# Cyclization Reactions of Perfluoroalkyl-Substituted Radicals

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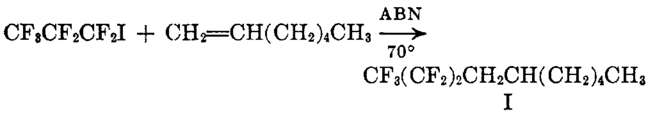
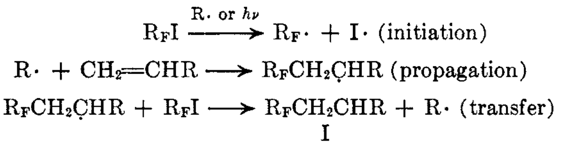
Two pathways to cyclization products from 1,6-heptadiene and iodoperfluoroalkanes ($R_FI$) have been discovered. Ring closure of the intermediate radical, $R_FCH_2\dot{C}H(CH_2)_3CH{=}CH_2$, may occur or the open-chain adduct, $R_FCH_2CHI(CH_2)_3CH{=}CH_2$, may itself rearrange to its cyclic isomers. The latter is a much slower process, although free radical in nature, since it is accelerated by an azonitrile initiator. The influence of reactant ratios or dilution on the relative amount of open-chain and cyclic isomers was determined. Both diallyl ether and 1,6-heptadiene cyclize to five-membered rings rather than to a six-membered ring product.

This paper discusses an unusual radical cyclization reaction which was encountered during a study of the free-radical addition of iodoperfluoroalkanes ($R_FI$) to olefins.[1] Usually a high yield of a single adduct is obtained[2,3] from a large variety of unsaturated compounds and $R_FI$. In a typical example 1-heptene, 1-iodoperfluoropropane, and 1% of azobisisobutyronitrile (ABN) initiator in 6 hr at 70° gave a 99% yield of 1-perfluoropropyl-2-iodoheptane. Less than 1% of 1-hydroperfluoropropane was formed.



$$CF_3CF_2CF_2I + CH_2{=}CH(CH_2)_4CH_3 \xrightarrow[70°]{ABN} CF_3(CF_2)_2CH_2\underset{I}{C}H(CH_2)_4CH_3$$

The commonly assumed mechanism for such reactions comprises three steps.



$$R_FI \xrightarrow{R\cdot \text{ or } h\nu} R_F\cdot + I\cdot \text{ (initiation)}$$

$$R\cdot + CH_2{=}CHR \longrightarrow R_FCH_2\dot{C}HR \text{ (propagation)}$$

$$R_FCH_2\dot{C}HR + R_FI \longrightarrow R_FCH_2\underset{I}{C}HR + R\cdot \text{ (transfer)}$$

Since the reaction depends on efficient transfer of the intermediate radical with $R_FI$ for its maintenance, side reactions which affect this radical usually are harmful. Nevertheless, the alkyl chain may contain a variety of functional groups such as carboxyl, hydroxyl, amido, keto, or a second center of unsaturation.[3] When 1,5-hexadiene or 1,7-octadiene was employed, one or two $R_FI$ molecules were added to one or both ends of the diene, respectively. With 1,6-heptadiene, however, cyclization occurred.[4] Beside a small amount of the monoadduct and bisadduct, the major product was a mixture of isomeric saturated adducts.

$$R_FI + CH_2{=}CH(CH_2)_3CH{=}CH_2 \longrightarrow$$

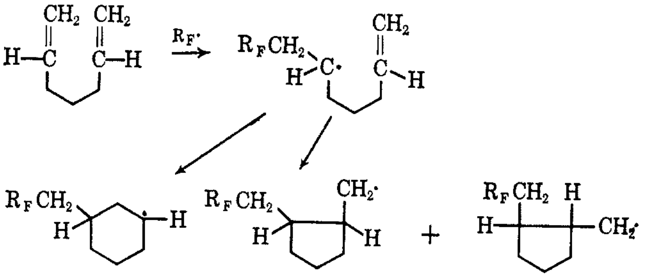
$$\underset{\text{I}}{R_FCH_2CHI(CH_2)_3CH{=}CH_2} + \underset{\text{II}}{R_FCH_2CHI(CH_2)_3CHICH_2R_F} +$$

two saturated cyclic adducts (IIIa,b)

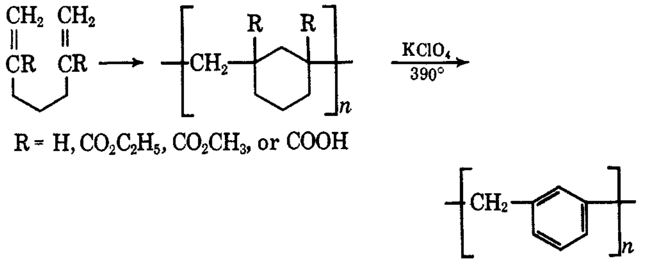
It seemed likely that the intermediate radical cyclized in part to either a six- or five-membered ring which could give *cis*- and *trans*-cyclohexane or cyclopentane adducts, respectively, by transfer with $R_FI$ (Chart I).

CHART I

CYCLIZATION TO SIX- OR FIVE-MEMBERED RINGS



Until recently it has been assumed that cyclization of the 5-hexen-1-yl radical to a six-membered ring would occur.[5-7] For example, in polymerization of various 1,6-heptadienes and analogous compounds soluble products containing very little residual unsaturation were obtained. Cyclohexane repeating units are present in the polymers as shown by conversion to aromatic or to cyclohexadiene rings by various means.[5,7] Two of the polymers prepared by Marvel were dehydrogenated by heating with potassium perchlorate. Ultraviolet and infrared spectra indicated that aromatic rings are present in the product. Also, free-radical addition of bromotrichloromethane, carbon tetrachloride, and the like to 1,6-heptadiene and analogous 1,6-dienes was postulated[8] to give six-membered ring products. These reactions bear a close analogy to the present work and are being studied currently.



R = H, $CO_2C_2H_5$, $CO_2CH_3$, or COOH

More recently, however, it was found that the 5-hexen-1-yl radical generated by two different methods[9,10] cyclizes preferentially to methylcyclopentane, and that certain substituted 5-hexen-1-yl radicals

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[1] This work was begun at the Du Pont Co. and has been continued with the support of the U. S. Army Research Office (Durham) and the Research Corp.

[2] N. O. Brace, *J. Org. Chem.*, **27**, 3027, 3033, 4491 (1962); **28**, 3093 (1963).

[3] N. O. Brace, U. S. Patent 3,145,222 (Aug 18, 1964), assigned to E. I. du Pont de Nemours and Co.

[4] N. O. Brace, *J. Am. Chem. Soc.*, **86**, 523 (1964).

[5] C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957); C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

[6] G. B. Butler and R. J. Angelo, *ibid.*, **79**, 3128 (1957).

[7] S. G. Matsoyan, G. M. Pogosyan, R. K. Skripnikova, and A. V. Mushegyan, *Vysokomolekul. Soedin.*, **5**, 183 (1963); S. G. Matsoyan, G. M. Pogosyan, A. O. Dzhogolyan, and A. V. Mushegyan, *ibid.*, **5**, 854 (1963).

[8] W. S. Friedlander and G. V. D. Tiers, German Patent 1,098,942 (Sept 29, 1958), assigned to Minnesota Mining and Manufacturing Co.

[9] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

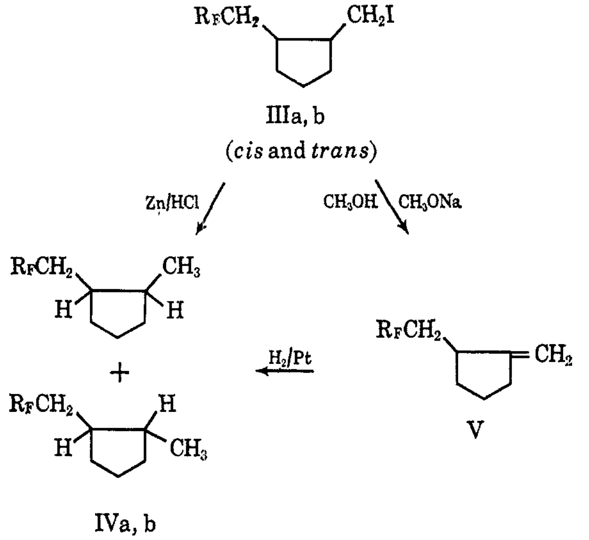
[10] C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

may cyclize to both five- and six-membered ring products.[11] These findings demonstrate that even closely related systems may differ in their behavior and that the products from each reaction must be carefully examined for their structures.

**Proof of Structure of Cyclic Adducts.**—Structures of the cyclic adducts from 1,6-heptadiene and iodoperfluoropropane were ascertained by the scheme shown in Chart II.[4]

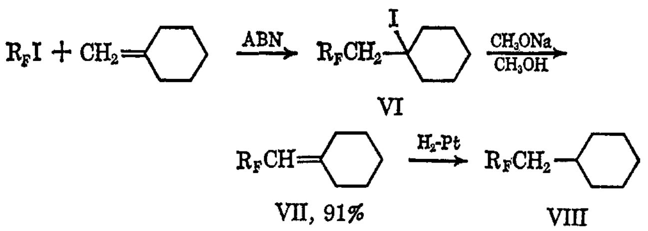
CHART II

REDUCTION AND DEHYDROHALOGENATION OF CYCLIC ADDUCTS



The cyclic adduct mixture IIIa,b was reduced by zinc and hydrogen chloride to a mixture of *cis*- and *trans*-methylcyclopentanes IVa,b bearing the fluoroalkyl side chain. Dehydrohalogenation by sodium methoxide gave but one methylenecyclopentane derivative, V, which was hydrogenated to the same mixture of methylcyclopentane isomers obtained from zinc reduction. Had the cyclic adduct been a cyclohexane, reduction would have given a *single* product, whereas elimination of HI should have given *two* cyclohexenes. These data, along with infrared and nmr spectra, are consistent only with a five-membered ring structure for the cyclic adducts.[4]

To check these conclusions, the fluoroalkylcyclohexane derivative was synthesized which would have resulted from these reactions had the cyclic adduct been a six-membered ring product. Addition of $R_FI$ to methylenecyclohexane gave in high yield 1-iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclohexane (VI) from which the iodine-free cyclohexane VIII was obtained by dehydrohalogenation of VI and catalytic hydrogenation of VII. The tertiary iodine in VI was readily solvolyzed or eliminated. This rendered unsatisfactory the attempted reduction of VI by lithium aluminum hydride or by zinc and hydrogen chloride in ethanol.



The spectrum and properties of VIII were readily distinguished from IVa,b.

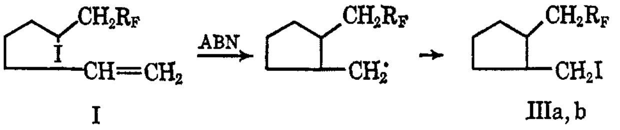
**Isomerization of Olefinic to Cyclic Adducts.**—Surprisingly, cyclization of the first-formed *open-chain* monoadduct I to the saturated cyclic isomers IIIa,b occurred during the course of the reaction (Table I). A tenfold increase in the relative amount of cyclic isomers to olefinic adduct was observed under the given reaction conditions over a 24-hr period.

TABLE I

EFFECT OF REACTANT RATIO ON CYCLIZATION[a]

| Mole ratio of $R_FI$/HPD | Adduct ratio Initial[b] | IIIa,b/I after 24 hr |
|---|---|---|
| | $CF_3CF_2CF_2I$ | |
| 2.0:1.0 | 0.31 | ... |
| 1.0 | 0.68 | 3.82 |
| 1.0:2.0 | 0.80 | 9.85 |
| 1.0:4.0 | ... | 47.7 |
| | $(CF_3)_2CFI$ | |
| 1.0 | ... | 2.60 |
| 1.0:2.0 | 1.1 | 13.3 |
| 1.0:4.0 | ... | 61.1 |

[a] Reaction was done at 60° for 24 hr using 2 mole % of ABN as initiator. [b] Adduct ratios for four runs up to 4.0-hr duration were extrapolated back to zero time (see Tables III, IV, and IX).



The ratio of cyclic isomers to open-chain product (IIIa,b/I) was also a function of reactant ratio, increasing from an initial ratio of 0.3 with a twofold excess of 1-iodoperfluoropropane to 0.8 using 1 mole of 1-iodoperfluoropropane to 2 moles of 1,6-heptadiene. The ratio of adducts rose from 3.82 to 9.85 after 24 hr of reaction for the same reaction mixtures. At a one-fourth reactant ratio IIIa,b/I reached a value as high as 61 for the reaction of 2-iodoperfluoropropane. In this case, gas chromatography showed that all of the $R_FI$ had reacted within 2 hr. When a mixture of approximately equal amounts of I and IIIa,b was heated in *n*-hexane solution at 60° with ABN (1%) as initiator, in 24 hr about half of I had isomerized to IIIa,b. In the absence of ABN less than 10% isomerization occurred. Reaction in each case occurred in sealed ampules which had been filled with nitrogen and evacuated at −70°.

Increasing concentration of 1,6-heptadiene also resulted in a dramatic decrease in II as well. For example, with 1-iodoperfluoropropane and 1,6-heptadiene at a 1:1 mole ratio II comprised 16.0% of the products formed after 24 hr of reaction time, while at 1:4 mole ratio it was only 0.5% of the product mixture.

Cyclization was also promoted by increasing dilution in a *nonreactive* solvent, *n*-hexane. A 3.5:1 ratio of IIIa,b to I was formed after 24 hr at a 1 mole/l. concentration (equimolar amounts of reactants were used). A fourfold dilution gave a 10:1 ratio of IIIa,b to I. In neat solution (Table I) the ratio of IIIa,b to I formed under analogous conditions was 3.82.

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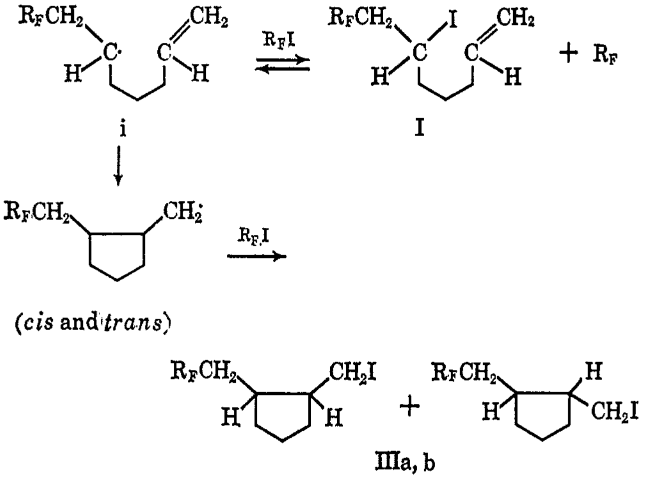
(11) M. Julia, J. M. Surzm, and L. Katg, *Compt. Rend.*, **251**, 1030 (1960); M. Julia and F. LeGoffic, *ibid.*, **255**, 714 (1962); M. Julia, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 3 (1964).

**Discussion of Results.** It appears that there are two processes leading to cyclic isomers running concurrently in the initial stages of the reaction (Chart III).

CHART III
REACTION PATHWAYS TO CYCLIC ADDUCTS



First, the open-chain radical i may cyclize to *cis* and *trans* cyclic radicals, which then transfer with $R_FI$ to give the saturated cyclic adducts (IIIa,b). Secondly, the open-chain adduct I may suffer abstraction of its iodine atom to reform the radical i again, which may then cyclize. This pathway would be expected to be a slower process, since it involves breaking the carbon–iodine covalent bond of I and requires a twisting of the chain into a very restricted conformation where cyclization can occur.

The fact that initial adduct ratios were dependent upon the concentration of perfluoroalkyl iodide indicates that the rate of the transfer step of I with $R_FI$ is the crucial factor. At higher dilution of $R_FI$ it is reasonable to expect that more intramolecular reaction, hence more cyclization of the intermediate radical i could occur before transfer. Thus, as collisions between $R_FI$ and radical i are reduced in frequency, cyclization if it is the slower step, could then better compete. This appears to be the case from the increase in cyclization product with time and with higher olefin concentrations. After all the $R_FI$ is used up it is the equilibrium between i and I which is affected by reaction parameters. Once cyclization has occurred it is not likely it will be reversed. Higher dilution of I, as in the *n*-hexane solution experiments, would then reasonably lead to a higher final concentration of IIIa,b.

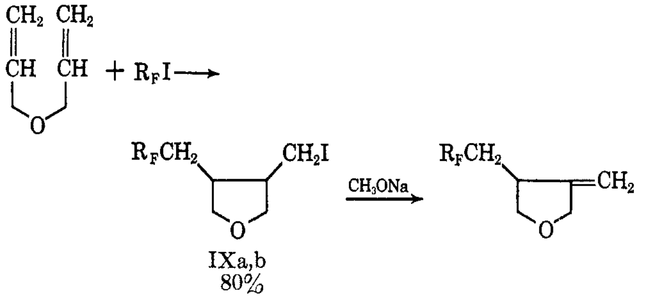
It is significant to note again that cyclization was not observed in analogous reactions of $R_FI$ with either 1,5-hexadiene or with 1,7-octadiene.

Looking at the system from a thermodynamic standpoint instead of the kinetic analysis just given, it appears that the greater stability of the cyclic adduct with its primary iodomethyl group and five-membered ring suffices to overcome the unfavorable entropy change which occurs in the transformation of open-chain to the more rigid ring structure. An estimate of the increase in stability of IIIa,b over I based on bond dissociation energies is about 30 kcal/mole.

Why has cyclization to a *five-membered* ring occurred? Reexamination of Chart I indicates that intramolecular transfer to a five-membered ring converts a secondary radical to the usually less stable primary radical.[10] However, the final product, a cyclopentane having an iodomethyl group, may be a more stable compound than would be the cyclohexane with a secondary iodine atom, since a primary carbon–iodine bond is stronger (by about 8 kcal/mole) than a secondary bond. Of course, the thermodynamic stability of a five-membered ring itself is less than the six-membered ring.[9] In this instance the thermodynamic stability of the final product, rather than the presumed intermediate radicals, apparently is more significant.

Walling[10] points out that models show there is little difference in the steric requirements for ring closure at either C-5 or C-6 of a 5-hexen-1-yl radical. However, with our particular substituted 5-hexen-1-yl radical ring closure to a cyclopentane can occur in two ways, and models show that only the isomer with the two alkyl groups on opposite sides of the ring is relatively free from strain. A preference for *trans* addition of $R_FI$ to cyclopentene in a related system was observed.[12] In cyclohexanes having such adjacent bulky and electronegative groups,[13] steric hindrance may be so great as to cause a twisting of the ring, itself. This may be an additional reason why a cyclopentane structure is favored in this free-radical process.

**Other Diene Systems.**—The cyclization reaction has been extended to analogous dienes such as diallyl ether. The major product formed in 80% yield was the cyclic adduct mixture (IXa,b); there was also isolated 10% of olefinic adduct X and 10% of bis-adduct XI. In this instance also, evidence was obtained which indicated isomerization of X to IXa,b occurred by a slow process. Dehydrohalogenation of IXa,b gave a single exocyclic olefin; infrared spectra showed that it was a 3-methylene–tetrahydrofuran derivative. Thus, a five-membered ring structure for IXa,b was confirmed. As reported previously[4] the cyclization process has been observed in reactions of other 1,6-dienes such as diethyl 1,6-heptadiene-4,4-dicarboxylate or diallyl cyanamide. These and other related reactions will be more fully discussed at a later date.



## Experimental Section

**Gas Chromatographic Analysis.**—The dienes (Table II) and their adducts were analyzed on several columns operated at various conditions given. A 2-m polypropylene glycol column (LB 550-X, 20% on Chromosorb W) is the "R" column. A 2-m column of 20% tetrafluoroethylene–propylene telomer oil on firebrick is indicated by "TFEP." A 2-m Apiezon L (20% on Chromosorb W) and a 6-ft column of Apiezon N (10% on 80–

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(12) N. O. Brace, *J. Org Chem.*, **28**, 3093 (1963).

(13) N. O. Brace, *J. Am. Chem. Soc.*, **86**, 665 (1964).

TABLE II

SOURCE AND PHYSICAL PROPERTIES OF STARTING MATERIALS

| Compd | Supplier | Bp, °C (mm) | $n^{25}\mathrm{D}$ |
|---|---|---|---|
| 1,5-Hexadiene | Columbia Organic Chemical Co. | 59 | 1.4011 |
| 1,6-Heptadiene[a] | Columbia Organic Chemical Co. | 67 (400) | 1.4120 |
| 1,7-Octadiene[b] | Union Carbide Co. | 118 | 1.4192 |
| 1-Iodoperfluoropropane | Columbia Organic Chemical Co. | 41 | 1.3250 |
| 1-Iodoperfluorobutane[c] | | 67 | 1.3252 |
| Biallyl ether[d] | Monomer-Polymer Corp. | 94 | 1.4125 |
| Tri-*n*-butylamine | Eastman Kodak Co. | 101–104 (20) | 1.4228 |
| Methylenecyclohexane[e] | Columbia Organic Chemical Co. | | 1.4475 |
| α,α′-Azobisisobutyronitrile (ABN) | E. I. du Pont de Nemours and Co. | mp 102 (dec) | |

[a] Reference 5b gave bp 90° (750 mm), $n^{25}\mathrm{D}$ 1.4142; analysis by glpc ("R" column at 80°) showed 96% purity. [b] C. S. Marvel and W. E. Garrison, Jr., *J. Am. Chem. Soc.*, **81**, 4737 (1959), reported bp 116–118°, $n^{20}\mathrm{D}$ 1.4236; glpc analysis, 99.5% pure ("R" column, 80°). [c] Prepared from iodopentafluoroethane and tetrafluoroethylene.[2] [d] Glpc analysis, "TFEP" column, 150°, showed a purity of 95%. [e] A. C. Cope and E. Ciganek, *Org. Syn.*, **39**, 41 (1959), reported $n^{25}\mathrm{D}$ 1.4474; glpc analysis ("R" column) gave only one peak.

100 mesh Chromosorb W) were used for the analysis of I, II, and IIIa,b.

**1-Iodoperfluoropropane and 1,6-Heptadiene.**—In a magnetically stirred flask heated to 73° in a bath purged with nitrogen and surmounted by condenser filled with Dry Ice were placed 1,6-heptadiene (19.2 g, 0.20 mole), ABN (0.60 g, 0.004 mole), and 1-iodoperfluoropropane (6.0 g of 60.0 g, 0.20 mole). The remaining 1-iodoperfluoropropane (54 g) was added during 1 hr at 72–75°, cooling as necessary. After 3 hr 1,6-heptadiene was still present; an additional 10.0 g (0.03 mole) of 1-iodoperfluoropropane was added and kept at 74° for 7 hr. Glpc analysis now showed that 98% of the 1,6-heptadiene had reacted, and that the proportion of monoadducts I to IIIa,b was 8/92. IIIa,b were present in a 14:73.4 ratio. Distillation in a 12-in. platinum spinning-band column (column A) gave the following cuts: (1) bp 72–82° (4.5 mm), 3.7 g, an infrared spectrum showed vinyl unsaturation bands; it contained 71% of I, 3.5% of tetramethylsuccinonitrile (mp 168–169°), and 25% of IIIa,b by glpc analysis; (2) bp 84–91° (5.1 mm), $n^{25}\mathrm{D}$ 1.4236, 3.6 g (a mixture similar to 1); (3–6) bp 92–93° (5.5 mm), $n^{25}\mathrm{D}$ 1.4295–1.4309, 53.5 g; (7) bp 50–58° (0.3–0.45 mm), $n^{25}\mathrm{D}$ 1.4302, 4.0 g, a total of 57.5 g of IIIa,b (a 73.5% yield, based on 1,6-heptadiene); (8) a mixture, bp 78–98° (0.40 mm), $n^{25}\mathrm{D}$ 1.4234, 3.1 g; (9–12) bisadduct II, bp 88° (0.10 mm), $n^{25}\mathrm{D}$ 1.4231 (a total of 21.0 g, 15.2% yield of II based on 1,6-heptadiene). A residue of 2.5 g and 1.2 g in the cold trap were recovered.

An nmr spectrum of IIIa,b (60 Mc, tetramethylsilane internal reference, Varian A-60 spectrometer) showed no proton resonance at −4.20 to −4.50 ppm characteristic of CHI (see Varian Spectrum No. 82[14]), but did show a resonance pattern of $CH_2I$ at −3.25 (2.00 proton area), two broad peaks −2.50 and 2.25 (4.00 proton area), and a sharp peak of ring protons at −1.85 ppm (6.00 proton area). An $F^{19}$ nmr spectrum at 56.4 Mc had a $CF_3$ peak at +2.78, $CF_2$ at 49.86, and $CF_2CH$ (broad peak) at 36.12 ppm relative to external trifluoroacetic acid. These data were consistent with the structures assigned. An infrared spectrum of IIIa,b showed no olefinic bands, but bands at 10.45, 11.85, and 13.75 μ.

*Anal.* Calcd for $C_{10}H_{12}F_7I$: C, 30.63; H, 3.09; F, 33.9; I, 32.4. Found: C, 30.9; H, 3.1; F, 34.0; I, 32.0.

The bisadduct II gave an nmr proton spectrum having a CHI peak at −4.50 ppm (2.0 proton area), a triplet of $n\text{-}C_3F_7CH_2$ ($J_{HF}$ = 20 cps) centered at −3.00 ppm (4.0 proton area), and a single peak of $(CH_2)_3$ at −1.90 ppm (6.0 proton area). The $F^{19}$ nmr peaks were $CF_3$, 2.75; $CF_2$, 51.5; $CF_2CH_2$, 35.5 to 36.3 ppm (broad peak). These data were consistent with the structure assigned to II. An infrared spectrum showed no olefinic bands, but bands at 10.50, 10.90, and 13.70 μ.

*Anal.* Calcd for $C_{13}H_{12}F_{14}I_2$: C, 22.7; H, 1.76; F, 38.7; I, 36.9. Found: C, 22.9; H, 1.7; F, 38.7; I, 36.6.

**Hydrolysis of IIIa,b.**—1-Iodomethyl-2-heptafluorobutylcyclopentane (IIIa,b, 20/80 mixture, 38.2 g, 0.007 mole) was added to a slurry of sodium methoxide (10.4 g, 0.20 mole) in methanol (anhydrous, 200 ml) at 67° while stirring. After 4 hr at 67°, the slurry was poured into 200 ml of water, and extracted three times with 20 ml of dichloromethane. The extract was dried (magnesium sulfate) and fractionated in column A. 1-Methylene-2-(2,2,3,3,4,4,4-heptafluorobutyl)cyclopentane (V), bp 97° (144 mm), $n^{25}\mathrm{D}$ .1.3638 (23.0 g, 90% yield), and a residual oil (0.50 g) were obtained. Glpc analysis showed only *one* compound, retention time of 17.9 min ("R" column, 80° (15 psi)).

An infrared spectrum showed a vinyl CH band at 3.24, the stretching band at 6.00, and a strong out-of-plane deformation band of $CH_2{=}CR_1R_2$ at 11.30 μ with the overtone band[15] (weak) at 5.62 μ. Two strong bands were at 10.45 and 10.85 μ. An nmr spectrum at 60 Mc showed a resonance for two vinyl protons (AB-type pattern) at −5.00 ppm analogous to methylenecyclopentane,[16] a broad four-proton peak at −2.40 and several sharp peaks belonging to protons on the ring and having no obvious pattern at −2.10 to −1.4 ppm.

*Anal.* Calcd for $C_{10}H_{11}F_7$: C, 45.46; H, 4.20; F, 50.34. Found: C, 45.6; H, 4.2; F, 50.2.

***cis*- and *trans*-1-Methyl-2(2,2,3,3,4,4,4-heptafluorobutyl)cyclopentane (IVa,b).**—Olefin V (13.2 g, 0.05 mole), 1.50 g of 20% platinum on carbon (Baker and Co.), and 35 ml of 90% ethanol were shaken in a Parr hydrogenator at 25° under 45 psi of hydrogen pressure. A pressure drop of 3.5 psi corresponding to *ca.* 0.05 mole of hydrogen occurred in 10 min, and no further change in 16 hr. The catalyst was filtered off, water was added, and the mixture was extracted with dichloromethane. Fractionation gave IVa,b in three cuts, bp 97° (138 mm), $n^{25}\mathrm{D}$ 1.3562, 11.3 g (an 85% yield). Glpc analysis ["R" column, 80° (15 psi)] showed two compounds were present (39% at 13.6 min and 60% at 17.0 min) and 1% of an impurity at 19.2 min. Analogous results were obtained using platinum oxide catalyst.

An infrared spectrum of the mixture showed no vinyl group bands, but a $CH_3C$ band at 7.24 and two bands at 10.45 and 10.85 μ present in V. The bands cited for cyclohexane derivatives[15] were absent. An nmr spectrum at 60 Mc gave broad resonances at −2.15 and −1.80 ppm, and three peaks at −1.10, −0.92, and −0.82 ppm in the region characteristic for $CH_3CH$.

**Zinc Reduction of IIIa,b.**—IIIa,b (20/80 mixture, 10.0 g, 0.026 mole), zinc (20–40 mesh, 6.5 g, 0.10 mole), and anhydrous ethanol (50 ml) were saturated with hydrogen chloride (gas) while stirring. The temperature rose to 70° and foaming occurred. After intermittent addition of hydrogen chloride for 2 hr at 60–70°, the liquid was decanted into 100 ml of water, and extracted with three portions of dichloromethane (15 ml each). After washing with water and drying (magnesium sulfate), the product was fractionated in column A, giving IVa,b, bp 97° (135 mm), $n^{25}\mathrm{D}$ 1.3561, 5.5 g (a yield of 82%), and residue, 0.2 g. Glpc analysis showed the IVa,b ratio was 20:80, identical with starting material. Infrared spectra of 10/90 and 45/55 mixtures of IVa,b were identical. An nmr spectrum of a 10/90 mixture at 60 Mc, however, showed a clean doublet at −0.84 ppm, and the additional peak at −1.10 ppm in the 45/55 mixture was very weak. The doublet ($J$ = 7 cps) is reasonably ascribed to a methyl group resonance split by an adjacent proton. The area was 2.5 protons (calcd 2.7).

*Anal.* Calcd for $C_{10}H_{13}F_7$: C, 45.12; H, 4.92; F, 50.0. Found: C, 45.6; H, 5.0; F, 50.0.

**Mass Spectrum Analysis.**—Time-of-flight mass spectra of IVa,b were obtained by F. Kitson. A base peak of 56, followed by 41, 55, 42, and parent peak 266 in decreasing intensity, was found for both isomers. Hence, the molecular weight of 266 was confirmed, as well as the methylcyclopentane structure for both isomers. Methylcyclopentane and *cis*- and *trans*-1,2-

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[14] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "N.M.R. Spectra Catalog," Varian Associates, Inc., Palo Alto, Calif., 1962.

[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 3, 34.

[16] Reference 14, Spectrum No. 132.

dimethylcyclopentane also have base peaks of 56, followed by 41 (API spectra).

**1-Iodoperfluoropropane and 1,5-Hexadiene.**—1,5-Hexadiene (8.2 g, 0.1 mole), 1-iodoperfluoropropane (60.0 g, 0.2 mole), and $\alpha,\alpha'$-azobis-$\alpha,\gamma$-dimethylvaleronitrile (AVN) (0.5 g, 0.002 mole) were heated under nitrogen for 7 hr at 60–65°. Distillation in column A gave 5-iodo-7(7,8,8,9,9,9)-heptafluoro-1-nonene (XII), bp 56° (5.0 mm), $n^{25}{}_{\mathrm{D}}$ 1.4109 (13.5 g, 36% conversion); and 1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-5,8-diiodododecane (XIII), bp 85° (0.5 mm), $n^{25}{}_{\mathrm{D}}$ 1.4198, mp *ca.* 28°, 40.3 g, 60% conversion. The cold trap contained 9.5 g (0.032 mole) of 1-iodoperfluoropropane and 1.5 g of residual liquid. The total yield of adducts based on reactants used was 96%. An infrared spectrum of XII showed vinyl CH stretching bands at 3.21 and 3.33, CH bands at 3.40 and 3.50, a vinyl double bond stretching band at 6.05, and associated bands at 10.05 and 10.90 $\mu$; XIII showed CH bands at 3.40 and 3.50, but no vinyl stretching band at 6.05 $\mu$.

*Anal.* Calcd for $C_9F_7H_{10}I$: C, 28.6; H, 2.67; F, 35.2. Found: C, 28.8; H, 2.7; F, 35.3.

*Anal.* Calcd for $C_{12}F_{14}H_{10}I_2$: C, 21.4; H, 1.50; F, 39.45. Found: C, 21.8; H, 1.7; F, 39.5.

Glpc analysis of cuts containing XII or of XIII showed only one substance was present ["TFEP" column, 173° (15 psi of helium)].

1-Iodoperfluoropropane was added slowly to 1,5-hexadiene over a 3.5-hr period at 70° and kept at 70° for a total of 12.5 hr; glpc analysis of the reaction mixture gave a ratio of XII to XIII of 0.18/1. No other products were present in more than 1% concentration.

**1-Iodononafluorobutane and 1,7-Octadiene.**—1,7-Octadiene (5.5 g, 0.05 mole), 1-iodononafluorobutane (35.0 g, 0.10 mole), and ABN (0.16 g, 0.001 mole) were heated at 70° under nitrogen while stirring for 18 hr. The colorless reaction mixture was sampled. Glpc analysis showed both reactants were present after 2.5 hr, but only 1-iodononafluorobutane after 18 hr. Distillation in column A gave 6-iodo-1,1,2,2,3,3,4,4,4-nonafluoro-11-dodecene (XIV), bp 56° (0.25 mm), $n^{25}{}_{\mathrm{D}}$ 1.4080, 4.81 g, 21% conversion (glpc analysis showed one peak); and 6,11-diiodo-1,1,1,2,2,3,3,4,4,13,13,14,14,15,15,16,16,16-octadecafluorohexadecane (XV), bp 118° (0.30 mm), $n^{25}{}_{\mathrm{D}}$ 1.4100 (three fractions of same $n^{25}{}_{\mathrm{D}}$), 31.6 g, 76% conversion. An oil residue (0.8 g) remained. 1-Iodononafluorobutane, 1-hydrononafluorobutane, and 1,7-octadiene were recovered (3.47 g). An infrared spectrum of XIV showed a vinyl CH stretching band at 3.20, the vinyl group band at 6.08 (moderate strength) with associated bands at 10.05 and 10.95 $\mu$. In the spectrum of XV no vinyl unsaturation was indicated, and no $CH_3C$ band at 7.25 $\mu$ was present in either XIV or XV, indicating that addition occurred at the terminal carbon.

*Anal.* Calcd for $C_{12}H_{14}F_9I$: C, 31.6; H, 3.09; F, 37.5; I, 27.8. Found: C, 32.0; H, 3.0; F, 38.8; I, 27.1.

*Anal.* Calcd for $C_{16}H_{14}F_{18}I_2$: C, 23.96; H, 1.76; F, 42.6; I, 31.65. Found: C, 24.0; H, 1.6; F, 42.7; I, 31.8.

**1-Iodo-1-(2,2,3,3,4,4,4-heptafluorobutyl)cyclohexane (VI).**—Methylenecyclohexane (9.6 g, 0.1 mole) and ABN (0.30 g, 0.002 mole) were heated under nitrogen in an oil bath at 70° while 1-iodoperfluoropropane (30.0 g, 0.1 mole) was added over a 1.5-hr period to control the temperature. After an additional 13 hr at 70–72°, distillation in column A gave 33.0 g of VI, bp 61° (0.80 mm) or 46° (0.5 mm), $n^{25}{}_{\mathrm{D}}$ 1.4378, 85% conversion. On a twofold scale using a 10% excess of 1-iodoperfluoropropane the conversion to VI was 92%; unreacted material (13 g) was recovered (100% yield). Infrared and nmr spectra were consistent with the structure VI. A triplet ($J_{\mathrm{HF}} = 20$ cps) centered at −3.10 ppm (relative to TMSi at 60 Mc) having the area for two protons of $R_FCH_2$ and proton resonance peaks of the remaining 10 protons at −2.32, −2.10, −1.65, −1.49, and −1.26 ppm were obtained. An $F^{19}$ spectrum at 56.4 Mc relative to external trifluoroacetic acid showed resonances at 2.73 ($CF_3$, a triplet), 32.09 (a complex multiplet of $CF_2CH_2$), and 50.35 ppm (a single line of $CF_2$).

*Anal.* Calcd for $C_{10}H_{12}F_7I$: C, 30.63; H, 3.09; F, 33.9; I, 32.37. Found: C, 30.9; H, 3.0; F, 33.5; I, 32.4.

**2,2,3,3,4,4,4-Heptafluorobutylidenecyclohexane (VII).**—Compound VI above (19.6 g, 0.05 mole) was added to a slurry of sodium methoxide (5.4 g, 0.1 mole) in 50 ml of methanol, and stirred for 4 hr at 70°. The mixture was poured into 100 ml of water, the lower layer was separated, and the aqueous layer was extracted three times with 10 ml of dichloromethane. After drying over magnesium sulfate and filtering, distillation (column A) gave VII, bp 102° (140 mm), $n^{25}{}_{\mathrm{D}}$ 1.3734, 12.0 g (91%). An infrared spectrum showed a vinyl stretching band at 5.95, and a weak band at 10.10 $\mu$. The nmr spectrum (TMSi reference) gave a triplet ($J_{\mathrm{HF}} = 16$ cps) (entered at −5.40 ppm, with integrated area of one proton, a broad double resonance peak of area for four protons at −2.45 and −2.25 ppm, and a single sharp resonance peak (six-proton area) at −1.78 ppm. The pattern was consistent for $R_FCH{=}C$. Peaks in the $F^{19}$ spectrum were $CF_3$ at +3.58, $CF_2CH{=}$ at +28.23, and $CF_2$ at +50.92 ppm (external $CF_3COOH$ reference). The substance gave only one peak in glpc analysis ("R" column, 150° (15 psi), 4.80 min). Retention time was 27 min at 80°.

**2,2,3,3,4,4,4-Heptafluorobutylcyclohexane (VIII).**—VII (6.0 g, 0.023 mole) and 1.0 g. of 20% platinum-on-carbon catalyst (Baker and Co.) in 25 ml of anhydrous ethanol were shaken at 45 psi of hydrogen pressure in a Parr hydrogenator at 25°. Hydrogen was absorbed for 10 min and stopped. After 16 hr the catalyst was filtered off and the solution was diluted with water and extracted into dichloromethane. Glpc analysis ("R" column) showed only one peak at 3.90 min (150°) or at 20.0 min (80°) and none of VII. Distillation gave 4.33 g of VIII, bp 100° (137 mm), $n^{25}{}_{\mathrm{D}}$ 1.3585 (65% recovery). An infrared spectrum showed no C=C or $CCH_3$ bands, but strong absorption bands at 9.60 and 10.23 $\mu$ in the regions cited[15] for cyclohexane rings. The nmr spectrum had only broad proton resonances at −2.30, −2.00, −1.35, and −1.25 ppm. The $F^{19}$ nmr spectrum gave $CF_3$ (+3.58 ppm), a triplet ($J = 9.5$ cps), $CF_2CH_2$ (+35.94 ppm, a broad peak), and $CF_2$ (+50.83 ppm unsplit peak).

*Anal.* Calcd for $C_{10}F_7H_{13}$: C, 45.12; H, 4.9; F, 49.96. Found: C, 45.1; H, 4.9; F, 50.5.

**Other Reduction Methods.**—An attempt to remove the iodine from VI by lithium aluminum hydride reduction (fourfold excess) in ether at reflux for 1.5 hr and the usual work-up conditions gave both reduction to VIII and elimination to VII; 40% of VI was recovered. An attempt to reduce VI (28.6 g, 0.71 mole) with zinc (28.0 g, 0.4 mole) added in portions to a solution of dry hydrogen chloride in 100 ml of ethanol at 40–65° gave 12.0 g of a mixture of VII (40%) and VIII (60%), according to glpc analysis. Total conversion was 64%. Higher boiling fractions (4.0 g) showed prominent hydroxyl group absorption in the infrared spectra. Solvolysis of the tertiary iodide evidently occurred.

**1-Iodoperfluoropropane and Biallyl Ether.**—Biallyl ether (9.8 g, 0.1 mole), 1-iodoperfluoropropane (60.0 g, 0.2 mole), and AVN (0.3 g, 0.001 mole) were heated at 59–64° for 12 hr. Distillation (column A) gave unreacted 1-iodoperfluoropropane (32.7 g, 55%) and monoadducts, IXa,b and X, bp 98–102° (5 mm), 29.8 g, (a yield of 76% based on biallyl ether), and residue 0.5 g. A liquid fraction, bp 80° (0.3 mm), $n^{25}{}_{\mathrm{D}}$ 1.4183, 2.8 g, probably contained bisadduct XI also. The cold trap (6.8 g) contained about equal amounts of the starting materials (glpc analysis). Refractionation of the adducts in column A gave (1) bp 65–69° (5.4 mm), $n^{25}{}_{\mathrm{D}}$ 1.4068, 0.6 g; (2) bp 72–93° (5.4 mm), $n^{25}{}_{\mathrm{D}}$ 1.4137, 1.9 g [cuts 1 and 2 contained three compounds by glpc analysis, principally (75–88%) X, having a retention time of 5.3 min; "TFEP" column, 150° (15 psi of helium)]; (3) bp 96–98° (5.6 mm), $n^{25}{}_{\mathrm{D}}$ 1.4250, 1.0 g (three compounds also, 25% of X); (4) bp 101° (5.0 mm), $n^{25}{}_{\mathrm{D}}$ 1.4293, 3.4 g; (5–7) bp 100° (5.0 mm), $n^{25}{}_{\mathrm{D}}$ 1.4311, 18.7 g, residue 0.9 g. Glpc analysis of cuts 5, 6, and 7 showed IXa,b were present: 16.1 min (*ca.* 30%) and 17.1 min (*ca.* 70%). An infrared spectrum of X showed vinyl absorption bands at 6.05 and 10.05 $\mu$; IXa,b showed none of these bands. Cut 3 gave a slow reaction with 1% $KMnO_4$ solution in acetone; IXa,b gave no reaction.

A series of ampoules was charged with 1-iodoperfluoropropane, biallyl ether, and ABN as above. After heating at 60° for varying periods of time, glpc analysis showed that the ratio of X to IXa,b decreased after 31 hr.

*Anal.* Calcd for $C_9H_{10}F_7IO$: C, 27.45; H. 2.56; F, 33.8; I, 32.2. Found: C, 27.5; H, 2.7; F, 34.0; I, 32.2.

**Dehydrohalogenation of IXa,b.**—IXa,b (cuts 5 and 6 above, 8.0 g, 0.02 mole) and tri-*n*-butylamine (7.4 g, 0.04 mole) were heated at 162–193° in column A for 1 hr and at 180° (112 mm) for 1 hr taking off distillate (3.91 and 1.14 g). The cuts were shaken with 10% aqueous sulfuric acid (5.0 ml) and redistilled: (1) bp 102–112° (190 mm), $n^{25}{}_{\mathrm{D}}$ 1.3770, 1.02 g; (2) 113° (185 mm), $n^{25}{}_{\mathrm{D}}$ 1.3638, 2.46 g; and (3) holdup, $n^{25}{}_{\mathrm{D}}$ 1.3631, 0.60 g. Residue was 0.30 g. Glpc analysis of 1 and 2 showed only one main peak (99%) using three different columns [1-m tricresyl phosphate at 127° (1.5 of psi helium); 2-m bismethoxyethyl phthalate, 80° (10 psi); the "R" column, 80° (20 psi of helium)], 36.6-min retention time. An nmr spectrum at 60 Mc showed two vinyl protons at −5.10 ppm (an AB pattern), a two-proton resonance. Infrared spectrum showed $CH_2{=}C$ (exocyclic) at 11.20 and at 5.98 μ, just as also found in V.

**Reaction of 1-Iodoperfluoropropane or 2-Iodoperfluoropropane and 1,6-Heptadiene at a 1:2 Mole Ratio for Varying Length of Time.**—A reaction mixture containing 1.567 g (0.0050 mole) of 1-iodoperfluoropropane, 0.962 g or 1.30 ml (0.010 mole) of 1,6-heptadiene, and 0.0164 g (0.0001 mole) of ABN was prepared and about 50.0 μl of the clear solution was placed in each of several ampoules. After heating for the periods of time indicated in Table III, two each of the ampoules were removed from a bath at 60°, quenched at −70°, and analyzed by glpc [Apiezon L column, 180° (15 psi)]. The per cent conversion to adducts was determined by averaging the two measured values, which were generally within ±1%.

TABLE III

$CF_3CF_2CF_2I$ AND 1,6-HEPTADIENE FOR VARYING TIMES

| Reaction time, hr | % conversion to adducts: I | IIIa,b | | II | Adduct ratio: III/I | III/I + II |
|---|---|---|---|---|---|---|
| 1 | 43.2 | 9.34 | 45.16 | 2.3 | 1.26 | 1.20 |
| 4 | 29.3 | 10.0 | 56.76 | 4.0 | 2.28 | 2.00 |
| 7 | 24.9 | 12.0 | 59.5 | 3.6 | 2.86 | 2.50 |
| 12 | 15.8 | 14.5 | 67.6 | 2.1 | 5.19 | 4.58 |
| 24.5 | 8.6 | 17.3 | 67.3 | 4.0 | 9.85 | 6.70 |
| 46 | 2.9 | 16.8 | 76.1 | 1.3 | 32.0 | 31.0 |

The glpc curves were quite clean and the only products present in significant amount after 4 to 12 hr of reaction time were I, II, and IIIa,b. After 24.5 hr there was a trace of substance appearing after I and another compound with retention slightly longer than IIIa,b. The 1-iodoperfluoropropane was incompletely reacted in 1 hr; an estimated 41% was present. After 4 hr less than 0.3% was present in any of the product mixtures.

Another reaction mixture (see Table IV) contained 1.56 g (0.0050 mole) of 2-iodoperfluoropropane, 0.92 g (0.010 mole) of 1,6-heptadiene, and 0.0164 g (0.00010 mole) of ABN. After 1 hr there was only about 5.9% of 2-iodoperfluoropropane unreacted.

TABLE IV

$(CF_3)_2CFI$ AND 1,6-HEPTADIENE AT 60° FOR VARYING TIMES

| Reaction time, hr | % conversion to adducts: I | IIIa,b | II | Adduct ratio: IIIa,b/I | III/I + II |
|---|---|---|---|---|---|
| 1 | 41.5 | 51.9 | 7.00 | 1.25 | 1.07 |
| 4 | 34.0 | 58.7 | 7.11 | 1.73 | 1.43 |
| 7 | 27.9 | 66.3 | 5.5 | 2.38 | 2.00 |
| 11 | 22.3 | 78.75 | 4.6 | 3.54 | 2.93 |
| 22 | 7.85 | 89.0 | 3.4 | 11.34 | 7.94 |
| 24.5 | 6.7 | 90.0 | 3.3 | 13.3 | 9.0 |

**Free-Radical Reaction of 1-Iodoperfluoropropane and 1,6-Heptadiene in *n*-Hexane Solution.**—A mixture of equimolar amounts of reactants and 1 mole % of ABN was used for running the reaction at three levels of concentration in *n*-hexane solution. The total volume was 1.00 ml in each case (see Table V).

TABLE V

REACTION IN *n*-HEXANE AT 60° FOR 24.5 HR

| Reactants: $R_FI$, *M* | HPD, *M* | Concn, mole/l. | % conversion to adducts: I | IIIa,b | II | Adduct ratio: III/I | III/I + II |
|---|---|---|---|---|---|---|---|
| 0.001 | 0.001 | 1.0 | 20.9 | 72.6 | 6.0 | 3.5 | 2.7 |
| 0.0005 | 0.0005 | 0.5 | 12.2 | 84.2 | 3.6 | 6.9 | 5.3 |
| 0.00025 | 0.00025 | 0.25 | 7.8 | 90.3 | 1.5 | 9.7 | 7.6 |

The same procedure with 2-iodoperfluoropropane gave similar results. The results of glpc analysis are listed in Table VI.

TABLE VI

REACTION IN *n*-HEXANE AT 60° FOR 24.5 HR

| Reactants: $R_FI$, *M* | HPD, *M* | Concn, mole/l. | % conversion to adducts: I | IIIa,b | II | Adduct ratio: III/I | III/I + II |
|---|---|---|---|---|---|---|---|
| 0.001 | 0.001 | 1.0 | 14.5 | 77.2 | 8.3 | 5.31 | 3.8 |
| 0.0005 | 0.0005 | 0.5 | 9.4 | 86.1 | 4.4 | 9.15 | 6.15 |
| 0.00025 | 0.00025 | 0.25 | 6.0 | 91.7 | 2.3 | 15.3 | 11.2 |

**Isomerization of Olefinic to Cyclic Compounds in *n*-Hexane Solution.**—A sample of I ($R_F$ = $CF_3CF_2CF_2$, 53.3%) and IIIa,b (41%), which also contained an unknown impurity (5.0%), was made up to 1 mole/l. concentration in *n*-hexane. To one-half of the solution, ABN was added at 1 mole % concentration based on I and IIIa,b. Ampoules were charged, evacuated, and filled with nitrogen twice and sealed *in vacuo*. After 6, 11, and 24 hr at 60° in an oil bath, two ampoules each were quenched and the composition determined by glpc analysis [Apiezon N, 170° (20 psi of helium)]. Peaks corresponding to I (3.2 min) and IIIa,b (6.8 and 7.8 min) were measured. The unknown impurity was essentially unchanged by the reaction (see Table VII).

TABLE VII

ABN-INDUCED ISOMERIZATION OF I AT 60°

| Time, hr | With ABN, %: I | IIIa,b | Without ABN, %: I | IIIa,b |
|---|---|---|---|---|
| 0 | 53.3 | 41 | 53.3 | 41 |
| 6 | 51 | 43 | 52 | 42 |
| 9 | 46.7 | 48 | 51.3 | 43 |
| 24 | 27.5 | 67.5 | 45.5 | 50.0 |

While a small amount of isomerization occurred without ABN, a 50% change occurred with the free-radical initiator present.

**Competitive Reaction of 1-Iodoperfluoropropane and 2-Iodoperfluoropropane with 1,6-Heptadiene.**—A solution of 1-iodoperfluoropropane and 1,6-heptadiene both 0.5 *M* in *n*-hexane and containing 1 mole % of ABN (based on 1-iodoperfluoropropane) and an exactly similar solution of 2-iodoperfluoropropane and 1,6-heptadiene were mixed. Samples were distributed in five ampoules, and sealed in the usual manner. After heating at 60° for the times indicated below, the contents were analyzed by glpc (see Table VIII).

TABLE VIII

COMPETITIVE REACTION OF $CF_3CF_2CF_2I$ AND $(CF_3)_2CFI$

| Time, hr | Olefinic adducts: $CF_3CF_2$-$CF_2$ | $(CF_3)_2CF$ | Cyclic adducts: $CF_3CF_2$-$CF_2$ | $(CF_3)_2CF$ | Total adducts: $CF_3CF_2$-$CF_2$ | $(CF_3)_2CF$ |
|---|---|---|---|---|---|---|
| 0.50 | 7.2 | 5.8 | 27.3 | 59.7 | 34.5 | 65.5 |
| 1.0 | 6.7 | 4.4 | 29.3 | 59.5 | 36.0 | 64.0 |
| 2.5 | 6.4 | 4.2 | 33.4 | 55.9 | 39.9 | 60.1 |
| 5.5 | 4.2 | 2.0 | 44.2 | 49.6 | 47.5 | 52.5 |

Extrapolation of these values back to zero time showed that the ratio of total $(CF_3)_2CF$ adducts to $CF_3CF_2CF_2$ adducts was 2 to 1. After 5.5 hr this ratio approached unity as the more slowly reacting $CF_3CF_2CF_2I$ formed an increasing amount of its adducts in the product mixture. Isomerization of some of the initially formed olefinic adducts is also evident.

**Varying Mole Ratios of $R_FI$ and 1,6-Heptadiene at 60°.**—Mixtures were prepared and treated as described above. The results of reaction under various conditions and mole ratios are given in Table IX.

These data are generally consistent with the results shown in Tables III and IV, but in common with other free-radical reactions; differences in reaction rates and conversion are apparent. The important effects of reactant ratio and of reaction time on product distribution are clearly evident.

Table IX

Reactions of $CF_3CF_2CF_2I$ and of $(CF_3)_2CFI$ with 1,6-Heptadiene

| Reaction time, hr | Reactants, $M$ | | | | % conversion to adducts | | | Adduct ratio | |
|---|---|---|---|---|---|---|---|---|---|
| | $CF_3CF_2CF_2I$ | HPD | ABN[a] | $R_FI$[b]/HPD | I | IIIa,b | II | III/I | III/I + II |
| 0.16 | 0.0050 | 0.0050 | 1.00 | 1.0/1.0 | 57.4 | 40.8 | 1.8 | 0.71 | 0.69 |
| 0.16 | 0.0050 | 0.0100 | 1.00 | 1.0/2.0 | 55.5 | 43.3 | 1.0 | 0.78 | 0.77 |
| 0.33 | 0.0100 | 0.0050 | 1.00 | 2.0/1.0 | 68.0 | 26.3 | 5.5 | 0.39 | 0.36 |
| 0.33 | 0.0050 | 0.0050 | 1.00 | 1.0/1.0 | 60.0 | 39.0 | 1.0 | 0.65 | 0.65 |
| 0.33 | 0.0050 | 0.0100 | 1.00 | 1.0/2.0 | 55.5 | 43.3 | 1.0 | 0.78 | 0.77 |
| 0.50 | 0.010 | 0.0050 | 1.00 | 2.0/1.0 | 62.5 | 23.8 | 13.7 | 0.38 | 0.31 |
| 0.50 | 0.0050 | 0.0050 | 1.00 | 1.0/1.0 | 57.0 | 37.4 | 5.7 | 0.66 | 0.60 |
| 0.50 | 0.0050 | 0.010 | 1.00 | 1.0/2.0 | 55.7 | 43.8 | 0.6 | 0.78 | 0.78 |
| 1.50 | 0.010 | 0.0050 | 1.00 | 2.0/1.0 | 57.5 | 25.7 | 16.8 | 0.45 | 0.35 |
| 1.50 | 0.0050 | 0.0050 | 1.00 | 1.0/1.0 | 56.4 | 37.4 | 6.3 | 0.66 | 0.60 |
| 4.00 | 0.010 | 0.0050 | 1.00 | 2.0/1.0 | 44.5 | 27.6 | 27.9 | 0.62 | 0.38 |
| 24.0 | 0.010 | 0.010 | 1.00 | 1.0/1.0 | 17.0 | 64.2 | 16.0 | 3.82 | 1.94 |
| 24.0 | 0.0050 | 0.010 | 1.00 | 1.0/2.0 | 8.6 | 84.5 | 4.0 | 9.85 | 6.70 |
| 24.0 | 0.0025 | 0.010 | 1.00 | 1.0/4.0 | 2.0 | 95.5 | 0.5 | 47.7 | 38.1 |
| 46.0 | 0.010 | 0.010 | 1.00 | 1.0/1.0 | 15.0 | 63.9 | 20.9 | 4.25 | 1.77 |
| 46.0 | 0.0050 | 0.010 | 1.00 | 1.0/2.0 | 4.06 | 92.95 | 1.3 | 23.2 | 17.5 |
| 46.0 | 0.0025 | 0.020 | 1.00 | 1.0/4.0 | 2.0 | 98.0 | 0.0 | 46.0 | 46.0 |
| | $(CF_3)_2CFI$ | | | | | | | | |
| 7.5 | 0.010 | 0.010 | 1.35 | 1.0/1.0 | 37.3 | 39.0 | 22.6 | 1.04 | 0.65 |
| 7.5 | 0.0050 | 0.010 | 1.10 | 1.0/2.0 | 32.2 | 58.0 | 9.74 | 1.80 | 1.38 |
| 7.5 | 0.0025 | 0.020 | 0.86 | 1.0/4.0 | 30.4 | 68.4 | 1.4 | 2.25 | 2.16 |
| 24.5 | 0.010 | 0.010 | 1.00 | 1.0/1.0 | 21.0 | 54.5 | 24.5 | 2.60 | 1.2 |
| 24.5 | 0.0050 | 0.010 | 1.00 | 1.0/2.0 | 6.70 | 90.0 | 3.3 | 13.3 | 9.0 |
| 24.5 | 0.0025 | 0.010 | 1.00 | 1.0/4.0 | 1.55 | 98.4 | trace | 61.1 | 61.1 |

[a] $M \times 10^{-4}$. [b] $R_FI$ is either $CF_3CF_2CF_2I$ or $(CF_3)_2CFI$.

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# Isomerization of Propargylic Amines to Conjugated Dienes. 2-Dialkylamino-1,3-butadienes

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A new class of reactive compounds, 2-dialkylamino-1,3-butadienes, may be obtained in good yield by the base-catalyzed isomerization of 3-dialkylamino-1-butynes.

Although base-catalyzed acetylene–allene and acetylene–acetylene interconversions have been reported frequently since the early work of Favorskii,[1-9] only recently have many examples of acetylene–allene–conjugated diene interconversions been reported. For instance Smadja has successfully isomerized 1-heptyne and 1-octyne to conjugated systems using potassium tertiary butoxide in dimethyl sulfoxide.[10] Subsequent investigations by Julia and Baillarge have shown that 1,1,4,4-tetraphenyl-1,2-butadiene gives 1,1,4,4-tetraphenyl-1,3-butadiene upon treatment with methanolic potassium hydroxide; 1,4-diphenoxy-2-butyne undergoes a similar rearrangement.[11] Recently an interesting example of an enyne system undergoing isomerization has been reported. The naturally occurring methyl crepenynate has been isomerized to *trans,cis,trans*- and *trans,cis,cis*-8,10,12-octadecatrienoic acids in 70% yield plus other conjugated trienes when heated with potassium hydroxide.[12] Sondheimer has converted cyclic polyynes and related compounds to fully conjugated ring systems with ease.[13] 1,2-Cyclodecadiene or cyclodecyne when heated with potassium hydroxide in diethyl "Carbitol" results in the formation of 69–73% *cis,cis*-1,3-cyclodecadiene.[14] Phenyl-substituted propargylic ethers and thio ethers have been easily isomerized to the allenes with potassium tertiary butoxide in dimethyl sulfoxide.[15] Under similar conditions, 1,3-diphenyl-3-dimethylamino-1-propyne and 1,3-diphenyl-3-dimethylamino-1,2-propadiene were equilibrated. However, in all cases when phenyl groups were replaced by alkyl groups, difficulties were reported.

We wish to report an example of a facile base-catalyzed isomerization of certain acetylenic compounds to 1,3-dienes; the reaction has been applied to propargylic amines and to hexynes, the former providing some heretofore unreported 3-dialkylamino-1,3-conjugated dienes. Since the propargylic amines are

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