Cyclization of Ethyl Diallylacetate or Ethyl Diallylmalonate to Cyclopentane Derivatives during the Addition of Perfluoroalkyl and Trichloromethyl Radicals

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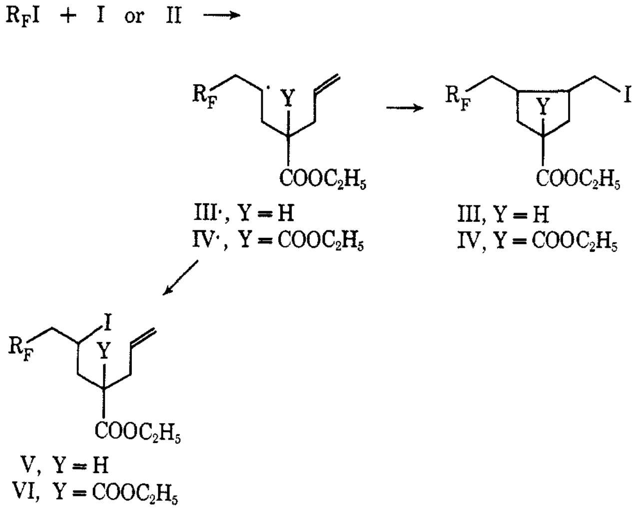
Radical cyclization reactions of 4-substituted 1,6-heptadienes were studied. Five- but not six-membered rings were obtained from iodoperfluoroalkanes or carbon tetrachloride with ethyl diallylacetate (I) or with ethyl diallylmalonate (II). Various derivatives of the cyclic adducts were prepared which confirmed the structures suggested by spectroscopic and other evidence. These reactions provide an entry into the area of partially fluorinated alicyclic carboxylic acids. Free-radical reaction of I with a variety of thiols or with diethyl phosphite is reported to have given five- *and* six-membered ring products; cyclopolymerization of II also is supposed to lead to six-membered ring structures.

Cyclization of 1,6-heptadiene during the addition of perfluoroalkyl ($R_F\cdot$) radicals or trichloromethyl ($Cl_3C\cdot$) radicals gave substituted 1,2-dimethylcyclopentanes bearing various addenda.[1] This behavior has been recently observed[2] for the addition of the dialkyl phosphono radical[2] or $NF_2\cdot$ radical[3] to 1,6-heptadiene. A generalized pattern of reaction of 6-hepten-2-yl or 5-hexen-1-yl radicals seems to be emerging,[4-7] with a preference for five-membered ring formation. However, in a brief communication[8] in which reactions of ethyl diallylacetate (I) with n-$C_4H_9S\cdot$, $CH_3COS\cdot$, $C_2H_5O_2CCH_2S\cdot$, and $(C_2H_5O)_2P(O)\cdot$ radicals were given, six-membered ring products were reported to predominate over five-membered-ring compounds to the extent of two or three to one. Allusion was made to complex results from similar addition reactions involving related systems.[8] Other instances of five- and six-membered ring formation in free-radical cyclizations are known.[9] It seemed interesting and important, therefore, to determine if the addition of $R_F\cdot$ to I would give cyclization to five- *and* six-, or to only five *or* six-membered ring products. Analogous reaction of $CCl_3\cdot$ with I was also of interest. The related addition of $R_F\cdot$ radicals to ethyl diallylmalonate (II) was previously disclosed[1a] but is now described in detail. Cyclopolymerization of II has been stated[10,11] to give repeating units containing substituted cyclohexane rings, which have generally been accepted as the basic structural unit in analogous polymers.

Results and Discussion

As in previous cases studied[1] the $R_F\cdot$ radical [from R_FI, R_F = $CF_3CF_2CF_2$ or $CF_3(CF_2)_3$–] readily added to I or II with azonitrile initiator, giving an excellent yield of the substituted cyclopentane products (III or IV) and a much smaller amount of olefinic adducts (V or VI) (Scheme I). Bis adducts or telomers were not obtained under these conditions. Reaction of I or II with CCl_4 gave analogous products, VII, VIII, and also some telomer (IX), from II (Scheme II). The amount of IX formed was very sensitive to reaction conditions, being greatly decreased when initiation by a Fe^{2+}/Fe^{3+} redox transfer system[1b,12] was used, or by increased

SCHEME I

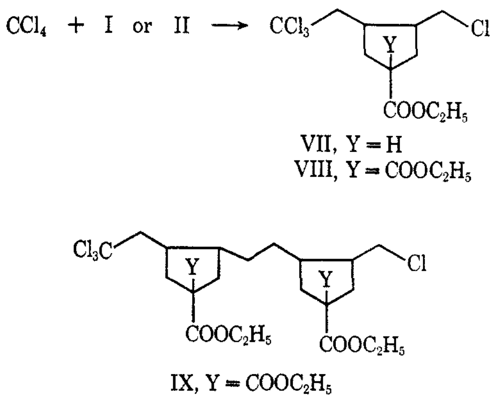


III·, Y = H
IV·, Y = $COOC_2H_5$

III, Y = H
IV, Y = $COOC_2H_5$

V, Y = H
VI, Y = $COOC_2H_5$

SCHEME II



VII, Y = H
VIII, Y = $COOC_2H_5$

IX, Y = $COOC_2H_5$

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CCl_4 concentration. These results are summarized in Table I. Little telomer was obtained from I and CCl_4 using the Fe^{2+}/Fe^{3+} catalyst system.

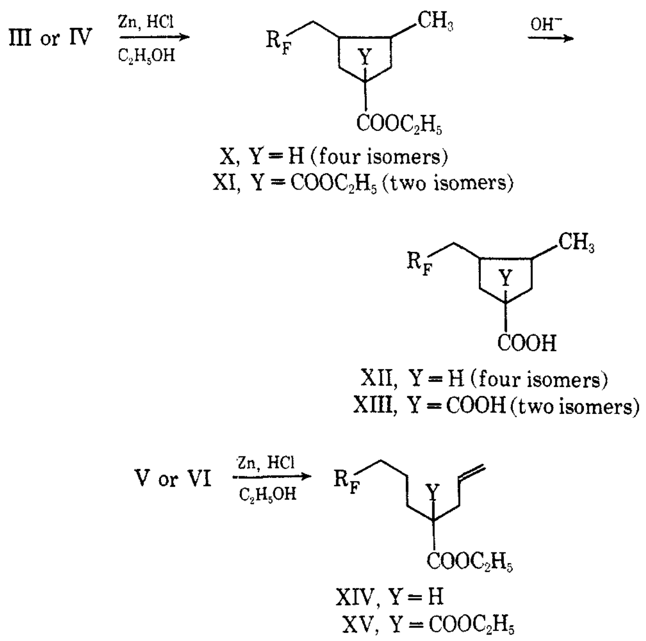
Table I
Free-Radical Reaction of Carbon Tetrachloride and II

CCl_4/II, mol	Reaction Time, hr	Reaction Temp, °C	Mol % initiator[a]	% convn VIII	% convn IX
1.2	12	82	1.8	20	49
2.4	12	82	3.7	55	28
5.0	16	82	2.0	68	18
5.0	22	77	(Fe^{3+})	87	8.4

[a] Based on II.

A detailed study of the distribution of products from R_FI (or CCl_4) and I or II as a function of reaction conditions was not made since these high-boiling and heat-sensitive compounds could not be readily separated by distillation or by gas–liquid partition chromatography (glpc). Instead, product mixtures were converted into stable, distillable iodine-free derivatives by zinc reduction and the relative amounts of isomers (X and XIV or XI and XV, Scheme III) determined by glpc and nmr analysis. Little if any VI or XV was present in reaction products. One reason for the small amount of V observed in reaction product mixtures was that cyclization to a γ-lactone occurred during attempted isolation.[13] A sample of XVI was trapped from glpc separation and showed ir bands consistent with this structure ($\nu_{C=O}$ 1770 cm^{-1}; bands of CH_2=CH at 3090, 1640, 990 and 920 cm^{-1}).

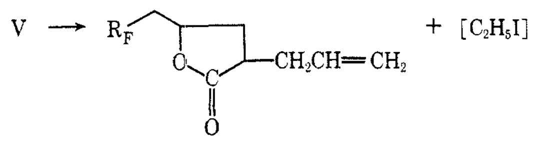
Scheme III



X, Y = H (four isomers)
XI, Y = $COOC_2H_5$ (two isomers)

XII, Y = H (four isomers)
XIII, Y = COOH (two isomers)

XIV, Y = H
XV, Y = $COOC_2H_5$



XVI

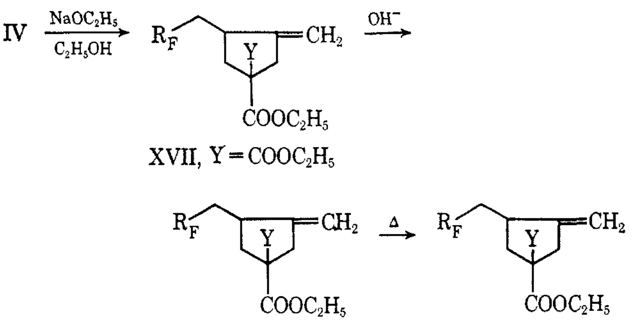
The methylcyclopentane structure of cyclic adducts III, IV, and their derivatives was clearly indicated by ir and nmr spectra. From the relative area of the proton resonances in nmr spectra and the number of peaks in glpc curves it was concluded that cyclohexane products were not present in significant amount on these reaction products.

For example, zinc reduction of a sample of III and V gave 92% yield of product containing isomers X and XIV, which was analyzed by glpc using five different columns. There were nine substances present in greater than 0.5% relative amount. However, the four isomers of X comprised 89% of the total, three early peaks (8% total) were olefinic compounds, I, XIV, and an unknown substance, and two later peaks (3%) were not identified. The possible amount of cyclohexane products in X could not have been greater than 5%. Similarly, zinc reduction of a reaction product containing IV (and possibly VI) gave reduced compounds in 94% yield, for which glpc analysis showed 19.3 and 76% *cis* and *trans* isomers of XI. An early peak (0.5%) and a late peak (2.8%) were not identified. Again the amount of cyclohexane isomers in XI could not have exceeded 5%.

Hydrolysis of samples containing X (four isomers) gave a mixture of acids, XII, with the corrent ratio for CH_3C– at δ 1.00 relative to COOH at δ 12.42 in nmr spectra. A cyclohexane–methylcyclopentane mixture could not have given this result. Hydrolysis of XI gave a crystalline isomer of XIII in 85% yield, again with the correct area for CH_3C– relative to COOH protons in nmr spectra. The oil residue was reconverted into ethyl esters and glpc showed formation of X isomers *via* decarboxylation. An acid chloride and amide from X isomers thus obtained were prepared in a separate experiment.

Reaction of IV with sodium ethoxide in anhydrous ethanol gave a mixture of dehydrohalogenation products in which XVII and XIX predominated. Reaction conditions were too vigorous to give clean reaction, and hydrolysis occurred in part to give XVIII which decarboxylated to XIX (Scheme IV). The CH_2=C and $COOC_2H_5$ groups in XVII and XIX were shown by ir: ν_{CH} 3090, $\nu_{C=C}$ 1655, $\nu_{C=O}$ 1735, and $\gamma_{CH_2=C}$ 890 cm^{-1}. These are absorption bands unique to this structure,[14] which could not have been obtained from an isomeric cyclohexane product. Nmr spectra also

Scheme IV



XVII, Y = $COOC_2H_5$

XVIII, Y = COOH

XIX, Y = H

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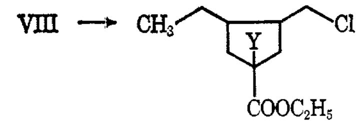
[13] N. O. Brace, *J. Org. Chem.*, **29**, 1247 (1964).

[14] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 100–104.

displayed a clean doublet at δ 5.10, $J = 7\text{–}8$ Hz, indicative of the $CH_2{=}C$ group.

Reduction of VIII by zinc gave a product bearing the CH_2Cl group. Nmr analysis showed proton resonances at δ 2.84 for CH_2CCl_3 and at δ 3.50 for CH_2Cl in VIII


XX, Y = $COOC_2H_5$

compared with δ 2.82 and δ 3.50 in the analogous 1-chloromethyl-2(2,2,2-trichloro)ethylcyclopentane from CCl_4 and 1,6-heptadiene.[1b] After reduction to XX nmr showed a CH_3 of ethyl at δ 1.00 and CH_2Cl at δ 3.50. Had the cyclization product VIII been a cyclohexane derivative there would have been a Cl_3CCH_2 but no $ClCH_2$ group present. By analogy with III and IV, it is believed that VII has a structure similar to VIII.

These data all are consistent with our previous results[1] showing cyclization of 6-hepten-2-yl radicals to five-membered rings. We are continuing our efforts to define more closely this radical cyclization process and must leave open the question of how and under what conditions cyclization to five- and six-membered rings from 1,6-heptadiene systems can occur.

It should be observed that synthesis of compounds such as III and IV from radical cyclizations presents a new and potentially valuable entry into interesting cyclopentylcarboxylic acid derivatives. A variety of substances having fluorinated or halogenated side chains and various functional groups can be readily prepared from the reactive intermediates III and IV, or from the analogous VII and VIII. The potential for new chemistry of these and related substances should be readily apparent.

Experimental Section[15]

Source of Materials.—1-Iodoperfluoropropane, Pierce Chemical Co., was redistilled, bp 40–41°, and kept cold before use. 1-Iodoperfluorobutane, bp 67°, $n^{25}\mathrm{D}$ 1.3252, was a gift from E. I. du pont de Nemours and Co.

Ethyl Diallylacetate (I).—Ethyl allylacetoacetate was prepared:[16,17] bp 92–7° (12 mm); $n^{25}\mathrm{D}$ 1.4360; 85% yield [lit.[18] bp 96–97° (14 mm); $n^{26}\mathrm{D}$ 1.4365]. A slightly altered procedure gave this compound in 55% yield and a 14% yield of ethyl diallylacetoacetate: bp 112° (12 mm); $n^{25}\mathrm{D}$ 1.4540. However, reaction of allyl bromide with ethyl allylacetoacetate by the same procedure gave alcoholysis of the aceto group[19] and a 73% yield of I: bp 85° (21 mm); $n^{25}\mathrm{D}$ 1.4352 (lit.[20] bp 189–191°; $n^{20}\mathrm{D}$ 1.4364); ir (CCl_4) $\nu_{CH=CH}$ 3090, ν_{CH} 2890, $\nu_{C=O}$ 1730, $\nu_{C=C}$ 1640, $\gamma_{=CH}$ 995, 920 cm^{-1}. Elemental analysis also was consistent. Glpc (6 ft × 0.25 in. Carbowax 20M, 20% on Chromosorb W, at 160°) gave 99% area under one peak.

Ethyl Diallylmalonate (II).—Ethyl malonate was alkylated with 2 equiv of allyl bromide.[16] Fractional distillation using column A gave ethyl allylmalonate (7%) and II: bp 129° (15 mm); $n^{25}\mathrm{D}$ 1.4436 (79%) [lit.[21] bp 120–122° (12 mm); $n^{20}\mathrm{D}$ 1.4435].

Ethyl 3-Iodomethyl-4-(perfluoropropyl)methylcyclopentyl-1-carboxylate Isomers (III).—1-Iodoperfluoropropane (60.0 g, 0.20 mol), I (16.8 g, 0.10 mol) and azobis-2-methyl-2-propionitrile ABN (0.26 g, 0.0015 mol) were charged to a Fischer–Porter aerosol tube, purged with nitrogen and evacuated to 0.1 Torr at −78° three times and heated in an oil bath at 70° for 21.5 hr. The reaction mixture became brown in 1 hr. The tube when cool was opened, 1-iodoperfluoropropane, 31.8 g, pumped off into a trap at −70° and the product (A), 43.5 g, distilled in column A, using an oil bath. Iodine was formed. Fractions taken were (1) bp 42° (0.15 mm), $n^{20.5}\mathrm{D}$ 1.4352, 2.9 g, I, 17.3% recovery; (2) bp 72–88° (0.15 mm), $n^{20.5}\mathrm{D}$ 1.4316, 4.6 g, a mixture of I, III, V and other substances; (3) bp 92° (0.15 mm), $n^{20.5}\mathrm{D}$ 1.4400, 17.3 g; (4) 92–94° (0.13 mm), $n^{20.5}\mathrm{D}$ 1.4390, 14.0 g; (5) residue, 0.2 g. Cuts 3 and 4 comprised isomers of III (67% conversion), with essentially no bis adduct or telomeric products being formed. An ir spectrum (neat) of 3 and 4 showed no detectable unsaturation but bands listed below for III. Product B from a second run was distilled without a column: bp 30–33° (0.13 mm), 2.25 g, 13.5% recovery of I; and bp 90–93° (0.13 mm), $n^{25}\mathrm{D}$ 1.4379, 34.8 g, 73% conversion into cyclic isomers; residue 1.2 g. Samples of product B and fractions 3 and 4 gave identical nmr spectra (neat): δ 1.23, CH_3CH_2O (t, $J = 7$ Hz, 3.04 H); δ 1.24–3.00, R_FCH_2CH, $(CH_2)_2CH$–, CH (unresolved, 8.85 H); δ 3.22, CH_2I (unresolved, 2.05 H); δ 4.10, CH_3CH_2O (q, $J = 7$ Hz, 1.88 H). There were no olefinic proton resonances. The $-CH_2I$ resonance appeared at δ 3.25 in a product of similar structure.[1b] Infrared spectra of product B showed that a small amount of V was present (weak olefinic bands), and the bands of III isomers: ν_{CH} 2980, 2960, 2910, 2870; $\nu_{C=O}$ 1730; δ_{CH} 1450 and 1380 (CH_3), 1440, 1365, 1345; and bands at 1230, 1200, 1185, 1120 (COC), 1065, 1030, 1010, 958, 925, 860, 760, 730 and 710 cm^{-1}. Glpc analysis was attempted with a variety of columns and conditions to determine the relative amounts of isomers present, and a 6 ft × 0.25 in., 10% QF-1 fluorosilicone oil on Chromosorb WA (DMAC treated) column, run at 185° and 25-psi helium pressure, was selected. Glpc of fraction 2 gave 0.9 min, 3.59% (I); 2.5 min, 2.76%; 3.2 min, 23.2% (probably V); 3.6 min, 23.6% (probably a γ-lactone (XVI) derived from V; see below for ir); 4.8 min, 9.55%; 10.1 min, 28.7%, an isomer of III; 11.1 min, 5.24% (same); 13.5 min, 3.3% (same). Fractions 3 and 4 contained only isomers of III in varying ratios. The various peaks were trapped and ir spectra recorded using a microcell (AgCl plates). Insufficient amount of V was isolated for complete characterization; ir showed olefinic bands at 3090, 1640, 990 and 920 cm^{-1} ($CH_2{=}CH$–), $\nu_{C=O}$ 1735 cm^{-1}, CH_3, CH_2, and COC absorption bands in the peak trapped. XVI gave bands at 3090, 1640, 990 and 920 cm^{-1} ($CH_2{=}CH$—); $\nu_{C=O}$ 1770 cm^{-1} (strong); δ_{CH} 1450, 1440, 1400 and 1350, but no δ_s of CH_3 at 1370 cm^{-1}; CF bands 1280, 1220; COC bands at 1180 and 1120; and bands at 960, 790, 745, 735, 700, 660 and 635 cm^{-1}. Product B showed 0.85% of I, 2.4% each of peaks at 3.2 and 3.6 min, and 94% of four peaks of III isomers at 10.1–16.8 min. A major part of III isomers decomposed on a Carbowax 20M (20%) on Chromosorb WA column at 185°. The mixture of substances trapped included (from ir) XV and III isomers. The trapped isomers of III were analyzed.

Anal. Calcd for $C_{13}H_{16}F_7O_2I$: C, 33.6; H, 3.47. Found (cut 3): C, 33.9; H, 3.55.

Ethyl 3-Methyl-4-(perfluoropropyl)methylcyclopentyl-1-carboxylate Isomers (X) **and Ethyl 2-Allyl-6,6,7,7,8,8,8-heptafluorooctanoate** (XIV).—Distilled product B above (34.0 g, 0.073 mol), ethanol (125 ml), and zinc (20–40 mesh, 6.5 g, 0.10 g-atom) were stirred rapidly while being saturated with hydrogen chloride at 75–80°. The yellow slurry began to foam, and became colorless after 15 min. Additions of zinc (three 3.0-g samples) were made after 15 min, 1 hr, and 1.5 hr. The colorless solution was decanted into 150 ml of water and extracted three times with a 1:1 mixture of benzene and ether. The organic extract was rinsed with sodium sulfite solution and with

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(15) Melting points were determined with a Thomas–Hoover Unimelt apparatus. Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer. Nmr spectra were obtained from neat samples with a Varian A-60 instrument at ambient temperature and are reported in parts per million from tetramethylsilane as an internal standard. Integrated areas measured by the instrument are given as number of H, calculated from the empirical formula and the total area. Distillations were done in a 16-in. Nester–Faust stainless steel spinning-band column (column A). Gas chromatographic analyses (glpc) were done with a Microtek 1500 instrument using columns and conditions indicated. Per cent relative areas were measured by a disk integrator on the recorder.

(16) "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1947, p 250.

(17) A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Amer. Chem. Soc.*, **63**, 1843 (1941).

(18) M. S. Schechter, N. Green, and F. B. LaForge, *ibid.*, **71**, 3165 (1949).

(19) *Cf.* ref 17 where reaction time was limited to 0.5 hr, even though reaction was incomplete, to reduce alcoholysis.

(20) K. Auwers and W. Moosbrugger, *Ann.*, **387**, 167 (1912).

(21) R. Ya Levina and N. N. Godovikov, *Zh. Obshch. Khim.*, **24**, 1572 (1954); *Chem. Abstr.*, **49**, 11667 (1955).

water, dried over $MgSO_4$ and distilled without a column: bp 71–83° (1.25–0.50 mm); $n^{25}\mathrm{D}$ 1.3825, 22.8 g (92%). Glpc, 6 ft × 0.25 in. XE-60 silicone resin (15%) on Chromosorb WA column at 145°, with 25-psi helium pressure, showed retention times, relative areas: (1) 6.0 min, 0.4%; (2) 7.0 min, 1.5%; (3) 11.1 min, 6.4%; (4) 13.8 min, 10.6%; (5,6) 17.0 min, 52.7% (two peaks); (7) 18.8 min, 25.3%; (8) 22.6 min, .83%; (9) 25.2 min, 2.27%. Peak 1 was I; peaks 2 and 3 were XIV and another olefinic compound since ir showed $CH_2{=}CH-$ bands at 3090, 1640, 995, 910, $\nu_{C=O}$ at 1730, and other identical bands; peaks 4–7 were isomers of X (four possible); and peaks 8 and 9 were unknown. A portion of the product, 10.9 g, was redistilled in column A: cut 1, bp 98–107° (11 mm), $n^{25}\mathrm{D}$ 1.3876, 1.1 g; cut 2, bp 110° (11 mm), $n^{25}\mathrm{D}$ 1.3829, 6.9 g; cut 3, bp 108° (9 mm), $n^{25}\mathrm{D}$ 1.3836, 2.1 g; column holdup, 0.6 g. These cuts were examined by ir, nmr, and glpc. Ir (cut 3) showed ν_{CH} 2960, 2920, 2880; $\nu_{C=O}$ 1730; δ_{CH} 1460, 1450, 1440, 1430, 1380, 1370, 1350, ν_{CF} 1280–1260; bands at 1170, 1120, 1080, 1050, 1000, 960, 925, 850, 760, 720 (s), 630, 540, and 520 cm^{-1}. Glpc (QF-1 fluorosilicone oil column at 150°, 15-psi helium pressure): cut 1 gave (1) 2.8 min, 12.9%; (2) 4.0 min, 0.75%; (3) 5.1 min, 7.45%; (4) 7.4 min, 19.4%; (5) 9.3 min, 13.5%; (6) 11.0 min, 39.6%; (7) 12.0 min, 9.2%; cut 2 showed 7.2% of peak 3 and the remainder of peaks 4–7; cut 3 gave only peaks 4–7 and 0.66% of a later peak. Cut 1 nmr showed δ 0.8–1.0, CH_3CH (two d, 1.7 H); δ 4.7–6.4, $CH_2{=}CH-$ (m, 1.5 H); ir ν_{CH} 3090, 1640; $\nu_{C=O}$ 1735. Cuts 2 and 3 had δ 0.9 CH_3CH (d, J = 7 Hz, 3.08 H); δ 1.20, CH_3CH_2O (t, J = 7 Hz, 3.4 H); δ 1.2–2.6 $(CH_2)_2CH$, R_FCH_2CH and CH_3CH (unresolved, 7.85 H); δ 2.85, $CHCOOC_2H_5$ (t, J = 7 Hz, 1.0 H); δ 4.15 CH_3CH_2O (q, J = 7 Hz, 1.7 H). These data confirm that cut 1 contained I, XIV and isomers of X, and that cuts 2 and 3 were substantially pure isomers of X. Careful refractionation in column A was unsuccessful in separating isomers of X, bp 115° (20 mm); only four peaks appeared in glpc analysis, also run on a 6 ft × 0.25 in. cyanosilicone oil (XE 60, 15%), on a Chromosorb WA column at 145° and 25-psi helium, and on Carbowax 20M, "Craig polyester" and "FFAP" columns under similar conditions. Samples of X and XIV from cut 1 were trapped from glpc separation on the QF-1 column. Peak 4 at 7.4 min was XIV: ir ν_{CH} 3090, 2990, 2950, 2880; $\nu_{C=O}$ 1730; $\nu_{C=C}$ 1640; δ_{CH} 1455, 1435, 1370, 1350; bands at 1250–1170, 1120, 1020, 995, 960, 950, 920, 910, 880, 850, 785, 750, 730, 700, 650, 640, 555, 550 and 535 cm^{-1}. Bands at 3090, 1640, 995 and 910 revealed the vinyl group; all the other bands were consistent with the structure of XIV.

Anal. Calcd for $C_{13}H_{17}F_7O_2$: C, 46.15; H, 5.07. Found (XIV): C, 46.08; H, 4.95. Found (X isomers): C, 46.3; H, 5.24.

Preparation of 3-Methyl-4-(perfluoropropyl)methylcyclopentyl-2-carboxylic Acid Isomer Mixture (XII).—Mixture of X isomers (10.0 g, 0.0325 mol) and KOH (3.36 g, 0.06 mol) dissolved in 90% aqueous ethanol (56 ml) was kept at 80° for 7.8 hr, diluted with 100 ml of water, acidified with 10 ml of concentrated HCl and extracted three times with ether. The ether extract was dried ($MgSO_4$) and evaporated off, leaving 8.8 g (84%) of XII isomer mixture. Fractional distillation in column A gave cuts: (1) bp 98–107° (1.5 mm), $n^{25}\mathrm{D}$ 1.3894, 1.2 g; (2) bp 110° (1.2 mm), $n^{25}\mathrm{D}$ 1.3872, 2.65 g; (3 and 4) bp 100° (0.30 mm), $n^{25}\mathrm{D}$ 1.3882, 3.7 g (no residue). Cuts 2 and 3 (5% in CCl_4) gave ir $\nu_{COOH,CH}$ 3100–2880; $\nu_{C=O}$ 1705; δ_{CH_3} 1450, 1380; $\delta_{CH_2,CH}$ 1470, 1430, 1420, 1350; bands at 1230, 1203, 1180, 1140, 1070, 1050, 980 (sh), 965, 925, 690, 645, 550 and 530 cm^{-1}; nmr neat δ 1.00, CH_3CH (overlapping doublets, 3.02 H measured by hand and machine); δ 1.6–2.7, $(CH_2)_3$ and $(CH)_2$ (m, unresolved, 8.0 H); δ 2.7–3.55, $-CHCOOH$ (t, J = 7 Hz, 1.0 H); δ 12.42, COOH (s, 1.0 H). No vinyl proton resonances appeared; XII isomeric structures were confirmed by relatives areas of CH_3 and COOH groups. Cut 1 contained X, XII and some olefinic substances according to nmr.

Anal. Calcd for $C_{11}H_{13}F_7O_2$: C, 42.58; H, 4.22. Found: C, 42.76; H, 4.30.

Ethyl 3-Iodomethyl-4-(perfluoropropyl)methylcyclopentyl-1,1-dicarboxylate (IV).—1-Iodoperfluoropropane (60.0 g, 0.20 mol), II (16.8 g, 0.069 mol), and ABN (0.32 g, 0.0020 mol) were heated at 70° for 24 hr as previously done with III. 1-Iodoperfluoropropane (37.4 g, 96%) was recovered, leaving residual oil, 35.4 g (95%): ir (no $CH_2{=}CH$ bands) ν_{CH} 2980, 2940, 2920, 2880; $\nu_{C=O}$ 1735; δ_{CH} 1460, 1440, 1380, 1360 and 1350; bands at 1260, 1220, 1180, 1100, 1065, 1045, 1030, 990 (shoulder), 960, 930, 860, 760, 730 and 715 cm^{-1}. A 2:1 reactant ratio gave 93% yield of IV. Distillation from an oil bath in a short-path still gave IV: $R_F = CF_3CF_2CF_2-$; bp 132° (0.25 mm); $n^{22}\mathrm{D}$ 1.4402; 32.6 g (88%); residue 1.0 g. A portion, 6.3 g, redistilled in column A: bp 118° (0.15 mm); $n^{22.5}\mathrm{D}$ 1.4404; 5.7 g; ir same as above; nmr δ 3.17, CH_2I (m, 2.3 H), and no olefinic protons.

Anal. Calcd for $C_{16}H_{20}F_7IO_4$: C, 35.8; H, 3.76; F, 24.8. Found: C, 36.1; H, 3.87; F, 25.2.

1-Iodoperfluorobutane and II gave IV: $R_F = CF_3(CF_2)_3-$; bp 116° (0.20 mm); $n^{25}\mathrm{D}$ 1.4295; 26.4 g (95%); ir $\nu_{C=O}$ 1735 cm^{-1} and no olefinic bands.

Anal. Calcd for $C_{17}H_{20}F_9IO_4$: C, 34.83; H, 3.44; I, 21.65. Found: C, 34.8; H, 3.5; I, 21.5.

Ethyl 3-Methyl-4-(perfluoropropyl)methylcyclopentyl-1,1-dicarboxylate (XI).—Zinc reduction of IV, $R_F = CF_3CF_2CF_2-$ (19.0 g, 0.0365 mol), was done as above with III. XI, $R_F = CF_3CF_2CF_2-$, 14.0 g, 94%, was distilled without a column: cut 1, bp 88–110° (1.30 mm), $n^{25}\mathrm{D}$ 1.3983, 1.55 g; 2, bp 110–112° (1.00 mm), $n^{25}\mathrm{D}$ 1.3964, 10.0 g; 3, holdup, $n^{25}\mathrm{D}$ 1.3975, 0.45 g; and residue, 1.5 g (80% yield); ir, neat, KBr plates, ν_{CH} 2970 cm^{-1}, ν_{as} CH_3; ν_s CH_3 at 2870 was stronger in XI than in IV; $\nu_{C=O}$ 1735 cm^{-1}. Glpc, using a 6 ft × 0.25 in. Carbowax 20M (10%) on Chromosorb W at 178°, with 25-psi helium, gave peaks: cut 1, 7-min retention time, 0.25%; 8.8 min, 0.15%; 11.1 min, 19.2%; 13.4 min, 79.5%. Cut 2 gave 11.2 min, 20.5%; 13.4 min, 79.5%. Cut 3 gave 11.1 min, 4.7%; 13.4 min, 94%; 17.5 min, 1.6%. The isomer ratio in XI based on relative areas was thus 20:80; nmr (neat) δ 0.90, CH_3CH- (d, J = 6 Hz, 2.2 H); δ 1.2, $(CH_3CH_2O)_2$ (t, J = 7 Hz, 5.1 H); δ 1.87, CH_3CH- (m, unresolved, 1 H); δ 2.0–2.8, $(CH_2)_2$ and R_FCH_2CH- (m, 8.0); δ 4.14, $(CH_3CH_2O)_2$ (q, J = 7 Hz, 4.0 H).

Anal. Calcd for $C_{16}H_{21}F_7O_4$: C, 46.71; H, 5.38. Found: C, 46.31; H, 5.10.

Ethyl 3-methyl-4-(perfluorobutyl)methylcyclopentyl-1,1-dicarboxylate (XI) [$R_F = CF_3(CF_2)_3-$] was obtained from IV in 90% yield, bp 112–114° (1.2 mm), $n^{25}\mathrm{D}$ 1.3896.

Anal. Calcd for $C_{17}H_{21}F_9O_4$: C, 44.36; H, 4.60; F, 37.15. Found: C, 44.5; H, 4.6; F, 37.2.

3-Methyl-4-(perfluoropropyl)methylcyclopentyl-1,1-dicarboxylic Acid (XIII).—XI (8.2 g, 0.020 mol) was added to a solution of KOH (2.24 g, 0.040 mol) in 90% aqueous ethanol (50 ml) and heated at 80° for 10 hr. At 25° water (100 ml) and concentrated HCl (7 ml) were added; the mixture was extracted three times with ether. The ether extract was dried ($MgSO_4$) and evaporated off giving solid XIII: $R_f = CF_3CF_2CF_2-$, 6.9 g, 97%, mp (sinter 103°) 115–125° dec. Essentially all the solid dissolved at the boil in CCl_4 (125 ml), and at 25° deposited 5.95 g of XIII (84%), mp 132.2–132.9°. Recrystallization again from CCl_4 (125 ml) gave 5.93 g of XIII, mp 129.5–130.5°. The filtrates evaporated off gave an oil (0.9 g) which was soluble in ligroin. It was reesterified with ethanol, taking off the ternary azeotrope with benzene. Glpc analysis (6 ft × 0.25 in. Carbowax 20M, 20% on Chromosorb W, 192°, 20-psi helium) gave (1) 2.0 min, 35.6%; (2) 4.0 min, 4.55%; (3) 5.0 min, 2.60%; (4) 5.70 min, 10.4%; (5) 6.75 min, 40.1%; (6) 8.50 min, 6.78%. Peaks 2, 4, 5, and 6 were present in the original mixture. By comparison with a known sample of X isomers run under these conditions, peak 1 was an isomer of X, formed by decarboxylation of XIII and reesterification. Peaks 4 and 5 were isomers of XI, recovered in altered ratio from the original mixture. The solid XIII was evidently isolated in only one isomeric form.

An nmr spectrum of XIII was obtained from 0.26 g in 0.30 ml of acetone-d_6. Insufficient sample dissolved in $HCCl_3$ or CCl_4 to give a spectrum. Resonances were at δ 0.90, CH_3CH- (3.1 H); δ 1.8–3.0, $(CH_2)_3$ and $(CH)_2$ (m, not resolved, 8.2 H); δ 10.8, $(COOH)_2$ (s, 2.0 H); the ratio of CH_3 to COOH again confirmed the postulated structure; ir (KBr disk) ν_{CH} 2975, 2925 (CH_3, CH_2); $\nu_{C=O}$ 1697; δ_{CH_3} 1450; bands at 1430, 1400, 1350, 1280, 1226, 1170, 1110, 960, 922 and 740 cm^{-1}. Titration with 0.0100 N KOH solution using a pH meter gave breaks at pH 5.15 and pH 9.30; neut equiv, 204 (202 theory).

Anal. Calcd for $C_{12}H_{13}F_7O_4$: C, 40.68; H, 3.69; F, 37.54. Found: C, 40.4; H, 3.59; F, 37.4.

3-Methyl-4-(perfluorobutyl)methylcyclopentyl-1,1-dicarboxylic acid, XIII ($R_f = CF_3CF_2CF_2CF_2$), was obtained in similar fashion from XI in 87% yield, mp (sinter 92–99°) 108–120°. A sample (5.0 g) was recrystallized from 1,1,2-trichloro-1,2,2-trifluoroethane ("F-113", 30 ml) and then from benzene, 4.0 g, mp 130–132° (gas evolution). A residual oil (0.46 g) was recovered: nmr (α,α'-dichlorotetrafluoroacetone dihydrate) δ 0.92, CH_3CH– (m, unresolved, 3 H); δ 1.70–2.8, $(CH_2)_3$ and $(CH)_2$ (m, unresolved, 8 H); ir (KBr disk) gave a spectrum very similar to XIII, $R_F = CF_3CF_2CF_2$.

Anal. Calcd for $C_{13}H_{13}F_9O_4$: C, 38.6; H, 3.24; F, 42.3. Found: C, 38.3; H, 3.2; F, 42.3.

Preparation of 3-Methyl-4-(perfluorobutyl)methylcyclopentyl-1-carboxamide.—XIII ($R_f = CF_3CF_2CF_2CF_2$, 2.02 g, 0.0050 mol) in xylene (10 ml) was heated to reflux for 23 hr, giving evolution of carbon dioxide. Solid did not separate from the clear yellow solution upon cooling, but an oily mixture of XII isomers (1.8 g, 95%) was obtained by evaporation. The oil was heated with 5.0 ml of thionyl chloride for 2 hr at 80°; the acid chloride of XII isomers was distilled, bp 108–114° (10 mm), 1.3 g (69%), and poured slowly while stirring into 5.0 ml of concentrated ammonium hydroxide at 0°. White solid amide of XII was collected, washed with water and dried, 1.25 g (100%), mp (sinter 99°) 102–103°. The XII amide ($R_F = CF_3CF_2CF_2CF_2$) was recrystallized from methylcyclohexane, 0.90 g, mp 104–105°, and 0.05 g, mp 101–103.5°.

Anal. Calcd for $C_{12}H_{14}F_9NO$: C, 40.0; H, 3.94. Found: C, 40.0; H, 3.96.

Ethyl 3-Methylene-4-(perfluoropropyl)methylcyclopentyl-1,1-dicarboxylate (XVII) and Ethyl 3-Methylene-4-(perfluoropropyl)-methylcyclopentyl-1-carboxylate (XIX).—Adduct mixture IV (24.9 g, 0.04 mol) was added to a solution of sodium ethoxide prepared from sodium (5.8 g, 0.25 g-atom) in ethanol (100 ml). The temperature rose to 65° and then to 89° when warmed externally; the mixture became dark brown. It was cooled to 52°, kept for 4 hr, and poured into 300 ml of water. Hydrochloric acid (6 *N*, 50 ml) was added, extracted three times with ether, and the ether extracts were rinsed with water, dried ($MgSO_4$), and distilled. The distilled product mixture [bp 135–150° (20 mm), 10.3 g] was fractionated in column A. Cuts 1, 2, and 3, bp 107–127° (12 mm), 3.3 g, contained XIX (21% conversion) and some XVII. Cuts 4, 5, and 6, bp 120–2° (3.2 mm), n^{25}D 1.4020, 7.4 g, were principally XVII (40% conversion). Cuts 1–3 were refractionated to give pure XIX, bp 105° (11 mm), n^{25}D 1.3930. Reaction of IV (0.03 mol) and sodium ethoxide (0.04 mol) in ethanol at 29–30° for 15 hr also gave a mixture of XVII (37%) and XIX (13%). Glpc analysis (QF-1 column, 150°, 30 psi) showed 99% under a peak at 4.3 min (XIX); and 99% under one peak at 20.6 min for XVII in cut 5. At a slower flow rate (15-psi helium pressure) refractionated XIX gave 95.9% at 11.8 min and 4.1% at 19.4 min: XVII, ir ν_{CH} 3090, 3000, 2950, 2920 and 2880; $\nu_{C=O}$ 1730; $\nu_{C=C}$ 1655; δ_{CH} 1470, 1450, 1430, 1380, 1370 and 1350; bands at 1260, 1180, 1120, 1070, 1045, 1020, 960, 930, 890, 860, 760, 725, 715, 660, 650, 550 and 530 cm^{-1}. The ir spectrum of XIX was identical with XVII's from 3090 to 1100 cm^{-1}, but gave bands at 1040, 960, 925, 890, 860, 822, 760, 725, 715, 660, 650, 550 and 530 cm^{-1}. The carbonyl band at 1730 was stronger in XVII, but bands at 1650 and 890 ($C{=}CH_2$) were stronger in XIX than in XVII, as would be expected from the difference in structure. The nmr spectrum of XVII showed CH_3CH_2O at δ 1.25 (t, J = 7 Hz, 6.1 H) and 4.30 (q, J = 7 Hz, 3.9 H); $CH_2{=}C$, δ 5.10 (d, J = 8 Hz, 1.8 H). The nmr spectrum of XIX showed CH_3CH_2O at δ 1.25 (t, J = 7 Hz, 3.2 H) and 4.21 (q, J = 7 Hz, 2.0 H); R_FCH_2CH–, δ 1.9 (t, J = 7 Hz, 1.0 H); $(CH_2)_2CH$, R_FCH_2, δ 1.9–3.4 (m, unresolved, 6.7 H); $CH_2{=}C$, δ 5.08 (d, J = 7 Hz, with additional 1-Hz splitting with protons on the ring, 1.9 H).

Anal. Calcd for $C_{16}H_{19}F_7O_4$ (XVII): C, 47.06; H, 4.69. Found: C, 47.05; H, 4.63.

Anal. Calcd for $C_{13}H_{15}F_7O_2$ (XIX): C, 46.43; H, 4.50; F, 39.55. Found: C, 46.60; H, 4.58; F, 39.23.

Ethyl 3-Chloromethyl-4-(2,2,2-trichloroethyl)cyclopentyl-1,1-dicarboxylate (VIII).—CCl_4 (77.0 g, 0.50 mol), II (24.0 g, 0.10 mol), and a solution of acetonitrile (8.2 g, 0.20 mol), ferric chloride hexahydrate (0.27 g, 0.001 mol), benzoin (0.21 g, 0.002 mol), and diethylamine hydrochloride (0.16 g, 0.0015 mol) were charged to a Fischer–Porter aerosol tube, purged by CO_2 from a piece of Dry Ice, and heated at 77° for 22 hr. The contents were extracted with 5% aqueous hydrochloric acid (25 ml) and dried ($MgSO_4$). VIII was distilled in a short-path still, bp 149–155° (0.15–0.25 mm), with the oil-bath temperature up to 192°; n^{22}D 1.4929; 34.2 g (87%); residue, 2.6 g. Reaction induced by 2 mol % ABN gave 68% of VIII and telomer IX (5.8 g) too high boiling to distil. Elemental analysis and physical properties were consistent with this formulation of IX. VIII was redistilled: bp 145° (0.08 mm); n^{22}D 1.4930; ir (CCl_4) ν_{CH} 2980, 2960, 2910, 2870; $\nu_{C=O}$ 1725; δ_{CH} 1475, 1460, 1440, 1425, 1370, 1360; bands at 1300, 1260, 1180, 1160, 1110, 1070, 1040, 935, 860, 800, 730, 705 cm^{-1}; nmr (10% in CCl_4) δ 1.24 $(CH_3CH_2O)_2$ (t, J = 7 Hz, 6 H); δ 2.2–2.4, $(CH_2)_2$ and $(CH)_2$ (m, unresolved, 5.5 H); δ 2.84, CH_2CCl_3 (m, 2.2 H); δ 3.50, CH_2Cl (m, 2.2 H); and δ 4.13, $(OCH_2CH_3)_2$ (q, J = 7 Hz, 3.8 H).

Anal. Calcd for $C_{14}H_{20}O_4Cl_4$: C, 42.66; H, 5.12; Cl, 35.85. Found: C, 42.8; H, 5.15; Cl, 36.1.

Anal. Calcd for $C_{28}H_{40}O_8Cl_4$ (n = 2 telomer): Cl, 22.7. Found: Cl, 24.8.

Zinc Reduction of VIII to Ethyl 3-Chloromethyl-4-ethylcyclopentyl-1,1-dicarboxylate (XX).—VIII (22.3 g, 0.058 mol) and ethanol (140 ml) was stirred vigorously while anhydrous hydrogen chloride was bubbled in at 75°, and zinc (20 mesh, 26 g, 0.4 g-atom) was added in four portions during 1 hr; the mixture foamed while stirring and gassing with HCl was continued for 17 hr. The liquid was decanted into 200 ml of water and extracted with ether and benzene four times; the organic layer was washed with 5% bicarbonate solution, with water and dried ($MgSO_4$). Fractionation in column A gave XX: bp 110° (0.20 mm); $n^{21.5}$D 1.4630; 10.7 g (65%); brown oil residue, 4.1 g (18.5% as VIII); ir ν_{CH} 2960, 2870 CH_3 stronger in XX than in VIII; no band at 705 cm^{-1} in XX; other bands very similar; nmr δ 1.00, CH_3CH_2 (m, partially obscured by adjacent proton resonance, 3.1 H); δ 1.2, CH_3CH_2O (t, J = 7 Hz, 6.5 H); δ 1.8–2.8, $(CH_2)_2$, CH_2CH_3 and $(CH)_2$ (m, unresolved, 7.9 H); δ 3.50, CH_2Cl (m, 2.1 H); δ 4.12, OCH_2CH_3 (q, J = 7 Hz, 3.9 H).

Anal. Calcd for $C_{14}H_{23}ClO_4$: C, 57.8; H, 7.97; Cl, 12.2. Found: C, 58.0; H, 8.1; Cl, 12.0.

Ethyl 3-Chloromethyl-4-(2,2,2-trichloro)ethylcyclopentyl-1-carboxylate (VII).—CCl_4 (77.0 g, 0.50 mol), I (16.8 g, 0.10 mol), and acetonitrile–$FeCl_3 \cdot 6H_2O$–benzoin–diethylamine hydrochloride exactly as above reacted at 79° for 20 hr gave 27.2 g (84%) of a yellow oil. An 11.1-g portion was distilled in a short-path sublimer apparatus at 90–110° (0.10 mm), n^{24}D 1.5031; and at 98–112° (0.05 mm), n^{24}D 1.5048; less than 0.1 g remained undistilled; ir (CCl_4) ν_{CH} 2980, 2960, 2945, 2920, 2875; $\nu_{C=O}$ 1730; δ_{CH} 1470, 1460, 1440, 1380, 1360, 1345; bands at 1290, 1280, 1180, 1160, 1095, 1035, 920, 880, 860, 700 and 580 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}Cl_4O_2$: C, 41.0; H, 5.00. Found: C, 41.0; H, 5.06.

Registry No.—I, 18-325-74-1; II, 3195-24-2; III ($R_F = CF_3CF_2CF_2$), 20116-37-4; IV ($R_F = CF_3CF_2CF_2$), 20116-24-9; IV [$R_F = CF_3(CF_2)_3$–], 20147-88-0; VII, 20116-25-0; VIII, 20116-26-1; VIII (n = 2 telomer), 20116-27-2; X ($R_F = CF_3CF_2CF_2$–), 20116-28-3; XI [$R_F = CF_3CF_2CF_2$–], 20116-29-4; XI [$R_F = CF_3(CF_2)_3$–], 20116-30-7; XII [$R_F = CF_3(CF_2)_2$–], 20116-31-8; XII amide [$R_F = CF_3(CF_2)_3$–], 20122-03-6; XIII [$R_F = CF_3(CF_2)_3$–], 20116-32-9; XIII ($R_F = CF_3CF_2CF_2$–), 20116-33-0; XIV ($R_F = CF_3CF_2CF_2$–), 20116-34-1; XVII ($R_F = CF_3CF_2CF_2$–), 20116-35-2; XIX ($R_F = CF_3CF_2CF_2$–), 20116-36-3; XX, 20122-02-5.

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