to exist in the commercial hydrocarbon solvents are too unreactive for this proton exchange and must be broken down by ether.

The acetates of I and II were prepared and were found to rearrange at 450° but not at 400°. The best synthetic route to the acetates was *via* the reaction of acetyl chloride with the unhydrolyzed lithium salts obtained from trifluorovinyllithium and the carbonyl compound. Using this procedure, the acetates of I and II were obtained in yields of 70% and 74%, respectively. The products from the rearrangement of the acetate of I were acetyl fluoride and perfluoro-2-methyl-2-butenoyl fluoride (50% yield). The acetate of II gave 4-chloro-3-(chlorodifluoromethyl)-2,4,4-trifluoro-2-butenoyl fluoride in 73% yield. The products from the pyrolyses were identified as acid fluorides from their infrared spectra and then converted to esters which were characterized by elemental analysis and ^{19}F nmr spectra. Presumably the reaction follows the mechanism postulated[4] for the rearrangement of $CF_2{=}CFC(OH)(CF_3)CH_3$ which gives 2-fluoro-3-trifluoromethyl-2-butenoyl fluoride.

Barna[5] has reported that phenyltrifluoromethylchlorodifluoromethyl carbinol reacts rapidly with alcoholic potassium hydroxide to give 2-phenyl-2,3,3,3-

(1) Presented at the 5th International Fluorine Symposium, Moscow, U. S. S. R., July 21–25, 1969.

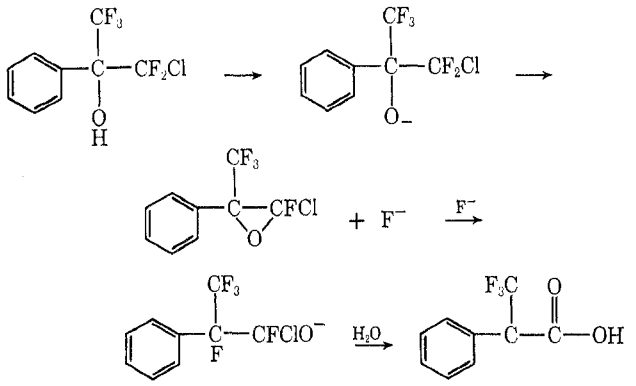
(2) R. N. Sterlin, R. D. Yatsenko, and I. L. Knunyants, *Khim Nauka Prom.*, **3**, 540 (1958); *Chem. Abstr.*, **53**, 4195 (1959).

(3) P. Tarrant, P. Johncock, and J. Savory, *J. Org. Chem.*, **28**, 839 (1963).

(4) F. G. Drakesmith, R. D. Richardson, O. J. Stewart, and P. Tarrant, *ibid.*, **33**, 286 (1968).

(5) P. M. Barna, *Aust. J. Chem.*, **21**, 1089 (1968).

tetrafluoropropionic acid quantitatively. He postulated the following mechanism.

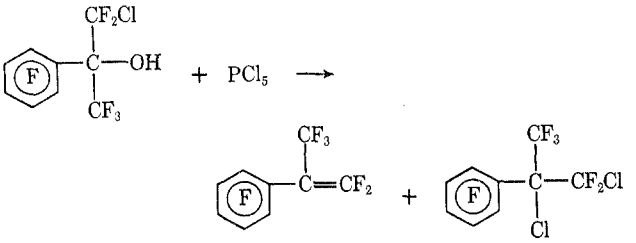


It was felt that II might undergo a similar rearrangement to CF_2=CF-CF(CF_2Cl)CO_2H. When the reaction was carried out an inseparable mixture of two compounds resulted. These were complex products which were not identified although the ^{19}F nmr spectrum was indicative of small ring compounds or compounds with a CHF group. On the basis of the reactions described below it appears more likely that the latter type of compound was obtained.

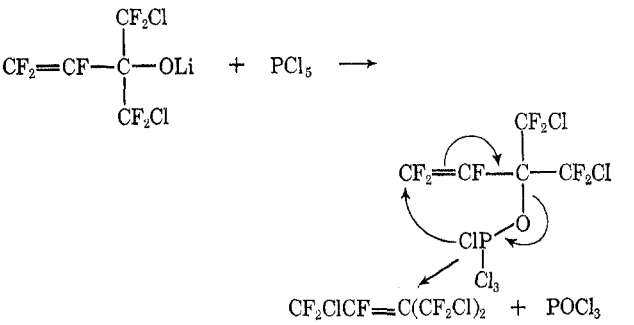
The reaction was repeated with CF_2=CFC(CF_3)$_2$OH, and the products were readily identified. Thus when I was refluxed for 24 hr with methanolic potassium hydroxide, a 13% yield of methyl 3-hydroxy-3-trifluoromethyl-2,4,4,4-tetrafluorobutanoate was formed. When heating was carried out for a shorter period, the alcohol adduct, 4-methoxy-3-trifluoromethyl-1,1,1,3,4,4-hexafluoro-2-butanol was obtained. Obviously this latter product is transformed to the former upon prolonged treatment with base. The products can be accounted for by the addition of alcohol across the double bond and subsequent reaction of the fluoro ethers to give the ester. The formation of ethers and esters from the reaction of alcohols and compounds containing the difluoromethylene group is well known.

1,3-Dichloropropanes, when treated with zinc, gives cyclopropanes. An experiment was carried out to determine if a small ring compound would be obtained from CF_2=CFC(CF_2Cl)$_2$OH; however, it appears difficult to effect cyclization as attempts to close the ring by the use of zinc in 2-propanol failed. The fact that the zinc reacted was shown by the formation of CF_2=CFC-(CF_2Cl)(CF_2H)OH in 44% yield. The ^1H nmr spectrum of this compound shows a broad singlet at τ 6.0 and a triplet at 3.84 (J = 57 cps), in a ratio of 1:1 indicative of the OH and isolated CF_2H group. Infrared, mass, and ^{19}F nmr spectra also confirmed the assigned structure.

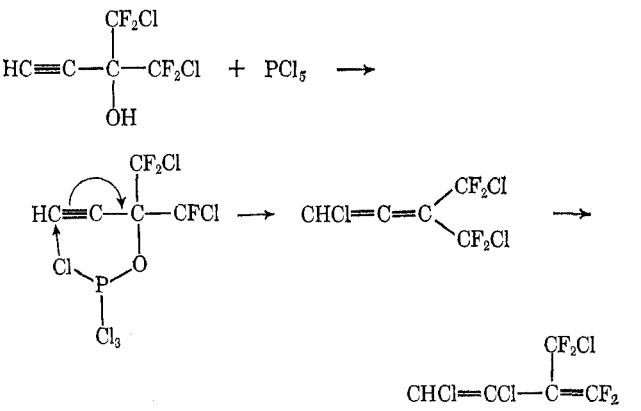
Kaufman and Braun[6] reported that phosphorus pentachloride reacts with 2-pentafluorophenyl-1,1,1,3,3-pentafluoro-3-chloro-2-propanol to give perfluoro-α-methylstyrene and its dichloride.



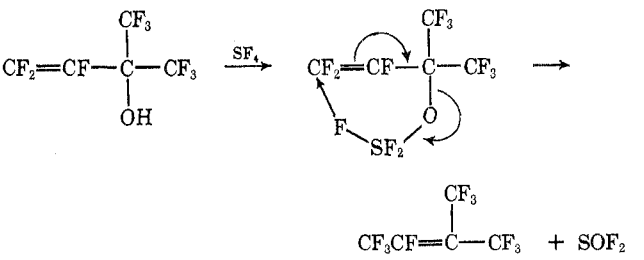
When II was treated with PCl_5 the reaction proceeded slowly, presumably because of the low nucleophilicity of the alcohol; however, the lithium salt of II reacted rapidly to give a rearranged product in 58% yield. Since the reaction of hydroxy compounds with PCl_5 is known to involve an intermediate phosphite ester, the following mechanism is postulated.



This result is similar to that reported by Dear and Gilbert[7] who found that HC≡C—C(CF_2Cl)$_2$OH gave a diene when treated with PCl_5 *via* the postulated allene intermediate.



The reaction of I and sulfur tetrafluoride gave perfluoro-2-methyl-2-butene, presumably by a cyclic intermediate as shown.



This type intermediate has been postulated for reactions of SF_4 with acetylenic alcohols containing CF_3 groups;[7] however, the reaction with I required much higher temperatures and longer reaction time.

Experimental Section[8]

Preparation of Trifluorovinyllithium in Hexane–Ether and Its Reaction with Hexafluoroacetone: The Preparation of 2-Trifluoromethylperfluoro-3-buten-2-ol (I).—In a 500-ml flask with

(6) M. H. Kaufman and J. P. Braun, *J. Org. Chem.*, **31**, 3090 (1966).

(7) R. E. A. Dear and E. E. Gilbert, *ibid.*, **33**, 819 (1968).

(8) Analyses were by Peninsular ChemResearch, Inc., Gainesville, Fla.

nitrogen sweep and magnetic stirrer, butyllithium (0.2 mol) in 130 ml of hexane and 40 ml of ether was cooled to −78° in a Dry Ice–acetone bath and trifluoroethylene (20 g, 0.25 mol) condensed into the solution. The reaction mixture was stirred for 2 hr and hexafluoroacetone (38 g, 0.23 mol), previously condensed in a cold trap, was distilled into the reaction mixture. The mixture was allowed to warm slowly to room temperature. (a) The reaction mixture was hydrolyzed with 20 ml of water and 20 ml of concentrated hydrochloric acid. The organic layer was separated, dried and distilled to give CF_2=$CFC(CF_3)_2OH$ (I), 24 g containing twenty per cent ether (40%), bp 80–85°. Ten grams of the crude product was dissolved in 50 ml of ten per cent sodium hydroxide. The solution was boiled for 5 min, cooled and acidified with concentrated hydrochloric acid. The alcohol layer was dried over Drierite and distilled to give 6 g of pure sample: bp 83–85°; $n^{24}D$ 1.3002. (Drake smith, *et. al.*,[4] reported bp 86°, $n^{24}D$ 1.3000.) (b) The reaction mixture was hydrolyzed with 40 ml of 15% sodium hydroxide. The aqueous layer was separated, acidified with hydrochloric acid and dried over Drierite. Distillation gave I, 27–32 g (54–65%), bp 80–85°, containing 5–10% ether. (c) The solvent from a duplicate of the above reaction was removed under an aspirator vacuum with a heat lamp. The residue was hydrolyzed with 25 ml of concentrated hydrochloric acid and the alcohol layer separated and dried. Distillation gave I, 35–37 g (71–75%), bp 83–85°, containing less than 5% ether.

1-Chloro-2-chlorodifluoromethyl-1,1,3,4,4-pentafluoro-3-buten-2-ol (II).—To the lithium reagent from butyllithium (0.2 mol) and trifluoroethylene (20 g, 0.25 mol) was added dropwise 1,3-dichlorotetrafluoroacetone (44 g, 0.22 mol) in 30 ml of ether, precooled in a dropping funnel containing Dry Ice–acetone mixture. The bright yellow solution was allowed to warm slowly. (a) The mixture was hydrolyzed with 20 ml of water and 20 ml of concentrated hydrochloric acid. The organic layer was separated, dried and distilled to give CF_2=$CFC(CF_2Cl)_2OH$, II, 28 g (50%) containing 15% ether, bp 118–123°. A sample of II was purified by preparative glpc to give pure II: bp 120°; $n^{23}D$ 1.3666; ir 2.95 (m), 5.65 (m) and 13.65 (s) μ; ^1H nmr broad singlet at τ 4.5; mass spectrum 280 (M) (2 Cl), 198 (M − CF_2Cl) (1 Cl), 85 (CF_2Cl), and 81 (CF_2=CF).

Anal. Calcd for $C_5HCl_2F_7O$: C, 21.43; H, 0.36. Found: C, 21.28; H, 0.51.

(b) The reaction mixture was then subjected to hydrolysis with 40 ml of 15% sodium hydroxide. The aqueous layer was separated and acidified with concentrated hydrochloric acid. The alcohol layer was separated and dried over Drierite. Distillation gave II, 32–36 g (57–65%), bp 118–122°, with 5–10% ether.

Perfluoro-3-methyl-1,4-pentadien-3-ol.—Trifluoroacetyl chloride (13.2 g, 0.1 mol) was added to a flask containing the lithium reagent from butyllithium (0.2 mol) and trifluoroethylene (0.2 mol) at −78°. The reaction mixture was allowed to warm slowly to room temperature. The solvent was removed under reduced pressure and the residue hydrolyzed with hydrochloric acid. The organic layer was separated, dried and distilled to give $(CF_2$=$CF)_2C(CF_3)OH$ (22 g, 85%): bp 91°; $n^{25}D$ 1.3351; ir 2.9 (m), 5.65 (vs), 7.55 (s), 7.95 (m), 8.3 (m), 8.8 (m), 9.35 (m), 10.6 (m) 11.19 (m), and 13.6 (m) μ; ^1H nmr spectrum had a broad singlet centered at τ 4.7; mass spectrum 260 (M), 241 (M − F), 191 (M − CF_3), and 69 (CF_3).

Anal. Calcd for C_6HF_9O: C, 27.69; H, 0.38. Found: C, 27.47; H, 0.52.

Attempted Reaction of II with Sulfuric Acid.—In a glass tube, II (3.0 g, 0.011 mol) was sealed with 95% sulfuric acid (0.5 g, 0.002 mol) and allowed to stand at room temperature for 2 weeks. The insoluble sulfuric acid was removed with a transfer pipet and the alcohol transferred to a trap under vacuum. No residue remained. No product other than II appeared on the glpc.

Attempted Reaction of II with Aqueous Sulfuric Acid.—Alcohol II (8.0 g, 0.029 mol) was refluxed with 20 ml of 60% aqueous sulfuric acid for 36 hr. The lower alcohol layer was separated and dried. Transfer of the alcohol under vacuum gave 7.6 g of recovered alcohol but no residue. No peak except II appeared in the glpc.

Reaction of II with Aqueous Sodium Hydroxide.—A solution of II (6.0 g, 0.022 mol) in 10 ml of 20% sodium hydroxide was refluxed for 18 hr. Acidification yielded II (5.2 g). No residue remained on vacuum transfer and no reaction product could be detected on the glpc.

Reaction of II with Zinc Dust in 2-Propanol.—Alcohol II (20 g, 0.07 mol) was added to a rapidly stirred mixture of zinc dust (17 g, 0.26 g-atom) in 20 ml of refluxing 2-propanol. The refluxing mixture was stirred for 72 hr. The flask was connected to a trap cooled in Dry Ice–acetone, evacuated, and the volatile liquid was transferred. The residue was poured into 75 ml of water and the lower layer was separated, dried over Drierite and distilled to give II (4.8 g) and 1-chloro-2-difluoromethyl-1,1,3,4,4-pentafluoro-3-buten-2-ol (IV), 6.2 g (44%): bp 73–75° (180 mm); $n^{32}D$ 1.3540; ir 2.8 (m), 3.0 (m), 3.32 (w) and 5.65 (s) μ; ^1H nmr triplet at τ 3.84 (J = 57 cps), broad singlet τ 6.0 with areas in the ratio 1:1; the ^{19}F nmr spectrum was consistent with this structure; mass spectrum peaks at 246 (M) (1 Cl), 195 (M − CF_2H) (1 Cl), and 161 (M − CF_2Cl).

Preparation of 2-Acetoxy-2-trifluoromethylperfluorobutene-3 (V).—(a) Alcohol I (18.6 g, 0.075 mol) was added to acetyl chloride (25 g, 0.32 mol) containing 2.0 g of sodium acetate and the mixture was refluxed for 72 hr. The reaction mixture was hydrolyzed with 50 ml of water, the organic layer separated and washed with 50 ml water, 50 ml of 10% sodium hydroxide solution, another 50 ml of water, and dried over $CaSO_4$. The basic extract was acidified to give 8 g of unreacted alcohol. The dried product was distilled to give V, 6.4 g (48%): bp 102–104°; $n^{24}D$ 1.3186; ^1H nmr sharp singlet at τ 7.92; ir 3.40 (m) and 5.67–7 (s) μ; mass spectrum base peak at 43 ($COCH_3$) and peaks at 290 (M), 231 (M − $COCH_3$), and 221 (M − CF_3).

Anal. Calcd for $C_7H_3F_9O_2$: C, 28.97; H, 1.04. Found: C, 29.11; H, 1.12.

(b) To lithium chips (1.2 g, 0.17 g-atom) in 50 ml of ether under an argon atmosphere I (12.4 g, 0.05 mol) was added. The reaction was left to stir under argon for 24 hr. Excess lithium was removed with tweezers, and acetyl chloride (10 g, 0.13 mol) was added slowly. The reaction mixture was stirred for 2 hr and worked up as in (a). No alcohol was recovered. Distillation yielded 11.3 g of acetate (78%). (c) To the lithium reagent from butyllithium (0.2 mol in 130 ml of hexane plus 40 ml of ether) and trifluoroethylene (20 g, 0.25 mol), hexafluoroacetone (0.33 g, 0.2 mol) was added. When the solution warmed to room temperature, the solvent was removed under reduced pressure (aspirator). Acetyl chloride (25 g, 0.32 mol) was added to the syrupy residue. The vigorous reaction was stirred for 4 hr and worked up as in (a). Distillation yielded 43 g (74%) of acetate. 74% yield.

Preparation of 2-Acetoxy-1-chloro-2-chlorodifluoromethyl-3,4,4-trifluoro-3-butene (VI).—(a) Alcohol II (20 g, 0.071 mol), sodium acetate (1 g), and acetyl chloride (25 g, 0.32 mol) were refluxed for 72 hr. The mixture was poured into ice water and the organic layer was separated, washed twice with 25 ml of 10% sodium hydroxide and dried over calcium chloride. Distillation gave CF_2=CF—$C(CF_2Cl)_2OAc$ (VI): 18.5 g (81%); bp 155–157°, $n^{22}D$ 1.3773; ir 3.35 (vs), 5.65 (m), and 5.70 (m) μ; ^1H nmr sharp singlet at τ 8.01; mass spectrum base peak at 43 ($COCH_3$) and 287 (M − CCl) (1 Cl), 263 (M − $COCH_3$) (2 Cl), and 273 (M − CF_2Cl).

Anal. Calcd for $C_7H_3Cl_2F_7O_2$: C, 26.00; H, 0.91; F, 41.28. Found: C, 25.86; H, 1.06; F, 41.44.

Reactions of Perfluorovinylcarbinols with Phosphorus Pentachloride.—Alcohol II (14.0 g, 0.05 mol) and phosphorus pentachloride (10.5 g, 0.05 mol) were refluxed for 24 hr with stirring. The reaction mixture was hydrolyzed by pouring it over 100 g of crushed ice. The organic layer was separated, washed with 25 ml of water, 40 ml of 15% sodium hydroxide solution, and 20 ml of water, and was dried over calcium chloride. The basic extract was acidified to give 5.5 g of II. Distillation of the product gave 1,4-dichloro-2-chlorodifluoromethyl-1,1,3,4,4-pentafluorobutene-2, (XIII), 6.2 g (58%): bp 112–113°; $n^{23}D$ 1.3676; ir 5.90 (m), 6.05 (m), 9.55 (vs), 10.01 (s), 11.7 (s), and 12.65 (s) μ; mass spectrum 298 (M) (3 Cl) 279 (M − F) (3 Cl), 263 (M − Cl) (2 Cl), 213 (M − CF_2Cl) (2 Cl) and no peak at 81 (CF_2=CF).

Anal. Calcd for $C_5Cl_3F_7$: C, 20.02. Found: C, 19.91.

Reaction of the Lithium Salt of I with Phosphorus Pentachloride.—Crude (90%) lithium salt of I from reaction of trifluorovinyl lithium with hexafluoroacetone (14 g, 0.85 mol) was placed in a 50-ml flask with phosphorus pentachloride (14 g, 0.07 mol). A vigorous reaction began immediately. The flask was connected to a trap cooled in Dry Ice–acetone. After the reaction subsided, the trap contained essentially pure 4-chloro-2-trifluoromethyl-1,1,1,3,4,4-hexafluorobutene-2, 4.4 g (33%): bp 53–55°; $n^{24}D$ <1.3000; ir 2.98 (s), 7.45 (s), 10.0 (s), 10.3 (s) and 12.1 (s) μ.

Anal. Calcd for C_5ClF_9: C, 22.51. Found: C, 22.21.

Thermal Reactions of Perfluorovinylcarbinols. Attempted Pyrolysis of I.—Alcohol I (6.0 g, 0.024 mol) was added dropwise under nitrogen to a glass-packed column heated to 550°. The

trap contained 5.5 g of brown liquid which showed only I on the glpc.

Attempted Pyrolysis of II.—Alcohol II (6.5 g, 0.023 mol) was added dropwise to the glass packed column under nitrogen heated to 475°. The yellow liquid recovered left an infinitessimal residue on removal of the volatile liquid which the glpc showed to be only II (6.1 g).

Attempted Dimerization of I.—Alcohol I (6.0 g, 0.024 mol) was sealed in a thick-walled glass tube and heated to 225° for 40 hr. The liquid remained colorless and showed no reaction products on the glpc. It left no residue on distillation and 5.9 g of I were recovered.

Pyrolysis of 2-Acetoxy-2-trifluoromethylperfluorobutene-2.—Acetate V (20.0 g, 0.69 mol) was pyrolyzed at 450°. After three passes 15.5 g of material were found in the two traps. Distillation gave a mixture of acetyl fluoride, 6.0 g, bp 20–60°; 5.5 g (43.8%) of perfluoro-3-methyl-2-butenoyl fluoride, VIII, bp 63–63°; and 4.7 g of residue (85% V by vpc). The two low boiling fractions were combined, added to 10 ml of absolute ethanol and allowed to stand overnight. The mixture was washed with 50 ml of water, 20 ml of 5% sodium hydroxide, and 15 ml of water. Drying over $CaCl_2$ and distillation gave 6.2 g of (44.3%) ethyl perfluoro-3-methyl-2-butenoate (X): bp 108°; $n^{23}D$ 1.3286; pmr of X showed a quartet at τ 5.47 (J = 7 cps) and (triplet τ 8.60 (J = 7 cps), the areas being in the ratio 2:3; ir 3.3–3.4 (m), 5.78 (s), 5.98 (s), 10.0 (s), 10.75 (s), 11.70 (s), 13.65 (s) and 14.71 (s) μ; mass spectrum 254 (M), 239 (M − CH_3), 209 (M − C_2H_2O) and 69 (CF_3).

Anal. Calcd for $C_7H_5F_7O_2$: C, 33.08; H, 1.97. Found: C, 33.32; H, 2.17.

Pyrolysis of 2-Acetoxy-1-chloro-2-chlorodifluoromethyl-3,4,4-trifluoro-3-butene (VI).—Acetate (VI) (30.0 g, 0.094 mol) was pyrolyzed at 550°. After one pass, conversion was approximately 90%. Distillation of material in the taps gave acetyl fluoride, 4.2 g (80%), and 4-chloro-3-chlorodifluoromethyl-2,4,5-trifluoro-2-butenoyl fluoride (IX), 16.5 g (73%): bp 95–97°, $n^{23}D$ 1.3650; ir 5.45 (m), 6.02 (m), 7.60 (s), 9.55 (s), and 11.5 (s) μ. For further characterization IX was converted to the ethyl ester. Compound IX (8,0 g, 0.031 mol) was dissolved in 20 ml of absolute ethanol and allowed to stand overnight. Distillation gave ethyl 4-chloro-3-chlorodifluoromethyl-2,4,4-trifluoro-2-butenoate (XI), 4.0 g (45%): bp 95–97° (85 mm); $n^{24}D$ 1.3911; ir 3.43 (w), 3.45 (w), 5.70 (s), and 6.00 (s) μ; pmr (quartet τ 5.72 J = 7 cps) and (triplet 8.65 J = 7 cps), with areas in the ratio 2:3.

Anal. Calcd for $C_7H_5Cl_2F_5O_2$: C, 29.27; H, 1.74. Found: C, 29.59; H, 1.78.

Reaction of I with Methanolic Potassium Hydroxide.—(a) In 20 ml of absolute methanol, I (10.0 g, 0.04 mol) was refluxed for 24 hr with potassium hydroxide (7.0 g, 0.1 mol). A gelatinous solid precipitated. The reaction mixture was acidified with 25 ml of concentrated hydrochloric acid and 20 ml of water, and the lower layer separated and dried. Separation on preparative glpc gave methyl 3-hydroxy-3-trifluoromethyl-2,4,4,4-tetrafluorobutanoate (XV), 1.4 g (13.5%): bp 160°; $n^{24}D$ 1.3416; ir 2.9 (vs), 3.34 (m), 5.8 (s), 6.2 (m), 10.45 (vs) and 14.3 (vs) μ; pmr doublet at τ 4.78 (J = 46 cps), broad singlet at τ 5 and a sharp singlet at τ 6.00; ^{19}F nmr spectrum was consistent with this structure; mass spectrum base peak at 59 (CH_3OCO) and peaks at 239 (M − F), 227 [M − CH_3O], 199 (M − CH_3OCO), and 189 (M − CF_3).

Anal. Calcd for $C_6H_5F_7O_3$: C, 27.91; H, 1.94. Found: C, 28.39; H, 2.21.

(b) In 20 ml of absolute methanol, compound I (10.0 g, 0.04 mol) was refluxed for 18 hr with potassium hydroxide (7 g, 0.1 mol). The mixture was acidified with gaseous hydrogen chloride and the methanol distilled off. Purification on preparative glpc gave 4-methoxy-2-trifluoromethyl-1,1,1,3,4,4-hexafluoro-2-butanol (XVI), 2.2 g (19%): bp 76° (100 mm); $n^{24}D$ 1.1316; ir 2.82 (s), 3.32 (m), 14.0 (vs), and 14.65 (vs) μ; pmr had a doublet at τ 5.32 ($J_{H-\alpha F}$ = 45 cps, $J_{H-\beta F}$ = 11 cps) a broad singlet at τ 6.07 and a sharp singlet at τ 6.52 in the ratio 1:1:3; ^{19}F nmr spectrum was consistent with this structure; mass spectum had a base peak at 81 (CH_3OCF_2) and peaks at 261 (M − F) and 191 (M − F–CF_3).

Anal. Calcd for $C_6H_5F_9O_2$: C, 25.61; H, 1.79. Found: C, 25.75; H, 1.79.

Reaction of the Lithium Salt of I with Potassium Methoxide in Methanol.—Potassium metal (8.0 g, 0.2 mol) was dissolved in 50 ml of absolute methanol under nitrogen and crude lithium salt of I (25 g, 0.1 mol) (from the reaction trifluorovinyllithium and hexafluoroacetone) was added. A vigorous reaction began immediately and the refluxing solution was left to stir for 12 hr. Acidification with 95% sulfuric acid, and distillation gave XVI, 6.5 g (25%), and 11 g of a mixture of XV with a third product inseparable by glpc or distillation.

Reaction of II with Potassium Hydroxide in Methanol.—In 40 ml of absolute methanol, II (20.0 g, 0.071 mol) and potassium hydroxide (14 g, 0.2 mol) were refluxed for 6 hr. Potassium fluoride (4.9 g, 0.081 mol) precipitated. The solution was acidified with gaseous hydrogen chloride. Addition of 20 ml of water gave a lower layer which when dried and distilled gave a liquid, 5.5 g: bp 100–102° (mm) (this was a mixture of two compounds or isomers inseparable by glpc); pmr spectrum showed a complex group of peaks between τ 5.0 and 6.5; the ^{19}F nmr spectrum suggested the presence of a small ring or a CFH group; ir spectrum 2.91 (s), 3.36 (m), 2.91 (s), 3.36 (m), 5.8 (s), 10.0 (s), and 13.45 (s) μ; mass spectrum with an ionizing voltage of 10 eV had peaks at 207, 209, 292, 293, 294, and 295.

Registry No.—I, 15052-92-3; II, 25055-22-5; $(CF_2{=}CF)_2C(CF_3)OH$, 25055-23-6; IV, 25055-24-7; V, 25055-25-8; VI, 25080-61-9; VIII, 24499-79-4; IX, 25055-27-0; X, 24449-44-3; XI, 25055-29-2; XIII, 25055-30-5; XV, 25055-31-6; XVI, 25055-32-7; 4-chloro-2-trifluoromethyl-1,1,1,3,4,4-hexafluorobutene-2, 25055-33-8.

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