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# The Preparation and Cycloaddition Reactions of Pentafluoro-1,3-pentadienes

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3,4,5,5,5-Pentafluoro-1,3-pentadienes were prepared from 1 : 1 adducts of perfluoropropylene and alcohols by dehydration followed by dehydrofluorination. When 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene was heated at 130—220°C, an intramolecular cyclization occurred to give 1-methyl-2,3-difluoro-3-trifluoromethylcyclobutene in 73—87% yields. $\alpha$-Trifluoromethyl-$\beta$-acetylacrylic acid and 1-trifluoromethyl-2-fluoro-3-methylenecyclobutene were synthesized from the cyclobutene by oxidation and dehydrofluorination, respectively. Several polyfluorocyclobutanes with a perfluoropropenyl group were prepared by the cross-cycloaddition of the pentafluoro-1,3-pentadienes with the fluoroolefins such as 1,1-difluoro-2,2-dichloroethylene, trifluorochloroethylene, and perfluoropropylene.

Though fluorine-containing 1,3-butadienes have been prepared by various methods,[1] only a few papers[2] dealt with the syntheses of the polyfluoro-1,3-pentadienes. As the (2-hydroperfluoropropyl)-alkylcarbinols were found to be prepared in an excellent yield by the addition of alcohols to perfluoropropylene under $\gamma$-irradiation,[3] these carbinols were considered to be suitable intermediates for the syntheses of pentafluoro-1,3-pentadienes. Accordingly, (2-hydroperfluoropropyl)dimethylcarbinol was treated with phosphorus pentoxide to yield 2-methyl-3,3,4,5,5,5-hexafluoro-1-pentene,[3] which was subsequently dehydrofluorinated with potassium hydroxide to give 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene.

$$CF_3CF{=}CF_2 + CH_3CHROH \xrightarrow{\gamma\text{-ray}}$$

$$CF_3CHFCF_2CR(CH_3)OH \xrightarrow{P_2O_5}$$

$$CF_3CHFCF_2CR{=}CH_2 \xrightarrow{KOH} CF_3CF{=}CFCR{=}CH_2$$

(Ia R=H; Ib R=$CH_3$)

The pentafluoro-1,3-pentadienes (Ia,b) consisted of *cis* and *trans* isomers, the former being predominant.[4] The ratio of *cis* to *trans* varied with the condition of dehydrofluorination. Whereas the *cis* isomer was formed almost exclusively in dehydrofluorination with solid potassium hydroxide in the absence of a solvent, the ratio of *cis* to *trans* was about 2 : 1 in the presence of methanol or ethanol.

The assignment of the isomers to *cis* and *trans* were made unambiguously on the basis of the coupling constants[5] between vicinal F and $CF_3$, and those between vicinal F and F in their $^{19}F$ NMR spectra, whose parameters are shown in Table 1. Both isomers of pentafluoro-1,3-pentadienes polymerized upon standing in air and the rates of polymerization of the *trans* isomers were much greater than those of the *cis* isomers. From the NMR spectra, the structures of the polymers were found to be $[-CF(CF_3)CF{=}CRCH_2-]_n$, formed through the 1,4-polymerization.

Several papers have reported on the intramolecular cyclization of polyfluoro-1,3-dienes. Perfluoro-,[6] 2,3-dichloro-1,1,4,4-tetrafluoro-,[7] and 1,4-dichloro-1,2,3,4-tetrafluoro-1,3-butadiene[8] have produced the corresponding perhalocyclobutenes upon heating. When 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene was heated at 130—220°C, an intramolecular cyclization took place to give 1-methyl-2,3-difluoro -3- trifluoromethylcyclobutene (II) in approximately 80% yield. The effect of reaction temperature on the yield was shown in

1) A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York (1958), p. 100.

2) A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954); P. Tarrant and E. G. Gillman, *ibid.*, **76**, 5423 (1954); P. Tarrant and M. R. Lilyquist, *ibid.*, **77**, 3640 (1955).

3) H. Muramatsu, K. Inukai and T. Ueda, This Bulletin, **40**, 903 (1967).

4) The predominance of the *cis* form over the *trans* form has been observed in the preparation of perfluoropropenes and chlorofluoroethylenes containing an ethereal group; H, Muramatsu *et al.*, *ibid.*, **40**, 1284 (1967).

5) The coupling constants of $J_{F,F}$ and $J_{F,CF_3}$ were in agreement with those of polyfluoropropenes reported in the literature; J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, (1966), p. 909.

6) M. Prober and W. T. Miller, *J. Am. Chem. Soc.*, **71**, 598 (1949); Ref. 7.

7) W. T. Miller, U. S. Pat. 2729613 (1956).

8) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, **1955**, 3880.

TABLE 1. $^{19}F$ NMR SPECTRAL PARAMETERS OF PENTAFLUORO-1,3-PENTADIENES, $CF_3CF_a=CF_bCR=CH_2$

| R | Isomer | Chemical shift,* ppm | | | Coupling constant, cps | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\delta_{CF_3}$ | $\delta_{F_b}$ | $\delta_{F_a}$ | $J_{CF_3,F_a}$ | $J_{CF_3,F_b}$ | $J_{F_a,F_b}$ | $J_{F_b,H}$** |
| H | *cis* | −9.7 | 61 | 78 | 12 | 8 | 2 | 24 |
| | *trans* | −8.1 | 78 | 94 | 11 | 22 | 128 | 22 |
| $CH_3$ | *cis* | −10.7 | 42 | 79 | 13 | 8 | 8 | — |
| | *trans* | −9.0 | 68 | 90 | 10 | 23 | 129 | — |

* The chemical shifts of fluorines are with respect to external trifluoroacetic acid increasing to upfield.
** Coupling between the fluorine and hydrogen on vicinal carbon atoms.

TABLE 2. RESULTS OF CYCLIZATION REACTIONS*

| Reaction temp. °C | Pentadiene added g | Pentadiene recovered g | Cyclobutene g | Polymer g | Yield** of cyclobutene % |
|---|---|---|---|---|---|
| 130 | 73 | 13 | 47 | 11 | 78 |
| 140 | 107 | 8 | 87 | 11 | 87 |
| 150 | 93 | 4 | 75 | 11 | 84 |
| 160 | 112 | 4 | 87 | 17 | 80 |
| 180 | 109 | 5 | 87 | 16 | 84 |
| 200 | 95 | 5 | 75 | 13 | 84 |
| 220 | 140 | 6 | 98 | 30 | 73 |

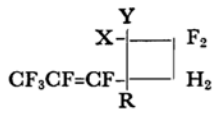
* In each run, about 10 g of Terpene B was added as an inhibitor and the reaction mixture was heated for a period of 21 hr.
** Based on the amount of pentadiene charged.

TABLE 3. NMR SPECTRAL PARAMETERS OF ESTERS OF $\alpha$-TRIFLUOROMETHYL-$\beta$-ACETYLACRYLIC ACIDS, $CH_3COCH=C(CF_3)COOR$

| R | Isomer | Chemical shifts,* ppm | | | | | Coupling constant, cps |
|---|---|---|---|---|---|---|---|
| | | $\delta_{CF_3}$ | $\tau_{COCH_3}$ | $\tau_{CH_3}$ | $\tau_{CH_2}$ | $\tau_{=CH}$ | $J_{CF_3,H}$ |
| $CH_3$ | *cis* | −12.5 | 7.68 | 6.24 | | 2.95 | 1.5 |
| | *trans* | −13.1 | 8.31 | 6.76 | | 2.28 | 1.8 |
| $C_2H_5$ | *cis* | −12.1 | 7.69 | 8 74 | 5.82 | 2.99 | 1.3 |
| | *trans* | −12.7 | 8.34 | 8.85 | 6.57 | 2.28 | 2.0 |
| H | | −12.7 | 8.30 | | | 2.52 | 1.6 |

* The chemical shifts of fluorines are with respect to external trifluoroacetic acid increasing to upfield.

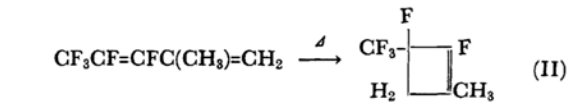
TABLE 4. YIELDS AND PHYSICAL PROPERTIES OF POLYFLUOROCYCLOBUTANES WITH A PERFLUOROPROPENYL GROUP,




| R | X | Y | Yield % | Bp °C(mmHg) | $n_D^{20}$ | $d_4^{20}$ | C, % | | H, % | | $\nu_{C=C}$ $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Found | Calcd | Found | Calcd | |
| H | F | Cl* | 49 | 119—120 | 1.3602 | 1.568 | 31.47 | 30.62 | 1.68 | 1.10 | 1729 |
| H | Cl | Cl | 55 | 84— 85(77) | 1.3882 | 1.593 | 29.75 | 28.89 | 1.37 | 1.04 | 1723 |
| H | F | $CF_3$ | 6 | 117—118 | 1.3234 | 1.617 | 31.49 | 31.19 | 1.05 | 0.98 | 1723 |
| $CH_3$ | F | Cl* | 49 | 91— 92(44) | 1.3690 | 1.600 | 34.87 | 33.30 | 2.10 | 1.75 | 1723 |
| $CH_3$ | Cl | Cl | 36 | 90— 92(64) | 1.3950 | 1.552 | 32.46 | 31.50 | 1.86 | 1.65 | 1720 |
| $CH_3$ | F | $CF_3$ | 3 | 126—132 | 1.3350 | 1.545 | 33.13 | 33.56 | 1.59 | 1.56 | 1726 |

* Contained a small amount of the dimer of pentafluoropentadiene.

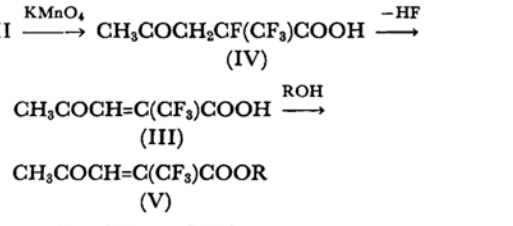
Table 2. The cyclization of 3,4,5,5,5-pentafluoro-1,3-pentadiene was unsuccessful due to polymerization to give viscous polymeric substance.



(II)

The structure of II was confirmed by elemental analysis, IR, and NMR spectra. In the $^{19}F$ NMR spectrum, a peak for the $CF_3$ group appeared as a doublet at 3.4 ppm caused by the splitting of a geminal fluorine ($J_{CF_3,F}$ 8.1 cps) and those for the -CF- and -$\dot{C}$F- as a triplet and a multiplet at 37 and 100 ppm, respectively. The triplet may be due to a long range coupling with hydrogens of methylene group ($J_{F,H}$ 13.2 cps).[9]

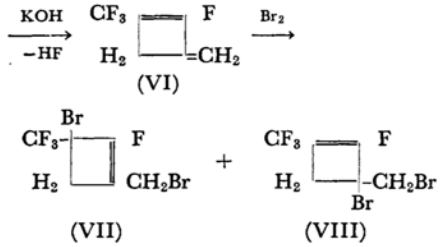
The structure of II was further substantiated by the following reactions. Oxidation of II with potassium permanganate gave $\alpha$-trifluoromethyl-$\beta$-acetylacrylic acid (III), which was obviously formed by dehydrofluorination of an intermediate, $\alpha$-fluoro-$\alpha$-trifluoromethyl-$\beta$-acetylpropionic acid (IV). Though two isomers of the disubstituted acrylic acid were possible, only the *trans* isomer was identified.



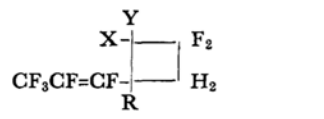
In esterification of III using *p*-toluenesulfonic acid as a catalyst, an isomerization took place to give a mixture of the *trans* and *cis* isomers, the *trans* ester being predominant (about 8 to 1 for R=$CH_3$; 6 to 1 for R=$C_2H_5$).

It has already been known[10] that carbonyl-containing groups in substituted olefins have long range deshielding effects on *cis*-$\beta$-hydrogen atoms and *cis*-$\beta$-methyl groups. The peak for the vinylic hydrogen of one isomer obtained in esterification appeared in a lower field by 0.7 ppm than that of the other isomer, but the peak for the methyl hydrogens in acetyl group of the former isomer appeared in a higher field by 0.6 ppm than that of the latter isomer. These chemical shifts of protons indicate the former to have the *trans* structure and the latter the *cis*. For the trifluoromethyl group, a deshielding effect of 0.6 ppm by the carbonyl group in the *cis* position was also observed in the $^{19}F$ NMR spectra. Table 3 gives the NMR parameters for methyl and ethyl $\alpha$-trifluoromethyl-$\beta$-acetyl acrylates. It is seen that $J^{cis}_{H,CF_3}$ is smaller than $J^{trans}_{H,CF_3}$ in each of the esters.[11]

Treatment of II with potassium hydroxide produced 1-trifluoromethyl-2-fluoro-3-methylenecyclobutene (VI) through a 1,4-elimination. To a mixture of II and VI was added bromine under ultraviolet irradiation to yield the dibromocyclobutenes, (VII) and (VIII) in a ratio of 1 : 1.2. Debromination of VII and VIII gave the pure VI, which polymerized upon standing overnight, yielding a white solid polymer.



The cross-cycloaddition reaction of 3,4,5,5,5-pentafluoro-1,3-pentadiene with the fluoroolefins (1,1-difluoro-2,2-dichloroethylene, 1,1,2-trifluoro-2-chloroethylene and perfluoropropylene) gave exclusively (perfluoropropenyl)cyclobutanes (IXa), no cyclohexenes being found.[12] In all the cases, the telomers of the pentadiene were formed as by-products. Similarly, 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene reacted with the fluoroolefins to give the (perfluoropropenyl)polyfluorocyclobutanes (IXb) together with II.



(IXa R=H; IXb R=$CH_3$)
(X, Y=Cl, F or $CF_3$)

Table 4 summarizes the yields based on the pentadienes added and the physical properties of polyfluorocyclobutanes containing a perfluoropropenyl group.

The cycloadducts IXa,b were identified by their NMR spectra and IR spectra ($\nu_{C=C}$ 1723—1729cm$^{-1}$ for R=H, 1720—1726 cm$^{-1}$ for R=$CH_3$). Further the 1-perfluoropropenyl-2-halo-3,3-difluorocyclobutenes (Xa,b) were synthesized by dehydrochlorination of the cycloadducts IXa. Xa was identical

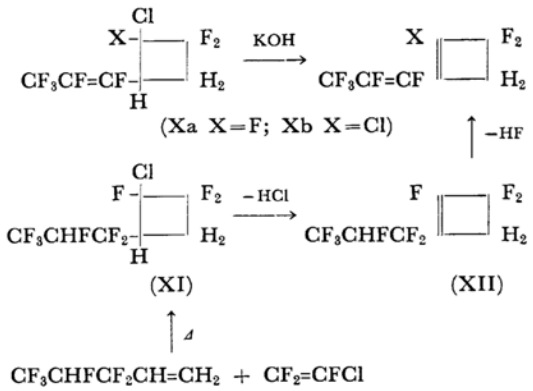
9) In some polyfluorocyclobutenes such as 1-phenyl-3,3,4-trifluoro-4-chlorocyclobutene and 1-phenyl-2,3,3-trifluorocyclobutene, the cross-ring couplings between H and F with $J_{H,F}$ of 8—12 cps were reported; C. M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1008 (1957).

10) Ref. 5, p. 735.

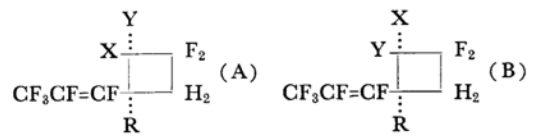
11) For coupling constants between the vicinal F–F, F–$CF_3$, F–$CH_3$, or $CF_3$–$CF_3$ on the double bond in fluoroalkenes, it was found that $J^{cis}_{F,F}<J^{trans}_{F,F}$; $J^{cis}_{F,CF_3}>J^{trans}_{F,CF_3}$; $J^{cis}_{F,CH_3}<J^{trans}_{F,CH_3}$; $J^{cis}_{CF_3,CF_3}>J^{trans}_{CF_3,CF_3}$.

12) For a recent review on Diels-Alder reactions of organic fluorine compounds, see D. R. A. Perry, "Fluorine Chemistry Reviews," Vol. 1, P. Tarrant, ed., Marcel Dekker, Inc., New York (1967), p. 253.

with the product obtained in the dehydrohalogenation of the (2-hydroperfluoropropyl)polyhalocyclobutanes (XI), which was prepared by the cycloaddition of 3,3,4,5,5,5-hexafluoro-1-pentene and trifluorochloroethylene.




The cycloadducts formed in the cycloadditions of trifluorochloroethylene or perfluoropropylene with I were found from their $^{19}F$ NMR spectra to consist of the two isomers A and B in approximately equal amounts.




## Experimental[13]

The NMR spectra were obtained using a JNM-C-60 high resolution spectrometer (60 Mc for $^1H$ and 56.4 Mc for $^{19}F$). Tetramethylsilane was used for $^1H$ as an internal standard and trifluoroacetic acid for $^{19}F$ as an external standard.

**3,4,5,5,5-Pentafluoro-1,3-pentadiene (Ia).** 3,3,4,5,5,5-Hexafluoro-1-pentene was prepared as reported in a previous paper.[3] In a 200 m*l* flask equipped with a stirrer and a reflux condenser was placed 105 g (0.59 mol) of the hexafluoro-1-pentene. After powdered potassium hydroxide (30 g) was added, the mixture was heated at 65—75°C for 1 hr with stirring. A gas chromatogram of the reaction mixture indicated that about 20% of the reactant was dehydrofluorinated. Addition of potassium hydroxide (30 g) and heating of the reaction mixture (65—75°C, 1 hr) were repeated four times. Distillation of the mixture gave 81 g (0.51 mol, 86% yield) of 3,4,5,5,5-pentafluoro-1,3-pentadiene, bp 40—41°C, $n_D^{20}$ 1.3372, $d_4^{20}$ 1.266, $\nu_{C=C}$ 1696 and 1612 $cm^{-1}$. The gas chromatogram and $^{19}F$ NMR spectrum of the pentadiene indicated that it consisted of almost exclusively the *cis* form.

Found: C, 38.65; H, 2.90%. Calcd for $C_5H_3F_5$: C, 37.99; H, 3.19%

When the pentadiene was stored in air, it polymerized gradually to yield viscous polymer, whose structure was confirmed to be $[-CF(CF_3)CF{=}CHCH_2-]_n$ from its $^{19}F$ NMR spectrum. $\delta_{CF_3}$ 2.3 ppm, $\delta_{-CF=}$ 41 ppm (broad doublet, $J_{H,F}$ 30 cps), $\delta_{-\underset{|}{CF}-}$ 95 ppm.

**2-Methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene (Ib).** *a) Dehydrofluorination with Solid Potassium Hydroxide.* 2-Methyl-3,3,4,5,5,5-hexafluoro-1-pentene (86 g, 0.43 mol) prepared as reported[3] was treated with powdered potassium hydroxide (144 g) as mentioned above to give 63 g (0.37 mol, 86% yield) of 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene, bp 61—62°C, $n_D^{20}$ 1.3357, $d_4^{20}$ 1.211, $\nu_{C=C}$ 1719 and 1644 $cm^{-1}$. The gas chromatogram (DOP column, 2 m, 84°C, carrier gas He, 37 m*l*/min) of the pentadiene obtained showed two peaks, that of the *cis* isomer (retention time, 5.0 min) and of the *trans* isomer (6.7 min), in a ratio of 97: 3.

Found: C, 41.81; H, 2.95%. Calcd for $C_6H_5F_5$: C, 41.87; H, 2.93%.

*b) Dehydrofluorination with Alcoholic Potassium Hydroxide Solution.* In a 300 m*l* flask with a stirrer was placed 50.2 g (0.26 mol) of the 2-methylhexafluoro-1-pentene. A solution of 25 g (0.45 mol) of potassium hydroxide in 150 m*l* of ethanol was added drop by drop and the mixture was poured into water. The organic layer (39.5 g) was separated, dried and distilled to give 34.5 g (0.20 mol, 77% yield) of the 2-methylpentafluoro-1,3-pentadiene, whose gas chromatogram showed presence of the *cis* and *trans* isomers in a ratio of 7: 3.

A similar treatment of the 2-methylhexafluoro-1-pentene with potassium hydroxide in methanol gave the 2-methylpentafluoro-1,3-pentadiene in a yield of 45%. The ratio of *cis* and *trans* was 6: 4.

**1-Methyl-2,3-difluoro-3-trifluoromethylcyclobutene (II).** A 300 m*l* stainless-steel autoclave was charged with 93 g (0.54 mol) of 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene (*cis* : *trans* 97: 3) and 10 g of Terpene B. The mixture was kept at 150°C for 21 hr. The resultant mixture was distilled to give a fraction boiling at 78—82°C and a viscous residue (20 g), which was presumed to be a mixture of Terpene B and the telomer of the pentadiene. The distillate consisted of 3.6 g of the unchanged pentadiene and 74 g (0.43 mol, 80% yield) of 1-methyl-2,3-difluoro-3-trifluoromethylcyclobutene, which was redistilled to give the pure II, bp 79—80°C, $n_D^{20}$ 1.3291, $d_4^{20}$ 1.263, $\nu_{C=C}$ 1738 $cm^{-1}$.

Found: C, 42.09; H, 2.99%. Calcd for $C_6H_5F_5$: C, 41.87; H, 2.93%.

The effect of the reaction temperature on the yield was shown in Table 2, which indicates an optimum temperature to be in 140—200°C. Above 200°C, the yield decreased presumably because of the polymerization of the pentadiene.

**α-Trifluoromethyl-β-acetylacrylic Acid (III).** An aqueous solution of potassium permanganate (58 g, 0.37 mol) was added to 42 g (0.24 mol) of 1-methyl-2,3-difluoro-3-trifluoromethylcyclobutene in acetone. After removal of manganese dioxide by filtration, the filtrate was acidified with sulfuric acid and extracted with ether. Vacuum distillation of the extract gave 24 g (0.13 mol, 54% yield) of crude α-trifluoromethyl-β-acetyl acrylic acid, bp 106—107°C/7 mmHg, and a tarry residue (11 g). The crude acid containing a small amount of α-fluoro-α-trifluoromethyl-β-acetylpropionic acid, $\delta_{CF_3}$ 2.1 ppm (doublet), $J_{CF_3,F}$ 7.5 cps, $\delta_{-\underset{|}{CF}-}$ 87 ppm (multiplet), was recrystallized from benzene to give white needles, mp 70—71°C.

Found: C, 38.72; H, 2.65%; Neut. equiv. 180.

13) All temperature readings are uncorrected.

Calcd for $C_6H_5O_3F_3$: C, 39.57; H, 2.77%; Neut. equiv. 182.

**Methyl and Ethyl α-Trifluoromethyl-β-acetylacrylate (V).** A mixture of α-trifluoromethyl-β-acetylacrylic acid (9 g), methanol (50 m*l*), benzene (30 m*l*), and *p*-toluenesulfonic acid was refluxed for 6 hr and extracted with ether. Distillation of the extract gave 3.5 g of methyl α-trifluoromethyl-β-acetylacrylate (a mixture of *trans* and *cis* isomers), bp 90—92°C/18 mmHg, $n_D^{20}$ 1.3992, $d_4^{20}$ 1.305.

Found: C, 42.53; H, 2.65%. Calcd for $C_7H_7O_3F_3$: C, 42. 87; H, 3.60%.

The gas chromatogram (Silicone DC-550 column, 2 m, 167°C, carrier gas He, 58 m*l*/min) of the methyl ester showed two peaks of the *trans* isomer (retention time, 6.6 min) and the *cis* isomer (10.7 min) in an area ratio of 8: 1.

Ethyl α-trifluoromethyl-β-acetylacrylate (10 g) was prepared from the acrylic acid (9 g) in a similar way as described above. The gas chromatogram of the ethyl ester showed two peaks, that of the *trans* (8.8 min) and of thd *cis* (19.8 min) in a ratio of 6: 1. bp 95—99°C/18 mmHg, $n_D^{20}$ 1.3998, $d_4^{20}$ 1.248.

Found: C, 45.40; H, 4.25%. Calcd for $C_8H_9O_3F_3$: C, 45.72; H, 4.32%.

**1-Fluoro-2-bromomethyl-4-bromo-4-trifluoromethylcyclobutene (VII) and 1-Fluoro-2-trifluoromethyl-4-bromo-4-bromomethyl-cyclobutene(VIII).** A mixture of 130 g (0.76 mol) of 1-methyl-2,3-difluoro-3-trifluoromethylcyclobutene and 30 g of powdered potassium hydroxide was heated at about 110°C for 1 hr with stirring. Addition of potassium hydroxide (30 g) was repeated seven times and the gas chromatogram of the reaction mixture indicated the formation of 27 g (0.18 mol, 24% yield) of 1-trifluoromethyl-2-fluoro-3-methylenecyclobutene. To the reaction mixture, bromine (29 g, 0.18 mol) was added drop by drop under UV irradiation, and the distillation of the mixture gave a fraction boiling at 63—68°C/18.5 mmHg (43 g, 0.14 mol, 78% yield), which was a mixture of the dibromocyclobutenes, 1,4-adduct VII and 1,2-adduct VIII in a ratio of 1: 1.2. The dibromocyclobutenes were separated by a preparative gas chromatograph.

VII: $n_D^{20}$ 1.4630, $d_4^{20}$ 1.953, $\nu_{C=C}$ 1724 $cm^{-1}$, $\delta_{CF_3}$ −4.0 ppm (singlet), $\delta_{-CF=}$ 21 ppm (triplet), $J_{CH_2,F}$ 13 cps.

Found: C, 23.11; H, 1.37%. Calcd for $C_6H_4F_4Br_2$: C, 23.11; H, 1.29%.

VIII: $n_D^{20}$ 1.4441, $d_4^{20}$ 1.927, $\nu_{C=C}$ 1736 $cm^{-1}$, $\delta_{CF_3}$ −14.0 ppm (doublet), $\delta_{-CF=}$ 11 ppm (triplet of quartet), $J_{CF_3,F}$ 10 cps, $J_{CH_2,F}$ 13 cps.

Found: C, 22.71; H, 1.42%. Calcd for $C_6H_4F_4Br_2$: C, 23.11; H, 1.29%.

**1-Trifluoromethyl-2-fluoro-3-methylenecyclobutene (VI).** The dibromocyclobutenes described above was treated with zinc dust in hexanol to give quantitatively 1-trifluoromethyl-2-fluoro-3-methylenecyclobutene, bp 42—43°C, $n_D^{20}$ 1.3640, $d_4^{20}$ 1.191, $\nu_{C=C}$ 1720 and 1671 $cm^{-1}$, $\delta_{CF_3}$ −13.6 ppm (doublet), $\delta_{-CF=}$ 17 ppm (multiplet), $J_{CF_3,F}$ 12 cps.

Found: C, 42.37; H, 2.85%. Calcd for $C_6H_4F_4$: C, 42.61; H, 2.89%.

**Preparations of the (Perfluoropropenyl)polyfluorocyclobutanes (IXa).** A mixture of 136 g (0.86 mol) of 3,4,5,5,5-pentafluoro-1,3-pentadiene, 99 g (0.85 mol) of trifluorochloroethylene, and 10 g of Terpene B in a 300 m*l* autoclave was heated at 200°C for 21 hr. The content was poured into methanol to yield white polymers (48 g), which were separated by filtration. The filtrate was treated with water to remove methanol, and an organic layer was distilled to give the unchanged pentadiene, hexafluorodichlorocyclobutane (14.2 g), and 116 g (0.42 mol, 49% yield) of 1-(perfluoropropenyl)-2-chloro-2,3,3-trifluorocyclobutane, bp 119—120°C.

The cross-cycloaddition of 3,4,5,5,5-pentafluoro-1,3-pentadiene and other polyfluoroolefins was carried out under similar conditions.

**Preparations of the (Perfluoropropenyl)methylpolyfluorocyclobutanes (IXb).** A mixture of 85 g (0.49 mol) of 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene, 70 g (0.53 mol) of 1,1-difluoro-2,2-dichloroethylene, and 10 g of Terpene B was charged into an autoclave and heated at 202°C for 24 hr. The contents were poured into methanol to give dark colored polymers (27 g), which were then filtered. After the filtrate had been treated with water, the organic layer was separated, dried, and distilled to give a small amount of tetrafluorotetrachlorocyclobutane, 8 g (0.04 mol, 9% yield) of II, and 54 g (0.18 mol, 36% yield) of 1-methyl-1-perfluoropropenyl -2,2- dichloro - 3,3 - difluorocyclobutene, bp 90—92°C/64 mmHg.

The cross-cycloaddition of 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene and other polyfluoroolefins was carried out under similar conditions.

**1-Perfluoropropenyl-2, 3, 3 - trifluorocyclobutene (Xa).** To 49 g (0.18 mol) of 1-perfluoropropenyl-2,3,3-trifluoro-2-chlorocyclobutane, 15 g (0.27 mol) of potassium hydroxide in 100 m*l* of ethanol were added drop by drop over a 1 hr period at room temperature. The mixture was stirred for 30 min and then poured into water. The organic layer (42 g) was separated, dried, and distilled to give 20 g (0.085 mol, 48% yield) of Xa, bp 80—81°C, $n_D^{20}$ 1.3551, $d_4^{20}$ 1.219, $\nu_{C=C}$ 1715 and 1663 $cm^{-1}$.

Found: C, 35.69; H, 1.19%. Calcd for $C_7H_2F_8$: C, 35.31; H, 0.85%.

**1-Perfluoropropenyl-2-chloro - 3,3 - difluorocyclobutene (Xb).** 1-Perfluoropropenyl-2,2-dichloro-3,3-difluorocyclobutane (33 g, 0.11 mol) was treated with potassium hydroxide as mentioned above to give 19.4 g (0.076 mole, 67% yield) of Xb, bp 120—121°C, $n_D^{20}$ 1.3958, $d_4^{20}$ 1.561, $\nu_{C=C}$ 1687 and 1601 $cm^{-1}$.

Found: C, 32.03; H, 0.79; Cl, 13.2%. Calcd for $C_7H_2F_7Cl$; C, 31.18; H, 0.87; Cl, 13.9%.

**1-Hexafluoropropyl-2-chloro - 2,3,3-trifluorocyclobutane (XI).** A mixture of 117 g (0.65 mol) of 3,3,4,5,5,5-hexafluoro-1-pentene, 98 g (0.84 mol) of trifluorochloroethylene, and 5 g of Terpene B was charged into a 300 m*l* autoclave and heated at 200°C for 48.5 hr. Distillation yielded 32 g (0.11 mol, 17% yield) of 1-hexafluoropropyl-2-chloro-2,3,3-trifluorocyclobutane, bp 80—82°C/138 mmHg, $n_D^{20}$ 1.3504, $d_4^{20}$ 1.592.

Found: C, 28.54; H, 1.37%. Calcd for $C_7H_4F_9Cl$: C, 28.72; H, 1.24%.

**1 - Hexafluoropropyl - 2,3,3 - trifluorocyclobutene (XII).** To 28 g (0.094 mol) of XI, 6.3 g (0.11 mol) of potassium hydroxide in 50 m*l* of ethanol were added dropwise at room temperature. The mixture was poured into water and the organic layer (25 g) was separated and distilled to give 8.2 g (0.032 mole, 34% yield) of 1-hexafluoropropyl-2,3,3-trifluorocyclobutene, bp 93—96°C, $n_D^{20}$ 1.3202, $d_4^{20}$ 1.529, $\nu_{C=C}$ 1733 $cm^{-1}$.

Found: C, 32.57; H, 1.17%. Calcd for $C_7H_3F_9$: C, 32.01; H, 1.33%.

Treatment of XII with powdered potassium hydroxide produced (perfluoropropenyl)trifluorocyclobutene Xa in a yield of 50%.

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