were swept with a stream of dry nitrogen into a trap cooled in Dry Ice. A sample of the volatile products was collected during the first 3 hr and another during the last 3 hr. In each case, the infrared spectrum of the trapped products indicated a trace of formaldehyde. In another reaction, 300 ml of DME was heated under reflux for 2.5 days. The vapors were passed through a 10% solution of bromine in carbon tetrachloride. Vpc of the products from the carbon tetrachloride failed to reveal any 1,2-dibromomethane.

Registry No.—**1,** 15649-35-1; **2,** 15649-36-2; **3,** 15649-37-3; benzoic anhydride, 93-97-0; 1,2-dimethoxyethane, 110-71-4; sodium trichloroacetate, 650-51-1.

Acknowledgment.—The use of the research facilities of Union Carbide Corp., South Charleston, W. Va., by D. E. B. is gratefully appreciated. We thank Mr. Robert R. Smith for recording the nmr spectra.

A Synthesis of Perfluoroalkyl Trifluorovinyl Ketones

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Contribution No. 1313 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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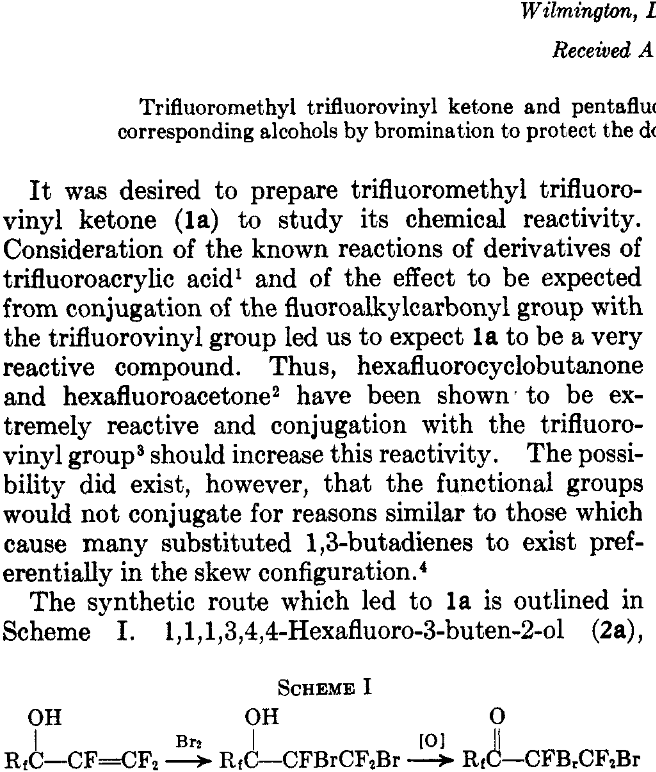
Trifluoromethyl trifluorovinyl ketone and pentafluoroethyl trifluorovinyl ketone have been prepared from corresponding alcohols by bromination to protect the double bond, oxidation, and debromination.

It was desired to prepare trifluoromethyl trifluorovinyl ketone (**1a**) to study its chemical reactivity. Consideration of the known reactions of derivatives of trifluoroacrylic acid[1] and of the effect to be expected from conjugation of the fluoroalkylcarbonyl group with the trifluorovinyl group led us to expect **1a** to be a very reactive compound. Thus, hexafluorocyclobutanone and hexafluoroacetone[2] have been shown to be extremely reactive and conjugation with the trifluorovinyl group[3] should increase this reactivity. The possibility did exist, however, that the functional groups would not conjugate for reasons similar to those which cause many substituted 1,3-butadienes to exist preferentially in the skew configuration.[4]

The synthetic route which led to **1a** is outlined in Scheme I. 1,1,1,3,4,4-Hexafluoro-3-buten-2-ol (**2a**), prepared by a route similar to that used for other perfluoroalkyl trifluorovinyl carbinols,[5] was brominated to form 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanol (**3a**), obtained as a mixture of diastereomeric forms. The secondary alcohol was oxidized with acid dichromate[6] to form 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanone (**4a**) in good yield. When the dibromo ketone was debrominated with zinc in boiling dioxane[7] under carefully controlled conditions, a mixture of ketone **1a** and solvent distilled which contained only small amounts of other components according to gas chromatographic analysis on several columns. Large scale chromatography was used to separate **1a**, a colorless, volatile liquid boiling near room temperature.

SCHEME I



The unsaturated ketone was very sensitive to nucleophilic attack; it decomposed rapidly in protonic solvents with formation of fluoride ion. Purified samples were stable to storage at room temperature if sealed in ampoules with careful exclusion of moisture.

The observed reactivity of **1a** undoubtedly explains the failure of direct oxidation of **2a** to **1a** with a number of oxidizing agents. Even if **2a** is preferentially attacked by an oxidizing agent at the proton on carbon, the double bond of any **1a** formed is probably attacked immediately by the same reagent. Among oxidizing agents which destroyed **2a** without evidence of formation of **1a** were manganese dioxide, N-bromosuccinimide in acetone, and chromic acid in pyridine.

The structure of **1a** is confirmed by spectral data. The ultraviolet spectrum of **1a** shows that it is similar to methyl vinyl ketone. The peaks are λ_{max} 237 mμ (ϵ_{max} 6340), λ_{max} 316 mμ (ϵ_{max} 19), compared with λ_{max} 212 (ϵ 7100), λ_{max} 320 mμ (ϵ_{max} 27), for methyl vinyl ketone.[8] These data appear to indicate that the functional groups are coplanar. F^{19} nmr spectrum at 56.4 Mc showed four peaks centered at +703, +724, +1424, and +7028 cps from symmetrical difluorotetrachloroethane in the ratio of 1:3:1:1. Coupling constants were first order and of the expected magnitudes. The infrared spectrum showed strong bands at 5.6 and 5.9 μ for carbonyl and trifluorovinyl groups, but specific bands could not be assigned to each functional group.

The synthetic route was repeated starting from 1,1,2,4,4,5,5,5-octafluoro-1-penten-3-ol (**2b**) and pentafluoroethyl trifluorovinyl ketone (**1b**) was obtained. Compound **1b**, a colorless volatile liquid, bp 62°, was somewhat less reactive than **1a**, possibly owing to re-

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[1] (a) J. D. Lazerte, D. A. Rausch, R. J. Koshar, J. D. Park, W. H. Pearlson, and J. R. Lacher, *J. Amer. Chem. Soc.*, **78**, 5639 (1956). (b) A. L. Henne and C. J. Fox, *ibid.*, **76**, 479 (1954).

[2] (a) D. C. England, *ibid.*, **83**, 2205 (1961). (b) H. E. Simmons and D. W. Wiley, *ibid.*, **82**, 2288 (1960).

[3] R. D. Chambers and R. H. Mobbs in "Advances in Fluorine Chemistry," Vol. 4, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth, Inc., Washington, D. C., 1965, pp 50–112.

[4] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3445 (1965).

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

[6] A. M. Lovelace, D. A. Rausch, W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Co., New York, N. Y., 1958, p 185.

[7] See ref 6, p 105.

[8] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 100.

duced solubility. Spectral data were very similar for the two compounds.

The relatively poor yields obtained in the debromination step of the synthesis of **1a** and **b** coupled with the difficulty of studying their complex reactions prevented further characterization of the chemical reactivity of these interesting materials.

Experimental Section

1,1,1,3,4,4-Hexafluoro-3-buten-2-ol (2a).—A 1-l., four-necked flask fitted with a condenser protected by a drying tube, a thermometer, a dropping funnel, and a Truebore stirrer was dried in an oven at 140° overnight, assembled while hot, and allowed to cool. The flask was charged with 100 ml of tetrahydrofuran (freshly distilled from sodium hydride) and 13.6 g of magnesium. The stirred mixture was cooled to $-30°$ and a solution of 90 g of trifluorovinyl bromide (distilled from calcium chloride) in 100 ml of freshly distilled tetrahydrofuran was added during 1 hr. A vigorous exothermic reaction occurred and the temperature reached $-20°$ on several occasions. The mixture was stirred 1 hr and freshly distilled trifluoroacetaldehyde (25 ml of liquid at $-80°$) was distilled into the solution slowly. Maximum temperature during the reaction was $-5°$. After 1 hr, the mixture was warmed to room temperature and stored at about 5° for 64 hr. The solvent was removed under reduced pressure and the resulting dark, viscous residue treated with 250 ml of cold, concentrated sulfuric acid. The tarry residue was largely unaffected by sulfuric acid at 0° but was decomposed at 100°, at which temperature volatile products distilled. The three-layer mixture of products collected in a cold trap with the reaction flask at 100° under reduced pressure was distilled through a small column to give 27.8 g, about 25%, of 1,1,1,3,4,4-hexafluoro-3-buten-2-ol: bp 79–85°, n^{25}D 1.3219–1.3297. When redistilled in a spinning-band still, the material distilled at 82° and had n^{25}D 1.3164. A sample was purified for analysis by gas chromatography on a 16 ft × 0.75 in. silicone oil column at about 50°.

Anal. Calcd for $C_4F_6H_2O$: C, 26.68; H, 1.12; F, 63.31. Found: C, 26.66; H, 1.54; F, 61.54.

Infrared and nuclear magnetic resonance spectra agreed very well with the structure. The proton magnetic resonance was especially informative. The hydroxylic proton resonance was at -293 cps (60 Mc) from tetramethylsilane as an internal standard. Addition of trifluoroacetic acid caused this resonance to shift well downfield so that the resonance pattern of the other proton was revealed as a 32-line multiplet centered at -290 cps from tetramethylsilane. The protons do not split each other as shown by the single line for the OH; therefore, the 32 lines result from simple first-order splitting by each of the four chemical shifts of the six fluorine atoms, and the J values could be extracted simply. The fluorine resonance is very similar, with some of the splits too small to be measured.

3,4-Dibromo-1,1,1,3,4,4-hexafluoro-2-butanol.—In a 250-ml, round-bottomed flask, fitted with a magnetic stirrer and a condenser protected by a drying tube, were placed 79.8 g of trifluoromethyl trifluorovinyl carbinol and 71 g of bromine. The mixture was stirred and irradiated with an AH-3 lamp for 50 hr. The excess bromine was removed with a stream of nitrogen, and the product was distilled in a 9 in. × 0.25 in. Vigreux column. The fraction, bp 145–162°, was redistilled. There was obtained 120.9 g, or 89% of the theoretical amount, of material, bp 145–152°. A sample, bp 150°, n^{25}D 1.148, was analyzed.

Anal. Calcd for $C_4H_2Br_2F_6O$: C, 14.13; H, 0.59; Br, 47.02, F, 33.54. Found: C, 14.33; H, 0.55; Br, 46.60; F, 33.37.

The infrared spectrum was consistent with the structure and the nuclear magnetic resonance spectrum, and gas chromatographic analysis of constant boiling fractions was consistent with the presence of two diastereoisomeric forms of the compound.

3,4-Dibromo-1,1,1,3,4,4-hexafluoro-2-butanone.—In a 500-ml, four-necked flask were placed 124 g of 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanol and 39 ml of concentrated sulfuric acid. A solution prepared from 111 g of sodium dichromate dihydrate, 155 ml of water, and 64.5 ml of concentrated sulfuric acid was placed in a dropping funnel connected to the flask. The material in the flask was heated to 65° and dropwise addition of the sodium dichromate solution was begun. The temperature rose to 95° and then fell. When it reached 80°, the mixture was heated on a steam bath and the speed of addition was increased to keep the temperature between 80 and 90°. The addition required 45 min. The mixture was heated under reflux (pot temperature, 92°) for 2 days. Concentrated sulfuric acid (150 ml), was added and the product was distilled under reduced pressure into a Dry Ice cooled receiver. The product (125 g) was added to 50 g of phosphorus pentoxide in the pot of a 9 in. × 0.25 in. Vigreux still, and the product was distilled. The product (114 g) which boiled at about 95–100°, was redistilled through a small spinning-band still to give 93.2 g (73.5% yield) of 3,4-dibromo-1,1,1,3,4,4-hexafluoro-2-butanone: bp 98.5–99.5°; n^{25}D 1.3717.

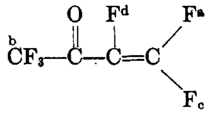
Anal. Calcd for $C_4Br_2F_6O$: C, 14.22; F, 33.74. Found: C, 14.56, 14.60; F, 33.54, 33.07.

Trifluoromethyl Trifluorovinyl Ketone.—A spinning-band still was fitted with a pot with a sidearm and dried by a stream of nitrogen. The pot was charged with 20 g of zinc dust and 50 ml of dioxane (freshly distilled from sodium). The solvent was heated to reflux and stirred and 10 g of 3,4-dibromo-1,1,3,4,4-hexafluoro-2-butanone was added dropwise. When the addition was begun, fractions were taken overhead. Gas chromatographic analysis of the distillate showed a new peak thought to be the desired ketone. Large scale gas chromatography allowed separation of a fraction identified by nmr spectroscopy as trifluoromethyl trifluorovinyl ketone.

Anal. Calcd for C_4F_6O: C, 26.98; F, 64.03. Found: C, 27.24; F, 63.28.

The infrared spectrum showed characteristic bands at 5.6 and 5.9 μ. The ultraviolet spectrum of the compound in octane showed λ_{max} 237 mμ (ϵ_{max} 6340) and λ_{max} 316 mμ (ϵ_{max} 19). This ultraviolet spectrum is comparable with that of methyl vinyl ketone, λ_{max} 212 mμ (ϵ_{max} 7100) and λ_{max} 320 mμ (ϵ_{max} 27).

The structure was confirmed by F^{19} nmr.



$$\overset{b}{C}F_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{F^d}{|}}{C}=C\begin{matrix}F^a\\F_c\end{matrix}$$

Resonance a is a pair of doublets centered at +703 cps from symmetrical tetrachlorodifluoroethane (CCl_2FCCl_2F), one doublet of which falls under resonance b. Resonance b is a pair of doublets centered at +724 cps. Resonance c is a widely split pair of peaks, each of which is a 14641 resulting from overlap of two 1,3,3,1's. It is centered at 1424 cps.

Resonance d is a widely split pair of peaks, each of which is a slightly overlapping pair of quadruplets. It is centered at 7028 cps.

Coupling constants were none for ab, 6 or 7 for ac, 34 or 35 for ad, 6 for bc, 14 for bd, and 110 cps for cd.

1,1,2,4,4,5,5,5-Octafluoro-1-penten-3-ol.—A 3-l., four-necked flask fitted with a stirrer, condenser, dropping funnel, and nitrogen inlet was dried in an oven, assembled hot, and cooled in a nitrogen stream. It was charged with 1 l. of tetrahydrofuran (distilled from sodium hydride) and 49 g of magnesium turnings. Trifluorovinyl bromide (360 g) (dried over calcium chloride) was added to the flask during 2 hr. The temperature of the reaction was kept at -20 to $-30°$. The mixture was stirred 2.5 hr at $-25°$ and then 80 ml (measured at $-80°$) of pentafluoropropionaldehyde in 150 ml of dry tetrahydrofuran was added during 1 hr to the stirred mixture maintained at -20 to $-10°$. The mixture was warmed to room temperature and stirred overnight. Tetrahydrofuran (700 ml) was removed by distillation, and the residue was transferred to a 5-l. flask. Sulfuric acid (1 l.) was added and the flask was fitted with a distillation column. The tarry residue was alternately heated and cooled. Material began to distil when the flask reached 120° and continued to distil during a vigorous exothermic reaction. The product was taken up in ether, dried over magnesium sulfate, and filtered. The filtrate was stored over potassium fluoride pellets, again filtered, and distilled in a spinning-band still. Material boiling at 83–91°, 66.4 g., was identified as 1,1,2,4,4,5,5,5-octafluoro-1-penten-3-ol according to infrared and nmr analyses.

1,2-Dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanol.—A mixture of 64 g of 1,1,2,4,4,5,5,5-octafluoro-1-penten-3-ol and 48 g of bromine was stirred for 1 hr to allow a slight exothermic reaction to subside and then it was irradiated with ultraviolet light for 18 hr. Distillation of the residue through a small column with a spinning band provided 86.9 g or 80% of the theoretical amount of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-

pentanol. A sample having bp 90-91° (97 mm) and $n^{25}D$ 1.3861 was analyzed.

Anal. Calcd for $C_5H_2Br_2F_8O$: Br, 40.00; F, 38.98. Found: Br, 40.46, 40.43, 40.68; F, 38.24.

Nmr examination of both of the products above indicated that they were alcohols (strong unsplit resonance with chemical shift moved by trifluoroacetic acid) containing another proton (complex splitting).

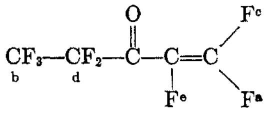
1,2-Dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone.—A 300-ml, four-necked flask fitted with a stirrer, thermometer, dropping funnel, and condenser was charged with 83.7 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanol and 23 ml of concentrated sulfuric acid. A solution prepared from 65.5 g of sodium dichromate dihydrate, 92 ml of water, and 38 ml of concentrated sulfuric acid was added from a dropping funnel during 15 min. The mixture was stirred and heated on a steam bath for 24 hr. Concentrated sulfuric acid, 90 ml, was added and liquid products were evaporated with vacuum into a Dry Ice cooled receiver. Phosphorus pentoxide was added to the distillate, and it was vacuum-distilled into the receiver of a Vigreux column. Phosphorus pentoxide (15 g) was added and the mixture was distilled. There was obtained 66.3 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone, bp 112-116.5°. A sample, bp 116.5°, $n^{25}D$ 1.3587, was analyzed.

Anal. Calcd for $C_2Br_2F_8O$: Br, 41.20; F, 39.17. Found: Br, 40.33, 40.56; F, 38.08.

Pentafluoroethyl Trifluorovinyl Ketone.—The pot of a small spinning band still with a side arm closed by a serum stopper was charged with 30 ml of sodium-dried dioxane and 20 g of zinc dust. The mixture was stirred and heated and 5 ml of dioxane was distilled. The column was set to a slow take off and 4.8 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone was added from a syringe through the serum stopper in small portions. A vigorous reaction occurred and distillate boiling at 85-100°, about 20 ml in all, was collected. Gas chromatography indicated the presence of a new compound in the material, and a quantity of this material was collected by large scale gas chromatography on a 20 ft × $^3/_8$ in. column of Dow Corning silicone 200 oil on 48-65 mesh firebrick. The pentafluoroethyl trifluorovinyl ketone had bp 62° and was pure.

Anal. Calcd for C_5F_8O: C, 26.33; F, 66.66. Found: C, 25.85; F, 66.62.

The ultraviolet spectrum was similar to that of the methyl compound having λ_{max} 242 mμ (ϵ_{max} 5500) and λ_{max} 318 mμ (ϵ_{max} 27). Infrared bands at 5.6 and 5.9 μ were characteristic. The structure was confirmed by F^{19} nmr.



$$\underset{b}{CF_3}-\underset{d}{CF_2}-\overset{O}{\overset{\parallel}{C}}-\underset{F^e}{C}=C(F^c)(F^a)$$

The resonance due to a, a pair of doublets, was centered at 680 cps from symmetrical tetrachlorodifluoroethane; that due to b, a doublet, was centered at 990 cps; that due to c, a pair of resonances, each of which was overlapping triplets, was centered at 1397 cps; that due to d, a pair of doublets, was centered at 3253 cps; the resonance due to e, a pattern of 21 lines formed by the overlapping of a pair of triplets split to quadruplets, was centered at 7029 cps. Coupling constants were 36 for ae, 12 for ac, 7 for be, 113 for ce, 8 for cd, and 22 cps for de.

Debromination of 22.5 g of dibromo ketone followed by gas chromatography of the product afforded 7.27 g, or 45% yield, of pentafluoroethyl trifluorovinyl ketone, about 98% pure according to gas chromatography. It had a boiling point of 62° with some decomposition.

Registry No.—**1a**, 15322-89-1; **1b**, 15322-70-0; **2a**, 15152-24-1; **2b**, 2070-67-9; **3a**, 15448-32-5; **3b**, 15448-33-6; **4a**, 15448-34-7; **4b**, 15448-35-8.

The Chemistry of Photodimers of Maleic and Fumaric Acid Derivatives. VI[1]

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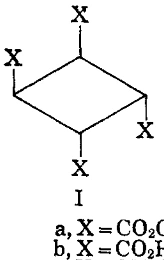
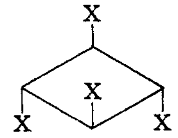
A number of 1,2,3,4-tetrasubstituted cyclobutanes have been prepared from *cis,trans,cis-* and *trans,trans,trans-*1,2,3,4-tetracarbomethoxycyclobutane. Two of these compounds, *cis,trans,cis-* and *trans,trans,trans-*1,2,3,4-tetraiodomethylcyclobutane, undergo an unexpected Grob-type cleavage with lithium aluminum hydride. A novel tricyclic system, namely, the bis anhydride of *trans,trans,trans-*1,2,3,4-cyclobutanetetracarboxylic acid, has also been prepared.

In earlier communications[1] it was reported that tetramethylenecyclobutane could be generated from a variety of substrates, including the 1,2,3,4-tetraiodomethyl- and tetrabromomethylcyclobutanes. At this time we wish to describe the synthesis of these precursors, as well as a variety of related compounds which are of interest in connection with independent studies of small ring systems.

The 1,2,3,4-tetrahydroxymethylcyclobutanes Ic and IIc were initially prepared by catalytic reduction of their respective methyl esters Ia and IIa at 250°.[5] Considerable isomerization and ring opening were encountered in the preparation of the *cis,trans,cis* isomer Ic under the rather drastic catalytic reduction conditions. Lithium aluminum hydride was subsequently found to provide homogeneous samples of Ic and IIc in high yields.



I



II

a, X = CO_2CH_3
b, X = CO_2H
c, X = CH_2OH
d, X = CH_2Br
e, X = CH_2I
f, X = CH_2OTs
g, X = CH_3
h, X = $COCH_3$
i, X = $COCHN_2$
j, X = CH_2CO_2H

The tetraols Ic and IIc were converted into their respective tetrabromides Id and IId with phosphorus tribromide. The nmr spectrum of the *cis,trans,cis*-tetrabromide Id showed peaks at τ 6.35 (eight protons) and 7.25 (four protons). A similar spectrum was observed for the *trans,trans,trans* isomer IId (τ 6.44, eight protons

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[1] For the last paper in this series, see G. W. Griffin and L. I. Peterson, *J. Amer. Chem. Soc.*, **85**, 2268 (1963).

[2] National Institutes of Health Fellow, 1960-1962.

[3] National Institutes of Health Fellow, 1959-1960.

[4] Author to whom inquiries regarding this paper should be addressed: Louisiana State University in New Orleans, New Orleans, La. 70122.

[5] G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Amer. Chem. Soc.*, **83**, 2725 (1961).