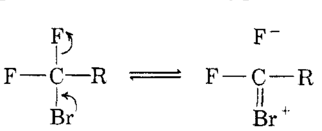
ucts caused the yield of olefin to be low. This reaction, however, was of interest in two respects. First, both possible dehydrohalogenation products were isolated (VI and VII). This is in contrast to

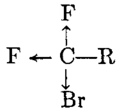
$$CH_2{=}CF_2 + CCl_3Br \xrightarrow{(C_6H_5COO)_2} \underset{V}{CCl_3CH_2CF_2Br} \xrightarrow{(C_2H_5)_3N} \underset{VI}{CCl_3CH{=}CF_2} + \underset{VII}{CCl_2{=}CHCF_2Br}$$

the results of Nesmeyanov[5] in the dehydrohalogenation with triethylamine of analogous compounds which contained no fluorine, when compounds of the type, $CCl_3CH{=}CHR$ were obtained from CCl_3CH_2CHBrR. This demonstrates the shielding effect afforded by adjacent fluorine atoms which arise, either through resonance of the type:



$$\begin{array}{c}F\\|\\F{-}C{-}R\\|\\Br\end{array} \rightleftharpoons \begin{array}{c}F^-\\ \\F{-}C{-}R\\ \|\\Br^+\end{array}$$

or a strictly inductive effect which results in a shortening of the bond between the electron-poor carbon atom and its bromine substituent:



$$\begin{array}{c}F\\ \uparrow\\F \leftarrow C{-}R\\ \downarrow\\Br\end{array}$$

Secondly, the structure of the initial adduct is shown to be 1,1,1-trichloro-2-bromo-3,3-difluoropropane, rather than 1,1,1-trichloro-2,2-difluoro-3-bromopropane, since removal of HX (X = Br or Cl) would yield only an olefin in the former case.

EXPERIMENTAL

Preparation of 1,5-dibromo-1,1,3,3,5,5-hexafluoropentane. A procedure similar to that of Tarrant, Lovelace, and Lilyquist[1] was used, in which a 5.2:1.2 ratio of the halomethane to the olefin was employed, with the exception that about three times as much benzoyl peroxide was used. These materials were combined in a 1.4 l. steel autoclave, cooled in Dry Ice, then heated and rocked for 6 hr. at 80°. Yields of the one-to-one adduct were 33–55% and the two-to-one adduct were 23–29%.

Anal. Calcd. for $C_5H_4F_6Br_2$: C, 17.7; H, 1.2; F, 33.7; Br, 47.3. Found: C, 17.4; H, 1.2; F, 33.8; Br, 46.7.

Dehydrohalogenation of 1,5-dibromo-1,1,3,3,5,5-hexafluoropentane. The method of Tarrant, Lovelace, and Lilyquist[1] was used. The haloalkane was added to 33% aqueous potassium hydroxide at 80° and the olefins distilled as they were formed. The 1,1,3,3,5,5-hexafluoropentadiene-1,3 (b.p. 44.6–45.1°/760 mm., n_D^{20} 1.3583, d_4^{20} 1.3935, $MR_{D(calcd.)}$ 24.36) and 5-bromo-1,1,3,3,5,5-hexafluoropentene-1 (b.p. 104–106°/738 mm., n_D^{20} 1.3583, d_4^{20} 1.7053, $MR_{D(calcd.)}$ 32.59) were obtained in a combined yield of 45%.

Anal. Calcd. for $C_5H_3BrF_6$: C, 23.4; H, 1.17; F, 43.4; Br, 32.0. Found: C, 25.4; H, 1.83; F, 43.1; Br, 32.6.

Anal. Calcd. for $C_5H_2F_6$: C, 34.1; H, 1.14; F, 64.8. Found: C, 34.1; H, 1.81; F, 64.8.

Preparation of 1,1,1-trichloro-3-bromo-3,3-difluoropropane. A 1.4 l. steel autoclave was charged with 990 g. (5.0 moles) of bromotrichloromethane and 12 g. (0.05 mole) of benzoyl peroxide, sealed, cooled in Dry Ice–acetone to −75°, and evacuated. Then 64 g. (1.0 mole) of 1,1-difluoroethylene was passed into the vessel. The vessel was rocked and heated at 90° for 8 hr. The autoclave was cooled, vented, and the contents distilled at 125 mm. to obtain 745 g. of unchanged bromotrichloromethane and 123 g. of product boiling at 90.5–94.5° with a yield of 62% based on unrecovered starting material. The product thus obtained was shown to be 95% pure by means of vapor phase chromatography. Upon careful redistillation through a Podbielniak Mini-cal column a cut was obtained which was shown to be essentially pure by the same means. The properties of this material were: b.p. 85.0°/100 mm., n_D^{20} 1.4678, d_4^{20} 1.8272, $MR_{D(calcd.)}$ 24.36.

Anal. Calcd. for $C_3H_2BrCl_3F_2$: C, 13.7; H, 0.76; Br, 30.5; Cl, 40.5; F, 14.5. Found: C, 13.7; H, 1.00; Br, 29.5; Cl, 39.7; F, 13.9.

Dehydrogenation of 1,1,1-trichloro-3-bromo-3,3-difluoropropane. In a three neck, 300-ml. flask equipped with stirrer, reflux condenser, thermometer, and funnel, the halopropane, 131 g. (0.5 mole) was added and heated to 70°. The triethylamine, 50.5 g. (0.5 mole) was added dropwise into the flask over a period of an hour. The temperature of the reaction was maintained between 70–90° during the addition. The mixture was stirred for 0.5 hr. after the addition was complete and then allowed to stand overnight. The reaction mixture was added to 300 ml. of water, the organic layer separated and dried over calcium chloride. The crude product weighed 98 g. Distillation gave 37 g. boiling from 94–125° and 58 g. of starting material boiling from 125–160°. Redistillation through the Podbielniak column gave 8 g. of 1,1,1-trichloro-3,3-difluoropropene-2, b.p. 96–97°, n_D^{25} 1.4273, d_4^{25} 1.5460; $MR_{D(calcd.)}$ 31.29 and 5 g. of 1-bromo-1,1-difluoro-3,3-dichloropropene-2, b.p. 116.1–116.3°; n_D^{25} 1.4568; d_4^{25} 1.8301; $MR_{D(calcd.)}$ 34.19.

Anal. Calcd. for $C_3HCl_3F_2$: C, 19.7; H, 0.55; Cl, 58.2; F, 20.8. Found: C, 20.2; H, 0.11; Cl, 57.1; F, 19.9.

Anal. Calcd. for $C_3HCl_2BrF_2$: C, 15.9; H, 0.44; Cl, 31.3; Br, 35.8; F, 16.8. Found: C, 16.2; H, 0.20; Cl, 31.8; Br, 35.4; F, 17.2.

MATERIALS CENTRAL
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(5) A. N. Nesmeyanov, R. Kh. Freĭdlina, L. I. Zakharkin, and A. B. Belyavskiĭ, *Zhur Obshcheĭ Khim.*, **26**, 1070 (1956); *Chem. Abstr.*, **50**, 16658f (1956).

Some Reactions of Vinyl and Allyl Acetate with Haloalkanes

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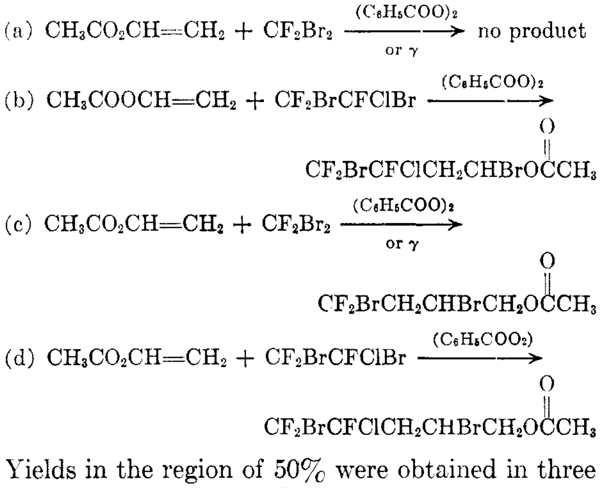
In attempting to prepare polymers containing oxygen, either in pendant groups or in the polymer chain itself, several methods involving free radical additions were briefly investigated. The first attempt was the reaction of perfluoroalkyl radicals with ethylene oxide and the other involved the addition of haloalkanes to vinyl and allyl esters followed by conversion to the unsaturated epoxides. Although both methods were fruitless, some new materials were prepared and characterized.

The ability of ethylene oxide to enter into free radical polymerization processes with fluoroolefins was demonstrated by Hauptschein and Lesser.[1] It was thought that the reaction of perfluoropropyl iodide and ethylene oxide under free radical conditions might proceed to produce perfluoropropyl-β-iodoethyl ether, and subsequent dehydroiodination would give the corresponding vinyl ether. An exploratory reaction carried out at 200° gave a 15% yield of a liquid subsequently identified as 1-iodo-1,1,2,2-tetrahydroperfluoropentane. A repeat of this experiment gave a yield of 27% of the same alkane. Dehydrohalognation of the isolated product produced the corresponding olefin ($CF_3CF_2CF_2CH{=}CH_2$). The fate of the oxygen in the original synthesis was not determined. Elucidation of the mechanism for the formation of the alkane was not undertaken.

The addition of haloalkanes to the vinyl and allyl esters should proceed analogously to the additions with bromotrichloromethane carried out by Kharasch[2] in which addition of the trichloromethyl group took place on the terminal methylene group. The additions were carried out and the products are listed below:



$$\text{(a)}\ CH_3CO_2CH{=}CH_2 + CF_2Br_2 \xrightarrow[\text{or } \gamma]{(C_6H_5COO)_2} \text{no product}$$

$$\text{(b)}\ CH_3COOCH{=}CH_2 + CF_2BrCFClBr \xrightarrow{(C_6H_5COO)_2} CF_2BrCFClCH_2CHBrO\overset{O}{\overset{\|}{C}}CH_3$$

$$\text{(c)}\ CH_3CO_2CH{=}CH_2 + CF_2Br_2 \xrightarrow[\text{or } \gamma]{(C_6H_5COO)_2} CF_2BrCH_2CHBrCH_2O\overset{O}{\overset{\|}{C}}CH_3$$

$$\text{(d)}\ CH_3CO_2CH{=}CH_2 + CF_2BrCFClBr \xrightarrow{(C_6H_5COO_2)} CF_2BrCFClCH_2CHBrCH_2O\overset{O}{\overset{\|}{C}}CH_3$$

Yields in the region of 50% were obtained in three of the above reactions. In the case of (a) no product was obtained in either a benzoyl peroxide initiated reaction at 80° in a rocking autoclave or in a sealed tube exposed to a cobalt^{60} source. In the case of (b) a fair yield of crude product was obtained, but on redistillation, the material tended to decompose and only a small portion of the purified material could be obtained. It is interesting to note that the decomposition, which occurred at 100°, resulted in the formation of volatile products which could be condensed in a Dry Ice–acetone trap. The material formed had a pronounced aldehydic odor and was extremely lachrymatory. Kharasch[2] similarly reported the relative ease with which the bromotrichloromethane vinyl acetate adduct was converted to β,β-dichloroacrolein by the action of aqueous acid.

The additions of both dibromodifluoromethane and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to allyl acetate gave good yields of the desired adducts. Elementary analysis and the infrared spectra were consistent with the proposed structure. In the benzoyl peroxide initiated reaction product, it was obvious that there was an aromatic contaminant present which could not be removed by distillation. In order not to resort to purification by chemical means, analytical samples were obtained by irradiation of the materials in sealed glass vials until a specified dosage was obtained. This method was originally reported by Postelnek *et al.*[3,4] for the additions of bromotrichloromethane to various olefins. The allyl acetate adducts were separated by fractional distillation through the Podbielniak minical column. The spectra thus obtained were identical with the others, but no aromatic residues arising from the peroxide initiator were present.

Finally, the adduct of 1,2-dibromo-2-chloro-1,1,-2-trifluoroethane and allyl acetate was reduced with zinc dust to give the reported pentadiene, 1,1,2-trifluoropentadiene-1,4,[5] indicating that 2,5-dibromo-4-chloro-4,5,5-trifluoropentylacetate rather than 2,5-dibromo-5-chloro-4,4,5-trifluoropentyl acetate.

EXPERIMENTAL

Reaction of perfluoropropyl iodide and ethylene oxide. In a steel autoclave cooled to 5° were placed 59.2 g. (0.2 mole) of perfluoropropyl iodide and 8.8 g. (0.2 mole) of ethylene oxide. The autoclave was sealed and rocked while being rapidly heated to 200°. The pressure rose to 250 p.s.i. but dropped to 110 p.s.i. after 4 hr. At this time the autoclave was allowed to cool and the contents, which were somewhat carbonaceous and contained solid iodine, were fractionally distilled. The fraction boiling at 64.0 to 64.2°/108 mm. had the following properties: n_D^{20} 1.3787, d_4^{20} 1.9210, $MR_{D(obsd.)}$ 38.2, $MR_{D(calcd.)}$ 38.19.

Anal. Calcd. for $C_5H_4F_7I$: C, 18.5; H, 1.23; F, 41.0; I, 38.8. Found: C, 18.6; H, 0.60; F, 41.5; I, 38.8.

Dehydrohalogenation of 1-iodo-1,1,2,2-tetrahydroperfluoropentane. The adduct, 34 g. (0.1 mole) was added slowly to a solution of 12 g. (0.2 mole) of potassium hydroxide in 200 ml. of 95% ethanol kept at 0°. A white precipitate was formed immediately. Stirring was maintained for an hour after the addition was complete and then the reaction mass was added to 400 ml. of ice and water and the organic layer was separated and dried over calcium chloride. Upon distillation a cut was obtained, b.p. 32°/750 mm.; lit.[6] b.p. 31°, with the physical properties n_D^{20} 1.2752, d_4^{20} 1.3391, $MR_{D(obsd.)}$ 25.2, $MR_{D(calcd.)}$ 24.8.

Anal. Calcd. for $C_5H_3F_7$: C, 30.6; H, 1.53; F, 67.9. Found: C, 31.1; H, 1.52; F, 67.1.

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(1) M. Hauptschein and J. Lesser, *J. Am. Chem. Soc.*, **78**, 676 (1956).

(2) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).

(3) W. Postelnek, D. A. Rausch, and A. M. Lovelace, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

(4) E. I. Heiba and L. C. Anderson, *J. Am. Chem. Soc.*, **79**, 4940 (1957).

(5) P. Tarrant and E. G. Gilman, *J. Am. Chem. Soc.*, **76**, 5423 (1954).

(6) O. R. Pierce, E. T. McBee, and C. F. Judd, *J. Am. Chem. Soc.*, **75**, 5618 (1953).

Dehalogenation of the product of the addition of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to allyl acetate. Zinc, 28.8 g. (0.44 g.-atom) and 150 cc. of dioxane were placed in a 500-cc. flask equipped with a stirrer, reflux condenser, and pressure-compensated addition funnel. A few drops of concd. hydrochloric acid were added, and the flask was stirred and heated to reflux. The addition product, 78 g. (0.2 mole) was placed in the addition funnel and slowly added. The condenser was allowed to warm to 40° and any material that passed through was collected in a cooled trap. About 10 ml. of product was obtained which on redistillation had a boiling point 37–38°, n_D^{20} 1.3424; reported[5] b.p. 38°, n_D^{27} 1.3435.

The peroxide initiated addition of dibromodifluoromethane to allyl acetate. The halomethane, 1110 g. (5.2 moles), allyl acetate, 130 g. (1.3 moles) and benzoyl peroxide, 8 g. (0.03 mole) were placed in a cooled 1.4-l. steel autoclave and sealed. After heating and rocking at 90° for 12 hr., the autoclave was cooled and the contents were distilled. Excess dibromodifluoromethane, 800 g., boiling at 22.5–24.5° was recovered, and then a product boiling at 95–109°/5 mm. This material was redistilled at 71–73°/2 mm. A yield of 163 g. (41%) was obtained. No reaction occurred under similar conditions with vinyl acetate.

The gamma radiation-induced reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and dibromodifluoromethane with allyl acetate. In a 60-ml. glass tube (22 mm. in diameter) were sealed 77 g. (0.28 mole) of the haloethane and 7.0 g. (0.07 mole) of allyl acetate. The tube was wrapped with friction tape and the sample was then exposed to a cobalt[60] source with a flux rate of 4.5 × 10[5] roentgens per hr. After exposure for an hour the tube was cooled and opened. Upon distillation 12 g. of pure product, b.p. 85–86°/3.5 mm., n_D^{25} 1.4654, d_4^{25} 1.8196, $MR_{D(obsd.)}$ 56.55, $MR_{D(calcd.)}$ 57.3, was obtained.

Anal. Calcd. for $C_7H_8BrClF_3O_2$: C, 22.3; H, 2.10; F, 15.1. Found: C, 21.4; H, 2.0; F, 15.3.

In the same manner, 100 g. (0.48 mole) of dibromodifluoromethane and 6 g. (0.06 mole) of allyl acetate were treated to give 8 g. of pure product boiling at 72°/2.4 mm. n_D^{20} 1 4631, d_4^{20} 1.8153, $MR_{D(obsd.)}$ 47.13, $MR_{D(calcd.)}$ 46.6.

Anal. Calcd. for $C_6H_8Br_2F_2O_2$: C, 23.2; H, 2.58; Br, 51.6; F, 12.52. Found: C, 23.7; H, 2.49; Br, 52.3; F, 12.0.

The gamma radiation-induced reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and dibromodifluoromethane to vinyl acetate. These reactions were carried out in an identical manner with those in the previous section. The dibromodifluoromethane addition gave no higher boiling materials while the other addition product decomposed during distillation.

The peroxide initiated addition of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to vinyl acetate and allyl acetate. In a 500-cc. three-neck flask equipped with stirrer, reflux condenser, and pressure-compensated addition funnel were placed 10 g. (0.04 mole) of benzoyl peroxide and 400 g. (1.45 moles) of the perhalo compound, which had been prepared by the addition of bromine to chlorotrifluoroethylene, according to the method of Park, Lycan, and Lacher.[7] The flask was heated to 90° and 31 g. (0.36 mole) of redistilled vinyl acetate added at such a rate as to maintain mild reflux. The flask was heated an additional 4 hr. at 90° and then distilled at 150 mm. to recover the excess 1,2-dibromo-2-chloro-1,1,2-trifluoroethane, 200 g. boiling at 43.47° being obtained. The pressure was lowered to 2 mm. and 198 g. of material boiling from 72–85° (largely 78°) was distilled. Upon redistillation through a more efficient column the product obtained distilled at 73°/2 mm. and had the following physical properties: n_D^{25} 1.4531, d_D^{25} 1.9905, $MR_{D(calcd.)}$ 51.4.

Anal. Calcd. for $C_6H_6Br_2ClF_3O_2$: C, 19.9; H, 1.66; Br, 43.8; F, 15.8. Found: C, 20.4; H, 1.58; Br, 44.5; F, 15.6.

A similar reaction using allyl acetate was also performed. Allyl acetate, 45 g. (0.45 mole) was slowly added to 500 g. (1.81 moles) of the haloethane and 10 g. (0.04 mole) of benzoyl peroxide. The product boiling at 84–88°/1.4 mm. was obtained, 128 g. (76%), n_D^{20} 1.4670. A solid had sublimed over the product. Upon drying this material melted at 110–112°.

MATERIALS CENTRAL
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(7) J. D. Park, W. R. Lycan, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 711 (1951).

Synthesis of 2,4-Dimethyl-3-hydroxy-6-oxoheptanal

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In connection with another problem 2,4-dimethyl-3-hydroxy-6-oxoheptanal was synthesized. The synthetic route used is outlined in the accompanying flow sheet. The reduction of *m*-xyloquinone was never very satisfactory. The crude product was a complex mixture, and purification resulted in low yields of I. It was assumed that use of a limited amount of chromic oxide would result in oxidation of I at the less hindered hydroxyl to give II rather than the isomeric hydroxyketone although this point was never unequivocally shown.