[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Free-Radical Catalyzed Addition of Unsaturated Alcohols to Perhaloalkanes[1]

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Perhaloalkanes, such as trifluoromethyl iodide, pentafluoroethyl iodide, *n*-heptafluoropropyl iodide, 1,1,2-trifluoro-2-dichloro-2-iodoethane and 1,1,2-trifluoro-1,2-dibromo-2-bromoethane, were found to react with both allyl and propargyl alcohols in photochemical reactions. Peroxide catalysis was also effective. The only adducts isolated from the allyl alcohol addition were of the general structure R_f—CH_2—CHI—CH_2OH, while propargyl alcohol gave only R_f—CH=CI—CH_2OH. The halohydrins were converted to glycols *via* the epoxide. The reduction of the epoxides under varying conditions yielded only secondary alcohols. Various plausible mechanisms for the glycol and alcohol formations are discussed. The physical properties of all the above new compounds are tabulated.

The use of free radical reactions for the preparation of fluorine-containing alcohols has received attention in the past decade.

Thus, methanol in the presence of peroxide catalysts has been found to add to hexafluoropropene to form 2,2,3,4,4,4,-hexafluorobutanol.[2] In the presence of peroxides, Joyce[3] found that methanol will also form telomers with tetrafluoroethylene of the type $H(CF_2—CF_2)_nCH_2$ OH (where n = 1–12); other alcohols such as ethanol, 1-propanol, and 2-propanol were also found to telomerize with tetrafluoroethylene.

LaZerte and Koshar[2] have obtained only 1:1 adducts in the free radical reactions of alcohols and certain olefins. Methanol added to perfluorobutene-1 and perfluorobutene-2 to produce the corresponding alcohol in 70–90% yields. They found that ethyl, *n*-propyl, and *i*-propyl alcohols reacted similarly. In all cases, it is the α-hydrogen which undergoes homolytic scission.

DISCUSSION

In our study, a variety of perhaloalkanes was found to react with both allyl and propargyl alcohols in photochemical reactions. Peroxide catalysis was also effective, however, the yields were poor. Quartz or Vycor vessels were not necessary in most of these reactions since it was found that enough ultraviolet penetrated "Double Tough" pyrex pipe along with the visible light to cleave homolytically the C—I bond of R_fI. The reactants were irradiated for a period of two weeks in most instances. The only adducts isolated from the allyl alcohol additions were $R_fCH_2CHICH_2OH$ while propargyl alcohol gave only $R_fCH{=}CICH_2OH$. These halohydrins proved to be useful intermediates for the preparation of epoxides, glycols, unsaturated alcohols, and olefinic compounds with terminal unsaturations.

Allyl alcohol, under the influence of ultraviolet light, was treated with the following perhaloalkanes: trifluoromethyl iodide, pentafluoroethyl iodide, heptafluoropropyl iodide, 1,2,2-trifluoro-1,2-dichloro iodoethane, and 1,2-dibromo-1-chloro-1,2,2-trifluoroethane. Only 1:1 adducts were obtained in each case. The structure of each adduct was proved by conversion to the glycol *via* the epoxide. All the glycols prepared gave a positive periodic acid test as expected for vicinal glycols. For this series of perhaloalkanes the structure of the halohydrin product is independent of the species attacking the unsaturated alcohol. In light of these results the following general mechanism is proposed:

$$R_fI \longrightarrow R_f\cdot + I\cdot \qquad K_I$$

$$R_f\cdot + CH_2{=}CH—CH_2OH \longrightarrow R_fCH_2—\dot{C}HCH_2OH \qquad K_A$$

$$R_fCH_2\,\dot{C}H—CH_2OH + R_fI \longrightarrow R_fCH_2CHICH_2OH + R_f\cdot \qquad K_D$$

$$2I\cdot \longrightarrow I_2$$

Since all the halohydrins have a similar structure (vicinal halohydrins), the stability of the radical produced in step K_I is not as important a factor as the stability of the intermediate radical obtained in the addition step, K_A. If the radical from step K_I was a highly reactive species, then a mixture of halohydrins would have formed since it would not have sufficient time to "select" the point of attachment.

A comparison of the C—Br bond distances and bond energies in methyl bromide and trifluoromethyl bromide is revealing. The C—Br distance and bond dissociation energy in methyl bromide is 1.936 Å[4] and 67.2[5] kcal./mole respectively, while trifluoromethyl bromide has values of 1.91 ± 0.02 Å[4] and 64.5[4] kcal./mole respectively. Thus, the C—Br

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[1] This paper represents part of a thesis submitted by F. E. Rogers to the Graduate School, University of Colorado, in partial fulfillment of the requirements of the Ph.D. degree, June 1958.

[2] J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, 77, 910 (1955).

[3] R. M. Joyce (to Du Pont), U. S. Patent 2,599,628 (July 10, 1951).

[4] J. Sheridan and W. Gordy, *J. Chem. Phys.*, 20, 591 (1952).

[5] C. Walling, *Free Radicals in Solution*, J. Wiley & Sons, Inc., New York, 1957, p. 50.

bond in trifluoromethyl bromide is the same distance or shorter than the corresponding bond in methyl bromide, but in trifluoromethyl bromide the bond is weaker. This anomaly can be explained if one assumes that the trifluoromethyl radical has some 3 kcal. of resonance energy[6a] (as compared to trichloromethyl with *ca.* 12 kcal.). If, as is true with the alkyl radicals, resonance energy increases with molecular weight then the CF_3-$CF_2\dot{C}F_2$ radical would be more reactive than the $\dot{C}F_3$ radical. This difference should be reflected in the increasing reactivity which parallels the decreasing strength of the C—I bond involved. While the kinetics of the radical reactions were not studied, some qualitative observations were made which support such a concept. Both trifluoromethyl iodide and heptafluoropropyl iodide were irradiated for seven days in the presence of propargyl alcohol. The yield of the adduct from heptafluoropropyl iodide was 60% while trifluoromethyl iodide only 45%. In the pressure reactions of both iodides with ethylene, heptafluoropropyl iodide reacts much faster.

The results of the free radical chlorination and bromination of trifluoromethane and pentafluoroethane also support the idea that the higher molecular weight perfluoroalkyl radicals are more stable. Park[6b] found that pentafluoroethyl iodide brominates and chlorinates smoothly at room temperature while trifluoromethane requires high temperature and the reaction is very slow. Both reactions presuppose the existence of the $\dot{C}F_3$ and $CF_3\dot{C}F_2$ radicals, the former being more unreactive, forms only with reluctance. Lawlor[7] found from a survey of investigations on the thermal telomerization of fluorine-containing compounds and olefins that certain generalizations can be made. For example, the rate of thermal initiation and consequently of telomerization is a function of the strength of the C—X bond being broken. Applying this to the results of the thermal addition of R_fI compounds to ethylene, it can be stated that since heptafluoropropyl iodide reacts much faster than trifluoromethyl iodide, the C—I bond in the former must be weaker. While no kinetic data are available to support this concept, all qualitative observations point in that direction.

Via these photochemical reactions the following halohydrins were prepared: $CF_3CH_2CHICH_2OH$, $C_2F_5CH_2CHICH_2OH$, $C_3F_7CH_2CHICH_2OH$, CF_3-$CH{=}CICH_2OH$, $C_3F_7CH{=}CICH_2OH$, CF_2ClCF-$ClCH_2CHICH_2OH$, and $CF_2BrCFClCH_2CHBr$-CH_2OH. The latter halohydrin resulted from the addition of $CF_2BrCFClBr$ to allyl aldohol. That the compound had this structure and not that of the isomer, $CFClBrCF_2CH_2CHBrCH_2OH$ was demonstrated by analogy with similar work reported by Tarrant[8,9] and observations on the relative stability of the $R\dot{C}FCl$ and $R\dot{C}F_2$ radicals.

By analogy, it is expected that of the radicals that can form from $CF_2BrCFClBr$, namely, $CF_2Br\dot{C}FCl$ and $CFClBr\dot{C}F_2$, the former should be more stable.

Since 1,2-dibromo-1-chloro-1,2,2-trifluoroethane behaves as do other halomethanes[9] and knowing the point of attack on allyl alcohol as demonstrated in the perfluoroalkyl iodide additions, the product is undoubtedly, $CF_2BrCFClCH_2{—}CH_2{—}BrCH_2$-$OH$. The halohydrins resulting from the photochemical reactions were converted to epoxides.

The reported methods for the conversion of fluorine-containing halohydrins to epoxides are consistent in the use of alkali but concentrations vary from powdered potassium hydroxide[10–13] to a 10% sodium hydroxide solution. In this investigation the procedure of Osterberg[14] was found suitable for the conversion of halohydrin such as $C_3F_7CH_2CHICH_2OH$ to the oxide $C_3F_7CH_2$-$\underline{CHCH_2O}$. In general, the procedure involved the agitation of a heterogeneous mixture of the halohydrin and 10% sodium hydroxide at room temperature for about one hour. The yields were generally on the order of 70%.

The epoxides prepared by this method were, $CF_3CH_2\underline{CHCH_2O}$, $C_2F_5CH_2\underline{CHCH_2O}$, $C_3F_7CH_2$-$\underline{CHCH_2O}$, and $CF_2BrCFClCH_2{—}\underline{CHCH_2O}$. These epoxides are quite stable and have a characteristic odor. The behavior of these oxides to prolonged irradiation by actinic light is complex. A solution of *n*-heptafluoropropyl iodide and $CF_2ClCFClCH_2$-$\underline{CHCH_2O}$ was irradiated for seven days and on distillation yielded almost all of the iodide. The residue was not the starting epoxide, but rather a thick polymeric liquid. The structure of this material is unknown. Whether a perfluoroalkyl group exerts any stabilizing influence on the three-membered epoxide ring is uncertain. McBee and Burton[12]

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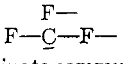
[6] (a) Resonance energy in this sense is composed of two factors: (1) electronic stabilization $F_2{—}C{—}\bar{\underline{F}}$ $F_2{—}\dot{C}{=}\bar{\underline{F}}$. etc. (2) relief of strain induced by polar C—F bonds,



$$\begin{array}{c} \quad F— \\ F—\underset{\smile}{C}—F— \end{array}$$

(6) (b) J. D. Park, private communication.

[7] F. E. Lawlor, Abstracts, 128th Meeting American Chemical Society, Minneapolis, Minn. (1955).

[8] P. Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3640 (1955).

[9] P. Tarrant and E. G. Gillman, *J. Am. Chem. Soc.*, **76**, 5423 (1954).

[10] I. L. Knunyants, *Compt. Rend. Acad. Sci., U.R.S.S.*, **55**, 223 (1947).

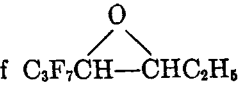
[11] I. L. Knunyants, O. V. Kildesheva, and I. P. Petrov, *Zhur Obshcheĭ Khim.*, **19**, 95 (1949).

[12] E. T. McBee and T. M. Burton, *J. Am. Chem. Soc.*, **74**, 3902 (1952).

[13] D. A. Rausch, A. Lovelace, and L. E. Coleman, *J. Org. Chem.*, **21**, 1328 (1956).

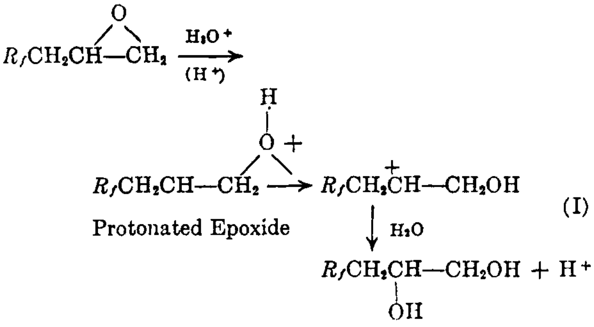
[14] A. E. Osterberg, *Org. Syntheses*, Coll. Vol. I, J. Wiley & Sons, Inc., New York, 1943, p. 185.

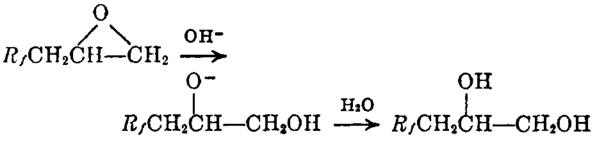
hydrolyzed $CF_3\underbracket{CHCH_2O}$ to $CF_3CH(OH)CH_2OH$ by refluxing with 1% sulfuric acid for twelve hours. However, Rausch *et al.*[13] found that the hydrolysis of



$C_3F_7\overset{O}{CH—CH}C_2H_5$ required heating with 20% sulfuric acid at 105° for sixty hours. In this investigation, hydrolysis was carried out with water and 10% sulfuric acid. With epoxides of the structure, $RCH_2\underbracket{CHCH_2O}$, where R is a perhaloalkyl group (with fluorine, chlorine, and bromine) it was found that hydrolysis took place at 95° with 10% sulfuric acid after sixteen hours to give the glycols in 70–90% yields. The best procedure for hydrolysis when R is a perfluoroalkyl group required heating with almost twice the stoichiometric amount of water at 140° in a sealed tube.[15] *Via* this procedure $C_2F_5CH_2\underbracket{CHCH_2O}$ gave $C_2F_5CH_2CH(OH)CH_2OH$ in 57% yield after three days at 140°.

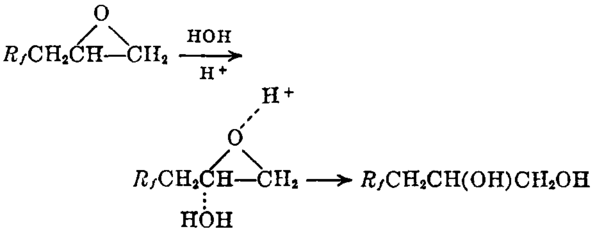
The presence of a perfluoroalkyl side chain on the epoxide ring places some informative restriction on the mechanism of hydrolysis. That the ring opening can be represented by "pure" acid catalysis is doubtful, since the intermediate carbonium ion (I) would be destabilized by the neighboring R_f group. That the R_f group deactivates the ring sufficiently so as to enhance the basic properties of water is possible.





Nonprotonated Epoxide

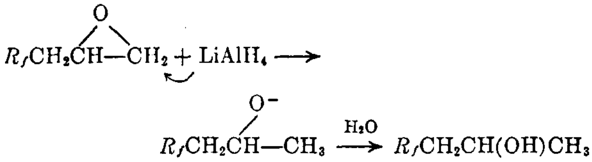
A concerted mechanism may be closer to reality however.



The glycols prepared by this method were: $C_2F_5CH_2CH(OH)CH_2OH$, $C_3F_7CH_2CH(OH)CH_2OH$, $CF_2BrCFClCH_2CH(OH)CH_2OH$, and $CF_2ClCFClCH_2CH(OH)CH_2OH$.

Some of the glycols could not be obtained pure by fractional distillation because of their extreme viscosity. These glycols were isolated as their 3,6-dinitrobenzoates prepared according to the procedure of Fuson.[16] The bisdinitrobenzoate of $C_3F_7CH_2CH(OH)CH_2OH$ decomposes at its melting point, 125–126°.

The epoxide, $C_2F_5CH_2\underbracket{CHCH_2O}$, was found to react with lithium aluminum hydride to produce the expected secondary alcohol,[17] $C_2F_5CH_2CH(OH)CH_3$, in 50% yield. The product carbinol was subjected to vapor phase chromatography and the results indicated only one alcohol. An NMR spectrum identified the carbinol as secondary. It is interesting to note, however, that this secondary alcohol would not give a positive test with the Lucas reagent. The S_{N1} nature of this test would require the formation of the carbonium ion, $C_2F_5CH_2\overset{+}{C}HCH_3$. The formation of such a carbonium ion is obviously suppressed by the neighboring perfluoroethyl group. Steric factors are evidently responsible for the selectivity manifest in the epoxide ring opening with lithium aluminum hydride, the reducing agent choosing the most accessible site, the primary carbon atom in this case



It was desired to determine how the negative pentafluoroethyl group would affect the reduction when a lithium aluminum hydride–aluminum chloride mixture was used. Eliel[18] has shown that this reagent reversed the mode of the ring opening in certain epoxides.

When $C_2F_5CH_2\underbracket{CHCH_2—O}$ was added to a solution of lithium aluminum hydride and aluminum chloride (in a ratio of 1:0.3 respectively) no reversal was observed and only secondary alcohol was isolated. Gas chromatography showed the carbinol to be a single pure compound.

It may be that the pentafluoroethyl group has no effect on the opening of the epoxide. The opening of the propylene oxide ring is reversed only to

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(15) L. Brunel, *Bull. Soc. Chem.*, 29, 882 (1903).

(16) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, J. Wiley & Sons, Inc., New York, third ed., 1948.

(17) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, New York, Interscience Publisher, Inc., 1950, pp. 646–73.

(18) E. Eliel and D. W. Selmonte, *J. Am. Chem. Soc.*, 80, 1744 (1958).

the extent of 7%[18] by the presence of aluminum chloride. Here, it is thought that the hydride shift is sluggish enough so that reduction by the weaker aluminum halohydrides can compete favorably.

The addition of perfluoroalkyl iodides to propargyl alcohol under free radical conditions was found to be faster than similar additions to allyl alcohol. Thus, trifluoromethyl iodide and *n*-heptafluoropropyl iodide reacted with propargyl alcohol over a period of seven days to form the corresponding unsaturated halohydrine, $R_fCH{=}CICH_2OH$, in 46 and 60% yields respectively, while allyl alcohol required fourteen days to give the halohydrins in 50 and 54% yields respectively. Whether this difference is significant or merely a manifestation of the relative purity of the reagents is not known.

The reaction of these unsaturated halohydrins with zinc was studied. Henne[19] had reported that $CF_3CCl{=}CClCF_3$ reacted with zinc in absolute ethanol at 40° to yield a mixture of products, *i.e.*, $CF_3C{\equiv}CCF_3$, $CF_3CH_2CH_2CF_3$, and $CF_3CCl{=}CHCF_3$. To learn more about the mechanism and general applicability of this reaction the same procedure was used with $C_3F_7CH{=}CICH_2OH$. If the double bond is saturated in the first step then the halohydrin, $C_3F_7CH_2CHICH_2OH$ would be formed which subsequently would react with zinc to yield the olefin, $C_3F_7CH_2CH{=}CH_2$ by elimination of hypoiodous acid. On the other hand, if the iodine atom is reduced off first, an unsaturated alcohol, $C_3F_7CH{=}CHCH_2OH$ results, which subsequently may be reduced to $C_3F_7CH_2CH_2CH_2OH$. The unsaturated halohydrin was treated with zinc in absolute ethanol at reflux for eighteen hours. Vacuum distillation gave only one product in 64% yield which was identified as the unsaturated alcohol, $C_3F_7CH{=}CHCH_2OH$. Thus, the removal of the iodine atom is clearly the first step.

The infrared spectrum of this compound showed a double bonded O-H absorption and a doublet around 6 μ indicating two types of double bonds, *cis* and *trans*. An initial pass through an "Aerograph" gas chromatographic instrument at 120°, at a flow rate of 88 ml./min. and a sensitivity of 30 did not give any resolution. However, a temperature of 90°, a flow rate of 60 ml./min. and a sensitivity of 20 resolved the compound into both isomers. Assignment of the *cis* and *trans* structures was made on the basis of their infrared spectra and relative boiling points. According to Bellamy[20a] it is a general—though not invariable—rule that the *trans* isomer absorbs at a lower wave length than the *cis*. The first fraction from the chromatographic instrument has a double bond peak at 6 μ, the last fraction at 5.95.[20b] This latter compound is therefore, assigned the *trans* structure.

The retention time in a chromatographic instrument is proportional to the relative boiling points of the compounds being separated, *i.e.*, the highest boiling liquid coming out last. Since *trans* isomers generally boil higher, the last fraction (5.95 μ) is assigned the *trans* structure. Both approaches give the same assignments.

When the halohydrin, $CF_3CH{=}CICH_2OH$, was treated with zinc in absolute ethanol in the manner described above the known unsaturated alcohol, $CF_3CH{=}CHCH_2OH$ was isolated. The infrared spectrum showed two types of double bond peaks, one at 5.90 μ (*trans*) and a shoulder at 5.95 μ (*cis*).

The preparation of this latter alcohol proves the structure of the intermediate halohydrin, $CF_3CH{=}CICH_2OH$ and therefore, clearly establishes the mode of addition of trifluoromethyl iodide and propargyl alcohol. By analogy, it is evident, then, that the *n*-heptafluoropropyl iodide adduct to propargyl alcohol is as written above, $C_3F_7CH{=}CICH_2OH$.

EXPERIMENTAL

4,4,4-Trifluoro-2-iodobutanol. (A) Reagent-grade allyl alcohol (18 g.) was placed in a "Double Tough" Pyrex pipe which was fitted with a pressure gage. The apparatus was cooled in a Dry Ice–acetone bath and evacuated. Trifluoromethyl iodide (40 g.) was distilled into the tube and the solution irradiated with a 100-watt ultraviolet source at room temperature. During a period of 14 days the pressure dropped from a maximum of 95 to 45 p.s.i.g. when the reaction was stopped. The tube was opened and the effluent gases (17 g.) that collected in a Dry Ice trap were later identified as the unchanged iodide. The high boiling residue was distilled at atmospheric pressure to remove unchanged allyl alcohol. Distillation *in vacuo* of the remaining liquid yielded the halohydrin, 15 g. (50%), b.p. 104.5–105° (60 mm.), n_D^{25} 1.4630, d_4^{25} 1.9983, MR_D: calcd. 35.10, obsd. 35.00.

Anal. Calcd. for $C_4H_6F_3IO$: C, 18.91; H, 22.44. Found: C, 18.64; H, 22.10.

This procedure was used in preparing the halohydrins that follow.

4,4,4-Trifluoro-1,2-epoxybutane. The procedure is similar to that reported by Osterberg.[14] To a flask fitted with a stirrer and reflux condenser were charged 25.8 g. (0.1 mole) of 4,4,4-trifluoro-2-iodobutanol and an aqueous sodium hydroxide solution (5 g. in 25 ml. of water). The pink color of the halohydrin was discharged immediately. The heterogeneous mixture was stirred at room temperature for 1 hr. after which time the organic layer was separated and dried over magnesium sulfate overnight. Atmospheric distillation gave 7.4 g. (59.5%) of the epoxide, b.p. 68–69° (627 mm.), n_D^{25} 1.3267, d_4^{25} 1.2487, MR_D: calcd. 20.13, obsd. 20.03.

Anal. Calcd. for $C_4H_5F_3O$: C, 38.10; F, 45.24; H, 3.96. Found: C, 37.86; F, 44.97; H, 3.82.

This procedure was used in preparing the epoxides that follow.

Perfluoroethyliodide. The procedure of Haszeldine[21] was used to prepare perfluoroethyl iodide from the silver salt of perfluoropropionic acid and iodine; yield 98%.

4,4,5,5,5-Pentafluoro-2-iodopentanol. From 40 g. of allyl alcohol, 142 g. of pentafluoroethyl iodide and benzoyl per-

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[19] A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71,** 298 (1949).

[20] (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley & Sons, Inc., New York, 1956.

(20) (b) Bellamy[20] reports that *cis* and *trans* isomers differ in absorption by about 0.5 μ.

[21] R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

oxide (0.5 g.) were obtained after 14 days 66.3 g. (55%) of 4,4,5,5,5-pentafluoro-2-iodopentanol, b.p. 81° (13.5 mm.), n_{D}^{25} 1.4310, d_4^{25} 2.036, MR$_{\mathrm{D}}$: calcd. 39.52, obsd. 38.64.

Anal. Calcd. for $C_5H_6F_5IO$: C, 19.75; H, 1.97. Found: C, 19.91; H, 1.85.

4,4,5,5,5-Pentafluoro-1,2-epoxypentane. From 40 g. of 4,4,5,5,5-pentafluoro-2-iodopentanol (0.13 mole) and 63 ml. of a 10% sodium hydroxide solution were obtained upon distillation 13.25 g. (57%) of 4,4,5,5,5-pentafluoro-1,2-epoxypentane, b.p. 84.5° (624 mm.), n_{D}^{25} 1.3178.

Anal. Calcd. for $C_5H_5F_5O$: C, 34.09; H, 2.84; F, 53.97. Found: C, 33.92; H, 2.94; F, 54.00.

4,4,5,5,5-Pentafluoro-1,2-pentanediol. 4,4,5,5,5-Pentafluoro-1,2-epoxypentane (2 g., 0.011 mole) and 0.5 ml. (0.028 mole) water were sealed in a small Pyrex combustion tube and heated in a mineral oil bath at 140°. The mixture became homogeneous after 36 hr. but heating was continued for another 36 hr. The solution was transferred to a small metro-ware distillation flask with a little anhydrous ether. Atmospheric distillation in a short path column gave a small amount of unreacted epoxide. Vacuum distillation of the residue gave 1.4 g. (63.5%) of the glycol, b.p. 80° (6 mm.), n_{D}^{25} 1.3586, d_4^{25} 1.4942, MR$_{\mathrm{D}}$: calcd. 28.34; obsd. 28.55. A micro boiling point determination gave 182° at 632 mm.

Anal. Calcd. for $C_5H_7F_5O_2$: C, 30.94; H, 3.62; F, 48.94. Found: C, 30.76; H, 3.81; F, 49.30.

This process was used in preparing the diols that follow.

4,4,5,5,5-Pentafluoro-2-pentanol. Lithium aluminum hydride (0.5 g., 0.015 mole) and 20 ml. of sodium-dried ether were charged to a 50-ml. metro-ware flask fitted with a condenser (and calcium chloride drying tube), dropping funnel, and magnetic stirring bar. The slurry was heated at reflux and stirred for 1.5 hr. A solution of anhydrous ether (15 ml.) and 4,4,5,5,5-pentafluoro-1,2-epoxypentane (5 g., 0.028 mole) was added dropwise so as to maintain gentle reflux (no external heating). Stirring was continued overnight.

The unchanged lithium aluminum hydride was decomposed with 10 ml. of water, which was added slowly. The oxides of aluminum were dissolved by the addition of 30 ml. of 10% sulfuric acid. The ether layer was separated and the aqueous layer continuously extracted for 20 hr. The combined ether solutions were dried over Drierite. Distillation in a short path column gave 2 g. (40%) of the secondary alcohol, b.p. 102.5 (632 mm.), n_{D}^{25} 1.3275.

Anal. Calcd. for $C_5H_7F_5O$: C, 33.71; H, 3.93; F, 53.37. Found: C, 33.78; H, 31.82; F, 53.10.

Gas chromatography indicated only one pure compound. The NMR spectrum identified the alcohol as being secondary. A negative test was obtained with the Lucas reagent for a secondary alcohol. However, this is not surprising for such a negatively substituted alcohol.

Reduction of 4,4,5,5,5-pentafluoro-1,2-epoxypentane with lithium aluminum hydride-aluminum chloride. The procedure was essentially that of Eliel.[18] Considerable difficulty was experienced in making a solution of lithium aluminum hydride. When lithium aluminum hydride from two previously used stock cans was employed in two separate attempts, no solution was obtained when the lithium aluminum hydride–ether (anhydrous) slurry was refluxed for 10 hr. However, lithium aluminum hydride from a new, unopened can gave almost complete solution in an equivalent time. Apparently lithium aluminum hydride forms an oxide coating when repeatedly exposed to air. This coating makes dissolution difficult or impossible.

Lithium aluminum hydride (0.3 g., 0.0079 mole) was pulverized and placed in a flask with 25 ml. of anhydrous ether. A condenser with a calcium chloride drying tube, magnetic stirrer, and dropping funnel were affixed. The slurry was stirred at reflux for 16 hr. After this period, when all but a very small amount of the lithium aluminum hydride had dissolved, a solution of aluminum chloride (3.74 g., 0.028 mole) in anhydrous ether (15 ml.) was added slowly. After 0.5 hr. the solution was clear except for a small amount of grey material on the sides of the flask. The epoxide (4.4 g., 0.025 mole) in ether (12 ml.) was added over a 25-min. period. Reflux was continued overnight.

Water (10 ml.) was added carefully, followed by enough 10% sulfuric acid (50 ml.) to dissolve the oxides formed. The aqueous layer was separated and extracted continuously with ether for 20 hr. The extract was combined with the original ether layer and dried over Drierite. Distillation yielded $C_2F_5CH_2CH(OH)CH_3$ (1.9 g., 43%), b.p. 102.5° (632 mm.), n_{D}^{25} 1.3272. A gas chromatographic run showed the material to be free of any primary alcohol.

4,4,5,5,6,6,6-Heptafluoro-2-iodohexanol. Two hundred and ten grams of heptafluoropropyl iodide and 40 g. of allyl alcohol were charged to a 200 ml. "Double Tough" Pyrex and the contents irradiated with a 400-watt Mercury Arc Lamp and a 100-watt ultraviolet source. Distillation yielded 90 g. (54%) of the desired halohydrin, b.p. 71–71.5° (7 mm.), n_{D}^{25} 1.4125, d_4^{25} 1.9635, MR$_{\mathrm{D}}$: calcd. 44.24, obsd. 44.91.

Anal. Calcd. for $C_6H_6F_7IO$: C, 20.35; F, 37.57. Found: C, 20.31; F, 36.95.

4,4,5,5,6,6,6-Heptafluoro-1,2-epoxyheptane. Eighty grams of 4,4,5,5,6,6,6-heptafluoro-2-iodohexanol treated with 50 ml. of a 15% sodium hydroxide solution upon distillation yielded 26.5 g. of unchanged halohydrin and 13.1 g. (38.4% of the epoxide, b.p. 103.5° (633 mm.), n_{D}^{25} 1.3149, d_4^{25} 1.4723; MR$_{\mathrm{D}}$: calcd. 29.36, obsd. 30.00.

Anal. Calcd. for $C_6H_5F_7O$: C, 31.86; H, 2.21. Found: C, 31.79; H, 2.55.

4,4,5,5,6,6,6-Heptafluoro-1,2-hexanediol. From 13.6 g. of 4,4,5,5,6,6,6-heptafluoro-1,2-epoxyhexane and 20% sulfuric acid (5 ml.) was obtained 4 g. of diol which came over at 114°, at 22 mm. n_{D}^{25} 1.3496, n_{D}^{25} 1.5759, MR$_{\mathrm{D}}$: calcd. 32.96, obsd. 33.29. A micro boiling point determination gave 193° at 632 mm. The infrared spectrum showed strong OH absorption. The compound gave a positive periodic acid test as would be expected from a vicinal glycol.

Preparation of 3,5-dinitrobenzoate.[16] The glycol (0.350 g.) and 3,5-dinitrobenzoyl chloride (0.9 g.) were taken up in anhydrous pyridine (2 ml.) and warmed on a steam bath for 1 hr. On pouring into water (10 ml.) an oil separated. The water was decanted and 10 ml. of 5% sodium carbonate added. The mixture was heated for 15 min. and then the sodium carbonate solution decanted. The oil was washed with hot water. Recrystallization from ethanol gave pale yellow crystals (0.175 g.), m.p. 118–125° dec. A second recrystallization from ethanol gave crystals which were air-dried and melted at 125–126° dec.

Anal. Calcd. for $C_{20}H_{11}F_7N_4O_{12}$: C, 37.97; H, 2.05; F, 21.04. Found: C, 38.07; H, 1.98; F, 20.75.

2-Iodo-4,5-dichloro-4,5,5-trifluoropentanol. From 211 g. of 1,2-dichloro-1,2,2-trifluoro-1-iodoethane, 52 g. of allyl alcohol, and 0.5 g. of benzoyl peroxide after irradiation for 22 days were obtained 112 g. of a fraction boiling at 110–125°/11 mm. The material was agitated in the presence of mercury to remove any entrained iodine. The precipitate of mercury and mercuric iodide was removed by filtration. The pink filtrate, vacuum distilled in a short path column yielded 106 g. (41.6%) of the halohydrin, b.p. 84.2° (1.6 mm.), n_{D}^{25} 1.4953, d_4^{25} 1.9984, MR$_{\mathrm{D}}$: calcd. 49.36, obsd. 49.20.

Anal. Calcd. for $C_5H_6Cl_2F_3IO$: C, 17.82; F, 16.92; I, 37.66. Found: C, 18.05; F, 16.87; I, 37.39.

4,5-Dichloro-4,5,5-trifluoro-1,2-epoxypentane. From 99.4 g. of 2-iodo-4,5-dichloro-4,5,5-trifluoropentanol and 15% aqueous sodium hydroxide (75 cc.) were obtained 39.8 g. of epoxide (70%), b.p. 145.5–145.8° (625 mm.), n_{D}^{25} 1.4033, d_4^{25} 1.4767, MR$_{\mathrm{D}}$: calcd. 34.48, obsd. 34.57.

Anal. Calcd. for $C_5H_5Cl_2F_3O$: C, 28.73; F, 27.27. Found: C, 28.70; F, 27.19.

4,5-Dichloro-4,5,5-trifluoro-1,2-pentanediol. 4,5-Dichloro-4,5,5-trifluoro-1,2-epoxypentane (6 g., 0.029 mole) and 15% sulfuric acid (5 cc.) yielded upon rectification a very viscous glycol (3.2 g., 53%), b.p. 101–102° (2.3 mm.), n_D^{25} 1.4330, d_4^{25} 1.5712, MR_D: calcd. 37.08, obsd. 37.57.

Anal. Calcd. for $C_5H_7Cl_2F_3O_2$: C, 26.45; F, 25.11. Found: C, 26.80; F, 24.80.

The infrared spectrum shows strong OH absorption. A positive periodic acid test was obtained as expected for a vicinal glycol.

2,5-Dibromo-4-chloro-4,5,5-trifluoropentanol. The following procedure was adapted from that used by Tarrant[22] for the free radical addition of 1,2-dibromo-1-chloro-1,2,2-trifluoroethane to vinyl silanes.

1,2-Dibromo-1-chloro-1,2,2-trifluoroethane (460 g., 1.65 moles) and allyl alcohol (90 g., 1.55 moles) were placed in a 500-cc., three-necked flask fitted with a condenser and attached drying tube, stirrer, and dropping funnel. The solution was heated to reflux and a solution of benzoyl peroxide (3.7 g., 0.015 mole) in a 1,2-dibromo-1-chloro-1,2,2-trifluoroethane (75 cc., 0.27 mole) was added over a 2-hr. period. The resultant solution was refluxed for 15 hr. and another 75 cc. of a similar solution was added over a 1.5-hr. period. Refluxing was continued for an additional 5 hr. The unreacted dibromide and alcohol were removed leaving the crude product. Rectification of this residue yielded the bromohydrin (21 g.), b.p. 97° (2.6 mm.), n_D^{25} 1.4808, d_D^{25} 1.9838, MR_D: calcd. 47.23, obsd. 47.96.

Anal. Calcd. for $C_5H_6Br_2ClF_3O$: C, 18.0; F, 17.2. Found: C, 18.2; F, 16.8.

Preparation of 4-chloro-5-bromo-4,5,5-trifluoro-1,2-epoxypentane. From 47.5 g. of 2,5-dibromo-4-chloro-4,5,5-trifluoropentanol (0.14 mole) and a 15% aqueous sodium hydroxide (50 cc.) were obtained 23.2 g. of the epoxide (73.5%), b.p. 72.5° (19 mm.), n_D^{25} 1.4294, d_4^{25} 1.7549, MR_D: calcd. 37.38 obsd. 37.27. This epoxide was not analyzed but converted directly to the glycol which was analyzed.

4-Chloro-5-bromo-4,5,5-trifluoro-1,2-pentanediol. From 10 g. of 4-chloro-5-bromo-4,5,5-trifluoro-1,2-epoxypentane (0.04 mole) and 10% sulfuric acid were obtained 3.6 g. of crude glycol (90%) with a boiling range of 112–118° (0.5 mm.), n_D^{25} 1.4554, d_4^{25} 1.8275, MR_D: calcd. 39.98, obsd. 40.33.

The agreement of the molar refractions may just be fortuitous since the extreme viscosity of the glycol prevents proper distillation. A micro boiling point determination gave 220° (625 mm.).

The infrared spectrum indicates strong OH absorption. A positive periodic acid test was obtained for the vicinal glycol.

The 3,5-dinitrobenzoate derivative of the glycol gave a m.p. of 109.5–110.5°.

Anal. Calcd. for $C_{19}H_{11}BrClF_3N_4O_{12}$: C, 34.57; H, 1.67; Cl, 5.38; Br, 12.11. Found: C, 34.59; H, 1.57; Cl, 5.56; Br, 11.82.

4,4,5,5,6,6-Heptafluoro-2-iodo-2-hexen-1-ol. Heptafluoropropyl iodide (87 g.) and propargyl alcohol (17 g.) charged to a "Double Tough" Pyrex tube was irradiated with a 100-watt ultraviolet source for 7 days. Distillation of the reaction mixture gave the halohydrin (62 g., 60%), b.p. 65.5° (3.4 mm.), n_D^{20} 1.4223, d_4^{20} 2.014, MR_D: calcd. 43.77, obsd. 44.43.

Anal. Calcd. for $C_6H_4F_7IO$: C, 20.45; H, 1.13; F, 37.76. Found: C, 20.22; H, 1.34; F, 37.61.

2(2-Iodo-4',4',5',5',6',6',6'-heptafluoro-2-hexeneoxy)dihydro pyran. The hydroxyl group of the halohydrin was protected according to the method of Parham[23] using dihydropyran.

Twenty grams of 4,4,5,5,6,6,6-heptafluoro-2-iodo-2-hexen-1-ol dihydropyran (10 g.) and 2 drops of concd. hydrochloric acid were combined. The addition of the acid gave rise to a highly exothermic reaction. The solution was allowed to stand for 4 hr. with occasional shaking. The reaction mixture was washed with 10% sodium hydroxide (40 ml.) and twice with water. The organic layer was separated and dried over "Drierite." The acetal was obtained in 88% yield, b.p. 98–99° (3.5 mm.), $n_D^{20.3}$ 1.4368, $d_4^{20.3}$ 1.6945, MR_D: calcd. 66.43, obsd. 67.30.

Anal. Calcd. for $C_{11}H_{12}F_7IO_2$: C, 30.29; F, 30.49. Found: C, 30.06; F, 30.08.

The infrared spectrum showed no O—H peak as expected.

4,4,5,5,6,6,6-Heptafluoro-2-hexen-1-ol. Zinc dust (5 g., 0.08 mole) and commercial absolute ethanol (75 ml.) were placed in a flask fitted with a stirrer, condenser, and dropping funnel. The slurry was heated to reflux. Over a period of 45 min. 4,4,5,5,6,6,6-heptafluoro-2-iodo-2-hexen-1-ol (17 g., 0.052 mole) was added. The reaction mixture was stirred at reflux for an additional 18 hr. Vacuum distillation gave the unsaturated alcohol (7.6 g., 64%), b.p. 65.5° (28 mm.), n_D^{25} 1.3363, d_4^{25} 1.4729, MR_D: calcd. 30.97, obsd. 31.84. A micro boiling point determination gave 137.5° at 632 mm.

The infrared spectrum showed two double bond absorption peaks, one at 5.95 μ and one at 6.0 μ. The liquid was run through the "Aerograph" gas chromatographic instrument at 90°, a flow rate of 60 ml./min. and a sensitivity of 20. A single peak which was unresolved in a preliminary run at 120°, a flow rate of 88 ml./min. and sensitivity of 30 was resolved into two peaks of equal intensity. Each fraction showed the expected O—H peaks and one double bond absorption band which differed by about 0.5 μ or the same difference between the doublet in the impure sample.

On the basis of their infrared absorption and the generally expected higher boiling point for a *trans* isomer, the fraction which absorbed at 6 μ is assigned the *cis* configuration; the 5.95 fractions, the *trans* structure.

Anal. Calcd. for $C_3F_7CH{=}CHCH_2OH$: C, 31.86; F, 58.84; H, 2.23. *cis* n_D^{25} 1.3360, found: C, 32.19; F, 59.12; H, 2.34. *trans* n_D^{25} 1.3365, found: C, 31.90; F, 59.02; H, 2.40.

2-Iodo-4,4,4-trifluoro-2-butenol. Propargyl alcohol (10 g., 0.18 mole) and trifluoromethyl iodide (31.5 g., 0.16 mole) were charged to a "Double Tough" Pyrex tube fitted with a pressure gage and irradiated for 7 days. Distillation using a glycerol "chaser" yielded the halohydrin (13 g., 46.5%), b.p. 75° (10 mm.), n_D^{20} 1.4782, d_4^{20} 2.076, MR_D: calcd. 34.7, obsd. 34.53.

Anal. Calcd. for $C_4H_4F_3IO$: C, 19.10; H, 1.59; F, 22.62. Found: C, 19.38; H, 1.74; F, 22.34.

4,4,4-Trifluoro-2-butenol. The halohydrin, 2-iodo-4,4,4-trifluoro-2-butenol, (14 g.), zinc dust (1.8 g.) and absolute ethanol (30 ml.) were treated in a manner similar to 2-iodo-4,4,5,5,6,6,6-heptafluoro-2-hexenol; the heating time was considerably shorter. This slurry was stirred at room temperature for 0.5 hr., then at 50° for 1 hr. Only the starting halohydrin (12.2 g.) was recovered.

The reaction was repeated at a higher temperature. Zinc dust (4 g., 0.06 mole) and absolute ethanol (12 ml.) were heated at reflux and the halohydrin (6.5 g., 0.026 mole) in absolute ethanol was added over a period of 1 hr. The slurry was stirred at reflux temperature for 18 hr. The zinc was removed by filtration and the entire liquid was separated from the dissolved and dispersed zinc iodide by distillation *in vacuo* at steam bath temperature. Distillation gave the unsaturated alcohol (1.5 g.) contaminated with some ethanol and water. Gas chromatographic analysis showed that the liquid contained 78% of the unsaturated alcohol, which was composed of about 60% *cis* and 40% *trans* isomers. Sufficient pure alcohol was collected in successive chromatographic runs to determine the following physical properties:

$CF_3CH{=}CHCH_2OH$: (36% yield); b.p. 118.5° (630 mm.); n_D^{25} (*cis*) 1.3546; n_D^{25} (*trans*) 1.3551; n_D^{20}, (mixture) 1.3565. (Lit.[24] reports: n_D^{20} 1.3578; b.p. 128° (760 mm.).)

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[22] P. Tarrant and G. W. Dykes, 128th Meeting, American Chemical Society, Minneapolis, Minn. (1955).

[23] W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.*, **70**, 4187 (1948).

[24] E. T. McBee, O. R. Pierce, and D. D. Smith, *J. Am. Chem. Soc.*, **76**, 3725 (1954).

The infrared spectrum shows strong O—H absorption at 3 μ and double bond peaks at 5.90 μ (*trans*) and a shoulder at 5.95 μ (*cis*).

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