Hydride-reduction of II. A suspension of 0.6 g. sodium borohydride in 5 ml. methanol was added to 0.19 g. II suspended in 5 ml. methanol. After 20 hr. at room temperature, 10 ml. 10% aqueous sodium hydroxide was added to the slightly opalescent solution, and the mixture was heated over a free flame for 5 min. The milky liquid was cooled, diluted with water, and extracted six times with chloroform. The combined extracts were washed three times with small amounts of water, dried (sodium sulfate), and evaporated (*in vacuo*). The white residue was brought into solution by refluxing with six successive portions of hexane, which deposited noncrystalline solids on cooling. Additional material was obtained by evaporation of the filtrates. Infrared spectroscopy showed the presence of two different nonketonic products having very similar but definitely nonidentical spectra. One of these was present in the first three hexane filtrates, while all other fractions consisted of the other compound. All fractions were noncrystalline and melted over a wide temperature range (approx. 155–175°). Numerous attempts to convert the bases or a variety of their salts to well characterized, crystalline products were unsuccessful.

Treatment of II with manganese dioxide. Thirty milligrams of II, dissolved in 10 ml. chloroform, was stirred at room temperature with 100 mg. active manganese dioxide[18] for 20 min. The mixture was filtered with suction, and the dioxide was washed several times with chloroform. Evaporation of the combined filtrates left a residue which crystallized on treatment with a few drops of ethanol. The crystalline product did not depress the melting point of an authentic sample of II, and had the same infrared spectrum. Complete evaporation of the mother liquors gave an additional amount of this material.

Parallel treatment of 0.5 g. of III in 50 ml. chloroform with 1.5 g. of the same batch of manganese dioxide gave, after purification *via* the crystalline perchlorate, 0.35 g. (70%) of pure I, m.p. and mixed m.p. 272–273°.

BETHESDA 14, MD.

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[18] T. Attenburrow *et al.*, *J. Chem. Soc.*, 1094 (1952).

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

Synthesis of Several Fluorinated Cyclobutanes and Cyclobutenes

J. D. PARK, H. V. HOLLER,[1] AND J. R. LACHER

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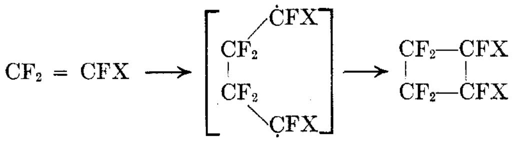
The synthesis of several fluorinated cyclobutanes by cyclization of $CF_2{=}CX_2$ olefins with themselves, and other olefins is reported. It appears that this cycloaddition takes place quite readily and easily only when X is halogen. The direction of addition of the unsymmetrical haloolefins can be rationalized and predicted by the assumption that in the product-determining transition state, the diradical of the lowest energy is preferentially formed with free (or nearly so) rotation about each single bond in the end positions (Equation 1). The physical properties of the fluorinated cyclobutanes and fluorinated cyclobutanes are described.

Many examples of the cyclization of $CF_2 = CX_2$-type olefins with themselves, alkenes and alkynes to form cyclobutanes and cyclobutenes are found in the literature. This cycloaddition appears to occur easily only when X is halogen.

Attempts to homocyclize trifluoroethylene, 2-bromo-1,1-difluoroethylene, and 2-chloro-1,1-difluoroethylene were unsuccessful. Propargyl chloride and tetrafluoroethylene also failed to cocyclize. Other studies have been carried out in this laboratory, but thus far all attempts to homocyclize fluoro-olefins of the type $CF_2 = CHX$ (where X is H, F, Cl, or Br) have been unsuccessful.

Recent work carried out in this laboratory has shown that chlorotrifluoroethylene dimerizes to give a product which is 50–50 (or nearly so) *cis-trans* 1,2-dichlorohexafluorocyclobutane. No differences in the distribution of the *cis-trans* isomers were observed when the dimerization reactions were carried out at temperatures ranging from 130 to 225°. This may be explained on the following basis. If the activated complex which forms when chlorotrifluoroethylene dimerizes has a rigid structure similar to the product molecules, then one would expect to get two parts of *cis* and one part of *trans*. The fact that the product is 50% of each suggests that the activated complex is a diradical with free (or nearly so) rotation, about each carbon single bond in the end position.

The direction of addition of unsymmetrical haloethylenes to themselves and to other unsymmetrical olefins can be rationalized and predicted by the assumption that in the product-determining transition state, the diradical of the lowest energy is preferentially formed. For example, in homocyclization:



(1)

cis and *trans* isomers

X = Cl, Br or I

The relative abilities of the halogens to stabilize free radicals appears to be: I>Br>Cl>F. The latter was determined by Haszeldine from the magnitudes of the bathochromic shifts in the ultraviolet spectra of halogenated alkyl iodides.[2]

The direction of cross-cyclization of haloethylenes with different alkenes or alkynes can likewise

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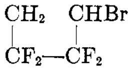
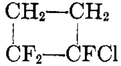
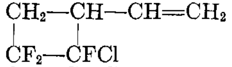
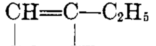
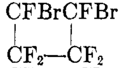
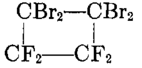
[1] From the Ph.D. dissertation submitted to the University of Colorado, August, 1957.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

TABLE I

THERMAL CYCLOADDITION REACTIONS

Reactants	G.	Time, Hr.	Temp.	Inhibitor	Product	G.	% Conversion
$CH_2{=}CHBr$ $CF_2{=}CF_2$	215 160	8	200	Terpene B[a]		40	12
$CH_2{=}CH_2$ $CF_2{=}CFCl$	126 685	9	200	Terpene B and hydroquinone		127	19.5
$(CH_2{=}CH)_2$ $CF_2{=}CFCl$	10 23	30	180	Terpene B and hydroquinone		24.6	78
$C_2H_5C{\equiv}CH$ $CF_2{=}CF_2$	109 250	8	170	Terpene B		86	28
$CF_2{=}CFBr$	96	8	210	Terpene B		24	25
$CF_2{=}CBr_2$	94	13	210	Terpene B and hydroquinone		26	28

[a] A terpene fraction, b.p. 176–196°, consisting primarily of dipentene and terpenolene.

be predicted. It is well known that the stability of alkyl free radicals stands in the order tertiary>secondary>primary. Unsaturation adjacent to a free radical is particularly effective in stabilizing that radical. Thus, with chlorotrifluoroethylene and butadiene the lowest energy diradical in the transition state would be ($\dot{C}FCl{-}CF_2{-}CH_2{-}\dot{C}H{-}CH{=}CH_2$), which leads to the product observed in the present work. The cycloaddition of chlorotrifluoroethylene with acrylonitrile leads to 3-cyano-2-chloro-1,1,2-trifluorocyclobutane[3] and with phenylacetylene leads to 1-phenyl-4-chloro-3,3,4-trifluorobutene.[4] These products can be rationalized assuming the most stable diradical intermediate. The cycloaddition of 1,1-dichloro-2,2-difluoroethylene to itself and other unsaturated materials leads to products predictable by assuming the lowest energy transitional diradical to be involved.

Similarly, the cyclobutanes formed by the cycloadditions of allenes[5] can also be rationalized by assuming the most stable intermediate diradical to be involved in the cyclization process.[6]

Cyclobutenes isomerize more or less readily to butadienes depending upon the position and nature of substituents.[7] The new cyclobutenes prepared in this work were thus brominated in order to determine chemically whether such an isomerization had occurred. In no case was this isomerization found. The surprising polymerization of 2,3,3-trifluorocyclobutene appears to be free radical in nature and could involve preliminary isomerization to the butadiene, but bromination data do not indicate this.

The thermal cyclization of tetrafluoroethylene, chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene give 80 to 90% yields of the cyclobutanes. The cyclization of bromotrifluoroethylene, 1,1-dibromo-2,2-difluoroethylene, and trifluoroiodoethylene give only 25 to 30% yields of simple cyclic products.[8] In the latter reactions, quantities of heavy oils, presumably linear low molecular weight polymers, are formed. This may result from the lower carbon-halogen bond strengths for bromine and iodine and their greater ionic radii. The product of iodotrifluoroethylene cyclization is the cyclobutene. Bromine is spontaneously lost from 1,1,2,2-tetrabromotetrafluorocyclobutane above its melting point.

EXPERIMENTAL

The thermal cycloaddition reactions summarized in Table I were carried out generally following the procedures of Coffman *et al.*[9] The reactants were heated in an air-free stainless steel autoclave or a glass tube in the presence of a free radical inhibitor. The physical properties of these compounds are given in Table II. The following section is concerned with reactions carried out with the cycloaddition products.

3,3,4,4-Tetrafluorocyclobutene. Thirty-six grams of 3-bromo-1,1,2,2-tetrafluorocyclobutane was added dropwise to a slurry of 75 g. of powdered potassium hydroxide in mineral oil at room temperature. The reaction was completed by stirring 5 hr. at 80°. Volatile materials were removed under reduced pressure to obtain 4.0 g. of starting material and 8.0 g. (36% conversion) of 3,3,4,4-tetrafluorocyclobutane, b.p. 50.4–50.5° (634 mm.), n_D^{20} 1.3114, d_4^{20} 1.358. This latter material is shown to be pure by gas-liquid partition chromatography. Molecular weight was determined by gas density and found to be 130 (theory for $C_4H_2F_4$ 126). The molar refraction calculated for the 3,3,4,4-tetrafluorocyclobutene structure was 18.72; that found was 17.96.

Anal. Calcd. for $C_4H_2F_4$: C, 38.1; F, 60.3. Found: C, 37.7; F, 60.1.

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(3) A. L. Barney and T. L Cairnes, *J. Am. Chem. Soc.*, **72**, 3193 (1950); F. J. Lorenzi-Thesis, University of Colorado, 1954.

(4) E. J. Smutny and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 3420 (1955).

(5) H. N. Cripps, J. R. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 751 (1958).

(6) W. H. Sharkey-Lecture, November 21, 1958, University of California, Berkeley, California.

(7) E. Vogel, *Ann.*, **615**, 14 (1958).

(8) R. J. Seffl, Thesis, University of Colorado (1950).

TABLE II

PHYSICAL PROPERTIES AND ANALYSES OF CYCLOADDITION PRODUCTS

Compound	B.P., °C./Mm. Hg	$n^{t°}_D$	$d^{t°}_4$	t, °C.	Molar Refraction Calcd.	Molar Refraction Found	Analyses, % Calcd. Calcd.	Analyses, % Calcd. Found	Analyses, % Calcd. Other	Analyses, % Found Calcd.	Analyses, % Found Found	Analyses, % Found Other
$CH_2—CHBr$ $CF_2—CF_2$	85.5/632	1.3787	1.777	20	26.90	26.90	23.2	36.7	Br, 38.6	23.4	36.3	Br, 36.6
$CH_2—CH_2$ $CF_2—CFCl$	75/634	1.3597	1.347	20	23.93	23.66	33.2	39.4	H, 2.79 Cl, 24.5	33.3	39.8	H, 3.04 Cl, 24.4
$CH_2—CH—CH{=}CH_2$[a] $CF_2—CFCl$	109/631	1.3927	1.344	25	32.75	32.70	42.3	33.4	H, 3.55 C, 20.8	42.5	33.2	H, 3.63 Cl, 20.7
$CH{=}CC_2H_5$ $CF_2—CF_2$	55/100	1.3472	1.199	20	28.01	27.46	46.8	49.3		47.1	49.3	
$CFBrCFBr$ $CF_2—CF_2$	90–90.5/ 638	1.3838		25								
$CBr_2—CBr_2$ $CF_2—CF_2$	Melting Point 153–154°						10.83	17.1	Br, 72.0	10.95	15.9	Br, 72.0

[a] See ref. 10.

3,4-Dibromo-1,1,2,2-tetrafluorocyclobutane. A mixture of 5.0 g. of 3,3,4,4-tetrafluorocyclobutene and 8.0 g. of bromine was sealed in a pyrex tube and irradiated for 1 day with ultraviolet light. Distillation yielded 7.2 g. (63%) of 3,4-dibromo-1,1,2,2-tetrafluorocyclobutane, b.p. 63–64° (79 mm.), n^{20}_D = 1.4220, d^{20}_4 2.129. The molar refraction calculated for this cyclobutane structure was 34.62, found: 34.12.

Anal. Calcd. for $C_4H_2Br_2F_4$: Br, 55.9. Found: Br, 55.7.

2,3,3-Trifluorocyclobutene. Forty grams of 1-chloro-1,2,2-trifluorocyclobutane was added dropwise to a slurry of 100 g. of potassium hydroxide in mineral oil containing 0.1 g. each of *t*-butylcatechol and diphenylamine and the mixture was allowed to stir for 1 day at room temperature. Volatile materials were removed under reduced pressure to yield 8.6 g. (21%) of 2,3,3-trifluorocyclobutene, b.p. 26.8° (631 mm.), n^{25}_D = 1.3170, d^{25}_4 1.190. This cyclobutene polymerized to a white solid on standing in the absence of traces of *t*-butylcatechol. The molar refraction calculated for the 2,3,3-trifluorocyclobutene structure was 18.64; that found was 17.86. The calculated molecular weight was 108.1; that found by gas density was 109.7.

Anal. Calcd. for $C_4H_3F_3$: C, 44.5; F, 52.7. Found: C, 44.1; F, 52.4.

2,3-Dibromo-1,1,2-trifluorocyclobutane. A mixture of 5.7 g. of 2,3,3-trifluorocyclobutene and 8.6 g. of bromine was sealed in a glass tube at liquid nitrogen temperatures. The reaction was complete by the time the mixture warmed to room temperature and 7.5 g. (53%) of 2,3-dibromo-1,1,2-trifluorocyclobutane was obtained, b.p. 76° (59 mm.), n^{25}_D 1.4544, d^{25}_4 2.125. The molar refraction calculated for this structure was 34.54; that found was 34.17.

Anal. Calcd. for $C_4H_3Br_2F_3$: C, 17.9; H, 1.13; Br, 59.7; F, 21.3. Found: C, 18.2; H, 1.26; Br, 59.5; F, 21.8.

3-Vinyl-2-chloro-1,1,2-trifluorocyclobutane. About 10 g. (0.185 mole) of 1,3-butadiene, 23 g. (0.198 mole) of chlorotrifluoroethylene, 0.1 g. of hydroquinone, and 0.5 ml. of terpene B (see Table I, footnote a) inhibitor were sealed in an air-free, heavy-walled Pyrex combustion tube. The tube was heated for 36 hr. at 100°, 12 hr. at 120°, 24 hr. at 150°, and 30 hr. at 180°. The tube was then cooled and opened. Distillation of the reaction products yielded 24.6 g. (78%) of 3-vinyl-2-chloro-1,1,2-trifluorocyclobutane, b.p. 109° (631 mm.), n^{25}_D 1.3927, d^{25}_4 1.244. Barrick[10] reported a boiling point of 115° for the same adduct but did not characterize the nature of the adduct.

Anal. Calcd. for $C_6H_6ClF_3$: C, 42.25; H, 3.55; F, 33.42; Cl, 20.79. Found: C, 42.49; H, 3.63; F, 33.16; Cl, 20.70.

Ozonolysis of 3-vinyl-2-chloro-1,1,2-trifluorocyclobutane. A mixture of ozone and oxygen was passed through a solution of 14.2 g. of 3-vinyl-2-chloro-1,1,2-trifluorocyclobutane in 65 ml. of methylene chloride at −75° until ozone uptake ceased. After warming to room temperature, this ozonide solution was added dropwise to a stirred mixture of 27 g. of 30% hydrogen peroxide, 0.8 ml. sulfuric acid and 35 ml. of water. Cooling with an ice bath was necessary initially. Ultimately the methylene chloride was distilled from the above mixture and it was stirred at 60° overnight. The resulting acidic reaction mixture was ether extracted, the acidic components were in turn taken into aqueous base, and the latter solution acidified and ether extracted. From the final extract, 8.7 g. of acidic brown oil was obtained which slowly crystallized. These crystals were recrystallized twice from toluene to yield 2 g. of α,α-difluoroglutaric acid, m.p. 102–103°; neut. equiv. Calcd. for $HO_2CCF_2CH_2CO_2H$: 84.05. Found: 82.6. This acid was previously obtained from the hydrolysis of 3-cyano-2-chloro-1,1,2-trifluorocyclobutane and the melting point reported as 103–105°.[3]

Anal. Calcd. for $C_5H_6O_4F_2$: C, 35.7; H, 3.60. Found: C, 35.6; H, 3.85.

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(9) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

(10) P. L. Barrick, U. S. Patent **2,462,345** (1949).

Bromination of 1-ethyl-3,3,4,4-tetrafluorocyclobutene. About 9.90 g. (0.0642 mole) of 1-ethyl-3,3,4,4-tetrafluorocyclobutene, 10.27 g. (0.0643 mole) of bromine, and 0.2 ml. of a saturated aqueous solution of acetamide were sealed in an air-free pyrex tube. The tube was wrapped in foil and heated for 24 hr. at 100°. The entire amount of bromine was consumed. On opening the tube a large amount of hydrogen bromide escaped and 15.5 g. of crude products were obtained. Distillation yielded 1.2 g. of recovered starting material, 5 g. of an unsaturated monobromide, and more highly brominated products. The monobromide had the following properties: b.p. 73–74° (50 mm.), n_D^{25} 1.4171, d_4^{25} 1.687. The molar refraction calculated for an unsaturated monobromocyclic compound, $C_6H_5BrF_4$, was 35.73, while that observed was 34.74.

Anal. Calcd. for $C_6H_5BrF_4$: C, 30.9; H, 2.16; Br, 34.3. Found: C, 30.4: H, 2.42; Br, 33.8.

Tribromination. Nine grams (0.058 mole) of 1-ethyl-3,3,4,4-tetrafluorocyclobutane and 16 g. (0.10 mole) of bromine were refluxed and irradiated with ultraviolet light for 1 day. All the bromine was consumed, hydrogen bromide evolved, and 17 g. of crude products obtained. Distillation revealed a complex mixture of products from which 1.9 g. of an unsaturated tribromide b.p. 88–90° (6 mm.), n_D^{25} 1.5095, was isolated.

Anal. Calcd. for $C_6H_3BrF_4$: Br, 61.34. Found: Br, 61.75.

Attempted cyclization of propargyl chloride and tetrafluoroethylene. An equimolar mixture of propargyl chloride and tetrafluoroethylene was heated in an air-free stainless steel autoclave in the presence of terpene B inhibitor. While heating, the mixture detonated at about 150°.

Debromination of 1,2-dibromohexafluorocyclobutane. About 18.6 g. of 1,2-dibromohexafluorocyclobutane from bromotrifluoroethylene cyclization was added dropwise to a stirred slurry of 24 g. of zinc dust, activated previously by 0.5 ml. concd. hydrochloric acid, in 30 ml. of dibutoxytetraethylene glycol applying no heat. In an exothermic reaction, 8.0 g. (88%) of hexafluorocyclobutene boiled from the mixture. The product was identified as hexafluorocyclobutene by comparison of its spectrum with that of an authentic sample and by gas density molecular weight determination. This product had a molecular weight of 160 while that calculated for C_4F_6 is 162.

1,2-Dibromo-3,3,4,4-tetrafluorocyclohutene. About 0.0585 mole of activated zinc dust, prepared from 5.86 g. of 93% zinc dust plus 4 ml. of concd. hydrochloric acid, was added in small portions to a stirred solution of 26 g. (0.0585 mole) of 1,1,2,2-tetrabromotetrafluorocyclobutane in 80 ml. of ether at −80°. After zinc addition was complete, the mixture was stirred for 4 hr. at −80°, then was allowed to warm slowly, and was stirred for 1 day at room temperature. Volatile materials were removed from the reaction mixture under reduced pressure and distilled to yield 4 g. (24%) of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene, b.p. 92–94° (635 mm.), n_D^{25} 1.4222, d_4^{25} 2.112. The molar refraction calculated for 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene structure was 34.14, while that observed was 34.17.

Anal. Calcd. for $C_4Br_2F_4$: C, 16.9; H, 0.0; Br, 56.3. Found: C, 16.9; H, 0.06; Br, 56.3.

Other attempted cycloadditions. Trifluoroethylene. Twenty-two grams of trifluoroethylene was treated for 30 hr. at 180° in an air-free Pyrex tube in the presence of hydroquinone and terpene B. From this reaction 86% of the trifluoroethylene was recovered and no 1,1,2,2,3,4-hexafluorocyclobutane formed. The latter is reported to boil at 27°.[11]

2-Chloro-1,1-difluoroethylene. Forty-two grams of 2-chloro-1,1-difluoroethylene was heated for 1 day at 180° and 1 day at 195° in the manner described above. No products boiling above room temperature were formed, but 86% of the starting material was recovered.

2-Bromo-1,1-difluoroethylene. Ninety-three grams of 2-bromo-1,1-difluoroethylene was heated for 1 day at 160° and 1 day at 180° as described above. No products boiling above room temperature were formed and 95% of the starting material was recovered.

Acknowledgment. We wish to express our appreciation to the Wright-Patterson Air Force Base, Ohio and to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, for their support of this work.

BOULDER, COLO.

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[11] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE]

Addition of Alcohols to Fluorinated Ethylenes

ARIEH DEMIEL[1a]

Received October 20, 1959

The sodium alkoxide-catalyzed addition of primary alcohols to 1-bromo-2,2-difluoro-, 1,1-dibromo-2,2-difluoro-, and 1-bromo-1,2,2-trifluoroethylene has been studied. Properties of the products and infrared data are reported.

This paper parallels to some extent and supplements the recent publication of Park[1b] on the addition of ethanol to fluorobromoethylenes in the presence of alcoholic potassium hydroxide. It reports the addition of methyl, ethyl, and *n*-propyl alcohol to 1-bromo-2,2-difluoro-, 1,1-dibromo-2,2-difluoro-, and 1-bromo-1,2,2-trifluoroethylene

$$F_2C{=}CHBr \qquad F_2C{=}CBr_2 \qquad F_2C{=}CFBr$$

using the respective sodium alkoxides as catalyst.[2]

$$RO{\cdot}CF_2{\cdot}CH_2Br,\ RO{\cdot}CF_2{\cdot}CHBr_2,\ RO{\cdot}CF_2{\cdot}CHBrF$$

The physical properties and the analytical data for the compounds so obtained are summarized in Table I. The three ethoxy compounds ($R = C_2H_5$)

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(1) (a) This paper forms part of the Ph.D. thesis, submitted by the author to the Hebrew University, Jerusalem.

(1) (b) J. D. Park, H. J. Cummings, and J. R. Lacher, *J. Org. Chem.*, **23**, 1785 (1958).

(2) See W. T. Miller, E. W. Fager and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).