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Synthesis of Tetrafluorocyclobutanes by Cycloalkylation

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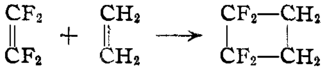
Introduction

Recent publications[1a,b,c,d] have described a new reaction which involves the addition of a fluoroolefin to itself, *e. g.*, the dimerization of tetrafluoroethylene[1a] or of chlorotrifluoroethylene,[1b] and to certain olefin derivatives such as chlorotrifluoroethylene,[1c] acrylonitrile[1d] and methyl methacrylate,[1d] to give cyclobutane derivatives. This new reaction has now been studied in considerable detail, and has been extended to the addition of tetrafluoroethylene to a wide variety of olefins. The general nature of this cycloalkylation method of preparing cyclobutane derivatives has been established. Thus, with ethylene, tetrafluoroethylene gives tetrafluorocyclobutane (I).



$$\begin{array}{c}CF_2\\ \|\\ CF_2\end{array} + \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} \longrightarrow \begin{array}{c}CF_2—CH_2\\ |\qquad |\\ CF_2—CH_2\end{array} \qquad \text{I}$$

Analogous reactions of tetrafluoroethylene with various unsaturated compounds have given the corresponding tetrafluorocyclobutanes substituted by halogen, vinyl, ethynyl or other groups.

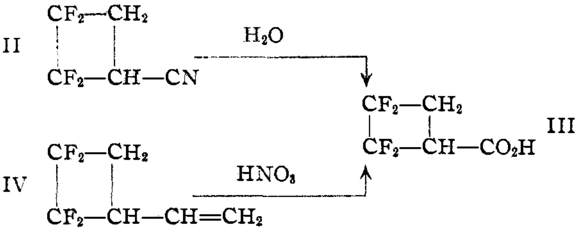
Generality of the Cycloalkylation

The cycloalkylation of tetrafluoroethylene with unsaturated compounds occurs at a lower temperature and apparently with greater facility than does the dimerization of tetrafluoroethylene.[1a] Under the conditions employed, the synthesis yields 4-membered ring compounds without the competitive dimerization of tetrafluoroethylene to octafluorocyclobutane and without the appreciable formation of 6-membered or larger rings and open-chain polymers. Qualitatively, the ease of reaction varies with the unsaturated reactant. Reactants containing a terminal methylene group combine more readily than do 1,2-disubstituted ethylenes such as 2-butene or trichloroethylene, while reactants having conjugated unsaturation, for example, 1,3-butadiene, acrylonitrile, methyl methacrylate and styrene, are even more reactive.

Reactions with Vinyl Compounds.—The cycloalkylation with vinyl and vinylidene compounds is illustrated by the formation of tetrafluorocyclobutane (I) from tetrafluoroethylene and ethylene, and by the substituted tetrafluorocyclobutanes formed in the reaction of tetrafluoroethylene with monolefins such as styrene, with chloroolefins typified by vinyl chloride, and with vinyl acetate, acrolein, allyl alcohol and the related unsaturates listed in Tables I, II, III.

Evidence for the tetrafluorocyclobutane structure is found in the mode of formation, the composition, and the properties of the products. The product from tetrafluoroethylene and a monoölefin has an empirical composition corresponding to that of one molecule of tetrafluoroethylene plus one molecule of olefin. The product is stable to aqueous permanganate, does not react with a solution of bromine in carbon tetrachloride, is unaffected under the usual conditions of catalytic hydrogenation, and its infrared absorption spectra show no absorption bands characteristic of the carbon–carbon double bond. The fluorohydrocarbon is resistant to oxidation as indicated by incomplete combustion in attempts to analyze the cyclobutanes from ethylene, propylene, isobutylene and 2-butene.

Further proof of structure is found in the transformations of products from acrylonitrile and from butadiene. Tetrafluoroethylene and acrylonitrile combine to form in good yield a nitrile which corresponds in composition to cyanotetrafluorocyclobutane (II). On acid hydrolysis, the nitrile gives the saturated tetrafluorocyclobutane carboxylic acid (III). The same acid (III) is obtained by the nitric acid oxidation of the unsaturated product (IV) formed by the addition of one molecule of tetrafluoroethylene to 1,3-butadiene. These transformations establish the identity of (III) as 2,2,3,3-tetrafluorocyclobutane carboxylic acid and of (IV) as 1-vinyl-2,2,3,3-tetrafluorocyclobutane formed by the 1,2-addition of butadiene to tetrafluoroethylene.



Reactions with 1,3-Dienes.—As already indicated, cycloalkylation occurs in the reaction of tetrafluoroethylene with terminally unsaturated dienes. The initial 1:1 products are tetrafluorocyclobutanes containing an unsaturated side chain. By further reaction with another molecule of tetrafluoroethylene, a bicyclic product containing two tetrafluorocyclobutane rings is formed. The simplest cases are the products from 1,3-butadiene and from allene. 1,3-Butadiene and tetrafluoroethylene form 1-vinyl-2,2,3,3-tetrafluorocyclobutane (IV) and not the tetrafluorocyclohexene that might have been expected by a Diels–Alder reaction. By hydrogenation, IV was converted to 1-ethyl-2,2,3,3-tetrafluorocyclobutane.

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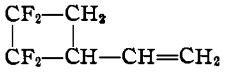
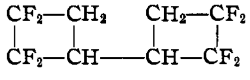
[1] (a) J. Harmon, U. S. Patent 2,404,374 (July 23, 1946); (b) A. L. Henne and R. D. Ruh, This Journal, 69, 279 (1947); (c) P. L. Barrick, U. S. Patent 2,427,116 (September 9, 1947); (d) P. L. Barrick and R. D. Cramer, U. S. Patent 2,441,128 (May 11, 1948).

Reaction of IV with another molecule of tetrafluoroethylene gave 2,2,2′,2′,3,3,3′,3′-octafluorobicyclobutyl (V). Similarly, in reactions with tetrafluoroethylene, allene gave the 1-methylene-2,2,3,3-tetrafluorocyclobutane (VI) and 1,1,2,2,5,5,6,6-octafluorospiro[3.3]heptane (VII).

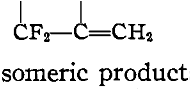
IV



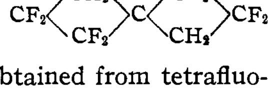
V



VI

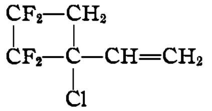


VII

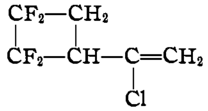


Isomeric products are obtained from tetrafluoroethylene and unsymmetrical dienes. Thus 2-chloro-1,3-butadiene gave the isomers VIII and IX.

VIII



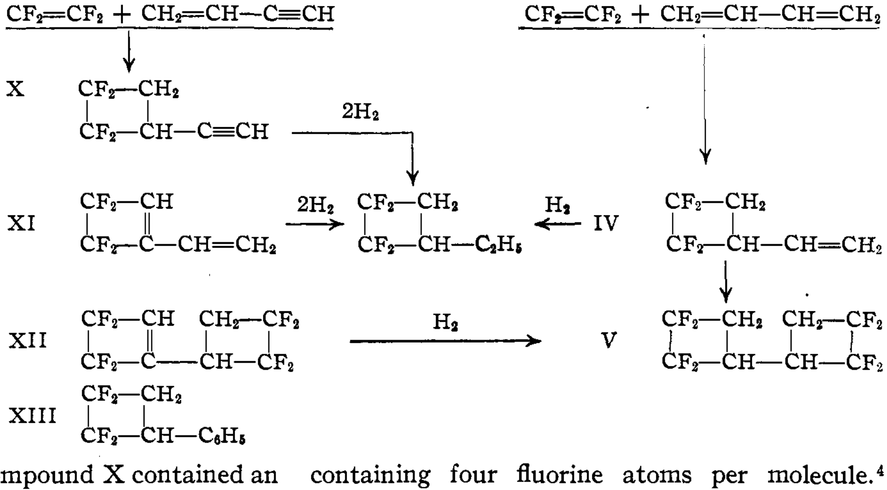
IX



The structures of compounds VIII and IX are believed to be those shown in view of (1) their compositions which correspond to a 1:1 tetrafluoroethylene/2-chloro-1,3-butadiene mole ratio; (2) their molecular refractivities which are in agreement with that for a tetrafluorocyclobutane derivative; (3) the conversion of IX to 1-ethyl-2,2,3,3-tetrafluorocyclobutane by hydrogenation; and (4) inability to obtain a chlorine-free product by the hydrogenation of VIII. Two isomeric 1:1 adducts were also obtained from tetrafluoroethylene and 2-fluoro-1,3-butadiene.

Reactions with Enynes.—Cycloalkylations with tetrafluoroethylene and an enyne proceed with participation of both the ethylenic and the acetylenic groups of the enyne. The products include the isomeric 1:1 tetrafluoroethylene/enyne adducts and also the bicyclic 2:1 adduct. Four clearly identified products have been obtained from monovinylacetylene. The first of these is 1-ethynyl-2,2,3,3-tetrafluorocyclobutane (X) Fig. 1, formed by reaction of tetrafluoroethylene at the ethylenic linkage of monovinylacetylene. Compound X contained an acetylenic hydrogen as shown by reaction with aqueous silver nitrate. By hydrogenation, X was converted to the 1-ethyl-2,2,3,3-tetrafluorocyclobutane independently synthesized from tetrafluoroethylene and 1,3-butadiene. Monovinylacetylene also reacted by 1,2-addition at the acetylenic linkage with the formation of compound XI. The structure XI was established as 1-vinyl-3,3,4,4-tetrafluorocyclobutene by its polymerizability, by its hydrogenation to 1-ethyl-2,2,3,3-tetrafluorocyclobutane, and by reaction with a second molecule of tetrafluoroethylene to obtain 2′,2′,3′,3′-tetrafluorocyclobutenyl-2,2,3,3-tetrafluorocyclobutane (XII). By hydrogenation, XII gave 2,2,2′,2′,3,3,3′,3′-octafluorobicyclobutyl (V), which was also synthesized from butadiene and two molecules of tetrafluoroethylene. The fourth product obtained from tetrafluoroethylene and monovinylacetylene was 1-phenyl-2,2,3,3-tetrafluorocyclobutane XIII, identical with the adduct of tetrafluoroethylene and styrene. The formation of XIII suggests that under the reaction conditions monovinylacetylene dimerized to styrene[2] which combined with tetrafluoroethylene.

Fig. 1.—Products from enynes and 1,3-dienes.



Physical Properties.—The physical properties of selected tetrafluorocyclobutane derivatives are given in Tables I to IV, inclusive. In general, the introduction of fluorine in the cyclobutane ring lowers the refractive index and increases the density of the products. The observed molecular refractivity was calculated by means of the Lorenz–Lorentz equation. The atomic refraction of fluorine was determined by subtracting the sum of the commonly used values (Eisenlohr's) of all the other increments from the experimental value and dividing the difference by the number of fluorine atoms. The atomic refraction of fluorine in these compounds, *AR*F, varied from 1.04–1.64 and averaged about 1.16.[3] The tetrafluorocyclobutanes containing only carbon, hydrogen and fluorine in Table I have an average *AR*F of 1.08 which agrees with the reported value for a fluorohydrocarbon containing four fluorine atoms per molecule.[4] The introduction of other atoms such as chlorine, oxygen, and/or nitrogen, and special configurations such as present in unsaturated substituents

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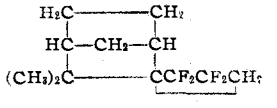
[2] H. B. Dykstra, THIS JOURNAL, **56**, 1625 (1934).

[3] Weissberger, "Physical Methods of Organic Chemistry," Volume I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 679.

[4] Grosse and Cady, *Ind. Eng. Chem.*, **39**, 373 (1947).

TABLE I

REACTION PRODUCTS FROM TETRAFLUOROETHYLENE AND MONO-OLEFINS

Tetrafluorocyclobutane	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	MR_D	AR_F	Analyses				Reactants[a] (g. C_2F_4/g. monoölefin)	Yield % based on C_2F_4
							Calcd. for	C	H	F		
$CH_2CF_2CF_2CH_2$	50–50.7		1.3046	1.2752	18.8	1.06	$C_4H_4F_4$	37.50	3.13	59.37	35/75	40
							Found	[c]	[c]	59.44	ethylene	
$CH_3CHCF_2CF_2CH_2$	68.5–68.8		1.3193	1.1961	23.5	1.08	$C_5H_6F_4$	42.25	4.22	53.53	50/125	72
							Found	[c]	[c]	53.73	propylene	
$CH_3CH_2CHCF_2CF_2CH_2$[b]	91		1.3370	1.1506	28.0	1.06	$C_6H_8F_4$	46.15	5.13	48.72		
							Found			48.25		
$(CH_3)_2CCF_2CF_2CH_2$	82–83		1.3395	1.1446	28.4	1.15	$C_6H_8F_4$	46.15	5.13	48.72	50/125	30
							Found	[c]	[c]	49.21	isobutylene	
$CH_3CH_2CH_2CHCF_2CF_2CH_2$[b]	113		1.3516	1.1190	32.62	1.05	$C_7H_{10}F_4$	49.40	5.90	44.70		
							Found	51.97	6.22	44.00		
$CH_3CH_2(CH_3)CCF_2CF_2CH_2$[b]	107.8		1.3529	1.1285	32.57	1.04	$C_7H_{10}F_4$	49.40	5.90	44.70		
							Found	54.23	6.83	45.98		
$CH_3CHCF_2CF_2CHCH_3$	87.5						$C_6H_8F_4$	46.15	5.13	48.72	50/125	5
							Found	[c]	[c]	50.35	butene-2	
$C_6H_5CHCF_2CF_2CH_2$	62	5	1.4512	1.2714	43.15	1.12	$C_{10}H_8F_4$	58.83	3.92	37.25	50/125	85
							Found	58.7	4.24	39.34	styrene	
	97–101	20	1.4352				$C_{12}H_{16}F_4$	61.02	6.83	32.18	70/95	7
							Found	61.38	7.08	31.0	camphene	
$CH_3CH_2CFCF_2CF_2CH_2$[b]	89–90		1.3295	1.2570	28.1	1.08	$C_6H_7F_5$	41.4	4.02	54.6		
							Found	[c]	[c]	54.79		

[a] The reactants were agitated at 150° under autogenous pressure for about eight hours. [b] These products were prepared by hydrogenation of the 1:1 reaction products of tetrafluoroethylene with 1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-butadiene and 2-fluoro-1,3-butadiene. [c] Extremely low C and H values were obtained due to incomplete combustion of the compounds.

appear to cause some variation in the values for the atomic refraction of fluorine. For example, the tetrafluorocyclobutanes from chloroölefins (Table II) have an average AR_F value of 1.30, while the products of Table III and IV have average AR_F values of 1.20 and 1.12, respectively.

Experimental

Preparation of Tetrafluorocyclobutanes.—The procedure for carrying out the cycloalkylation of tetrafluoroethylene with most of the unsaturated compounds listed in Tables I through IV consisted in charging 100 to 150 g. of the unsaturated compound containing a small amount of polymerization inhibitor, such as hydroquinone or "Terpene B" hydrocarbon,[5] into a 400 ml. high-pressure shaker tube lined with silver or stainless steel. A tube capable of withstanding operating pressures up to 500 atm. should be used when the unsaturated compound to be treated with tetrafluoroethylene is a gas at room temperature. The tube was cooled and evacuated to remove oxygen, and 50 g. of tetrafluoroethylene was added. The reaction mixture was heated under autogenous pressure with agitation at 150° for about eight hours. The pressure varied with the different reactants, but was initially about 45 atm. when the unsaturated compound was a liquid, and decreased as the reaction proceeded. After cooling and releasing any pressure, the liquid product was removed and steam distilled to separate the monomeric products from any non-volatile residue. The steam-volatile tetrafluorocyclobutane derivatives were fractionated.

A detailed study of synthesis conditions was not made. Accordingly, the yields given in the tables are not necessarily optimum. The yields are based on the amount of tetrafluoroethylene charged and are not corrected for the amount of tetrafluoroethylene which did not react. In general where low yields have been reported, reaction was incomplete and for the most part unaccompanied by polymerization of the individual reactants. Typical preparations are described in the following paragraphs.

Caution.—Information is not available concerning the toxicity of the various fluorine-containing products described. Accordingly, the products should be regarded with suspicion and handled with appropriate care.

Analysis.—It will be noted that the values obtained for carbon in the combustion analyses were frequently higher than the theoretical values. The apparently high carbon values for products containing appreciable proportions of fluorine result from the absorption of hydrogen fluoride formed during combustion and carried over into the Ascarite carbon dioxide absorber. Spongy silver placed in the absorption train preceding the Ascarite is beneficial in minimizing the carry over of hydrogen fluoride, but the silver must be replaced frequently.

1,1,2,2-Tetrafluorocyclobutane.—A silver-lined, high-pressure shaker tube was evacuated and charged with 35 g. of tetrafluoroethylene and 75 g. of ethylene. The sealed reactor was then heated under autogenous pressure at 150° with agitation for eight hours. After cooling the tube and bleeding off the gases slowly, there was obtained 17.9 g. of condensate (40% of theory). Characterization showed the condensate to be 1,1,2,2-tetrafluorocyclobutane which had the following properties: b. p. 50–50.7°, n^{25}_D 1.3046, d^{25}_4 1.2752, MR_D 18.8.

Anal. Calcd. for $C_4H_4F_4$: F, 59.37. Found: F, 59.44.

Warning.—Care should be exercised in preparing and heating mixtures of ethylene and tetrafluoroethylene since a violent explosion occurred when a mixture of 50 g. of tetrafluoroethylene and 125 g. of ethylene was heated at 160° and 480 atm. No difficulty was experienced with the other unsaturated compounds. Particular precau-

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(5) A terpene fraction consisting principally of dipentene and terpenolene boiling at 176–196° and having refractivity and density values of n^{20}_D 1.470–1.478, and $d^{15.5}_4$ 0.855–0.870.

TABLE II

REACTION PRODUCTS FROM TETRAFLUOROETHYLENE AND CHLOROÖLEFINS

Tetrafluorocyclobutane	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	MR_D	AR_F	Analyses Calcd. for	C	H	F	Cl	Reactants[a] (g. C_2F_4/g. chloroölefin)	Yield, %, based on C_2F_4
$ClHCCF_2CF_2CH_2$	73-74		1.3462	1.4251	24.15	1.18	$C_4H_3ClF_4$	29.53	1.84	46.8	21.85	50/132 vinyl	23
							Found	30.43	1.86	47.56	21.78	chloride	
$ClCH_2CHCF_2CF_2CH_2$	115-116		1.3745	1.3971	28.8	1.19	$C_5H_5ClF_4$	34.0	2.84	43.05	20.11	50/125 allyl	42
							Found	33.91	3.15	44.25	20.11	chloride	
$ClCH_2(CH_3)CCF_2CF_2CH_2$	122-124		1.3846	1.3161	33.85	1.30	$C_6H_7ClF_4$	37.8	3.67	39.9	18.65	46/150 methallyl	45
							Found	36.98	4.51	39.97	20.41	chloride	
$Cl_2CCF_2CF_2CH_2$	84-84.7		1.3702	1.5298	29.05	1.19	$C_4H_2Cl_2F_4$	24.35	1.01	38.6	36.05	50/125 vinyli-	46
							Found	27.13	0.91	38.84	35.82	dene chloride[b]	
$Cl_2CCF_2CF_2CHCl$	109-110.5		1.3995	1.5720	35.7	1.64	$C_4HCl_3F_4$			32.82	46.00	60/100 trichloro-	18
							Found			33.80	44.90	ethylene[c]	
$CH_3COCClCF_2CF_2CH_2$	56.7	36	1.3850	1.4478	35.75	1.36	$C_6H_5O_2ClF_4$	32.65	2.28	34.5	16.15	75/100 methyl	21
							Found	36.41	3.66	33.18	18.81	α-chloroacrylate	

[a] The reactants were agitated at 150° under autogenous pressure for about eight hours. [b] Added 0.5 g. of hydroquinone as polymerization inhibitor. [c] Heated at 225°.

tions should be taken to exclude all oxygen from tetrafluoroethylene and the reaction system.

Propylene, isobutylene and styrene reacted readily, yielding the methyl-, 1,1-dimethyl- and 1-phenyl-2,2,3,3-tetrafluorocyclobutanes, respectively, as given in Table I, whereas butene-2 and camphene were less reactive.

1-Chloro-2,2,3,3-tetrafluorocyclobutane.—A stainless steel-lined shaker tube was flushed with nitrogen, evacuated, cooled in a Dry Ice–methanol mixture, and then 132 g. of vinyl chloride and 50 g. of tetrafluoroethylene were added. The sealed tube was heated under autogenous pressure at 150° for eight hours. The tube was cooled and excess gas bled off slowly. The condensate amounted to 19 g. (23% yield) of 1-chloro-2,2,3,3-tetrafluorocyclobutane which had the following properties: b. p. 73–74°, n^{25}_D 1.3462, d^{25}_4 1.4251, MR_D 24.15.

Anal. Calcd. for $C_4H_3ClF_4$: C, 29.53; H, 1.84; F, 46.8; Cl, 21.85. Found: C, 30.43; H, 1.86; F, 47.56; Cl, 21.78.

Allyl chloride, methallyl chloride, vinylidene chloride, trichloroethylene and methyl α-chloroacrylate reacted with tetrafluoroethylene to yield the corresponding tetrafluorocyclobutanes listed in Table II.

1-Cyano-2,2,3,3-tetrafluorocyclobutane.[1d]—A 400 ml. stainless steel-lined shaker tube was flushed with nitrogen and charged with 125 g. of freshly distilled acrylonitrile. The tube was cooled and evacuated. After adding 50 g. of tetrafluoroethylene which contained approximately 0.1 g. of "Terpene B" hydrocarbon,[5] the sealed tube was heated at 150° with agitation under autogenous pressure for about eight hours. The reaction mixture was steam distilled, and the steam-volatile, lower, water-insoluble layer was separated, dried, and distilled. After separating a foreshot of unreacted acrylonitrile, an 84% yield (64 g.) of 1-cyano-2,2,3,3-tetrafluorocyclobutane was obtained which had the following properties: b. p. 148°, n^{25}_D 1.3568, d^{25}_4 1.3909. *Anal.* Calcd. for $C_5H_3NF_4$: C, 39.2; H, 1.96; F, 49.7; N, 9.15. Found: C, 37.0; H, 2.07; F, 49.19; N, 9.24. There was also obtained a non-volatile residue (1.2 g.) that contained about 7% fluorine.

The tetrafluorocyclobutanes which contain functional substituents undergo transformations characteristic of such substituents as illustrated by the hydrolysis of 1-cyano-2,2,3,3-tetrafluorocyclobutane to 2,2,3,3-tetrafluorocyclobutane carboxylic acid and by the conversion of this acid to simple carboxylic acid derivatives.

2,2,3,3-Tetrafluorocyclobutanecarboxylic Acid.[1d]—Ten grams of 1-cyano-2,2,3,3-tetrafluorocyclobutane was hydrolyzed by warming with 30 ml. of 70% sulfuric acid on a steam-bath for one-half hour. The upper oily layer was separated, and the lower sulfuric acid layer was diluted with cold water and extracted with ether. The combined oil and ether extracts were dried, and the ether was removed. An 87% yield (9.8 g.) of 2,2,3,3-tetrafluorocyclobutane carboxylic acid was obtained having the following properties: b. p. 100–100.5° at 24 mm., n^{25}_D 1.3684,[6] d^{25}_4 1.5103.[6] The acid solidified on cooling. It melted at 61.5–63°.

Anal. Calcd. for $C_5H_4O_2F_4$: C, 34.9; H, 2.33; F, 44.2; neut. equiv., 172. Found: C, 35.62; H, 2.60; F, 43.91; neut. equiv., 174.8.

2,2,3,3-Tetrafluorocyclobutanecarboxylic acid formed the customary acid derivatives such as the anhydride, the chloride, the amide, and the anilide.[1d]

Methyl 1-Methyl-2,2,3,3-tetrafluorocyclobutanecarboxylate.[1d]—A stainless steel-lined shaker tube was flushed with nitrogen and charged with 125 g. of methyl methacrylate containing 0.5 g. of hydroquinone as polymerization inhibitor. The tube was cooled in Dry Ice–methanol mixture, evacuated, and 50 g. of tetrafluoroethylene containing about 0.2 g. of "Terpene B" hydrocarbon[5] was added. The sealed tube was heated under autogenous pressure at 150° for eight hours. At the end of this time, there was no appreciable gas pressure in the tube. The reaction mixture was steam distilled, and the volatile, water-insoluble material was dried over anhydrous sodium sulfate and fractionated. The first fraction was unreacted methyl methacrylate (b. p. 32–36° at 57 mm.). Methyl 1-methyl-2,2,3,3-tetrafluorocyclobutanecarboxylate (64 g. or a 64% yield) was obtained next, boiling at 70° at 56 mm. and having the following properties: n^{25}_D 1.3656, d^{25}_4 1.2890, MR_D 34.6.

Anal. Calcd. for $C_7H_8O_2F_4$: C, 42.0; H, 4.00; F, 38.0; saponification number, 280.5. Found: C, 35.18; H, 4.24; F, 37.34; saponification number, 280.5. There was also obtained 5 g. of higher boiling liquid (b. p. 135–152° at 52 mm.), and 11 g. of polymer containing 6.8% fluorine.

Saponification of methyl 1-methyl-2,2,3,3-tetrafluorocyclobutane carboxylate with alkali gave the corresponding carboxylic acid[1d] melting at 41–43°.

A wide variety of ethylenically unsaturated oxygen-containing compounds including acrolein, methacrolein, vinyl acetate, allyl alcohol, methyl vinyl ketone, methyl vinyl ether, 2-vinylfuran, safrole and butadiene monoxide have been treated with tetrafluoroethylene to obtain the corresponding tetrafluorocyclobutane derivatives listed in Table III.

1-Vinyl-2,2,3,3-tetrafluorocyclobutane.—A stainless steel-lined high pressure shaker tube was flushed with nitrogen, evacuated, and charged with 125 g. of 1,3-buta-

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(6) Values were determined on the supercooled liquid.

TABLE III

REACTION PRODUCTS FROM TETRAFLUOROETHYLENE WITH UNSATURATED NITRILES AND OXYGEN COMPOUNDS

Tetrafluorocyclobutane	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	MR_D	AR_F	Analyses: Calcd. for	C	H	F	N	Reactants[a] (g. C_2F_4/g. unsaturant)	Yield, %, based on C_2F_4
$CNCHCF_2CF_2CH_2$	148		1.3568	1.3909	24.07	1.29	$C_5H_3NF_4$	39.2	1.96	49.7	9.15	75/100	84
							Found	37.0	2.07	49.19	9.24	acrylonitrile	
$CNCH_2CHCF_2CF_2CH_2$	192–195		1.3748	1.3459	28.2	1.16	$C_6H_5NF_4$	43.1	2.99	45.5	N 8.38	50/125	15
							Found	43.01	3.59	44.89	8.60	allyl cyanide	
$HC{=}OCHCF_2CF_2CH_2$	117–117.5		1.3768	1.5089	23.7	1.13	$C_5H_4OF_4$	38.5	2.56	48.75		50/125	12
							Found	40.5	2.57	47.67		acrolein[b]	
$HC{=}O(CH_3)CCF_2CF_2CH_2$	121–122		1.3625	1.3113	28.8	1.25	$C_6H_6OF_4$	42.35	3.53	44.7		50/125	50
							Found	45.44	4.25	43.27		methacrolein[b]	
$CH_3OC{=}O(CH_3)CCF_2CF_2CH_2$	70	56	1.3656	1.2890	34.6	1.13	$C_7H_8O_2F_4$	42.0	4.00	38.0	Sap. No. 280.5	100/125	84
							Found	35.18	4.24	37.34	280.5	methyl metha-acrylate[b]	
$CH_3C{=}OOCHCF_2CF_2CH_2$	138.5–139.5		1.3660	1.3310	31.2	1.44	$C_6H_6O_2F_4$	38.7	3.23	40.8		50/125	27
							Found	36.23	3.50	41.68		vinyl acetate	
$HOCH_2CHCF_2CF_2CH_2$	155–157		1.3670	1.3998	25.17	1.12	$C_5H_6OF_4$	38.0	3.80	48.1		50/125	45
							Found	39.34	3.95	47.86		allyl alcohol	
$CH_3C{=}OCHCF_2CF_2CH_2$	134–135.5		1.3582	1.3114	28.35	1.14	$C_6H_6OF_4$	42.35	3.53	44.7		50/125	18
							Found	41.95	4.12	43.78		methyl vinyl ketone	
$CH_3OCHCF_2CF_2CH_2$	88–91.8		1.3380	1.2612	26.0	1.30	$C_5H_6OF_4$	38.0	3.80	48.1		50/125	13
							Found	38.72	3.46	48.05		methyl vinyl ether[b]	
$OCH{=}CHCH{=}CCHCF_2CF_2CH_2$	86.5	80	1.4073	1.3341	35.75	1.06	$C_8H_6OF_4$	49.5	3.09	39.2		50/125	77
							Found	47.26	3.93	38.59		2-vinylfuran[b]	
$o\text{-}OCH_2OC_6H_4CH_2CHCF_2CF_2CH_2$	133.5–135.5	11	1.4770				$C_{12}H_{10}O_2F_4$	54.99	3.85	29.00		70/110	18
							Found	54.61	3.89	29.2		safrole	
$OCH_2CHCHCF_2CF_2CH_2$	74–76	67	1.3730				$C_6H_6OF_4$	42.36	3.56	44.7		70/37	9
							Found	43.45	3.96	42.7		butadiene monoxide[c]	

[a] The reactants were agitated at 150° under autogenous pressure for about eight hours. [b] Added 0.5 g. of hydroquinone as polymerization inhibitor. [c] Heated at 135° for ten hours.

diene and 100 g. of tetrafluoroethylene. The tube was heated under autogenous pressure at 125° with agitation for eight hours. After cooling to room temperature and releasing the pressure, the reaction mixture was steam distilled. The volatile water-insoluble liquid was dried and fractionated to give 140 g. (90%) of 1-vinyl-2,2,3,3-tetrafluorocyclobutane having the following properties: b. p. 83–85°, n^{25}_D 1.3489, d^{25}_4 1.1866; MR_D 27.87.

Anal. Calcd. for $C_6H_6F_4$: C, 46.76; H, 3.92; F, 49.32. Found: C, 46.45; H, 4.11; F, 50.02.

The nitric acid oxidation of 1-vinyl-2,2,3,3-tetrafluorocyclobutane[1d] gave a dense, green oil only sparingly soluble in water. By extraction with sodium bicarbonate solution and acidification, there was obtained 18 g. of an oil denser than water. Distillation gave a colorless product which boiled at 100° at 25 mm. and was identified as 2,2,3,3-tetrafluorocyclobutane carboxylic acid.

Anal. Calcd. for $C_5H_4O_2F_4$: C, 34.9; H, 2.33; F, 44.2; neut. equiv., 172. Found: C, 36.9; H, 2.60; F, 44.2; neut. equiv., 180.

2,2,2′,2′,3,3,3′,3′-Octafluorobicyclobutyl.—A stainless steel-lined shaker tube was charged with 90 g. of 1-vinyl-2,2,3,3-tetrafluorocyclobutane. After cooling the tube in Dry Ice–methanol mixture and evacuating, 50 g. of tetrafluoroethylene was added and the mixture was heated at 150° under autogenous pressure for eight hours. The tube was cooled to room temperature, and the pressure released. The liquid reaction mixture was fractionated to remove the unchanged 1-vinyl-2,2,3,3-tetrafluorocyclobutane, and then about 14 g. (11% conversion) of 2,2,2′,2′,3,3,3′,3′-octafluorobicyclobutyl distilling at 150–158° was obtained. The material solidified on cooling to room temperature and appeared to melt at 49–50°, but the boiling and melting points were not sharp.

Anal. Calcd. for $C_8H_6F_8$: F, 59.84. Found: F, 59.87.

A mixed melting point with the 2,2,2′,2′,3,3,3′,3′-octafluorobicyclobutyl obtained from the hydrogenation of 2′,2′,3′,3′ - tetrafluorocyclobutenyl - 2,2,3,3 - tetrafluorocyclobutane (a tetrafluoroethylene/monovinylacetylene reaction product) showed no depression.

1-Vinyl-1,2,2,3,3-pentafluorocyclobutane and 1-(1-fluorovinyl)-2,2,3,3-tetrafluorocycobutane.—A stainless steel-lined shaker tube was evacuated and charged with 128 g. of 2-fluoro-1,3-butadiene and 100 g. of tetrafluoroethylene. It was then heated at 125° with agitation for eight hours. After opening and discharging the tube, the reaction mixture was steam distilled to yield 142 g. of volatile, water-insoluble liquid. Fractionation gave equal amounts (each about 60 g.) of two isomeric products boiling at 85 and 95°, respectively, and 20 g. of a complex mixture of higher boiling products. The two isomeric products had the following properties: b. p. 85°,

TABLE IV

THE 1:1 REACTION PRODUCTS FROM TETRAFLUOROETHYLENE AND DIENES

Tetrafluorocyclobutane	B. p., °C.	B. p., Mm.	n^{25}D	d^{25}_4	*MR*D	*AR*F	Analyses: Calcd. for	C	H	F		Reactants[a] (g. C_2F_4/g. diene)	Yield, %, based on C_2F_4
$CH_2{=}CHCHCF_2CF_2CH_2$	83–85		1.3489	1.1866	27.87	1.14	$C_6H_6F_4$	46.76	3.92	49.32		100/125 1,3-butadiene	90
							Found	46.45	4.11	50.02			
$CH_2{=}CH(CH_3)CCF_2CF_2CH_2$	103		1.3649	1.1655	32.15	1.05	$C_7H_8F_4$	50.0	4.79	45.21		100/68 2-methyl-1,3-butadiene	83
							Found	51.34	5.26	44.86			
$CH_3CH{=}CHCHCF_2CF_2CH_2$	111		1.3698	1.1607	32.8	1.21	$C_7H_8F_4$	50.0	4.79	45.21		100/68 1,3-pentadiene	68
							Found	49.19	5.23	45.15	Cl		
$CH_2{=}C(Cl)CCF_2CF_2CH_2$	108		1.3838	1.3483	32.8	1.15	$C_6H_5ClF_4$	38.21	2.67	40.30	18.80	100/88.5 2-chloro-1,3-butadiene[b]	51
							Found	39.46	3.19	40.03	18.84		
											Cl		
$CH_2{=}CClCHCF_2CF_2CH_2$	122–124		1.3868	1.3654	32.4	1.05	$C_6H_5ClF_4$	38.21	2.67	40.30	18.80		10
							Found	37.37		40.03	18.69		
$CH_2{=}CHCFCF_2CF_2CH_2$	85		1.3405	1.2941	27.9	1.14	$C_6H_5F_5$	41.85	2.91	55.24		100/128 2-fluoro-1,3-butadiene	35
							Found	44.01	3.30	55.63			
$CH_2{=}CFCHCF_2CF_2CH_2$	95		1.3458	1.3193	27.5	1.05	$C_6H_5F_5$	41.85	2.91	55.24			35
							Found	42.90	3.14	56.36			
$CH_2{=}CCF_2CF_2CH_2$	64–66		1.3318	1.2288	23.4	1.17	$C_5H_4F_4$	42.87	2.88	54.25		75/30 allene[c]	14
							Found	43.08	3.71	53.2			
$CH{=}CHCH_2CH_2CHCHCF_2CF_2$	147–149		1.4019				$C_8H_8F_4$	53.3	4.45			75/30 dihydrobenzene[b]	50
							Found	54.35	4.98				
$CH_2CH{=}CHCHCHCF_2CF_2$	120–123		1.3865				$C_7H_6F_4$	50.61	3.64	45.75		70/46 dicyclopentadiene[d]	23
							Found	51.25	3.87	44.9	Iodine No.		
$CH_2{=}(CH_3)CH_2O$-$CH_2(CH_3)CCF_2CF_2CH_2$	70–72	19	1.3918				$C_{10}H_{14}OF_4$	53.2	6.18	33.6	112.3	50/150 dimethallyl ether	20
							Found	54.47	6.71	32.72	120.2		

[a] The reactants were agitated under autogenous pressure for about eight hours at 100–125°. [b] Added 1.0 g. of hydroquinone as polymerization inhibitor. [c] Heated at 150°. [d] Heated at 190°. A 9% yield of $C_2F_4{\cdot}2C_5H_6$, b. p. 102–107° (17 mm.), n^{25}D 1.4570, was also obtained.

N^{25}D 1.3405, d^{25}_4 1.2941, *MR*D 27.9; and b. p. 95°, n^{25}D 1.3458, d^{25}_4 1.3193, *MR*D 27.5.

Anal. Calcd. for $C_6H_5F_5$: C, 41.85; H, 2.91; F, 55.24. Found for 85° fraction: C, 44.01; H, 3.30; F, 55.63. Found for 95° fraction: C, 42.90; H, 3.14; F, 56.36.

Tetrafluorocyclobutanes from tetrafluoroethylene and other dienes are listed in Table IV.

1-Ethyl-1,2,2,3,3-pentafluorocyclobutane.—Fifteen grams of 1-vinyl-1,2,2,3,3-pentafluorocyclobutane (boiling at 85°) was dissolved in 100 g. of absolute ethyl acohol, and was hydrogenated using 4 g. of Raney nickel catalyst and 1500 lb./sq. in. hydrogen pressure at 80°. After removing the catalyst, the solution was diluted with water, the water-insoluble layer was separated, dried over calcium chloride and distilled. 1-Ethyl-1,2,2,3,3-pentafluorocyclobutane was obtained boiling at 89–90° and having the following properties: n^{25}D 1.3295, d^{25}_4 1.2570, *MR*D 28.1.

Anal. Calcd. for $C_6H_7F_5$: F, 54.6. Found: F, 54.79.

The structure of 1-ethyl-1,2,2,3,3-pentafluorocyclobutane was assigned because of the resistance of fluorine atoms substituted in the cyclobutane ring to elimination by hydrolysis.

Hydrogenation of 1-(1-fluorovinyl)-2,2,3,3-tetrafluorocyclobutane (boiling at 95°) under similar conditions gave a product which was hydrolyzed by water. Hydrolysis with loss of fluorine is evidence that a fluorine atom was present in an aliphatic side chain. The fluorine atoms in a tetrafluorocyclobutane ring are quite resistant to hydrolysis.

1-Vinyl-1-chloro-2,2,3,3-tetrafluorocyclobutane and 1-(1-chlorovinyl)-2,2,3,3-tetrafluorocyclobutane.—A silver-lined shaker tube was charged with 100 ml. of water, 88.5 g. of 2-chloro-1,3-butadiene and 1 g. of hydroquinone. After cooling and evacuating, 100 g. of tetrafluoroethylene was added, and the tube was heated with agitation at 100° for about eight hours. The recovered mixture was steam distilled to yield 115 g. of volatile liquid and 11 g. of non-volatile material. Fractionation of the liquid gave two distinct products: (1) 1-vinyl-1-chloro-2,2,3,3-tetrafluorocyclobutane (96 g.): b. p. 108°, n^{25}D 1.3838, d^{25}_4 1.3483, *MR*D 32.8, and (2) 1-(1-chlorovinyl)-2,2,3,3-tetrafluorocyclobutane (19 g.): b. p. 122–124°, n^{25}D 1.3868, d^{25}_4, 1.3654, *MR*D 32.4.

Anal. Calcd. for $C_6H_5ClF_4$: C, 38.21; H, 2.67; F, 40.30; Cl, 18.80. Found: (1) C, 39.46; H, 3.19; F, 40.03; Cl, 18.84. (2) C, 37.37; F, 40.03; Cl, 18.69.

The hydrogenation of fraction (1) in absolute ethyl alcohol using Raney nickel catalyst at 80° and 1500 lb./sq. in. pressure gave a product boiling at 113° which analyzed for nearly the theoretical amount of chlorine but which still contained a little unsaturated material as evidenced by oxidation with aqueous permanganate solution. The physical properties of the compound were n^{25}D 1.3690, d^{25}_4 1.2954, *MR*D 33.2. The increase in the molecular refraction of 0.4 checks with that expected from saturation of a double bond by two hydrogen atoms.

Anal. Calcd. for $C_6H_7ClF_4$: F, 39.9; Cl, 18.65. Found: F, 40.17; Cl, 15.25.

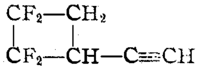
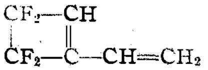
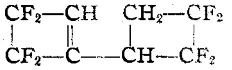
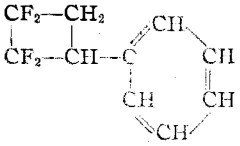
The hydrogenation of fraction (2) in absolute ethyl alcohol using Raney nickel catalyst at 80° and 1500 lb./sq. in. pressure resulted in practically complete removal of the chlorine to yield 1-ethyl-2,2,3,3-tetrafluorocyclobutane boiling at 90–91.5°.

The assignment of the structures for fractions (1) and (2) involves the assumption that chlorine in an aliphatic side chain is more readily eliminated during hydrogenation than is chlorine substituted in the ring.

1-Ethyl-2,2,3,3-tetrafluorocyclobutane.—One mole (154 g.) of 1-vinyl-2,2,3,3-tetrafluorocyclobutane was hydrogenated at 80° using about 10 g. of Raney nickel catalyst

TABLE V

REACTION PRODUCTS FROM TETRAFLUOROETHYLENE AND MONOVINYLACETYLENE

	Product	B. p., °C.	B. p., Mm.	$n^{25}D$	d^{25}_4	MR_D	AR_F	Calcd. for	C	H	F
X		82–84		1.3553	1.2498	26.5	1.18	$C_6H_4F_4$	47.47	2.63	50.0
								Found:	51.65	3.63	49.99
XI		98–99		1.3742	1.2588	27.5	1.16	$C_6H_4F_4$	47.37	2.63	50.0
								Found:	46.66	2.81	51.13
XII		49–50	13	1.3596	1.5147	36.6	1.27	$C_8H_4F_8$	38.1	1.58	60.3
								Found:	39.52	3.31	59.02
XIII		60–65	9		1.2703			$C_{10}H_8F_4$	58.8	3.92	37.25
								Found:	58.71	4.41	40.35

X. This product reacted with dilute aqueous silver nitrate, did not polymerize readily, and on hydrogenation gave 1-ethyl-2,2,3,3-tetrafluorocyclobutane.

XI. This product did not react with aqueous silver nitrate, polymerized readily, and on hydrogenation gave 1-ethyl-2,2,3,3-tetrafluorocyclobutane.

XII. Hydrogenation of XII gave a product identical with the 2,2,2′,2′,3,3,3′,3′ octafluorobicyclobutyl obtained from butadiene and two molecules of tetrafluoroethylene.

XIII. This compound was identical with the 1-phenyl-2,2,3,3-tetrafluorocyclobutane obtained from styrene and tetrafluoroethylene (see Table I).

and 1000–1500 lb./sq. in. hydrogen pressure. The hydrogenation was exothermic. About one mole of hydrogen was absorbed, and 150 g. (96% yield) of 1-ethyl-2,2,3,3-tetrafluorocyclobutane was obtained boiling at 90–91° and having the following properties: $n^{25}D$ 1.3370, d^{25}_4 1.1506, MR_D 28.0.

Anal. Calcd. for $C_6H_8F_4$: F, 48.7 Found: F, 48.25.

1-Ethyl-2,2,3,3-tetrafluorocyclobutane was also obtained by hydrogenation of the two isomeric products from tetrafluoroethylene and monovinylacetylene, namely, 1-ethynyl-2,2,3,3-tetrafluorocyclobutane and 1-vinyl-3,3,4,4-tetrafluorocyclobutene.

1-Ethynyl-2,2,3,3-tetrafluorocyclobutane and 1-Vinyl-3,3,4,4-tetrafluorocyclobutene.—A 400-ml. shaker tube was flushed with nitrogen, evacuated, and charged with 50 g. of monovinylacetylene and 50 g. of tetrafluoroethylene (containing less than 20 p. p. m. of oxygen). The sealed tube was heated at 100° for sixteen hours, and was then cooled to room temperature. After releasing the pressure, the light yellow liquid reaction product (82 g.) was removed and steam distilled to obtain about 60 g. of steam-volatile, colorless liquid which was heavier than water, and about 20 g. of light yellow, non-steam-volatile polymer. Analysis of the polymer indicated 26% fluorine, corresponding to a tetrafluoroethylene/monovinylacetylene mole ratio of 1:3.7. Fractionation of the liquid products through a precision column yielded the four products listed in Table V in about a 45:45:5:5 ratio, respectively. There was also a small amount of higher boiling material which was not identified.

1-Methylene-2,2,3,3-tetrafluorocyclobutane and 1,1,2,2,5,5,6,6-Octafluorospiro[3.3]heptane.—Thirty grams of allene and 75 g. of tetrafluoroethylene were heated in a silver-lined shaker tube at 150° under autogenous pressure for eight hours. The excess gas was bled through a Dry Ice-trap, and 18 g. of liquid was obtained from the tube. Fractionation of the liquid gave two distinct products: (1) 1-methylene-2,2,3,3-tetrafluorocyclobutane (14 g.), b. p. 64–66°, $n^{25}D$ 1.3318, d^{25}_4 1.2288, MR_D 23.4, and (2) 1,1,2,2,5,5,6,6-octafluorospiro[3.3]heptane (4 g.), b. p. 107–109°, $n^{25}D$ 1.3325, d^{25}_4 1.5137, MR_D 32.7, AR_F, 1.30.

Anal. (1) Calcd. for $C_5H_4F_4$: C, 42.87; H, 2.88; F, 54.25. Found: C, 42.98; H, 3.72; F, 52.9. (2) Calcd. for $C_7H_4F_8$: C, 35.01; H, 1.68; F, 63.31. Found: C, 35.69; H, 2.35; F, 61.8.

Fraction (1) instantly decolorized neutral permanganate solution, whereas fraction (2) did not. Ozonolysis of fraction (1) in carbon tetrachloride gave formaldehyde. When 10 g. of fraction (1) was heated with 30 g. of tetrafluoroethylene in a bomb for eight hours at 150° an 18% conversion to fraction (2) was obtained.

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Summary

A new family of substituted tetrafluorocyclobutanes has been synthesized by the cycloalkylation of tetrafluoroethylene under non-polymerizing conditions with terminally unsaturated ethylenic and acetylenic compounds, and with 1,3-dienes. Typical members of the family include 2,2,3,3-tetrafluorocyclobutane and this fluorohydrocarbon substituted in the 1 position by alkyl, halogen, cyano, carboxy, carbalkoxy, and other groups. As a class, the tetrafluorocyclobutanes are resistant to ring cleavage.

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