Cyclization during the Dehydrohalogenation of Perfluoroalkyl-Substituted Iodoalkylmalonates. Thermal Rearrangement of the Derived 2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylates

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3-Perfluoroalkyl-2-iodopropylmalonic esters (**1a–e**) cyclized during reaction with bases in aqueous and nonaqueous systems to give 2-(perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic acids (**6a–e**) and diesters (**5a–e**) in excellent yield. The higher homolog 4-perfluoroalkyl-3-iodobutylmalonate cyclized only in part, but was also dehydrohalogenated to $R_FCH{=}CHCH_2CH_2CH(COOR)_2$, R = Et, H. The cyclopropane diesters **5b** and **5c** rearranged thermally at 225–240° by a sigmatropic, 1,5-hydrogen shift to $R_FCH{=}CHCH_2CH(COOEt)_2$ (**3b, 3c**). The cyclopropanedicarboxylic acids **6b** and **6c** decarboxylated and rearranged at 175–200° to a mixture of $R_FCH{=}CHCH_2CH_2COOH$ (**13**) and *cis*- and *trans*-2-(perfluoroalkyl)methylcyclopropanecarboxylic acids (**15**). At reduced CO_2 pressure rearrangement was almost completely suppressed in favor of decarboxylation to **15**. *cis*-**15**, but not *trans*-**15**, slowly isomerized at a higher temperature to **13**. No reaction occurred under conditions which gave **13** from **6**. A concerted rearrangement and decarboxylation of **6** is probable, facilitated by both opening of the strained ring and release of CO_2.

The purpose of this research was to explore the behavior of perfluoroalkyl-substituted iodoalkylmalonic acids and esters, readily obtained by free-radical addition of iodoperfluoroalkanes (R_FI) to alkenylmalonic acids and esters.[1] These addition reactions were efficiently catalyzed by 2,2′-azobis-2-(methylpropionitrile) (ABN) initiator at 70°.

$$R_FI + CH_2{=}CH(CH_2)_mCH(COOEt)_2 \xrightarrow{ABN} R_FCH_2CHI(CH_2)_mCH(COOEt)_2$$

	R_F	m	convn	yield
1a	$(CF_3)_2CF$	1	87%	88%
1b–e	$CF_3(CF_2)_n$ n = 1–7	1	85	95
1f	$CF_3(CF_2)_3$	2	85	95
1g	$CF_3(CF_2)_5$	2	89	95

Certain perfluoroalkyl-substituted iodoalkenylmalonic esters were also prepared by addition of R_FI to 2-propynylmalonic ester. This was an inefficient reaction, however,

$$R_FI + HC{\equiv}CCH_2CH(COOEt)_2 \xrightarrow{ABN} R_FCH{=}CICH_2CH(COOEt)_2$$

	R_F	convn	yield
2b	$CF_3CF_2CF_2$	39%	85%
2c	$CF_3(CF_2)_3$	23	95

$$R_FCH{=}CICH_2CH(COOEt)_2 \xrightarrow{Zn/H^+} R_FCH{=}CHCH_2CH(COOEt)_2$$

	R_F	yield
3b	$CF_3CF_2CF_2$	86%
3c	$CF_3(CF_2)_3$	86

$$R_FCH{=}CHCH_2CH(COOEt)_2 \xrightarrow{OH^-} R_FCH{=}CHCH_2CH(COOH)_2$$

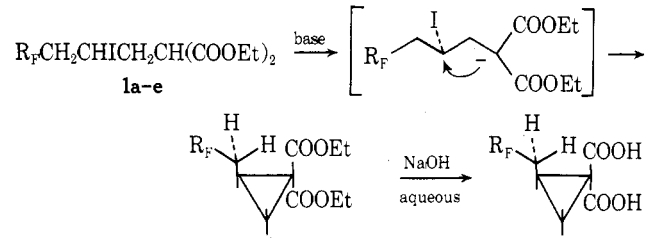
	R_F	yield
4b	$CF_3CF_2CF_2$	95%
4c	$CF_3(CF_2)_3$	96

and suffered from wastage of the initiator by the acetylenic ester. Reduction of adducts **2b** and **2c** by zinc and acid in anhydrous ethanol, followed by hydrolysis,[2] gave a group of related unsaturated esters (**3b, 3c**) and acids (**4b, 4c**) which were useful in comparing structures and properties. These syntheses were similar to those previously reported.[3,4] Reactions of diethyl perfluoroalkyl-2- or -3-iodoalkylmalonates **1a–g** were found to give unexpected and varied results. Additionally, thermal behavior of the novel cyclic products proved to be of unusual interest.

Results

Dehydrohalogenation of 3-perfluoroalkyl-2-iodopropylmalonic esters **1a–e** gave entirely cyclization to 2-(perfluoroalkyl)methylcyclopropanedicarboxylic acids and esters, as reported in a preliminary fashion.[5] Reaction of **1a–e** with ethoxide ion in anhydrous ethanol or by sodium hydride in benzene suspension took place via the carbanion (Chart I), and internal displacement of iodide ion gave cyclization to the cyclopropane-1,1-dicarboxylates **5a–e**. No olefinic product was formed by E2 elimination, as was shown by comparison with authentic compounds **3b** and **3c**.

Chart I
Cyclization of Diethyl 3-Perfluoroalkyl-2-iodopropylmalonates



5b, 88%, NaOEt-EtOH
5c, 85%, NaH-benzene

6a–e, 95–100%

Subsequent hydrolysis of **5b** in aqueous ethanol using sodium hydroxide as base gave crystalline 2-(perfluoropropyl)methylcyclopropane-1,1-dicarboxylic acid (**6b**) in 89% yield. In aqueous ethanol at 40–80° cyclization of iodopropyl esters **1a–e** (all R_F groups) with excess hydroxide went rapidly and exothermically; hydrolysis of the ester groups occurred inter alia and a quantitative yield of the corresponding R_F-substituted cyclopropane-1,1-dicarboxylic acids **6a–e** was obtained in each case. Reaction conditions and some physical constants of the acids are briefly recorded in Table I.

Reaction undoubtedly occurred by the sequence shown in Chart I, since reaction of the iodopropyl ester **1c** with a deficiency of base in aqueous ethanol gave some diethyl 2-(perfluorobutyl)methylcyclopropane-1,1-dicarboxylate

Table I
Preparation of 2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic Acids (6a–e)

Iodopropyl ester							
	R_F	mol	NaOH, mol	Time, hr	Temp, °C	Acid	Mp, °C
1a	$(CF_3)_2CF$	0.030	0.12	5	80	6a	128–129
1b	$CF_3(CF_2)_2$	0.030	0.15	7	80	6b	81–82[a]
1c	$CF_3(CF_2)_3$	0.0183	0.0652	5	40	6c	95
1d	$CF_3(CF_2)_5$	0.0200	0.0700	5	50	6d	127[b]
1e	$CF_3(CF_2)_7$	0.0100	0.0400	4	50	6e	132[b]

[a] Monohydrate, mp 94–95°, from benzene solution. [b] Monohydrate.

Table II
NMR Spectral Data for Isomeric 2-(Perfluoropropyl)methylcyclopropane-1,1-dicarboxylic Acids (6a and 6b)

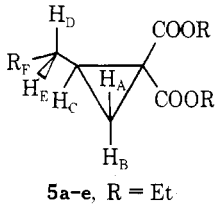
Proton	δ	Multiplicity	J, Hz (±0.2 Hz)
H_A	1.8	Doublet of doublets	$J_{AB} = 3.5^{a,b}$
H_B	2.02	Doublet of doublets	$J_{BC} = 9.0^a, 8.7^b$
H_C	2.49	Multiplet[c]	$J_{AC} = 7.5^{a,b}$
H_D, H_E[a]	2.75[a]	Multiplet of doublet[a]	$J_{DC} = J_{EC} = 7.7^a, 7.5^{b,d}$
H_D, H_E[b]	2.9[b]	Multiplet of doublet[b]	$J_{HF} = 21.5^a, 19.5^{b,d}$

[a] NMR spectrum of **6a**. [b] NMR spectrum of **6b**. [c] Actually a quintet owing to essentially equal values of coupling constants. [d] J_{DE} could not be determined owing to similar chemical shifts for H_D and H_E.

(**5c**), albeit in reduced yield. In subsequent studies it is hoped to determine whether it is possible to trap the carbanion in anhydrous systems before cyclization occurs, by reaction with another alkyl halide, for example.

Spectral Data. The R_F-substituted cyclopropane-1,1-dicarboxylic acids and esters were characterized by ir and nmr spectra. The dicarboxylic acids **6a–e** showed a carbonyl stretching band at 1735 cm^{-1} and a very strong band at 1640 cm^{-1}, not affected by method of analysis. This was unusual, as other 1,1-dicarboxylic acids such as **4b** or $R_F(CH_2)_3CH(COOH)_2$ had a single stretching band at 1705 cm^{-1}.[3] The diesters **5a–e** had a carbonyl band at 1735 cm^{-1} and CH bands at 1400 and 1325 cm^{-1} (cyclopropyl ring).[6] A band at 1350 cm^{-1} appeared in both **1b** and **5b** and is probably associated with R_FCH_2 deformation. It appears that bands at 1410, 1070, 990, and 940 cm^{-1} are characteristic of these substituted cyclopropanes and are absent in the straight-chain compounds.

NMR spectra of **6a–e** (acetone-d_6) at 60 HMz gave a cluster of lines for cyclopropyl ring protons (H_A, H_B, H_C) at δ 1.5–2.5, R_FCH_2 protons (H_D, H_E) at δ 2.9, and carboxyl group protons as a single line at δ 10.75, having correct areas for each type of proton. NMR spectra of isomeric 2-(perfluoropropyl)methylcyclopropane-1,1-dicarboxylic acids **6a** and **6b** were also run at 100.1 MHz in pyridine solution, as these structures afforded an opportunity to observe the effect of two closely related R_F groups in a well-defined structure (Table II).[7]



5a–e, R = Et
6a–e, R = H

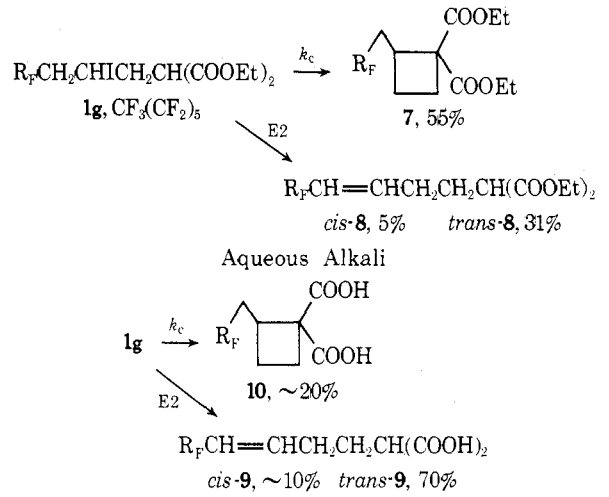
The R_FCH_2 protons (H_D, H_E) of **6a** appeared as a multiplet of a doublet, owing to coupling of the single F with adjacent nonequivalent CH_2 protons (J_{HF} = 21.5 Hz, J_{DE} = J_{EC} = 7.7 Hz). Further analysis, using ^{19}F resonance and decoupling showed the CF_3 groups to be nonequivalent and coupled to each other and to the CF group. Each CF_3 resonance appeared as five lines, having $J_{CF_3CFCF_3}$ = 8 ± 0.3 and J_{CF_3CF} = 6.5 ± 0.3 Hz. The CF resonance consisted of a multiplet of at least 16 lines, which were reduced to an approximate triplet having J_{HF} = 21.5 Hz by double ^{19}F resonance. The triplet nature of the CF resonance was only evident after decoupling from the CF_3 signals. The R_FCH_2 protons of **6b** gave a multiplet of a triplet as expected for two adjacent F atoms (J_{HF} = 19.5 Hz). The proton resonance for H_C turned out to be a quintet from nearly equal coupling constants of four adjacent hydrogens.

Diesters **5b** and **5c** gave two overlapping quartets at δ 4.18 for two methylenes of the ethyl ester groups, as the two CH_2 proton sets were evidently nonequivalent. By contrast, the unsaturated isomers **3a** and **3c** gave a single quartet at δ 4.2; they also showed typical olefinic proton resonances at δ 5.2–6.8 (very useful later for identification) and a multiplet near δ 3.0 for the methine proton.

Cyclization of Higher Homologs. Dehydrohalogenation of $R_FCH_2CHICH_2CH_2CH(COOEt)_2$ (**1g**) by sodium hydride at 60–70° gave 96% of an ester mixture (Chart II). Gas chromatography (GLC) of a sample removed before distillation showed 54.7% of cyclobutyl ester **7**, 5.0% of cis ester, and 31.4% of trans ester **8**. Pure **7** had no olefinic resonance in its pmr spectrum; cyclobutyl protons were seen at δ 1.8–2.7 and two quartets of the nonequivalent methylenes of the ester groups at δ 4.2 and 4.25. The cis and trans olefinic ester **8** showed the methine proton at δ 3.2 as a triplet (J = 6 Hz). Reaction of **1g** with sodium hydroxide in aqueous ethanol at 50° gave solid acid mixture **9–10** in quantitative yield. Recrystallization afforded pure *trans* **9** in a recovery of 70%, and a residue of *cis*- and *trans* **9** with **10**. Quantitative estimation was difficult because of the thermally sensitive nature of the malonic acid **9**. Similarly, reaction of **1f** gave the isomeric unsaturated malonic acid (*cis*- and *trans* **11**) as the chief product with a little of the cyclobutyl compound **12**, as shown by comparison of NMR spectra.

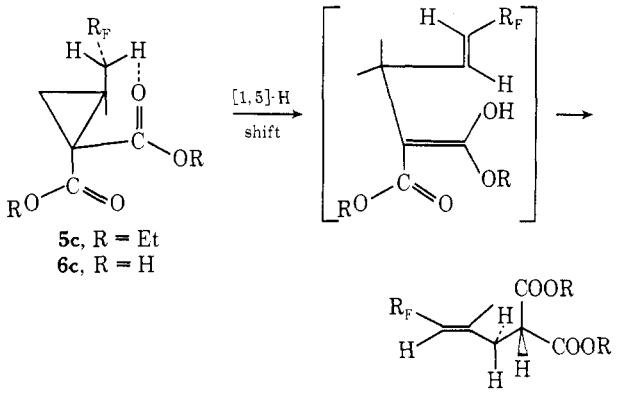
1,5-Hydrogen Shift Rearrangement of 2-(Perfluoroalkyl) Methylcyclopropanedicarboxylates. Isomerization of **5c** to diethyl 3-perfluorobutyl-2-propenylmalon-

Chart II
Cyclization vs. Elimination in Dehydrohalogenation of 4-Perfluoroalkyl-3-iodobutylmalonic Ester



ate (**3c**) occurred very slowly at 200° but more rapidly at 225–242° (Chart III). Reaction was followed by GLC, using as standard reference compound the diester **3c** previously prepared (see introduction). The course of isomerization is summarized in Table III, and was accompanied by the formation of two side products in small yield.

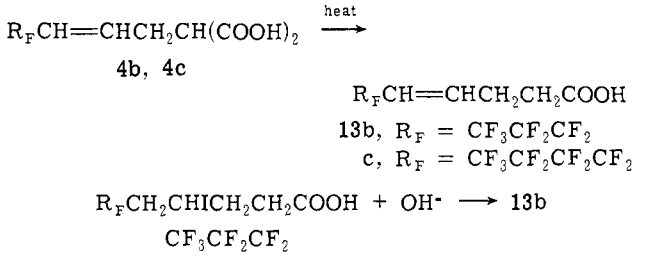
Chart III
Rearrangement of Perfluoroalkyl Methylcyclopropanedicarboxylates



The unsaturated dicarboxylic acid **4c**, obtained by the 1,5-hydrogen shift pathway (or synthesized by an independent route), was unstable and immediately decarboxylated. The malonic acid **4c** thus could not be isolated from this reaction. The conditions were too severe. The product actually isolated was $R_FCH{=}CHCH_2CH_2COOH$ (**13**), which does not cyclize to a cyclopropane derivative. Experimental evidence was obtained as follows. The malonic acids **4b** and **4c** were prepared via addition of perfluoroalkyl iodides to an alkynylmalonate and subsequent steps, as previously shown. The crystalline malonic acid **4b** or **4c**, with the double bond adjacent to the R_F group, when heated to just over 125° decarboxylated, giving the perfluoroalkyl-4-pentenoic acid **13**. This is the same acid as found in the thermal rearrangement of **6b** or **6c**. **13b** had been previously prepared by dehydrohalogenation as indicated, and its structure determined.[4]

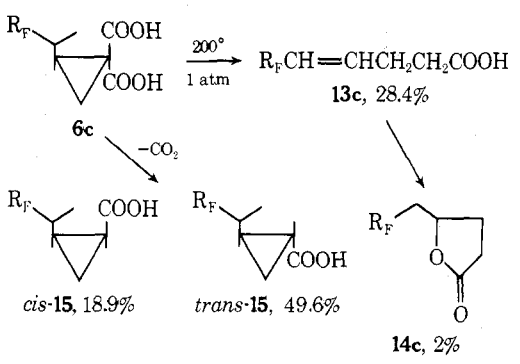
Table III
Isomerization of Diethyl 2-(Perfluorobutyl)-methylcyclopropane-1,1-dicarboxylate (5c) to Diethyl 3-Perfluorobutyl-2-propenylmalonate (3c)

Time, hr	Total, hr	Temp, °C	5c, %	3c, %	Others, %
3	3	200	90.3	2.8	1.5, 3.5
5	8	225	75.4	20.4	1.3, 2.5
4	12	242	57.7	42.4	4.6, 2.5
12	24	242	14.0	85.2	6.0



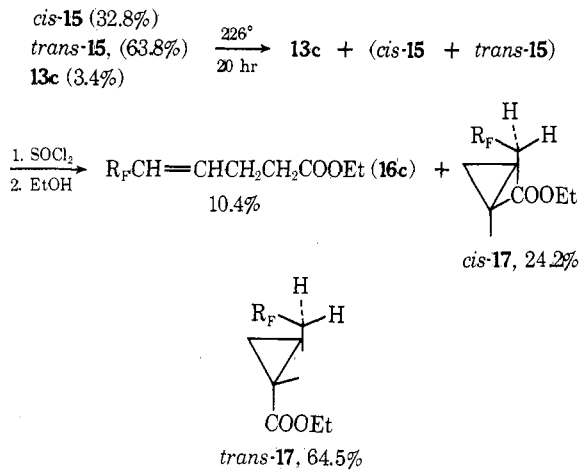
Thermal behavior of the cyclopropanedicarboxylic acids **6b** and **6c** was actually much more complex than that of the corresponding diesters **5b** and **5c**. It was found that two simultaneous reactions occurred when the diacids were heated and their relative rates depended on reaction conditions. Also the diacids were very much more labile than the diesters. At 200° in 1 hr *in an open flask* decomposition of **6c** was complete and the evolution of CO_2 (quantitative) had ceased. Subsequent analysis of the product mixture revealed that both 1,5-hydrogen shift and simple decarboxylation to *cis*- and *trans*-2-(perfluoroalkyl)methylcyclopropanecarboxylic acid (**15**) had occurred (Chart IV). The ratio of **13c** to **15** was 3:7. When **6c** was heated *in a sealed tube* at 196° for 3 hr the relative amounts of **13c** and *cis*- and *trans*-**15** was 3:2. If CO_2 was continuously swept out *under reduced pressure in a distilling apparatus*, thermal rearrangement was almost completely suppressed. At 165–173° and 15–25 mm pressure the ratio of **13c** to **15** was 3:97. Distillation afforded 3.4% of **13c**, 63.8% of *trans*-**15**, and 32.8% of *cis*-**15** in 95% yield. Even at 202° (65 mm) the product comprised nearly pure *cis*- and *trans*-**15**. *trans*-**15** crystallized from the mixture and was characterized by spectral and other means.

Chart IV
Rearrangement and Decarboxylation of 2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic Acids



The small amount of lactone **14** formed under certain conditions was indicated by a strong band at 1780 cm^{-1} in ir spectra, and a separate peak in GLC analysis. Lactonization had previously been observed in reactions of related substances.[3]

At a considerably higher temperature the *cis*-2-(perfluoroalkyl)methylcyclopropanecarboxylic acid (*cis*-**15**) slowly isomerized to **13.** A mixture of cis and trans or pure trans isomer of **15** was unchanged by heating at 196° for 3 hr or longer, but at 226° *cis*-**15** gave 7% of **13c** in 20 hr, while the amount of *trans*-**15** present remained unchanged. In order to quantify these reactions the acid mixtures (**13c,** *cis*- and *trans*-**15**) were converted to ethyl esters (**16c** and *cis*- and *trans*-**17**) by way of the acid chlorides. Conversions were quantitative and GLC analysis correlated well with area ratios of olefinic protons for **13c:15** or **16c:17.** Nearly pure *trans*-**17** was isolated by fractional distillation and served to identify GLC peaks.



Discussion

Dehydrohalogenation of perfluoroalkyl-2- or -3-iodoalkylmalonic esters (**1a–g,** Charts I and II) may be contrasted with analogous reactions of ω-halogenoalkymalonic esters [$X(CH_2)_nCH(COOEt)_2$, X = Cl or Br, *n* = 2, 3, 4, or 5] which gave as sole product the cycloalkane-1,1-dicarboxylic ester. Intramolecular nucleophilic substitution of the intermediate carbanion in the rate-determining step was demonstrated.[8–10] Formation of three-membered rings was very much faster than that of four-, five-, or six-membered rings. When X = Br relative rates were 3:5:4:6 ring = 80,000:800:2.5:1.[8] For the perfluoroalkyl-substituted esters the acidifying effect of an R_F group should increase the rate of base attack on the R_FCH_2 protons of **1a–g** at the expense of internal displacement (k_c) by the carbanion of the CHI group.[11,12] Steric hindrance for the approach of the carbanion to a secondary CHI would be greater than to a terminal CH_2I. These considerations help to explain the lack of specificity for base attack on the R_F-substituted iodobutylmalonates, **1f** and **1g.** For the 3-perfluoroalkyl-2-iodopropylmalonates **1a–e,** the unfavorable enthalpy of activation for three-membered ring formation may be partly offset by a higher entropy term, since closing the ring becomes more difficult as the ends become farther separated.[13,14]

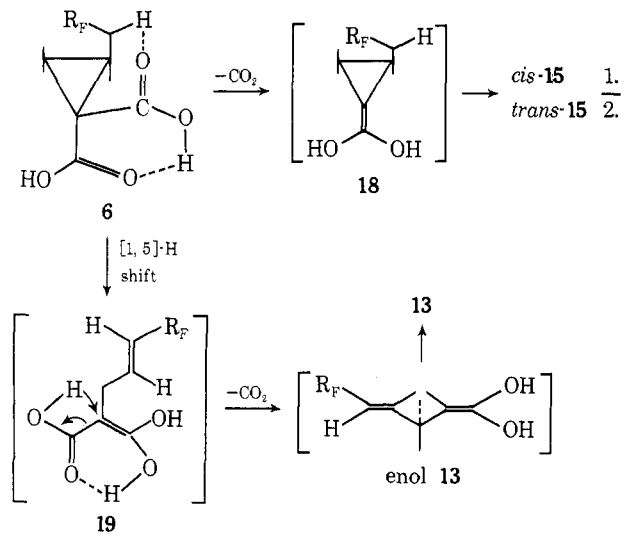
Knipe and Stirling further suggested that resonance interaction of the cyclopropane ring (as a conjugated unsaturated system) and a substituent serves to lower the enthalpy of activation.[8] There is good evidence for stabilization by cyclopropane, but not for higher homologs.[10] Thermal isomerization of R_FCH_2-cyclopropane-1,1-dicarboxylates belongs to the class of Cope rearrangements.[15] A six-membered transition state, drawn in the form of a chair (Chart III), is postulated. This type of reaction has been called an "enolene rearrangement" since the intermediate possesses an enol form, and the process generates an alkene.[16] It has formal similarity to other suprafacial sigmatropic 1,5-hydrogen shift processes.[17] Previous studies employing ethyl *cis*- and *trans*-1-methyl-2-methylcyclopropanecarboxylate[18] and *cis*- and *trans*-1-acetyl-2-methylcyclopropane[16] have shown that hydrogen transfers from the same side but not from the opposite side of the ring.[19] Conversion of *cis*-**15** to **13c** is another example and failure of *trans*-**15** to rearrange fits into this picture nicely.

Thermal rearrangement of diesters **5a–e** constitutes a potentially useful synthesis of R_F-substituted malonic esters **3** or the acids **4,** as free-radical addition of perfluoroalkyl iodides to the alkynylmalonates was an inefficient process.

The most surprising results of this study were (a) the remarkable dependence of thermal rearrangement–simple decarboxylation of diacids **6** on the conditions of reaction; and (b) the facility with which decomposition of the diacids **6** occurred compared with the diesters **5.** Decarboxylation of **6c** to *cis*- and *trans*-**15** was favored over Cope rearrangement to **13c** by reduced CO_2 pressure. This appears to involve an intermediate **18** leading to the final product **15,** and a competitive pathway leading to another intermediate **19** and final products, CO_2 and **13** (Chart V).[20]

Decarboxylation is known to proceed by means of a cyclic intermediate which achieves the highly strained structure **18** at the expense of release of energy in CO_2 formation.[21,22] The 2:1 preference for *trans*-**15** over *cis*-**15** (Chart IV) is then explained by proton transfer back to the ring in such a way as to minimize steric repulsion between the bulky and electronegative R_FCH_2 and COOH groups.

Chart V
Cope Rearrangement vs. Decarboxylation of 2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic Acids



The intermediate form **19** depicted in Chart V should be compared with the Cope intermediate shown in Chart III. It can be seen that simultaneously with enolene formation, transfer of a proton of the second carboxyl group to an ene carbon of **19** will permit the departure of the CO_2 molecule and generate directly the enol form of **13.** In this way the [1,5]-hydrogen shift and decarboxylation to **13** may become concerted. Indeed, relief of ring strain in opening the cyclopropane would assist the decarboxylation step as well.[21] These suggestions appear to offer a consistent explanation for the unusual results of this study. Further work will be necessary to determine thermodynamic values, rate factors, and the influence of structural variations on the course of this rearrangement.

Table IV
Preparation of Diethyl 3-Perfluoroalkyl-2-iodoalkylmalonates (1a-g)[a]

			Alkenyl malonate			Iodoalkyl ester					
R_F	R_FI, mol	ABN, mol × 10^{-3}	Compd	Mol	Reaction time, hr	Compd	Convn, %	Yield, %	Bp, C	(mm)	$n^{25}D$
$(CF_3)_2CF$	0.100	1.00	**20**	0.075	20	**1a**	87	88	97	(0.30)	1.4200
$CF_3(CF_2)_2$	0.100	1.00	**20**	0.075	19	**1b**	81	94	104	(0.30)	1.4210
$CF_3(CF_2)_3$	0.179	3.00	**20**	0.150	17	**1c**	85	96	100	(0.10)	1.4122
$CF_3(CF_2)_3$	0.0413	0.610	**21**	0.0325	17	**1f**	85	93	111	(0.20)	1.4168
$CF_3(CF_2)_5$	0.0500	1.00	**20**	0.050	20	**1d**	89	95	124	(0.50)	1.3994
$CF_3(CF_2)_5$	0.0500	1.00	**21**	0.050	20	**1g**	89	95	137	(0.60)	1.4040
$CF_3(CF_2)_7$	0.0250	0.500	**20**	0.0250	18	**1e**	87	94	142	(0.60)	1.3905

[a] Satisfactory analytical data (±0.4% for C, H, F, or I) were reported for all new compounds listed in the table.

Experimental Section

Source of Materials and Physical Measurements. Diethyl 2-propenylmalonate (**20**), bp 115° (19 mm), $n^{25}D$ 1.4307 [lit.[23] bp 116–124° (20 mm)], diethyl 3-butenylmalonate (**21**), 36% yield from 4-chloro-1-butene or 59% yield from 4-bromo-1-butene, bp 132° (23 mm), $n^{25}D$ 1.4315 [lit.[24] bp 116–121° (12 mm)], and diethyl 2-propynylmalonate (**22**), bp 117° (9 mm), $n^{25}D$ 1.4356 [lit.[25] bp 109.5° (13 mm), $n^{20}D$ 1.4384], were prepared by the literature method.[26] 2-Iodoperfluoropropane was a gift from E. I. du Pont de Nemours and Co. The perfluoroalkyl iodides, $CF_3(CF_2)_nI$ (n = 3, 5, 7), were a gift from Ciba-Geigy Corp., through the courtesy of Dr. E. K. Kleiner. The physical constants were those previously given.[2] 2,2′-Azobis-2-(methylpropionitrile) (ABN) was obtained from Eastman Kodak Co.

Melting points were observed using a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. NMR spectra were observed using a Varian T-60 spectrophotometer and as indicated, at 100.1 MHz.[7] Gas chromatographic analyses were done using a Sargent-Welch thermal conductivity instrument and under conditions which are listed where appropriate.

Preparation of Diethyl 3-Perfluoroalkyl-2-iodopropylmalonates and Diethyl 4-Perfluoroalkyl-3-iodobutylmalonates. Table IV summarizes the free-radical addition of perfluoroalkyl iodides to **20** and **21**. Analytical data for all new compounds are presented in Table V.[27] NMR and ir spectral data were consistent in each case. A typical procedure follows Table IV.

Diethyl 3-Perfluorooctyl-2-iodopropylmalonate (1e). A heavy-wall glass tube was charged with 1-iodoperfluorooctane (13.65 g, 0.0250 mol), **20** (5.00 g, 0.0250 mol), and ABN (0.0821 g, 5.00 mmol), cooled to −78°, evacuated and filled three times with nitrogen, and sealed. The tube was immersed in an oil bath at 70° for 18 hr, opened, and rinsed out with pentane through a sintered glass filter. The clear, colorless liquid was distilled in a short-path still without a column, heating with an oil bath up to 170°: **1e**, bp 142° (0.65 mm), $n^{25}D$ 1.3900, 16.3 g (87%); ir $\nu_{C=O}$ 1735 cm^{-1}; NMR δ 3.75 (t, J = 6 Hz, $CH_2CH(COOEt)_2$), 4.18 (m, overlapped peaks of CHI and $COOCH_2CH_3$). Residual oil (0.60 g), trap liquid (0.47 g), and a few drops of forerun were also obtained. Analyses are in Table V.

Preparation of Diethyl 3-Perfluoroalkyl-2-iodo-2-propynylmalonates. A. 2b from 1-Iodoperfluoropropane and Diethyl 2-Propynylmalonate (22). 22 (15.85 g, 0.0800 mol), 1-iodoperfluoropropane (29.6 g, 0.100 mol), and ABN (0.164 g, 1.00 mmol) under identical conditions with those given above gave recovered R_FI (19.4 g, 65%), **22** (9.0 g, 57%), and diethyl 2-iodo-4,4,5,5,6,6,6-heptafluoro-2-hexenylmalonate (**2b**), bp 122° (2.4 mm), $n^{25}D$ 1.4282, 12.7 g, and residual oil, 1.0 g. Redistillation of combined cuts in a 2-ft platinum spinning band column afforded pure **2b**, 14.4 g (39.2% conversion, 85% yield): ir ν_{OH} 3080 (w), $\nu_{C=O}$ 1750, $\nu_{C=C}$ 1640, bands at 1040, 975, 960, 940, 920, 860, 750, and 540 cm^{-1} (these results indicated that both cis and trans isomers were present);[4] NMR δ 3.30 (2 protons, d, J = 7 Hz, CH_2CH), 3.80 (1 proton, t, J = 7 Hz, CH_2CH), 6.60 (1 proton, t, J_{HF} = 14 Hz, $CF_2CH{=}CI$).

B. From 1-Iodoperfluorobutane and 22. 22 (19.8 g, 0.100 mol), 1-iodoperfluorobutane (27.6 g, 0.0800 mol), and ABN (0.164 g, 1.00 mmol) gave diethyl 2-iodo-4,4,5,5,6,6,7,7,7-nonafluoro-2-heptenylmalonate (**2c**), bp 98° (0.32 mm), $n^{24}D$ 1.4210, 10.3 g, 23% conversion and 95% yield based on recovered starting materials.

Zinc Reduction of Diethyl 2-Iodo-4,4,5,5,6,6,6-heptafluoro-2-hexenylmalonate (2b) to Diethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenylmalonate (3b). 2b (10.0 g, 0.0202 mol), ethanol (50 ml), and zinc (6.5 g, 0.10 g-atom, 30 mesh) was stirred while anhydrous hydrogen chloride was passed in at 75° until hydrogen gas evolution began. After 0.5 and 4 hr reaction times, zinc (6.5 g) was added. HCl gas was fed in momentarily as needed, to maintain gas evolution during the reaction. After 6.5 hr the liquid was poured into 100 ml of water and extracted three times with 20 ml of CCl_4. The organic layer was rinsed with water, dried over $MgSO_4$, and distilled in a 24-in. platinum spinning band column. Diethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenylmalonate (**3b**) had bp 120° (8.0 mm); $n^{25}D$ 1.3805; 6.4 g (86%); ir (neat, KBr) $\nu_{C=O}$ 1750, $\nu_{C=C}$ 1675, δ_{CH} 1470, 1450, 1375, 1350; and bands at 970, 940 (w), 860, and 750 cm^{-1}; NMR δ 1.25 (6 protons, t, J = 7 Hz, OCH_2CH_3), 2.85 (2 protons, m, CH_2CH), 3.3–3.9 (1 proton, m, $CH(COOC_2H_5)_2$), 4.2 (4 protons, q, J = 7 Hz, OCH_2CH_3), 5.0–6.8 (2 protons, m, cis and trans CH=CH.

Diethyl 4,4,5,5,6,6,7,7,7-Nonafluoro-2-heptenylmalonate (3c). In similar fashion diethyl 2-iodo-4,4,5,5,6,6,7,7,7-nonafluoro-2-heptenylmalonate (**2c**, 7.3 g, 0.013 mol) gave *cis*- and *trans*-**3c**, bp 116° (3.0 mm), $n^{25}D$ 1.3747, 4.4 g (70%).

Hydrolysis of 3b to $CF_3CF_2CF_2CH{=}CHCH_2CH(COOH)_2$ (4b) and Decarboxylation of 4b to $CF_3CF_2CF_2CH{=}CHCH_2CH_2COOH$ (13b). 3b (4.6 g, 0.0125 mol) was added to a solution of NaOH (1.1 g, 0.050 mol) in water (2.5 ml) and ethanol (23 ml), kept at 70° for 5 hr, diluted to 100 ml with water, and acidified with 6N HCl (20 ml). **4b** was extracted into dichloromethane (three times, 15 ml), dried over $MgSO_4$, and evaporated (2.7 g, 95%) to partly crystalline *cis*- and *trans*-**4b**: ir $\nu_{C=O}$ 1725, $\nu_{C=C}$ 1675 (w), δ_{CH} 1410, 1350, $\gamma_{C=C}$ 970 (s) and 940–930 cm^{-1}. The mixture when recrystallized from CCl_4 and then $HCCl_3$ gave pure *trans*-**4b**, mp (sinter 75°) 79–80°, evolved CO_2 at 122–130°. The residual oil was heated to ca. 150° for 10 hr and **13b** distilled, bp 68° (0.25 mm), $n^{25}D$ 1.3630, 1.4 g, identical with the sample previously prepared.[4]

2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic Acids (6a–e). Typical Procedure. NaOH (6.0 g, 0.15 mol) in water (7 ml) and ethanol (63 ml) was added while stirring to **1b** (14.8 g, 0.0299 mol) in ethanol (60 ml) and kept at 60–80° for 7 hr, diluted to 200 ml with water, and acidified with hydrochloric acid. Solid acid **6b**, dried at ambient temperature, was obtained as the monohydrate (9.4 g, 96% of theory), mp (sinter 89°) 91–92°, recrystallized from benzene, mp 94–95°. **6b** monohydrate lost water of hydration when stored over P_2O_5 for several weeks, or dried in a vacuum oven at 60° overnight; the melting point dropped to 81–82°. Samples of **6b** monohydrate and of **6b** were titrated in 50% aqueous ethanol with 0.02514 N sodium hydroxide solution, using a pH meter. A pH–volume plot for **6b** monohydrate gave midpoints of breaks in the curve at pH 5.6 and 10.6, with equivalent weights of 343 and 164. Anhydrous **6b** gave midpoints at pH 5.3 and 10.1, with equivalent weights of 318 and 155. Ir (KBr disk) ν_{COOH} 3560, $\nu_{C=O}$ 1730, 1640, δ_{CH} 1410, 1360, ν_{CF} 1290, 1270, 1225; bands at 1170, 1165, 1125, 1105, 1070, 1060, 995, 945, 805, 780, 775, 695, and 530 cm^{-1}. For NMR spectral data see Table II. Preparations of related compounds are listed in Table I.

Sodium Ethoxide Induced Cyclization. Diethyl 2-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,1-cyclopropanedicarboxylate (5b). 1b (10.0 g, 0.0200 mol) was added dropwise to a solution of sodium (0.4702 g, 0.0204 mol) in anhydrous ethanol [distilled from $Mg(OCH_3)_2$] at 56–62° during 20 min, with stirring by a magnet bar. The clear yellow solution was kept at 62° for 16 hr, 55 ml of 6.0 N HCl and 50 ml of water were added, and the orange oil

Table VI
Fractionation of 7, 8 Mixture

Fraction	Bp, °C (mm)	Wt, g	Retention time, min[a] 6.5	8.2	9.2	15.2	20.8	23.0
I	95(0.30)	0.79	5.0%	3.1%		89.1%	0.60%	1.2%
II	93–97 (0.25)	1.93	4.3	5.8		68.5		
III	97(0.20)	0.74	2.4	1.4	4.5	16.4	72.3	3.0
IV	82(0.15)	1.04	1.1	0.63	0.94	4.26	78.2	14.9
Original sample		6.4				54.7	31.4	4.95
Identity of substance								*cis*-8 7 *trans*-8

[a] GLC analysis using a 6-ft SE-30 silicone oil column at 160°.

was extracted with ether (3 × 15 ml) and benzene (15 ml), using salt to aid in separating layers. The organic extract was rinsed with dilute sodium sulfite solution and dried over $MgSO_4$. Distillation without a column gave **5b**, bp 79° (0.75 mm), $n^{25}D$ 1.3840, 6.5 g (88%), and an oil residue (0.2 g). Redistillation in a 2-ft platinum spinning band column gave **5b**, 99% pure by GLC analysis (SE-30 silicone oil column, up to 150°), bp 113° (8.0 mm), $n^{25}D$ 1.3802, having unchanged ir spectrum. **5b** reacted slowly with bromine in carbon tetrachloride solution or with dilute aqueous $KMnO_4$ solution in acetone. Ir ν_{CH} 2995, 2950, 2920, 2880, $\nu_{C=O}$ 1730, δ_{CH} 1470, 1445, 1400, 1370, 1350, ν_{CF} 1300–1200; bands at 1140, 1120, 1100, 1070, 1060, 1028, 995, 965, 940, 860, 830, 755, 735, 710, 640, and 530 cm^{-1}. Bands at 995, 965, 940, and 755 cm^{-1} were common to both **5b** and **6b**. NMR (50% in CCl_4) δ 1.33 [6 protons, t, J = 7 Hz, $(OCH_2CH_3)_2$], 1.49–2.18, [5 protons, m, CH_2CH (ring) and CF_2CH_2], 4.18 [4 protons, q, J = 7 Hz, $(OCH_2CH_3)_2$]. Hydrolysis of 2.00 g (5.40 mmol) of **5b** in 6.0 ml of 80% ethanol containing 0.65 g (0.016 mol) of sodium hydroxide at 80° for 7.5 hr gave **6b** as the monohydrate, 1.50 g (89%), mp (sinter 90°) 91–93°.

Sodium Hydride Induced Cyclization of 1c to Diethyl 2-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)-1,1-cyclopropanedicarboxylate (5c). **1c** (5.00 g, 9.16 mmol) in dry benzene (10 ml) under nitrogen atmosphere was added during 10 min to sodium hydride (0.40 g, 9.46 mmol, 57% dispersion in mineral oil) in benzene (10 ml) stirred by a magnet bar at 24°. The evolution of hydrogen was followed by displacing water from a vertical tube. At 62° reaction began and evolution of gas continued at 79–81° for 3 hr until quantitative. The tan slurry was kept at 26° for 18 hr and filtered through a fritted disk. Sodium iodide (1.34 g, 94%) was collected. Distillation through a 10-cm packed column was attended by much foaming at first. **5c** distilled without a column, bp 133° (17 mm), $n^{25}D$ 1.3762, 3.3 g (85%), leaving 1.0 g of hold-up and residue. GLC analysis gave 98.35% area under one peak, and the ir was identical with that of **5c**.

Sodium Hydroxide Induced Cyclization of 1c to 5c. **1c** (10.0 g, 0.0183 mol) was added to a solution of NaOH (0.732 g, 0.0183 mol) in water (75 ml), stirred and heated at 70° for 3 hr, without evident reaction. Ethanol (25 ml) was added and after 20 min the solution was neutral to litmus. Neutral product (**5c**) was extracted into benzene leaving **6c** (as salt) in the aqueous layer. **5c**, bp 103° (4.0 mm), $n^{25}D$ 1.3766, 4.40 g (58%), was recovered by distillation. GLC analysis gave 99% area at 7.4 min, using a 6-ft SE-30 silicone oil column, temperature programmed from 135 to 200° at 15°/min.

Sodium Hydride Induced Dehydrohalogenation of Diethyl 3-Iodo-4-(perfluorohexyl)butylmalonate (1g). Ester **1g** (8.316 g, 0.0126 mol), sodium hydride (0.5326 g, 57% in mineral oil, 0.0126 mol), and benzene (20 ml) were stirred by a magnet bar under nitrogen atmosphere. Gas evolution at 60–70° was followed by displacing water from a flask; when heated to reflux for 8 hr the slurry became noticeably tan in color. Ethanol (9 ml) gave a clear alkaline solution. Water (50 ml) and 6 N HCl (10 ml) were added, and the solution was extracted three times with benzene (10 ml) and with ether and dried over magnesium sulfate. Glpc analysis showed that olefinic and cyclobutyl compounds were present (Table VI). Product mixture was first distilled, bp 110–113° (0.50 mm), 6.4 g, $n^{25}D$ 1.3750 (96%), and then fractionated in a spinning band column (Table VI). Spectral data for **7**: ir $\nu_{C=O}$ 1730, a band at 1042 but not at 970 cm^{-1}; NMR δ 1.3 (6 protons, t, J = 7 Hz), 1.8–2.7 (broad multiplet, 6 protons), 3.4 (1 proton, m), 4.2 and 4.25 (4 protons, overlapping q, J = 7 Hz, nonequivalent ester groups); ir for *cis*- and *trans*-**8** $\nu_{R_FCH=CH}$ 1670 and a band at 970 cm^{-1}; NMR δ 1.3 (6 protons, t, J = 7 Hz), 2.2 (4 protons, broad multiplet, CH_2CH_2CH), 3.2 (1 proton, t, J = 6 Hz), 4.1 (4 protons, q, J = 7 Hz, ethyl ester), 5.0–6.8 (2 protons, broad multiplet of olefinic protons).

Dehydrohalogenation of Diethyl 3-Iodo-4-(perfluorobutyl)butylmalonate (1f) by Sodium Hydroxide in 90% Ethanol. Ester **1f** (5.6 g, 0.010 mol) and a solution of sodium hydroxide (2.0 g, 0.050 mol) in 25 ml of 90% aqueous ethanol was stirred at 65–72° for 7 hr, 15 ml of 6 N HCl and 50 ml of water were added, and the solution was extracted with ether (three times, 25 ml) and benzene (25 ml). The organic layer was rinsed with bisulfite solution, dried over magnesium sulfate, and evaporated to an oil, 3.3 g, 88% yield; ir and NMR indicated a mixture of olefinic and cyclobutylcarboxylic acids. Recrystallization twice from dichloromethane (50 ml) afforded pure *trans*-**11**: 1.30 g, mp 82–83° (gas evolution at 126°); ir (KBr disk) ν_{COOH} 3300–2800, $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1670, δ_{CH} 1460, 1420, 1360, 1300; ν_{CF} 1250–1200, 1170, 1130; bands at 1072, 1008, 970, 920, 880, 812, 775, 740, 700, and 675 cm^{-1}; NMR (acetone-d_6) δ 2.4 (4 protons, CH_2CH_2CH), 3.44 (1 proton, t, J = 7 Hz, $CH_2CH(COOH)_2$), 5.90 (1 proton, m, ca. 4 lines, J = 14 Hz, $CF_2CH=CH$), 6.55 (1 proton, complex multiplet, $CF_2CH=CHCH_2$), 11.0 [2 protons, s, $(COOH)_2$]. The large coupling constant for olefinic protons is consistent with a trans configuration for this substance.

Dehydrohalogenation of 1g by Sodium Hydroxide in 90% Ethanol Solution. Similar treatment of **1g** (6.60 g, 0.0100 mol) gave 5.00 g (100%) of **9, 10** acid mixture, mp 60–75°. NMR and ir spectra showed that olefinic and cyclobutyl compounds were present in proportion of **9**:**10** = 0.80, from integrated areas of nmr spectra. A 1.00 g sample recrystallized from CCl_4 (20 ml) gave *trans*-**9**, 0.631 g, mp 81.5–87°, a second crop, mp 71–72°, 0.0488 g, and an oil residue, 0.167 g. An NMR spectrum of *trans*-**9** was identical with that of *trans*-**11**.

Decarboxylation and Rearrangement of 2-(Perfluoroalkyl)methylcyclopropane-1,1-dicarboxylic Acids. A. *cis*- and *trans*-2-Perfluorobutyl)methylcyclopropanecarboxylic Acid (15c). **6c** (10.00 g, 0.02761 mol, mp 95–96°) was stirred by a magnet bar and heated in a 25-ml round-bottom flask, immersed in an oil bath at 169–176°; under reduced pressure CO_2 was evolved and *cis*- and *trans*-**15c** distilled, bp 122–111° (24–15 mm), 7.48 g, during 1 hr. Crystalline solid residue (1.13 g) remained (93% total recovery). Ir of both materials was identical and showed $\nu_{C=O}$ 1700, δ_{CH} 1470, 1440, 1350,; bands at 1130, 1075, 1050, 1025, 1000–995, 965–955, 915, 885, 840, 770, 740, 710, 690, 670, 550, and 530 cm^{-1}. Bands at 1075, 1030, 950, 770, 710, and 675 cm^{-1} were not present in **6c**, and a strong band at 1640 cm^{-1} in **6c** was also absent. Bands at 1675 and 975 cm^{-1} in **13c** were absent. [However, conversion of the product to ethyl esters showed that *cis*-**17c** (32.78%), *trans*-**17c** (63.83%), and **16c** (3.39%) (average of four analyses) were present.] Pure *trans*-**15c** was obtained from CCl_4 solution, mp 69–71°. Similarly, **6c** (7.00 g, 0.0220 mol) when heated at 202° under reduced pressure evolved CO_2 and gave *cis*- and *trans*-**15c**, bp 166° (65 mm), 6.02 g, as a crystalline solid (**13c** absent by ir and NMR analysis).

B. At Atmospheric Pressure. **6c** (6.00 g, 0.0165 mol) in the same flask connected to a gas bubbler system was heated to 188° (194° bath temperature) without evolution of CO_2; at 198° (202° bath) gas was evolved during 1 hr and stopped. The solid which remained (5.29 g) contained no **6c**, but *cis*-and *trans*-**15c** (about 70–80%) and **13c** (about 20–30%) were present, according to NMR area ratios and ir spectra. The product mixture (4.768 g) was con-

verted to ethyl esters (5.24 g) and analyzed by GLC before and after distillation; *cis*-**15c** (20.96%), *trans*-**15c** (50.6%), and **13c** (28.43%) were present.

C. In Closed Vessel. 6c (0.3076 g, 0.849 mmol) was heated at 196° for 3 hr in a tightly capped "Reactivial" and the products were analyzed by NMR and ir; none of **6c** remained but a mixture of approximately 60% of **13c**, 40% of *cis*- and *trans*-15c, and a small amount of **14c** (band at 1780 cm^{-1}) was present.

D. Decarboxylation of 6b to *cis*- and *trans*-2-(Perfluoropropyl)methylcyclopropanecarboxylic Acid (15b) and 5-Perfluoropropyl-4-pentenoic Acid (13b). 6b (5.00 g, 0.0152 mol, mp 91–92°, monohydrate) was heated at 152° for 2 hr in a 10-ml flask, fitted with a bubbler tube, without apparent reaction or change in ir spectrum of the melt. At 200° evolution of CO_2 occurred during 1 hr. Distillation gave *cis*- and *trans*-**15b, 13b,** and **14b,** bp 124° (21 mm), 2.8 g, and a residue (0.70 g). The distillate was neutralized with 15.0 ml of 5% sodium bicarbonate solution and extracted with dichloromethane; evaporation gave 0.6 g of γ-lactone (**14b,** ir band at 1780 cm^{-1}). The aqueous layer was acidified with 6 *N* HCl and an oil separated (1.8 g); ir and NMR showed it to consist of **13b** (about 60%) and *cis*- and *trans*-**15b (about 40%).**

E. NMR Spectra of *cis*- and *trans*-15c. The spectrum resembled that of **6c** in the region of δ 0.8–3.0, but the COOH proton was at δ 11.22, with the area of one proton. The ir spectrum gave $\nu_{C=O}$ 1700 cm^{-1} (only) and had bands at 1135, 1050, 965, 890, and 710 cm^{-1} not in **6b.**

Thermal Rearrangement of *cis*-2-(Perfluorobutyl)methylcyclopropanecarboxylic Acid (*cis*-15c) to 5-Perfluorobutyl-4-pentenoic Acid (13c). A mixture (1.9683 g, 0.1867 mmol) containing relative amounts of *cis*-**15c,** *trans*-**15c,** and **13c** of 33.78:63.83:3.39 (by GLC analysis of ethyl esters) was placed in a heavy-walled glass tube, evacuated and filled three times with nitrogen at −78°, and sealed. After heating in a stirred oil bath at 226° for 4 hr, a sample showed no change in NMR spectrum; after 14 hr about 12% of **13c** was present from integrated area of olefinic protons, and after 21 hr the area was unchanged. The remaining material (1.10 g) was converted to ethyl esters and analyzed by GLC (FFAP column, 105°) which showed relative amounts of *cis*-**15c,** *trans*-**15c,** and **13c** of 20.39:69.93:9.55 (average of four analyses). Analysis on another column (QF-1 silicone oil) with temperature programming to 180° showed about 1–2% of higher boiling substances also. There appeared to be a 12% decrease in *cis*-**15c** and an increase of about 6% in *trans*-**15c** and **13c.** An attempt to analyze the mixture of the three acids by means of the trimethylsilyl derivatives gave volatile product which could be separated into only two well-resolved peaks on four different columns.

B. Nonisomerization of *cis*- and *trans*-15c at 198°. A mixture of *cis*- and *trans*-**15c** (2.50 g, 0.786 mmol) in a small reactor under positive nitrogen pressure was heated by an oil bath at 198°, removing samples for NMR and ir analysis after 5, 8.5, and 21 hr reaction times. There was no detectable change in the spectra of the samples.

Preparation of Ethyl *cis*- and *trans*-2-(Perfluorobutyl)-methylcyclopropanecarboxylates (17c) and Ethyl 5-Perfluorobutyl-4-pentenoate (16c). A mixture containing *cis*-**15c,** *trans*-**15c,** and **13c** formed by heating **6c** at 200° and atmospheric pressure (4.768 g, 0.01499 mol) and thionyl chloride (5 ml) was heated at 60–80° for 1 hr in a flask connected to a trap; gas evolution ceased and the mixture was evacuated at the water pump to 20 mm. The mixture of acid chlorides showed ir bands for COCl at 1785 and for $R_FCH{=}CH$ at 1670 cm^{-1}. Ethanol (5.0 ml) was added and the mixture was heated for 2 hr at 60–80° and then allowed to distil up to 105° pot temperature. The residual oil [5.24 g (100%), ir weak band for lactone at 1790 and a strong band for ester at 1730 cm^{-1}] was fractionated in a 16-in. spinning band column. The three fractions were analyzed by GLC on an 8-ft FFAP column at 105° and on a 6-ft QF-1 silicone oil column, temperature programmed from 135 to 180° after 5 min. Fraction I, bp 79° (9 mm), 1.34 g (39.21% *cis*-**17c,** 29.47% *trans*-**17c** and 31.32% **16c**) gave the correct elemental analysis and its ir and NMR spectra were recorded. Fraction II, bp 79° (9 mm), 62° (2.0 mm), 1.30 g, also contained these three substances, but fraction III, bp 66° (0.35–0.12 mm), 0.53 g, contained 80% of *cis*- and *trans*-**17c** and **16c,** and also 20% of four higher boiling substances, which were also present in the hold-up and residue. The original undistilled mixture contained 19.1% of *cis*-**17c,** 48.6% of *trans*-**17c,** 24.4% of **16c,** and 1.5, 2.2, and 2.7% of three higher boiling substances. One of these was probably the lactone **14c** but the small quantity precluded firm identification.

Another mixture containing *cis*- and *trans*-**15c** and a little of **13c,** obtained by heating **6c** under reduced pressure at 176° (2.00 g, 0.629 mmol), was similarly converted to ethyl esters (2.04 g, 95%). No lactone was detected in the product (ir) and distillation in a microstill gave *cis*- and *trans*-**17c,** bp 82° (13 mm), $n^{25}D$ 1.3582, 1.64 g. GLC analysis (FFAP column, 105°) of the mixture before and after distillation was identical (±0.5%) and showed *cis*-**17c,** 32.78%, *trans*-**17c,** 63.83%, and **16c,** 3.39% (average of four). The sample gave the correct elemental analysis.

Thermal Rearrangement of Diethyl 2-(2,2,3,3,4,4,4-Heptafluorobutyl)cyclopropane-1,1-dicarboxylate (5b) to $CF_3(CF_2)_3CH{=}CHCH_2CH(COOEt)_2$ (3c). 5b (2.09 g, 0.00500 mol) was placed in a heavy-wall glass tube, cooled to 0°, evacuated and filled with nitrogen three times, and sealed. After periods of time indicated in Table III, the tube was opened and a sample removed for GLC analysis on two different columns, using a known mixture of **5b** and **3c** for comparison. A 6-ft SE-30 silicone oil column, 10% on Chromosorb W at 150°, and a 6-ft QF-1 silicone oil column, 10% on Chromosorb W at 150°, were used. The NMR and ir spectra also showed that the substances listed were formed.

Registry No.—**1a,** 54019-87-3; **1b,** 2094-35-1; **1c,** 54019-88-4; **1d,** 54019-89-5; **1e,** 54019-90-8; **1f,** 54019-91-9; **1g,** 54019-92-0; *cis*-**2b,** 54062-06-5; *trans*-**2b,** 54019-93-1; **2c,** 54019-94-2; *cis*-**3b,** 54019-95-3; *trans*-**3b,** 54019-96-4; *cis*-**3c,** 54019-97-5; *trans*-**3c,** 54019-98-6; *cis*-**4b,** 54019-99-7; *trans*-**4b,** 54020-00-7; **4c,** 54020-01-8; **5b,** 27311-61-1; **5c,** 54020-02-9; **6a,** 54020-03-0; **6b,** 27311-60-0; **6c,** 54020-04-1; **6d,** 54020-05-2; **6e,** 54020-06-3; **7,** 54020-07-4; *cis*-**8,** 54020-10-9; *trans*-**8,** 54020-11-0; *cis*-**9,** 54020-12-1; *trans*-**9,** 54020-13-2; *trans*-**11,** 54020-09-6; **13b,** 54020-14-3; **13c,** 54020-15-4; **14b,** 54020-16-5; **14c,** 54020-17-6; *cis*-**15b,** 54020-18-7; *trans*-**15b,** 54020-19-8; *cis*-**15c,** 54020-20-1; *trans*-**15c,** 54020-21-2; **16c,** 54020-08-5; *cis*-**17c,** 54020-22-3; *trans*-**17c,** 54020-23-4; **20,** 2049-80-1; **21,** 31696-00-1; **22,** 17920-23-9; 1-iodoperfluoropropane, 754-34-7; 1-iodoperfluorobutane, 423-39-2; 1-iodoperfluorohexane, 355-43-1; 1-iodoperfluorooctane, 507-63-1; 2-iodoperfluoropropane, 677-69-0.

Supplementary Material Available. Table V and infrared and NMR spectra of the substances **1d, 3c, 4c, 5c, 6b, 6c, 7, 14c,** and **15c** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washigton, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-851.

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Thermal Rearrangement of Trimethylsilyl Enol Ethers of Cyclopropyl Methyl Ketones. A Cyclopentanone Annelation Procedure[1]

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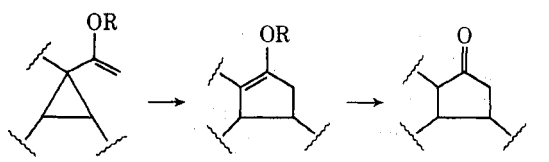
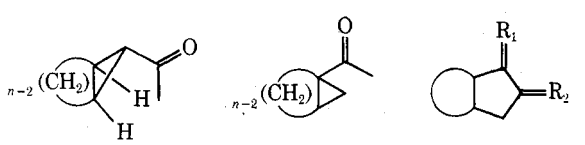
Pyrolysis of the conjugated enol trimethylsilyl ethers derived from methyl cyclopropyl ketone and methyl bicyclo[*n*.1.0]alkan-1-yl ketones (*n* = 3, 4, 5) at 450° yielded, after acidic hydrolysis of the resulting cyclopentene enol silanes, cyclopentanone (73%), bicyclo[3.3.0]octan-2-one (21%), bicyclo[4.3.0]nonan-7-one (99%), and bicyclo[5.3.0]decan-8-one (85%). Rearrangement of the enol silyl ether of methyl *exo*-bicyclo[4.1.0]heptan-7-yl ketone furnished a 1:2 mixture of *cis*- and *trans*-bicyclo[4.3.0]nonan-8-one (52%) and the γ,δ-unsaturated ketone, 2-cyclohexenylacetone (28%). The major products obtained from the enol silyl derivatives of methyl *exo*-bicyclo[3.1.0]hexan-6-yl and methyl *exo*-bicyclo[5.1.0]octan-8-yl ketones were the corresponding γ,δ-unsaturated ketones. This enol silane vinylcyclopropane–cyclopentene rearrangment pathway results in the regioselective annelation of a cyclopentanone ring onto an α,β-unsaturated ketone or an olefin. This overall process furnishes 1-hydroindanone and 1-hydroazulenone in good yields.

The occurrence of five-membered rings in an increasing number of natural products of biological importance has stimulated the development of a variety of new cyclopentane ring synthesis methods. These recent approaches include intramolecular ring closure of acyclic precursors,[2] formal [3 + 2][3] and [4 + 1][4] cycloaddition reactions, and ring contraction[5] and expansion[6] of cyclic substrates. In considering the various general routes to cyclopentanoid ring construction, it appeared to us that the well-established thermal vinylcyclopropane–cyclopentene rearrangement[7] could serve as the basis of a five-membered ring synthesis method in which the newly constructed ring contained a masked ketone functionality. In a general sense, rearrangement of conjugated cyclopropyl enol ethers of part structure **1** would yield cyclopentene enol derivatives **2**. Unmasking of the latent ketone functionality by acidic hydrolysis would then complete the sequence to give the cyclopentanone ring skeleton (eq 1). In particular, thermal



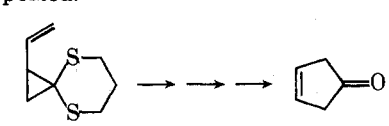
(1)

1 **2**

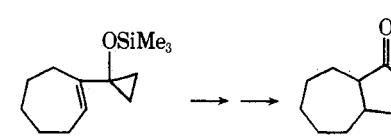


3a, *n* = 5 **4a**, *n* = 5 **5**, $R_1 = H_2$; $R_2 = O$
b, *n* = 6 **b**, *n* = 6 **6**, $R_1 = O$; $R_2 = H_2$
c, *n* = 7 **c**, *n* = 7

rearrangement of the enol derivatives derived from cyclopropyl methyl ketones **3** and **4** would furnish cyclopentanone **5** and **6** regioselectively. Since the cyclopropyl ketone substrates are readily prepared from olefin or α,β-unsaturated ketone precursors, the overall transformation constitutes a net cycloaddition of a one- or a three-carbon atom unit to an existing skeleton to give an annelated cyclopentanone. We have undertaken an examination of the thermal behavior of a series of cyclopropyl enol trimethylsilyl ethers (**1**, R = $SiMe_3$) and the results of this study are detailed below. During the course of our investigation two cyclopentanone ring synthesis methods based on the thermal vinylcyclopropane–cyclopentene rearrangement (eq 2[4a] and 3[6]) were reported.



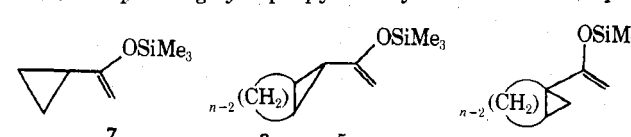
(2)



(3)

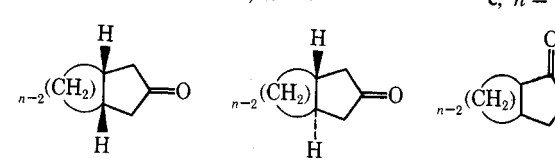
Results

The specific vinylcyclopropane substrates examined in this study, the parent trimethylsilyl enol ether **7**, and the two bicyclo[*n*.1.0]alkane series **8** and **9**, were prepared from the corresponding cyclopropyl methyl ketones under equil-



7

8a, *n* = 5 **9a**, *n* = 5
b, *n* = 6 **b**, *n* = 6
c, *n* = 7 **c**, *n* = 7



10a, *n* = 5 **11a**, *n* = 5 **12a**, *n* = 5
b, *n* = 6 **b**, *n* = 6 **b**, *n* = 6
c, *n* = 7 **c**, *n* = 7 **c**, *n* = 7