Acknowledgment.—We thank Professor Nakanishi for stimulating our interest in the Overhauser effect during his tenure as New York State Science and Technology Foundation Distinguished Visiting Professor at Fordham, and we thank Professor Kenneth Williamson for performing the NOE experiment.

Fluoroketenes. II.[1] Difluoroketene

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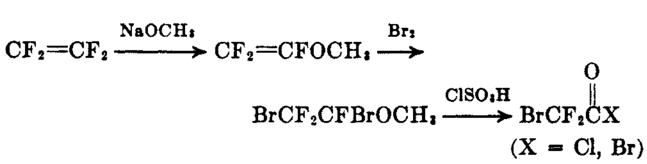
Difluoroketene, as obtained by zinc dehalogenation of bromodifluoroacetyl halides, is a reactive and unstable compound. The ketene itself has not been detected except by its dissociation at 35° to form carbon monoxide and tetrafluoroethylene and by trapping reactions. With excess bromodifluoroacetyl chloride it forms a vinyl ester, 1-chloro-2,2-difluorovinyl bromodifluoroacetate, and with acetone it forms α,α-difluoro-β,β-dimethylpropiolactone.

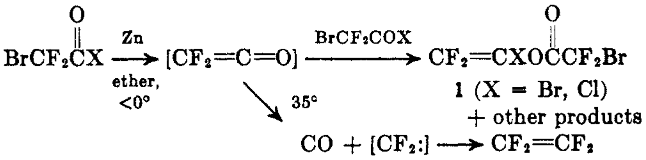
Dehalogenation of haloacetyl halides by zinc has recently been used successfully to prepare both dichloro-[2] and dibromoketene.[3] The preparation of difluoroketene in ether solution by zinc dehalogenation of chlorodifluoroacetyl bromide has also been reported,[4a] but the evidence for its existence is inconclusive.[4b] We now wish to report our findings on the subject, which indicate that difluoroketene is a highly reactive, short-lived material.

The finding of a convenient synthetic route to bromodifluoroacetyl halides furnished starting materials which are probably more easily dehalogenated than the chlorodifluoroacetyl derivatives used previously.[4a] The new three-step synthesis starts with a displacement of fluoride from tetrafluoroethylene by sodium methoxide at 60° and a few atmospheres of pressure to form the known methyl trifluorovinyl ether. This unsaturated ether reacts readily with bromine to give a material assumed to be the simple dibromo adduct, but which tends to liberate free bromine. The last step is an unusual and facile cleavage of the ether group by chlorosulfonic acid to give the acid halide function. This cleavage, which proceeds under much milder conditions than the more conventional reaction with sulfuric acid, is a useful general reaction as will be further illustrated in future publications.



$$CF_2{=}CF_2 \xrightarrow{NaOCH_3} CF_2{=}CFOCH_3 \xrightarrow{Br_2} BrCF_2CFBrOCH_3 \xrightarrow{ClSO_3H} BrCF_2\overset{\overset{O}{\|}}{C}X \quad (X = Cl, Br)$$

Results of dehalogenations of bromodifluoroacetyl chloride and bromide with zinc in ether indicate that difluoroketene or some form of it complexed with zinc halide is formed, and that it is very short-lived, even at the lowest possible reaction temperature (−5 to 0°). An ether solution resulting from such a low-temperature dehalogenation of bromodifluoroacetyl chloride, when kept cold and examined by infrared, showed no characteristic ketene band. Bands were observed for a vinyl ester 1 (X = Cl), and this compound could be separated in low yield by gas chromatography from the complex mixture of products. Compound 1 could be formed by reaction of difluoroketene with the starting material, bromodifluoroacetyl chloride. Another purified product showed very similar infrared and nmr spectra and had an empirical formula corresponding to 3 moles of difluoroketene to one of the acid chloride. A still higher boiling oil showed similar infrared and nmr spectra and contained more fluorine and less chlorine and bromine. Yields of isolated products were quite low, and some carbon monoxide was evolved. At a higher temperature (*ca.* 35°) much more carbon monoxide was evolved, and tetrafluoroethylene was detected. These two products are best accommodated by assuming the presence of free difluoroketene, which decomposes to CO and CF_2. The carbene could undergo a number of reactions, one of which is the known dimerization to form tetrafluoroethylene.



$$\begin{aligned} &BrCF_2\overset{\overset{O}{\|}}{C}X \xrightarrow[\text{ether, } <0°]{Zn} [CF_2{=}C{=}O] \xrightarrow{BrCF_2COX} CF_2{=}CXO\overset{\overset{O}{\|}}{C}CF_2Br \quad \mathbf{1}\ (X = Br, Cl) + \text{other products} \\ &[CF_2{=}C{=}O] \xrightarrow{35°} CO + [CF_2{:}] \longrightarrow CF_2{=}CF_2 \end{aligned}$$

The earlier evidence[4a] for the existence of difluoroketene rested mainly on the isolation of difluoroacetamide in low yield when an ether solution distilled from a zinc dehalogenation reaction was treated with ammonia. We have confirmed this reaction, but feel it is not convincing evidence, since difluoroacetamide could also result from the action of ammonia on a vinyl ester like 1 or on a product of reductive dehalogenation by zinc.[5] Yields of difluoroacetyl derivatives are not necessarily low, since we have further shown that difluoroacetic acid can be obtained in 52% yield by addition of water directly to the reaction mixture from zinc and bromodifluoroacetyl chloride. Reaction in methyl formate provided an indication that at least a portion of these difluoroacetyl derivatives are derived from zinc reduction products. With

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(1) For paper I, see D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 5582 (1966).

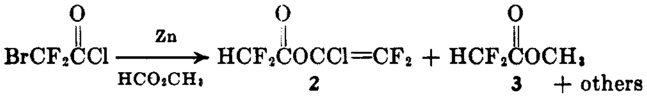
(2) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

(3) W. T. Brady, *ibid.*, **31**, 2676 (1966).

(4) (a) N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *J. Gen. Chem. USSR*, **27**, 2832 (1957). (b) R. E. Banks, R. N. Haszeldine, and D. R. Taylor [*J. Chem. Soc.*, 5602 (1965)] refer to some unpublished work by J. M. Birchall, R. N. Haszeldine, and M. Jefferies, who were unable to repeat this synthesis of difluoroketene.

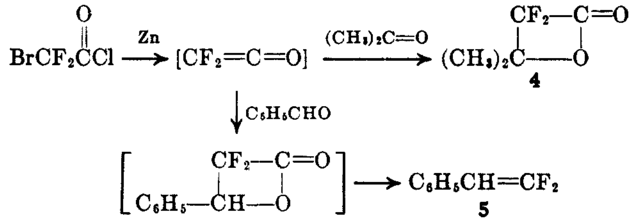
(5) Yu. A. Cheburkov, E. I. Mysov, and I. L. Knunyants [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1570 (1963)] describe the formation of reduction products from related α-bromoperfluoroacid halides and zinc.

methyl formate as solvent, 1-chloro-2,2-difluorovinyl difluoroacetate (**2**) and methyl difluoroacetate (**3**), both reduction products, were obtained directly.



$$\mathrm{BrCF_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow[HCO_2CH_3]{Zn} \underset{\mathbf{2}}{HCF_2\overset{\overset{O}{\|}}{C}OCCl{=}CF_2} + \underset{\mathbf{3}}{HCF_2\overset{\overset{O}{\|}}{C}OCH_3} + others}$$

In order to distinguish between formation of difluoroketene and formation of other reaction products which would give difluoroacetyl derivatives with active hydrogen compounds, the difluoroketene was trapped as a cycloadduct. When the zinc dehalogenation of bromodifluoroacetyl chloride was carried out in acetone, α,α-difluoro-β,β-dimethylpropiolactone (**4**) was isolated in 50% yield. Formation of **4** indicates not only that difluoroketene is an intermediate product, but that it is also exceptionally reactive, since acetone is reluctant to cycloadd to ketenes such as bis(trifluoromethyl)ketene.[6]



A conceivable alternative route to **4** is through an intermediate organozinc compound of the type $BrZnCF_2COCl$, but two pieces of evidence indicate otherwise. Perfluoroalkylzinc halides are of such low reactivity that heptafluoropropylzinc iodide has even been prepared in acetone.[7] In addition, if an organozinc intermediate were basic enough to attack acetone, the resulting anion would be expected to polymerize lactone **4** rather than ring close, since base-catalyzed polymerization of **4** has been found to proceed rapidly.

Dehalogenation of bromodifluoroacetyl chloride with zinc in benzaldehyde gave a low yield of difluorostyrene **5**, the decarboxylation product of the expected cycloadduct, α,α-difluoro-β-phenylpropiolactone.

Experimental Section[8]

Methyl Trifluorovinyl Ether[9a] from Tetrafluoroethylene and Sodium Methoxide.—This reaction was run in a modified Parr low-pressure hydrogenation apparatus.[9b] However, the end of the gas-inlet tube inside the bottle was a glass bubble perforated at the sides with large holes. This permitted bleeding vapors from the bottle while it was shaking without carrying over liquid and suspended solids. The bottle was charged with 0.25-lb, free-flowing sodium methoxide powder (Matheson Coleman and Bell) and 150 ml of tetrahydrofuran (distilled from sodium). This was done rapidly or in a dry box to avoid exposure to moisture in the air. The bottle was then clamped into position in the metal cage of the shaking apparatus, evacuated, and pressured to 40 psi with tetrafluoroethylene. The valve to admit tetrafluoroethylene, regulated to 40 psi, was left open.

Shaking was started, and in about 10 min cooling was necessary to keep the temperature at 60°. Cooling was accomplished by pouring ice water over the bottle and/or packing ice in the cage around the bottle. Overcooling was avoided, and the temperature kept as near 60° as possible.

When the temperature decreased to 40–50° without added coolant (2.5–3 hr from the time the reaction was started), the addition of tetrafluoroethylene was stopped and the vapors were bled into a Dry Ice trap while the bottle was shaken and heated at 60°.

The crude product in the trap was distilled to give 100–120 g (43–52%) of methyl trifluorovinyl ether, bp 10–11°.

Bromodifluoroacetyl Chloride and Bromide.—To 56 g (0.5 mole) of methyl trifluorovinyl ether was added dropwise with cooling and stirring 80 g (0.5 mole) of bromine. The reaction was very exothermic, and Dry Ice–acetone cooling was used to keep the temperature below −30°. Near the end of the addition the bromine color persisted. The product was washed with 5% sodium hydroxide and water, dried, and distilled to give 109 g (80%) of an oil presumed to be the dibromide: bp 62° (100 mm); $n^{25}\mathrm{D}$ 1.4200.

Anal. Calcd for $C_3H_3F_3Br_2O$: F, 20.96. Found: F, 20.85.

To 93 g (0.34 mole) of the above bromo compound was added with stirring and cooling (below −20°) 50 ml (87 g, 0.75 mole) of chlorosulfonic acid. Stirring was continued while the solution was allowed to come to room temperature slowly until evolution of hydrogen chloride, which began at about −5°, was complete. A vacuum (*ca.* 1 mm) was then applied through a Dry Ice–acetone trap with continued stirring and warming to keep the reaction mixture at room temperature or slightly above. Thus the products were collected in the trap, and overheating of the reaction mixture, which causes liberation of bromine, was avoided. The material in the trap was redistilled over mercury (to remove bromine) to give 38.5 g (58%) of bromodifluoroacetyl chloride[10] (bp 50°, $n^{25}\mathrm{D}$ 1.3853) and 12.5 g (15%) of bromodifluoroacetyl bromide[11] (bp 71° $n^{25}\mathrm{D}$ 1.4145). The acid chloride absorbed in the infrared at 5.43 and 5.53 μ and the acid bromide at 5.50 and 5.62 μ.

Anal. Calcd for C_2F_2BrClO: C, 12.42; F, 19.64. Found: C, 12.85; F, 19.69. Calcd for $C_2F_2Br_2O$: C, 10.09; F, 15.97. Found: C, 10.53; F, 16.19.

Dehalogenation of Bromodifluoroacetyl Chloride in Ether.—Granular zinc (12 g, 20 mesh, J. T. Baker Chemical Co.) was rinsed in 50 ml of 5% aqueous hydrochloric acid containing 0.1 g of mercuric chloride until the surface was bright. It was then filtered, washed with acetone, and dried under a current of nitrogen in a 250-ml, three-necked flask fitted with a thermometer, dropping funnel, and condenser with provision for collecting any off-gas over water. The zinc was then covered with 100 ml of ether, and bromodifluoroacetyl chloride (total of 20 g, 0.1 mole) was added dropwise with stirring. The addition was carried out at −10° after it was established that the very exothermic reaction had begun (the solution became cloudy and small gas bubbles were evolved). Some gas collected during the reaction (*ca.* 200 ml) was largely carbon monoxide (infrared analysis and combustible). When addition was complete, the reaction mixture was allowed to come to room temperature slowly. A vacuum (*ca.* 1 mm) was then applied, and volatile material was collected in a Dry Ice trap while the reaction mixture was stirred and heated on a boiling water bath. The residue in the flask was redissolved in ether and filtered to remove unreacted zinc (6.5 g, indicating 85% reaction). Removal of ether under vacuum left a syrupy residue (22.2 g) which contained, by analysis, 7.66% fluorine. This analysis corresponds to the presence of 3.5 g of "polymeric" difluoroketene in the residue. Extraction with benzene left a residue of crystalline, water-soluble salt, and evaporation of the benzene extract gave 1 g of water-insoluble oil with an infrared spectrum very similar to those of the purified products described below. The F^{19} nmr spectrum of the oil was also similar showing a single peak at 63.1 (area 1), an AB pattern (area 3) at 93.4, 94.4, 104, and 105, and unresolved peaks at 108 (area 6), 80 (area 3), and 91 ppm (area 3).

Anal. Found: C, 29.58; H, 0.88; F, 39.83; Br, 7.99; Cl, 2.45.

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(6) D. C. England and C. G. Krespan [*J. Am. Chem. Soc.*, **87**, 4019 (1965)] report cycloadditions of bis(trifluoromethyl)ketene to a variety of unsaturated compounds, but the reaction does not proceed with acetone.

(7) W. T. Miller, E. Bergman, and A. H. Fainberg, *ibid.*, **79**, 4159 (1957).

(8) Melting points and boiling points are uncorrected. F^{19} nmr spectra are reported in parts per million upfield from external trichlorofluoromethane. H^1 nmr resonances are relative to external tetramethylsilane.

(9) (a) S. Dixon, U. S. Patent 2,917,548 (1959); (b) D. C. England and L. R. Melby, *Org. Syn.*, **40**, 11 (1960).

(10) D. Goerrig, German Patent 1,020,970 (1957); *Chem. Abstr.*, **54**, 5469 (1960).

(11) H. Cohn and E. D. Bergmann, *Israel J. Chem.*, **2**, 355 (1965); *Chem. Abstr.*, **62**, 14488 (1965). The acid bromide was not purified but converted into an ester.

Ether was distilled from the volatile material initially evaporated into the Dry Ice trap. This left 3 g of liquid which was shown to contain at least fifteen compounds by gas chromatography. Two of the compounds (about 20% each of the total) were separated by preparative gas chromatography from fractions boiling, respectively, at about 50° (100 mm) and 120° (100 mm). Based on the following data the low-boiling product is believed to be $CF_2{=}C(Cl)OCOCF_2Br$ (**1**, X = Cl). It absorbed in the infrared at 5.51 (C=O) and 5.64 μ (C=C)[12] and showed no proton nmr. The F^{19} nmr spectrum consisted of a single sharp peak at 63.3 and an AB pattern of equal area at 93.3, 94.3, 103.5, and 104.5 ppm.

Anal. Calcd for $C_4F_4BrClO_2$: C, 17.70; F, 28.00; Br, 29.45; Cl, 13.06. Found: C, 18.04; F, 28.06; Br, 28.43; Cl, 12.68.

The second product, bp *ca.* 120° (100 mm), was also purified by preparative gas chromatography but has not been completely characterized. The infrared absorption spectrum was quite analogous to that of the above compound with bands at 5.49 and 5.64 μ. There was no proton nmr. The F^{19} nmr spectrum was also similar in that it contained a CF_2 peak and an AB pattern of about the same chemical shifts. The peaks were as follows: (1) a CF_2 peak at 63.0; (2) a CF peak at 80.8; (3) a CF peak at 91.4; (4) CF peaks (half of AB pattern) at 93.4 and 94.4; (5) CF peaks (half of AB pattern) at 104.0 and 105.0; and (6) a CF_2 peak at 108.5 ppm. Spin-spin coupling was interpreted as follows. Peak 1 was a 1.5-cps doublet split by peak 4. Peak 2 was a 26-cps doublet by peak 3 and a 7-cps triplet by peak 6. Peak 3 was a 22-cps triplet by peak 6, a 26-cps doublet by peak 2, and a 4-cps doublet by peak 4. Peaks 4 were 4-cps doublets by peak 3 and 1.5-cps triplets by peak 1. Peaks 5 showed no appreciable splitting. Peak 6 was a 22-cps doublet by peak 3 and a 7-cps doublet by peak 2.

Anal. Calcd for $C_8F_8BrClO_4$: C, 22.48; F, 35.55; Br, 18.70; Cl, 8.29. Found: C, 22.13; F, 35.98; Br, 17.97; Cl, 7.64.

When the dehalogenation of bromodifluoroacetyl chloride with zinc carried out without cooling so that the ether was allowed to reflux, evolution of gas was much greater. Infrared absorption of this gas showed carbon monoxide as a double peak at 4.6 and 4.7 μ and the two strongest bands characteristic of tetrafluoroethylene at 7.5 and 8.4 μ. These spectral bands were superimposable on those of authentic samples. Total distillable product from this run amounted to only 1.7 g.

In another zinc dehalogenation carried out with cooling as above, 5 ml of water was added to the mixture after completion of the reaction. The product was stripped of solvent and distilled (after drying over magnesium sulfate) as before; 5.0 g (52%) of difluoroacetic acid was isolated and characterized by comparison with an authentic sample (infrared and gas chromatography).

In still another run carried out on 0.3 mole of the bromodifluoroacetyl chloride at 5–10° the mixture was filtered after completion of the reaction. Distillation gave only a fraction with the boiling point of ether. Addition of ammonia to this fraction gave about 1 g of ether-soluble material from which the amide of difluoroacetic acid could be sublimed. It was characterized by melting point (45–47°) and mixture melting point with an authentic sample[13] (47–49°).

Zinc Debromination of Bromodifluoroacetyl Bromide.—To a mixture of 12 g of amalgamated zinc in 100 ml of ether was added dropwise 24 g (0.1 mole) of bromodifluoroacetyl bromide. Reaction was slow at low temperatures and was run at 20–30°. A total of 500 ml of gas was evolved. After reaction was complete, the pot was heated with boiling water, and all volatile material was transferred under vacuum to a liquid nitrogen trap. Distillation gave 3 g boiling mostly at 70° (72 mm). By gas chromatography the main peak was separated and characterized as $CF_2{=}C(Br)OCOCF_2Br$ (**1**, X = Br). It absorbed in the infrared at 5.48 (C=O) and 5.70 μ (C=C). The F^{19} nmr spectrum consisted of a singlet at 62.7 and an AB pattern of equal area at 88.0, 88.8, 100.3, and 101.1 ppm.

Anal. Calcd for $C_4F_4Br_2O_2$: C, 15.20; F, 24.05. Found: C, 15.97; F, 24.07.

Dehalogenation of Bromodifluoroacetyl Chloride in Methyl Formate.—A mixture of 13 g of amalgamated zinc and 25 ml of methyl formate was stirred and 10 ml (20 g, 0.1 mole) of bromodifluoroacetyl chloride was added dropwise, mostly below 10° where reaction was very slow. The reaction mixture was worked up as described above, the products being evaporated into a trap away from halide and zinc before being distilled. There was obtained 8.0 g of liquid, bp 42–102°, composed mostly of four products as shown by gas chromatography. One of them was $CF_2{=}C(Cl)OCOCF_2Br$ (**1**) described above. The reaction was repeated at reflux temperature (31–40°). There was obtained about 5 g of distillate similar to the above but with product 1 nearly eliminated. The three main products were characterized by infrared and nmr spectra and by elemental analyses as methyl difluoroacetate,[14] methyl bromodifluoroacetate,[4] and the vinyl ester $CF_2{=}C(Cl)OCOCF_2H$ (**2**).

Methyl difluoroacetate absorbed in the infrared at 5.63 μ (C=O). The proton nmr spectrum consisted of a triplet (J = 53 cps) centered at τ 4.4 (area 1) and a singlet at 6.5 (area 3). The F^{19} nmr was a doublet (J = 53 cps) centered at 129 ppm.

Methyl bromodifluoroacetate absorbed in the infrared at 5.60 μ (C=O). The proton nmr spectrum was a single sharp peak at τ 6.2 and the F^{19} nmr spectrum a single sharp peak at 61.4 ppm.

The vinyl ester $CF_2{=}C(Cl)OCOCF_2H$ absorbed in the infrared at 5.50 (C=O) and 5.62 μ (C=C). The proton nmr spectrum was a triplet (J = 53 cps) centered at τ 4.23. The F^{19} nmr spectrum was an AB quartet at 94.5, 95.5, 105, and 106 ppm and a doublet (J = 53 cps) of equal area centered at 129 ppm.

Anal. Calcd for $C_4HF_4ClO_2$: C, 24.95; H, 0.53; F, 39.48; Cl, 18.42. Found: C, 25.05; H, 0.69; F, 39.47; Cl, 17.88.

Dehalogenation of Bromodifluoroacetyl Chloride in Acetone.—A mixture of 100 ml of acetone and 24 g of amalgamated zinc was stirred and cooled at −10 to −5° while 20 ml (40 g, 0.2 mole) of bromodifluoroacetyl chloride was added dropwise. Stirring was then continued until the mixture had warmed to room temperature. Volatiles were then evaporated under vacuum into a Dry Ice trap while the pot was heated with a boiling-water bath. Material in the trap was redistilled to give 13.5 g (50%) of α,α-difluoro-β,β-dimethylpropiolactone (**4**): bp 54° (100 mm), 112° (atm); $n^{24}\text{D}$ 1.3571. Infrared absorption for C=O was at 5.37 μ. The proton nmr spectrum was a triplet (J = 1.6 cps) centered at τ 8.69. The F^{19} nmr spectrum was a septet (J = 1.6 cps) centered at 123 ppm.

Anal. Calcd for $C_5H_6F_2O_2$: C, 44.15; H, 4.45; F, 27.94. Found: C, 44.69; H, 4.53; F, 27.91.

When the above reaction mixture was worked up by pouring it into water, extracting with methylene chloride, drying, and distilling, there was obtained a 17% yield of lactone 4 and a 27% yield of the hydrolysis product, α,α-difluoro-β,β-dimethyl-β-hydroxypropionic acid (bp 110° (2.5 mm), mp 73–74°) after recrystallization from chlorform. Infrared absorption occurred at 2.96 (OH) and 5.73 μ (C=O). Proton nmr spectrum of a 20% solution in deuterioacetone showed a triplet (J = 1.6 cps) centered at τ 9.12 and a broad peak of about one-third the area at 2.7. The F^{19} nmr spectrum was a septet (J = 1.6 cps) centered at 119 ppm.

Anal. Calcd for $C_5H_8F_2O_3$: C, 38.99; H, 5.24; F, 24.68. Found: C, 38.61; H, 4.97; F, 24.10.

Polymerization of α,α-Difluoro-β,β-dimethylpropiolactone (4).—Lactone **4** (15 g) in 100 ml of purified hexane (stored over sodium) was brought to reflux under nitrogen, and a trace of sodium methoxide was added. The solution became cloudy,

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(12) These assignments correlate with those of related known compounds. D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, pp 454–455 reports infrared bands for various terminal ($CF_2{=}$) olefins in the 5.56–5.71-μ range, and fluorinated esters with negative substituents in the β position of the alkoxy group are noted to have carbonyl absorptions lowered in wavelength as far as 5.53 μ. More recently, I. L. Knunyants, M. D. Bargamova, N. S. Mirzabekyants, and Yu. A. Cheburkov [*Bull. Acad. Sci. USSR, Div. Chem. Sci., English Transl.*, 1068 (1966)], report a carbonyl band at 5.52 μ for $CF_3CHFCO_2CHFCF_3$. The vinyl group itself in vinyl esters acts as an electronegative unit which shifts the carbonyl band to shorter wavelengths. Carbonyl absorptions as low as 5.56 μ for substituted vinyl esters are cited by L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 182.

(13) Prepared from the acid chloride, bp 26°, available in 95% yield from the reaction of chlorosulfonic acid with $HCF_2CF_2OCH_3$, run as described in this paper for preparation of bromodifluoroacetyl halides. J. D. Park, H. J. Gerjovich, W. R. Lycan, and J. R. Lacher, *J. Am. Chem. Soc.*, **74**, 2192 (1952) report mp 51°.

(14) E. Gryszkiewicz-Trochimowski, A. Sporzynski, and J. Wnuk, *Rec. Trav. Chim.*, **66**, 413 (1947); *Chem. Abstr.*, **42**, 865 (1948).

but a negligible amount of polymer formed even after refluxing overnight. Addition of 0.25 g of sodium methoxide caused polymer to form rapidly. After refluxing overnight the solution was filtered and 9.9 g of dried polymer recovered.

Dehalogenation of Bromodifluoroacetyl Chloride in Benzaldehyde.—A mixture of 12 g of amalgamated zinc and 50 ml of benzaldehyde was stirred at 0 to −10° while 10 ml (20 g, 0.1 mole) of bromodifluoroacetyl chloride was added dropwise. Volatile material was then evaporated into a Dry Ice trap under vacuum while the pot was heated with boiling water. Redistillation of material in the trap gave 1.5 g of difluorostyrene, bp 78° (100 mm), $n^{25}\mathrm{D}$ 1.4855. The infrared spectrum agreed with that of a known sample.[15]

Registry No.—1 (X = Cl), 15080-17-8; 1 (X = Br), 15080-18-9; **2**, 15156-62-4; **3**, 433-53-4; **4**, 15156-63-5; difluoroketene, 683-54-5; methyl trifluorovinyl ether, 3823-94-7; methyl trifluorovinyl ether dibromide, 15080-20-3; bromodifluoroacetyl chloride, 3832-48-2; bromodifluoroacetyl bromide, 1796-12-9; methyl bromodifluoroacetate, 683-98-7; α,α-difluoro-β,β-dimethyl-β-hydroxypropionic acid, 15080-23-6.

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[15] J. L. Anderson, U. S. Patent 2,733,278 (1956); *Chem. Abstr.*, **50**, 15575 (1956).

Fluorinated Acetylenic Alcohols and Derived Allenes

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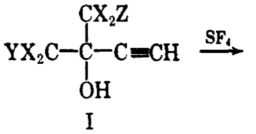
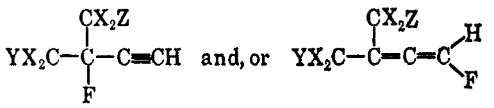
Acetylenic alcohols derived from several haloacetones were converted into novel fluorinated allenes by treatment with sulfur tetrafluoride. In some cases the corresponding fluorinated acetylenes were also formed by replacement of the hydroxyl group by fluorine and in one instance the fluorinated acetylene was the sole product. Two of the allenes were thermally rearranged to the corresponding butadienes. The mechanism of the reaction is discussed and the spectroscopic properties of the new compounds are reported.

As part of a general program of the reactions and derivatives of hexafluoroacetone and related compounds[1] the preparation of haloalkylacetylenes (II) was attempted by treatment of the corresponding acetylenic alcohols (I) with sulfur tetrafluoride.



$$\mathrm{YX_2C{-}\overset{CX_2Z}{\underset{OH}{C}}{-}C{\equiv}CH \xrightarrow{SF_4}}$$

I

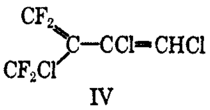


$$\mathrm{YX_2C{-}\overset{CX_2Z}{\underset{F}{C}}{-}C{\equiv}CH} \quad \text{and, or} \quad \mathrm{YX_2C{-}\overset{CX_2Z}{C}{=}C{=}C\genfrac{}{}{0pt}{}{H}{F}}$$

II III

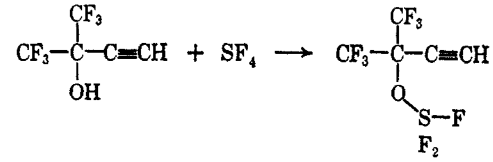
a, X = Y = Z = F
b, X = Y = F; Z = Cl
c, X = F; Y = Z = Cl
d, X = Y = F; Z = H
e, X = F; Y = Z = H
f, X = F; Y = Cl; Z = H

Alcohols Ia and Ic have been known for some time.[2,3] The remainder are new compounds. The use of SF_4 for the smooth replacement of hydroxyl by fluorine in other types of alcohols has been reported by England.[4] It was found in the present study, however, that the type II product was formed in only minor yield from alcohols Id, e, and f, and not at all from alcohols Ia, b, and c. The major (or sole) product in all of these cases was the corresponding allene III. It is noteworthy that the reaction proceeds easily even at room temperature or below, even though this type of alcohol, as pointed out by Simmons and Wiley[3] in the case of Ic, is unusually inert toward acidic reagents which normally afford replacement of the hydroxyl group. The only exception observed by these authors was the reaction of Ic with phosphorus pentachloride, which resulted in the formation of the 1,3-butadiene (IV). It is probable that the formation of IV from Ic is related to the chemistry described in the present paper.



IV

While the mechanism of the reaction resulting in allene formation has not been investigated, it is possible to postulate a reasonable pathway. It is suggested that the first stage is interaction of the alcohol and sulfur tetrafluoride. This is derived from a mechanism which has been suggested for the reaction of SF_4 with carbonyl groups in the presence of a suitable Lewis acid.[5] In our mechanism it is possible to make use of the fact that SF_4 itself is known to be a weak Lewis acid[6] and we might therefore postulate that first it forms a complex in which oxygen is the donor. The complex would then lose HF to form the intermediate V. However, in view of the strongly acidic nature of such fluorinated alcohols,[7] it is more likely that there is formed initially a strong hydrogen bond between the hydroxyl proton and a fluorine atom of SF_4. This would pave the way for electron donation by oxygen to sulfur, with subsequent elimination of HF to form V. The net result is shown in eq 1. This intermediate (V) can then rearrange by an



$$\mathrm{CF_3{-}\overset{CF_3}{\underset{OH}{C}}{-}C{\equiv}CH + SF_4 \longrightarrow CF_3{-}\overset{CF_3}{\underset{O{-}SF_3}{C}}{-}C{\equiv}CH + HF} \quad (1)$$

Ia V

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[1] This is paper XIII in the series on perhalo ketones and their derivatives. For paper XII, see *J. Org. Chem.*, **31**, 3174 (1966). Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill. Sept 1967.

[2] I. L. Knunyants, C. Ch'ing-yun, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. 4, 686 (1960).

[3] H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

[4] D. C. England, U. S. Patent 3,236,894 (1966).

[5] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[6] E. L. Muetterties, W. D. Phillips, and W. C. Smith, U. S. Patent 2,897,055 (1959).

[7] I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 923 (1964).