this suspension there was added 20 ml. of condensed butadiene and several crystals of hydroquinone to inhibit polymerization. The sealed tube was kept at 115° for 40 hr. After several crystallizations from ether 10.0 g. of white crystals, m.p. 126–127.5°, was obtained (85% yield). $\lambda_{\max}^{\mathrm{CHCl_3}} = 5.88\ \mu$ (unconjugated ketone), 6.04 μ (conjugated ketone), 6.24 μ (enol ether).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.30. Found: C, 68.36; H, 6.12.

2-Methoxy-4-oxo-1,4,4a,5,8,8a-hexahydro-1-naphthol (IIIa). Sodium borohydride (0.20 g.) was dissolved in 70 ml. of ethanol and a solution of 0.96 g. of II in 10 ml. of ethanol was added dropwise. The flask was allowed to stand for 3 hr., then water was added. The solution was saturated with sodium chloride and extracted with ether. Upon recrystallization from cyclohexane 0.20 g. (44% yield) of white, fibrous crystals, m.p. 134–135°, was obtained. $\lambda_{\max}^{\mathrm{CHCl_3}} = 6.05\ \mu, 6.20\ \mu$.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.03; H, 7.27. Found: C, 68.06; H, 7.18.

The *p-toluenesulfonate* (IIIb) crystallized from methanol as white crystals, m.p. 93°.

Anal. Calcd. for $C_{18}H_{19}O_5S$: C, 62.23; H, 5.51. Found: C, 62.35; H, 5.60.

2-Methoxy-4a,5,8,8a-tetrahydronaphthoquinone-1-oxime (V). To a solution of 0.35 g. (0.005 mole) of hydroxylamine hydrochloride in 5 ml. of pyridine and 5 ml. of absolute ethanol there was added 0.96 g. (0.005 mole) of II. The solution was refluxed for 1 hr. After it had cooled the solvents were blown off by a stream of air. The residue was triturated with 5 ml. of cold water and filtered. The oxime was recrystallized from methanol to give white crystals which begin to decompose at 200°. The yield amounted to 0.65 g. (68%). $\lambda_{\max}^{\mathrm{CHCl_3}} = 6.08\ \mu, 6.28\ \mu$.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 64.03; H, 6.28; N, 6.89.

Acknowledgment. The author wishes to express his gratitude to Professor Gilbert Stork for his interest in this work.

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Synthesis of Some Haloolefins. Addition of Dibromodifluoromethane and Bromotrichloromethane to Vinylidene Fluoride

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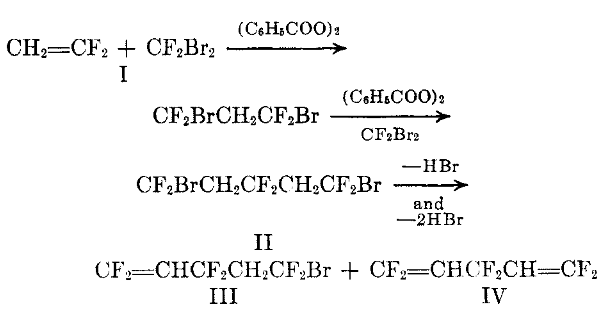
Received February 22, 1960

The addition reactions of dibromodifluoromethane to vinylidene fluoride, initiated by benzoyl peroxide, proceeded as described in the literature[1,2] and comparable yields were obtained. In addition to the simple one-to-one adduct (I) an approximately equivalent amount of the two-to-one adduct (II) was isolated. It is of interest to note that this



$$CH_2{=}CF_2 + CF_2Br_2 \xrightarrow{(C_6H_5COO)_2}$$
$$\underset{\mathrm{I}}{CF_2BrCH_2CF_2Br} \xrightarrow[CF_2Br_2]{(C_6H_5COO)_2}$$
$$\underset{\mathrm{II}}{CF_2BrCH_2CF_2CH_2CF_2Br} \xrightarrow[\text{and } -2HBr]{-HBr}$$
$$\underset{\mathrm{III}}{CF_2{=}CHCF_2CH_2CF_2Br} + \underset{\mathrm{IV}}{CF_2{=}CHCF_2CH{=}CF_2}$$

reaction occurred as it did, in spite of the fact that over 400% molar excess of the halomethane was used. The 1,5-dibromo-1,1,3,3,5,5-hexafluoropentane (II) was dehydrohalogenated to the unconjugated pentadiene (IV) 1,1,3,3,5,5-hexafluoropentadiene-1,4 and some pentene (III), the 5-bromo-1,1,3,3,5,5-hexafluoropentene-1. These results substantiate the work of Hauptschein, *et al.*,[3] on telomers of fluorinated olefins.

As a corollary of this work the polymerizability of the diene was studied.[4] While the diene did not homopolymerize, it formed copolymers with butadiene, styrene, and vinyl acetate. The diene is substituted with fluorine on the carbon atom *alpha* to the sites of unsaturation ($CF_2{=}CHCF_2CH{=}CF_2$) and thus not possessed of allylic hydrogen atoms. Therefore, it should not show the retarding influence of free-radical polymerization commonly associated with allylic compounds. This advantage was probably more than offset by the fact that free-radical attack would be predicted to occur at carbon atom 2 and would doubtlessly be sterically inhibited.

Another reaction investigated was that of the peroxide-initiated addition of bromotrichloromethane to vinylidene fluoride. Although this reaction has not been reported previously, it would be expected to occur quite readily. The complication of the formation of appreciable amounts of the two-to-one adduct should be lessened because of the high chain transfer tendency of bromotrichloromethane. This proved to be the case; yields of the adduct (V), 1,1,1-trichloro-3-bromo-3,3-difluoropropane, in the neighborhood of 60% were obtained consistently.

In attempting to dehydrohalogenate the halopropane, with aqueous and ethanolic base, no products could be isolated. In one reaction with aqueous sodium hydroxide, the reaction mixture sparked, possibly due to the formation of an unstable halogen substituted acetylene derivative. Triethylamine proved to be a useful reagent for effecting the dehydrohalogenation, although even here the high reactivity of the initial reaction prod-

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(1) P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Am. Chem. Soc.*, **76**, 944 (1954).

(2) P. Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **76**, 944 (1954).

(3) M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Am. Chem. Soc.*, **80**, 846 (1958).

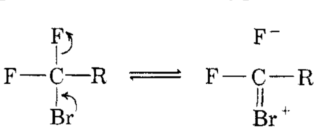
(4) F. B. Jones, C. A. Lichtenwalter, P. B. Stickney, and R. G. Heiligmann, *Polymerization Studies on Monomers and Evaluation of Derivative Polymers*, Wright Air Development Center, Dayton, Ohio; Technical Report 57-110, Pt I (1957).

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

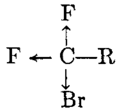
$$CH_2{=}CF_2 + CCl_3Br \xrightarrow{(C_6H_5COO)_2}$$

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

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_2-CHBrR. This demonstrates the shielding effect afforded by adjacent fluorine atoms which arise, either through resonance of the type:



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



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, $MR_{D(\text{calcd.})}$ 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, $MR_{D(\text{calcd.})}$ 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, $MR_{D(\text{calcd.})}$ 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; $MR_{D(\text{calcd.})}$ 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; $MR_{D(\text{calcd.})}$ 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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Received February 22, 1960

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.