[Contribution from the Department of Chemistry, University of Florida]

Free Radical Additions Involving Fluorine Compounds. VI. The Addition of Perhaloalkanes to Some Allyl Ethers

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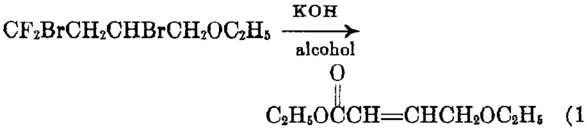
Perhaloalkanes such as bromotrichloromethane, dibromodifluoromethane and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane add to allyl ethers to give 1:1 adducts and telomers. The dehydrohalogenation of these products gave unexpected unsaturated ethers.

Perhaloalkanes such as bromotrichloromethane, dibromodifluoromethane, and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane have been shown to react with a variety of olefinic compounds.[1] However, unsaturated ethers have not been used widely in these radical induced reactions. This paper is the report of some additions made to allyl ethyl ether and to allyl α,α,β-trifluoro-β-chloroethyl ether and of some transformations carried out on the adducts.

The additions, even with the reactive bromochloromethane, gave relatively large amounts of compounds of higher molecular weight than the 1:1 addition products. These materials were not identified but were assumed to be the usual 2:1, 3:1, etc. telomers often encountered in addition reactions of this type.[2,3]

Interestingly enough, the formation of the 1:1 addition product proceeded to the same extent irrespective of the alkane used. Yields with the reactive bromotrichloromethane were essentially the same as with the relatively unreactive dibromodifluoromethane. However, the simple 1:1 addition of the alkanes to allyl trifluorochloroethyl ether gave yields of products about double the yields obtained with allyl ethyl ether. It is generally observed that telomerization occurs to a greater extent if the radical formed by the addition of the perhaloalkyl radical to an olefin is stabilized by the presence of other groups or atoms. For example, the reaction between dibromodifluoromethane and vinylidene fluoride gives appreciable quantities of 2:1 adduct whereas very little similar product is obtained from dibromodifluoromethane and ethylene.[3] Therefore it seems likely that radicals of the type $CX_3CH_2CHCH_2OCF_2CFClH$ are more reactive toward perhaloalkanes than $CX_3CH_2\underset{\cdot}{C}HCH_2OCH_2CH_3$. The reason for this behavior is not clear.

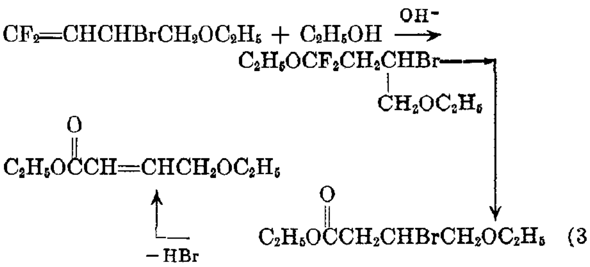
Some unusual results were encountered in the dehydrohalogenation of the addition products as shown in the following reactions.



$$CF_2BrCH_2CHBrCH_2OC_2H_5 \xrightarrow[\text{alcohol}]{\text{KOH}} C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}CH{=}CHCH_2OC_2H_5 \quad (1)$$

$$CF_2BrCH_2CHBrCH_2OC_2H_5 \xrightarrow[\text{KOH}]{\text{solid}} CF_2{=}CHCHBrCH_2OC_2H_5 \quad (2)$$

The products of the first reaction was identified as ethyl γ-ethoxycrotonate by comparison of its physical properties with those reported. Its formation can be accounted for *via* reaction 2 and further reaction with alcohol and base as shown.



$$CF_2{=}CHCHBrCH_2OC_2H_5 + C_2H_5OH \xrightarrow{OH^-} C_2H_5OCF_2CH_2\underset{\displaystyle CH_2OC_2H_5}{\underset{|}{C}HBr} \longrightarrow C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}CH_2CHBrCH_2OC_2H_5 \quad (3)$$

$$C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}CH_2CHBrCH_2OC_2H_5 \xrightarrow{-HBr} C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}CH{=}CHCH_2OC_2H_5$$

Ethers containing the $ROCF_2CH_2$—grouping are known to hydrolyze readily to esters.[4]

Reaction 2, above, is also unusual as elimination reactions of this type usually involve the loss of the bromine beta to the —CF_2Br group. The reaction of 1,4-dibromo 1,1-difluoroethane gives 3-bromo-3,3-difluoropropene and not 3-bromo-1,1-difluoropropene. There is no doubt that 3-bromo-4-ethoxy-1,1-difluoro-1-butene was formed in the reaction since the infrared absorption in the double bond region occurred at 5.72 μ which is characteristic of the $CF_2{=}CH$ group. No diene was produced in the reaction.

The reaction of the allyl trifluorochloroethyl adduct of dibromodifluoromethane, on the other hand, gave both olefin and diene. The olefin had a

$$CF_2BrCH_2CHBrCH_2OCF_2CHFCl \longrightarrow \xrightarrow[\text{solid}]{\text{KOH}} CF_2{=}CHCHBrCH_2OCF_2CHFCl \quad (4)$$

$$\downarrow$$

$$CF_2{=}CHCH{=}CHOCF_2CHFCl$$

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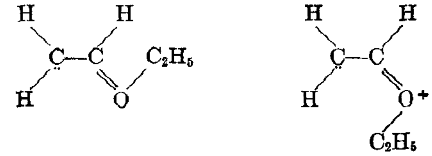
(1) Cheves Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., 1957.

(2) Paul Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3640 (1955).

(3) Paul Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 2783 (1955).

(4) J. A. Young and Paul Tarrant, *J. Am. Chem. Soc.*, **72**, 1860 (1950).

single absorption peak at 5.73 μ while the diene had peaks at 5.75 μ and 6.01 μ. Alkyl β-haloethyl ethers are not particularly easy to dehydrohalogenate. This situation can be attributed to the lessened acid character of the alpha hydrogen atoms resulting from the adjacent oxygen. However, the presence of an electron withdrawing group such as the —CF_2CHFCl on the oxygen would reduce its tendency to donate electrons to the α-carbon and hence make the α-hydrogen more susceptible to attack. It has been shown that vinyl alkyl ethers possess a doublet[5] in the carbon-carbon double bond stretching region whereas vinyl trifluorochloroethyl ether does not. An explanation has been offered that the doublet is due to the presence of the two forms of the vinyl alkyl ether as shown. This



type of isomerism is not encountered with the fluoroalkyl vinyl ethers because the fluoroalkyl group prevents the release of electrons needed to give these two structures.

EXPERIMENTAL[6]

Addition of bromotrichloromethane to allyl ethyl ether. A solution of 20 g. of benzoyl peroxide in 1000 g. (5.0 moles) of bromotrichloromethane was placed in a 2-l. three necked flask fitted with stirrer, condenser, and dropping funnel. The flask contents were heated to 90°, and a solution of 20 g. benzoyl peroxide, 168 g. (1.95 moles) of allyl ethyl ether, and 600 g. (3.0 moles) of bromotrichloromethane was added dropwise over a 3-hr. period. The flask contents were stirred for an additional 2 hr. at 90° and stripped of unchanged starting material. The remainder was washed with sodium bicarbonate solution, and the crude product separated and dried. Fractional distillation gave 173 g. (29% conversion) of 3-bromo-1,1,1-trichloro-4-ethoxybutane ($CCl_3CH_2CHBrCH_2OC_2H_5$). An analytical fraction had the following properties: b.p. 69°/0.5 mm., n_D^{23} 1.4940, d^{23} 1.535.

Anal. Calcd. for $C_6H_{10}BrCl_3O$: MR_D, 53.92; C, 25.34; H, 3.54. Found: MR_D, 54.10; C, 25.10; H, 3.58.

Addition of dibromodifluoromethane to allyl ethyl ether. A 1.5 l. autoclave fitted with a valve, pressure gauge, and rupture disk assembly was charged with 840 g. (4.0 moles) of dibromodifluoromethane, 66.5 g. (0.77 mole) of allyl ethyl ether, and 10 g. of benzoyl peroxide. It was then heated with rocking for 5 hr. at 90°. The unchanged starting materials were stripped, and the remainder washed with sodium bicarbonate solution. The crude product was separated and dried. Fractional distillation gave 64 g. (31% conversion) of 1,3-dibromo-4-ethoxy-1,1-difluorobutane ($CF_2BrCH_2CHBrCH_2OC_2H_5$). An analytical fraction had the following properties: b.p. 55°/2 mm., n_D^{23} 1.4510, d^{23} 1.670.

Anal. Calcd. for $C_6H_{10}Br_2F_2O$: MR_D, 47.08; C, 24.34; H, 3.41. Found: MR_D, 47.71; C, 23.98; H, 3.51.

Addition of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane to allyl ethyl ether. A solution of 10 g. of benzoyl peroxide, 650 g. (2.35 moles) of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane, and 48 g. (0.56 mole) of allyl ethyl ether was sealed in an autoclave and treated at 95° for 5 hr. Fractional distillation gave 53 g. (26% conversion) of 1,4-dibromo-2-chloro-5-ethoxy-1,1,2-trifluoropentane ($CF_2BrCFClCH_2CHBrCH_2OC_2H_5$). An analytical fraction had the following properties: b.p. 75°/1.5 mm., n_D^{23} 1.4534, d^{23} 1.743.

Anal. Calcd. for $C_7H_{10}Br_2ClF_3O$: MR_D, 56.56; C, 23.20; H, 2.78. Found: MR_D, 56.25; C, 23.97; H, 3.23.

Addition of bromotrichloromethane to allyl β-chloro-α,α-trifluoroethyl ether (I). A solution of 15 g. of benzoyl peroxide, 595 g. (3.0 moles) of bromotrichloromethane, and 175 g. (1.0 moles) of allyl β-chloro-α,α,β-trifluoroethyl ether were treated in an autoclave at 95° for 6 hr. The material was worked up as before and fractionally distilled to give 186 g. (50% conversion) of $CCl_3CH_2CHBrCH_2OCF_2CFClH$. An analytical fraction had the following properties: b.p. 99°/2 mm., n_D^{23} 1.4645, d^{23} 1.759.

Anal. Calcd. for $C_6H_6BrCl_4F_3O$: MR_D, 58.78; C, 19.38; H, 1.63. Found: MR_D 58.57; C, 20.32; H, 1.80.

Addition of dibromodifluoromethane to I. An autoclave was charged with 845 g. (4.0 moles) of dibromodifluoromethane, 175 g. (1.0 mole) of $CH_2{=}CHCH_2OCF_2CFClH$, and 8 g. of benzoyl peroxide. It was heated and rocked at 95° for 3 hr. The autoclave contents were treated as before and fractionally distilled to give 175 g. (46% conversion) of CF_2, $BrCH_2CHBrCH_2OCF_2CFClH$. An analytical sample had the following properties: b.p. 65°/2 mm., n_D^{23} 1.4301, d^{23} 1.911.

Anal. Calcd. for $C_6H_6Br_2ClF_5O$: MR_D, 51.95; C, 19.10; H, 1.72. Found: MR_D, 51.91; C, 18.75; H, 1.58.

Addition of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane to I. A solution of 4 g. of benzoyl peroxide in 260 g. (1.5 moles) of $CH_2{=}CHCH_2OCF_2CFClH$ and 553 g. (2.0 moles) of $CF_2BrCFClBr$ was added with stirring to a flask containing 4 g. of benzoyl peroxide in 1100 g. (4.2 moles) of $CF_2BrCFClBr$ at 90°. Addition was completed in 2 hr. and stirring at 90° was contained for 1 hr. The material was handled as previously described and fractionated to give 314 g. (47% conversion) of $CF_2BrCFClCH_2CHBrCH_2OCF_2CFClH$. An analytical sample had the following properties: b.p. 78.5°/0.6 mm., n_D^{22} 1.4350, d^{23} 1.902.

Anal. Calcd. for $C_7H_6Br_2Cl_2F_6O$: MR_D, 61.43; C, 18.64; H, 1.34. Found: MR_D, 61.72; C, 19.25; H, 1.51.

Dehydrohalogenation of 1,3-dibromo-4-ethoxy-1,1-difluorobutane ($CF_3BrCH_2CHBrCH_2OC_2H_5$). a. *With alcoholic potassium hydroxide.* Forty-four grams (0.149 mole) of the above ether was added over a 30-min. period to a stirred, refluxing solution of 30 g. (0.53 mole) of potassium hydroxide in 200 ml. of 95% ethanol. The solution was stirred at reflux for an additional 2 hr., and the ethanol stripped. Fractionation of the remaining solution gave 10 g. (42% conversion) of ethyl γ-ethoxy crotonate. An analytical sample had the following properties: b.p. 59°/0.9 mm. and 90°/12 mm., n_D^{23} 1.4332, d^{23} 0.987; reported[7] for ethyl γ-ethoxy crotonate: b.p. 86–87°/12 mm., n_D^{13} 1.4375, d^{13} 1.006.

Additional evidence leading to the assignment of the above structure was obtained from an infrared spectrum which showed strong absorption at 5.78 μ, characteristic of α,β-unsaturated esters.[8]

b. *With solid potassium hydroxide.* A slurry of 22 g. (0.35 mole) potassium hydroxide in 100 ml. of mineral oil was heated to 60° and 35 g. (0.12 mole) of $CF_2BrCH_2CHBrCH_2OC_2H_5$ added with rapid stirring over 30 min. at 20 mm. pressure. Pressure was then reduced to 0.5 mm. and the temperature raised to 100°. Crude product (21.5 g.) was collected in a Dry Ice–acetone cold trap, dried, and fractionated to give 7 g. (27% conversion) of $CF_2{=}CHCHBrCH_2OC_2H_5$, b.p. 56°/24 mm., n_D^{23} 1.482, d^{23} 1.393.

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[5] M. L. Brey and Paul Tarrant, *J. Am. Chem. Soc.*, **79,** 6533 (1957).

[6] Analyses by Galbraith Laboratories, Knoxville, Tenn.

[7] R. Rambaud, *Compt. rend.*, **228,** 1595 (1949).

[8] L. J. Bellamy, *The Infrared Structure of Complex Molecules*, John Wiley & Sons, Inc., New York, 1958.

Anal. Calcd. for $\mathrm{C_6H_9BrF_2O}$: $\mathrm{MR_D}$, 38.85; C, 33.51; H, 4.22. Found: $\mathrm{MR_D}$, 39.70; C, 34.68; H, 4.51.

An infrared spectrum showed a single strong, sharp absorption peak at 5.72 μ. It has been observed[9] that compounds having the $\mathrm{CF_2{=}CH}$— structure absorb around 5.7 μ.

Dehydrohalogenation of 1,4-dibromo-2-chloro-5-ethoxy-1,1,2-trifluoropentane ($\mathrm{CF_2BrCFClCH_2CHBrCH_2OC_2H_5}$). A slurry of 15.5 g. (0.25 mole) of potassium hydroxide in 150 ml. of mineral oil was heated to 100° and 46 g. (0.13 mole) of the above ether was added with vigorous stirring over a 1-hr. period. The mixture was stirred at 100° for an additional 1.5 hr., and the product stripped under vacuum into a trap cooled to −75°. The crude product (27 g.) was dried over Drierite and fractionated to give 9.5 g. (27% conversion) of $\mathrm{CF_2BrCFClCH{=}CHCH_2OC_2H_5}$. An analytical sample had the following properties: b.p. 54°/1.2 mm., n_{D}^{23} 1.4358, d^{23} 1.518.

Anal. Calcd. for $\mathrm{C_7H_9BrClF_3O}$: mol. wt., 281.7; $\mathrm{MR_D}$, 48.33; C, 29.87; H, 3.22. Found: mol. wt., 304; $\mathrm{MR_D}$, 48.46; C, 29.80; H, 3.15.

An infrared spectrogram showed a single absorption peak in the carbon-carbon double bond region at 5.97 μ.

Dehydrohalogenation of 1,3-dibromo-4-(2-chloro-1,1,2-trifluoroethoxy)-1,1-difluorobutane ($\mathrm{CF_2BrCH_2CHBrCH_2OCF_2CFClH}$). A slurry of 47 g. (0.75 mole) of potassium hydroxide in 300 ml. of mineral oil was treated at 100° as previously described with 99 g. (0.26 mole) of the above ether. The crude product (65 g.) was collected in a cold trap, dried over anhydrous calcium chloride, and separated into two fractions by distillation.

The first fraction consisted of 2.5 g. (5% conversion) of $\mathrm{CF_2{=}CHCH{=}CHOCF_2CFClH}$. This cut had the following properties: b.p. 62°/70 mm., n_{D}^{23} 1.3820, d^{23} 1.390.

Anal. Calcd. for $\mathrm{C_6H_4ClF_5O}$: mol. wt., 222.6; $\mathrm{MR_D}$, 35.48; C, 32.26; H, 1.94. Found: mol. wt., 234; $\mathrm{MR_D}$, 37.25; C, 32.38; H, 1.81.

The high molar refractivity observed may be due to optical exaltation. An infrared spectrum of this compound revealed two strong, sharp peaks in the carbon-carbon double bond region. One peak, at 5.75 μ, can be attributed to the $\mathrm{CF_2{=}CH}$— group while the higher wave length absorption at 6.01 μ is due to the —$\mathrm{CH{=}CH}$— group.

The second fraction, weighing 19 g. (25% conversion), was identified as $\mathrm{CF_2{=}CHCHBrCH_2OCF_2CFClH}$. This cut had the following properties: b.p. 112°/70 mm., n_{D}^{23} 1.4083, d^{23} 1.687.

Anal. Calcd. for $\mathrm{C_6H_5ClBrF_5O}$: mol. wt., 303.5; $\mathrm{MR_D}$, 43.72; C, 23.71; H, 1.66. Found: mol. wt., 295; $\mathrm{MR_D}$, 44.43; C, 23.77; H, 1.92.

An infrared spectrum showed a single peak in the carbon-carbon double bond region at 5.73 μ, indicating the $\mathrm{CF_2{=}CH}$— group.

Dehydrohalogenation of 1,4-dibromo-2-chloro-5-(2-chlorotrifluoroethoxy)-1,1,2-trifluoropentane ($\mathrm{CF_2BrCFClH_2CHBrCH_2OCF_2CFClH}$). A solution of 8.4 g. (0.15 mole) of potassium hydroxide in 100 ml. of 95% ethanol was added over a 20-min. period to 60 g. (0.14 mole) of the above ether in 50 ml. of ethanol. After addition was completed the solution was stirred for 2 hr. at 60°, decanted from the solid salt, washed, separated, and dried. Fractionation provided 29 g. (56% conversion) of $\mathrm{CF_2BrCFClCH{=}CHCH_2OCF_2CFClH}$. An analytical sample had the following properties: b.p. 57°/0.7 mm., n_{D}^{23} 1.4152, d^{23} 1.738.

Anal. Calcd. for $\mathrm{C_7H_5BrCl_2F_6O}$: $\mathrm{MR_D}$, 53.20; C, 22.69; 1.36. Found: $\mathrm{MR_D}$, 53.30; C, 23.09; H, 1.82.

An infrared spectrum showed a single absorption peak in the carbon-carbon double bond region at 5.92 μ.

Dehydrohalogenation of 5-bromo-4-chloro-1-(2-chloro-1,1,2-trifluoroethoxy-4,5,5-trifluoro-2-pentene ($\mathrm{CF_2BrCFClCH{=}CHCH_2OCF_2CFClH}$). A solution of 1.7 g. (0.03 mole) of potassium hydroxide in 25 ml. of ethanol was treated with 10.4 g. (0.028 mole) of the ether as described above. The mixture was worked up as before and fractionated to give 2.2 g. (24% conversion) of $\mathrm{CF_2BrCF{=}CHCH{=}CHOCF_2CFClH}$. This sample had the following properties: b.p. 41°/0.7 mm., n_{D}^{23} 1.4255, d^{25} 1.669.

Anal. Calcd. for $\mathrm{C_7H_4BrClF_6O}$: mol. wt., 333.5; $\mathrm{MR_D}$, 47.87; C, 25.21; H, 1.21; silver equivalent, 166.8. Found: mol. wt., 344; $\mathrm{MR_D}$, 51.05; C, 25.16; H, 1.48; silver equivalent, 167.0.

An infrared spectrum exhibited two peaks in the carbon-carbon double bond region at 5.91 μ and 6.06 μ and a carbon-hydrogen stretching absorption at 3.23 μ.

Dehalogenation of 1,4-dibromo-2-chloro-5-ethoxy-1,1,2-trifluoropentane ($\mathrm{CF_2BrCFClCH_2CHBrCH_2OC_2H_5}$). Fourteen grams (0.2 mole) of powdered zinc, 0.5 g. of zinc chloride, and 75 ml. of ethanol were heated to reflux and 36 g. (0.1 mole) of the above ether added dropwise to the stirred mixture. The mixture was stirred for 3 hr. and decanted. The solution was washed with water and the crude product dried and fractionated to give a single compound whose infrared spectrum was identical to a spectrum of an authentic sample. of $\mathrm{CF_2{=}CFCH_2CH{=}CH_2}$.[10]

Dehalogenation of 1,4-dibromo-2-chloro-5-(2-chloro-1,1,2-trifluoroethoxy)-1,1,2-trifluoropentane ($\mathrm{CF_2BrCFClCH_2CHBrCH_2OCF_2CFClH}$). A mixture of 23 g. (0.35 mole) of powdered zinc, 1.0 g. of zinc chloride, and 150 ml. of isopropyl alcohol was heated to reflux and 80 g. (0.177 mole) of the above ether added dropwise with stirring. After addition the mixture was stirred for 3 hr. and worked up as described above. On fractionation a sample, b.p. 47–49°/19 mm., was obtained whose infrared spectrum was identical to that of an authentic sample of $\mathrm{CFClHCOOCH(CH_3)_2}$.

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[9] P. Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3642 (1955).

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