[CONTRIBUTION FROM THE RESEARCH DIVISION, WYANDOTTE CHEMICALS CORP.]

Reactions of 4,4-Dihydro-3-iodoperfluoroheptane and 2,2-Dihydro-3-iodoperfluoropentane[1,2]

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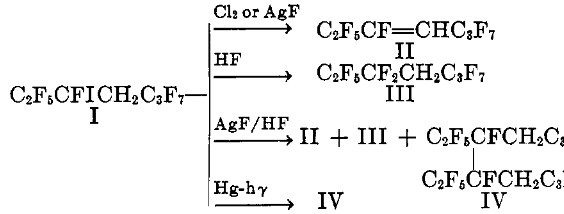
The reactions of 4,4-dihydro-3-iodoperfluoroheptane (I) with chlorine, silver fluoride, hydrogen fluoride (alone and in the presence of silver fluoride) and with mercury (under ultraviolet irradiation) are described. Chlorine afforded 4-hydroperfluoroheptene-3 (II), as did also silver fluoride. Hydrogen fluoride treatment resulted in the formation of 4,4-dihydroperfluoroheptane (III) exclusively, but hydrogen fluoride in the presence of silver fluoride gave in addition to II and III some coupled product, 5,6-diperfluoroethyl-4,4,7,7-tetrahydroperfluorodecane (IV). The latter was obtained readily by ultraviolet irradiation of I in the presence of mercury. 2,2-Dihydro-3-iodoperfluoropentane (XV) under these conditions afforded 3,4-diperfluoroethyl-2,2,5,5-tetrahydroperfluorohexane. The coupled compounds were each resolved by gas chromatography into the *meso*-form and the racemate. Synthesis of 2,4-dihydro-3-perfluoroethyl-2,4-perfluoroheptadiene (X) was accomplished by telomerization of 2,2-dihydro-3-iodoperfluoropentane (XV) with 1,1-dihydroperfluorobutene-1 (VIII), followed by base dehydrohalogenation of the resulting 2,2,4,4-tetrahydro-3-perfluoroethyl-5-iodoperfluoroheptane (IX). The direct telomerization of trifluoroiodomethane and VIII failed to give IX in good yield. Compound IX was resolved by gas chromatography into two diastereoisomers. The diastereoisomers and the olefins afforded interesting infrared spectra.

4,4-Dihydro-3-iodoperfluoroheptane (I) was synthesized initially[3] for model studies of the cross-linking mechanism of fluoro elastomers.[4] Subsequent investigations required either a chlorine or a fluorine substituent in place of iodine.

Treatment of I with two moles of chlorine at low temperatures resulted in an 83% yield of 4-hydroperfluoroheptene-3 (II). The procedure was a convenient one for dehydrohalogenation.

Substitution of the iodine by fluorine was accomplished by heating I with hydrogen fluoride at 130° for prolonged periods of time. No olefin, II, was formed during this reaction. The infrared spectrum of the product, 4,4-dihydroperfluoroheptane (III), showed the expected absorption at 7.0 μ, observed also in the starting material. This, in conjunction with the considerably lower refractive index, supported the structure III. The band at 7.0 μ, in the compounds of the general formula R_fCH_2X (X = F, Cl, Br or I), has been ascribed[5] to the methylene deformation, as influenced by the adjacent perfluoro grouping and the halogen substituent. It was observed in this laboratory that the 7.0-μ absorption was also exhibited by compounds containing the $R_f'CH_2CFXR_f''$ moiety (R_f' and R_f'' = $(CF_2)_n$ or CF_3; X = F, Cl, Br or I), but this was not surprising inasmuch as the effective electronegativity of CF_2 and CF_3 groups is known to be very high.[6]



When the reaction of I with hydrogen fluoride was conducted in the presence of silver fluoride, some coupled product IV formed along with III and olefin II, whereas silver fluoride alone afforded only the latter. Gas chromatography of 5,6-diperfluoroethyl-4,4,7,7-tetrahydroperfluorodecane (IV) showed the presence of two compounds, apparently the *meso*-form and the racemate, in the ratio of 1.42:1.

A 75% yield of the coupled compound IV was obtained by ultraviolet irradiation of 4,4-dihydro-3-iodoperfluoroheptane (I) in the presence of mercury.[7] Again the product was separated by gas chromatography into the same diastereoisomers in the ratio of 1.52:1. These materials exhibited somewhat different infrared spectra. In the methylene deformation region of the first eluted diastereoisomer a doublet was observed at 6.85 and 6.90 μ, whereas only a single band at 6.85 μ was present in the spectrum of the other diastereoisomer. There were slight variations, mainly in the relative intensities of the bands in the 8.5–10-μ region. Interestingly, a band observed at 11.70 μ in the spectrum of the first diastereoisomer appeared in the second compound at 11.83 μ. It is noteworthy that the first compound had a melting point of 21–23°, whereas the second did not appear to be crystalline even at −80°.

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[2] Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 1961.

[3] K. L. Paciorek, B. A. Merkl, and C. T. Lenk, *J. Org. Chem.*, in press.

[4] K. L. Paciorek, L. C. Mitchell, and C. T. Lenk, *J. Polymer Sci.*, **45**, 405 (1960).

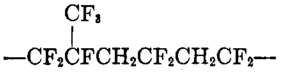
[5] G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

[6] J. J. Lagowski, *Quart. Revs.* (London), **13**, 233 (1959).

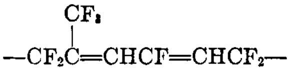
[7] M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Am. Chem. Soc.*, **80**, 846 (1958).

The mercury coupling of 2,2-dihydro-3-iodoperfluoropentane afforded 3,4-diperfluoroethyl-2,2-5,5-tetrahydroperfluorohexane in 76% yield. This material was also resolved into two diastereoisomers (ratio 1.93:1) by gas chromatography. The first compound had a melting point of 7–8°, whereas the second melted at 30–31°. Their infrared spectra had the same variations apparent in the methylene deformation region as noted for the diastereoisomers discussed above. However, in the 7–15 μ region the spectral differences between these two compounds were much more pronounced than those exhibited by the compounds derived from I.

In conjunction with fluoro elastomer studies,[3,4] an effort was made to synthesize a conjugated system resembling one which might arise in Viton A (vinylidene fluoride-perfluoropropene copolymer) during vulcanization processes. The predominating arrangement in Viton A has been found to be V.[8] As a potential diene intermediate, structure VI was chosen, inasmuch as one would expect the tertiary fluorine to be more susceptible to dehydrohalogenation than the difluoromethylene group.

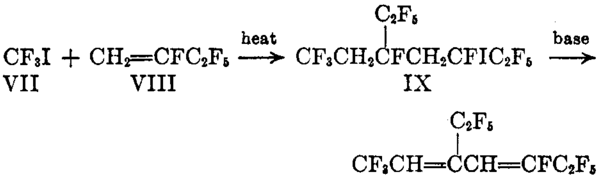

$-CF_2\overset{CF_3}{C}FCH_2CF_2CH_2CF_2-$

V


$-CF_2\overset{CF_3}{C}{=}CHCF{=}CHCF_2-$

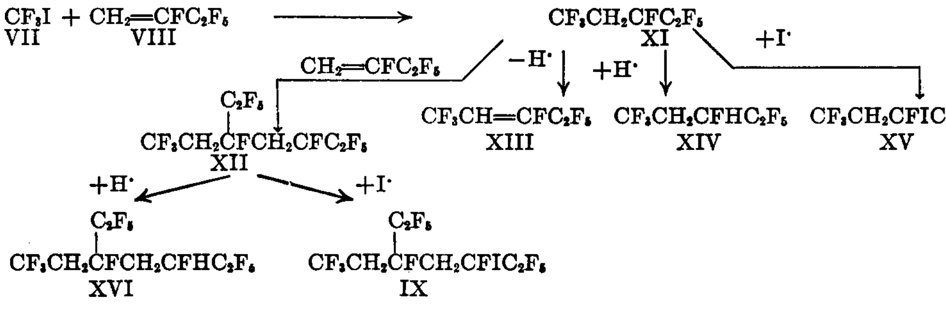
VI

To prepare such a system or one resembling it fairly closely, the following route was devised:


$CF_3I + CH_2{=}CFC_2F_5 \xrightarrow{heat} CF_3CH_2\overset{C_2F_5}{C}FCH_2CFIC_2F_5 \xrightarrow{base} CF_3CH{=}\overset{C_2F_5}{C}CH{=}CFC_2F_5$

VII VIII IX X

The thermal telomerization of trifluoroiodomethane (VII) and 1,1-dihydroperfluorobutene-1 (VIII) afforded very little of the desired product IX; mainly higher telomers were obtained. However, it is interesting that in addition to the expected products (IX, XIII, and XV) 2,2,4,4,5-pentahydro-3-perfluoroethylperfluoroheptane (XVI) was isolated. Thus, it is apparent that the free radical XI as well as higher homologues can undergo the type of reactions shown below.

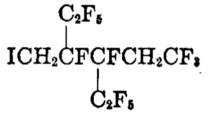

$CF_3I + CH_2{=}CFC_2F_5 \longrightarrow CF_3CH_2\dot{C}FC_2F_5$ (VII, VIII, XI)

XI $\xrightarrow{-H\cdot} CF_3CH{=}CFC_2F_5$ (XIII); XI $\xrightarrow{+H\cdot} CF_3CH_2CFHC_2F_5$ (XIV); XI $\xrightarrow{+I\cdot} CF_3CH_2CFIC_2F_5$ (XV)

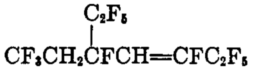
XI $\xrightarrow{CH_2=CFC_2F_5} CF_3CH_2\overset{C_2F_5}{C}FCH_2\dot{C}FC_2F_5$ (XII)

XII $\xrightarrow{+H\cdot} CF_3CH_2\overset{C_2F_5}{C}FCH_2CFHC_2F_5$ (XVI); XII $\xrightarrow{+I\cdot} CF_3CH_2\overset{C_2F_5}{C}FCH_2CFIC_2F_5$ (IX)

Using ultraviolet free radical initiation, the reaction between 1,1-dihydroperfluorobutene-1 (VIII) and trifluoroiodomethane resulted in a 54% yield of 2,2-dihydro-3-iodoperfluoropentane (XV). The latter when heated with an additional quantity of VIII in an autoclave at 185° gave 2,2,4,4-tetrahydro-3-perfluoroethyl-5-iodoperfluoroheptane (IX) in 36% yield. Gas chromatography resolved IX into two compounds in the ratio of 2:1. These materials exhibited somewhat different infrared spectra. The first compound showed a doublet in the CH stretching region, yet only a single band was observed for the second material. In addition, the first compound exhibited absorption at 6.87 and 7.00 μ. Only a single band appeared in the spectrum of the second compound. There were also significant differences in the 9–12 μ region. The band at 7.0 μ is ascribed to the deformation of the methylene group adjacent to the iodine-bearing carbon atom; the second band at 6.87 μ is most likely due to the other methylene group. The presence of only one band in this part of the spectrum of the second compound is unexplained. The two compounds had almost identical refractive indices, and the same mass-spectrographic spectra. It appeared possible that one of the compounds had structure XVII,


$ICH_2\overset{C_2F_5}{C}F\underset{C_2F_5}{C}FCH_2CF_3$

XVII


$CF_3CH_2\overset{C_2F_5}{C}FCH{=}CFC_2F_5$

XVIII

which could be derived from tail to tail addition. However, such an arrangement would be rather unlikely in view of the results obtained by Haszeldine and Steele.[9] Both compounds on treatment with an equimolar quantity of triethylamine afforded the olefin XVIII in a yield of over 80%, thus establishing structure IX. It is believed that the two compounds are diastereoisomers, inasmuch as there are present two centers of asymmetry in 2,2,4,4-tetrahydro-3-perfluoroethyl-5-iodoperfluoroheptane (IX). The pronounced differences in the infrared spectra are, however, unexpected.

The infrared spectrum of the olefin 2,2,4-trihydro-3-perfluoroethyl-4-perfluoroheptene (XVIII)

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[8] R. C. Ferguson, *J. Am. Chem. Soc.*, 82, 2416 (1960).

[9] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953).

showed the presence of the CH= entity (band at 3.22 μ). A band at 5.79 μ is ascribed to the C=C stretching vibration of $R_f'CF{=}CHR_f''$ grouping. The shift of the 6.87-μ band in the saturated material to 6.95 μ in compound XVIII can be attributed to the influence of the unsaturation upon the remaining methylene group.

The olefin XVIII on prolonged treatment with triethylamine or on heating with powdered potassium hydroxide afforded 2,4-dihydro-3-perfluoroethyl-2,4-perfluoroheptadiene (X). It is noteworthy that the formation of XVIII from IX occurred very readily, but the dehydrohalogenation to the diene X proceeded with difficulty. The latter compound exhibited a maximum in the ultraviolet at 214 mμ (log ϵ = 3.675), supporting the presence of a conjugated system. In the infrared spectrum of X, the separation of the doublet observed at 5.82 and 5.93 μ was much larger than that observed for butadiene; however, the shift to the lower wave length is in good agreement with the data reported by Haszeldine[10] for fluorinated butadienes. No absorption was present in the vicinity of 7 μ, confirming the absence of CH_2 grouping.

EXPERIMENTAL[11]

Treatment of 4,4-dihydro-3-iodoperfluoroheptane (I) *with chlorine.* Into a thick-wall glass tube (cooled in Dry Ice) containing I (5.80 g., 0.0126 mole) was distilled chlorine (0.9 g., 0.0126 mole). The tube was sealed, shaken and allowed to stand at 0° (protected from light) over a period of 2 days, when some yellow precipitate was observed. The mixture was allowed to stand for an additional 3 days at room temperature. Subsequently, it was kept at 50° for 24 hr., during which time the yellow precipitate disappeared and two distinct layers were formed. The bottom layer (dark red) solidified at 0°, suggesting the presence of iodine monochloride. The top part was drawn out to form a small ampoule while the tube was cooled in Dry Ice. The contents were then warmed to 0°, the liquid was decanted from the solid and sealed in the small ampoule. The liquid (3.48 g., 83.3%) was identified as 4-hydroperfluoroheptene-3 (II) by comparing its infrared spectrum with that of the authentic sample.

Treatment of I *with silver fluoride.* 4,4-Dihydro-3-iodoperfluoroheptane (I) (3.50 g., 0.00761 mole) was heated with silver fluoride (5.50 g., 0.0433 mole) at 157° for 2 hr. and at 165–170° for an additional 3 hr. The mixture was cooled, glass wool was added and the material was distilled *in vacuo* at room temperature. The product (3.01 g., n^{25}_D 1.3357) was collected in a Dry Ice cooled receiver. The infrared spectrum indicated the presence of II in addition to I. This was in agreement with the lowered refractive index. 4,4-Dihydro-3-iodoperfluoroheptane (I), n^{25}_D 1.3380; 4-hydroperfluoroheptene-3 (II), n^{25}_D 1.2720.

4,4-Dihydroperfluoroheptane (III). 4,4-Dihydro-3-iodoperfluoroheptane (I) (15 g., 0.0326 mole) was heated at 125–130° with hydrogen fluoride (10 g., 0.50 mole) in a 50-ml. stainless steel pressure vessel over a period of 14 days. The bomb was cooled (in ice), opened, and the contents were poured slowly onto crushed ice. The product (8.22 g.) was washed several times with cold water and dried over magnesium sulfate. Fractionation afforded 6.04 g. (52.8%) of III, b.p. 86.5–87.5°, n^{25}_D 1.2730.

Anal. Calcd. for $C_7H_2F_{14}$: C, 23.88; H, 0.57; F, 75.55. Found: C, 23.90; H, 0.84; F, 75.31.

Treatment of I *with silver fluoride and hydrogen fluoride.* 4,4-Dihydro-3-iodoperfluoroheptane (I) (14.60 g., 0.032 mole), silver fluoride (3.81 g., 0.030 mole) and hydrogen fluoride (10 g., 0.50 mole) were sealed in a 50-ml. stainless steel vessel and heated at 120–130° for 48 hr. The pressure vessel was cooled in Dry Ice, opened, and the contents poured onto crushed ice. The heavy bottom layer containing a solid (silver iodide) was washed several times with water (by decantation) and dried over anhydrous magnesium sulfate. Sodium fluoride and glass wool were added and the mixture was distilled *in vacuo* at room temperature. The product was collected in a Dry Ice cooled receiver. The material (4.06 g., n^{25}_D 1.3260) obtained at 2 mm. consisted (as shown by infrared spectra and gas chromatography) mainly of I, admixed with II and III, with very little of the coupled product IV. The material (1.5 g., n^{25}_D 1.3153) obtained at 0.25 mm. consisted of I and IV, whereas the distillate (0.80 g., n^{25}_D 1.3027) collected at 0.15 mm. consisted of IV only.

Anal. Calcd. for $C_{14}H_4F_{26}$: C, 25.24; H, 0.61; F, 74.15. Found: C, 25.43; H, 0.62; F, 74.22.

Gas chromatography using a 5-ft. column packed with Monoplex S-70 (Rohm and Haas) on Chromosorb-B (Johns-Manville) at 62°, helium flow 0.2 std. cu. ft per hr., afforded two peaks (the first after 2.7 min., the second after 5.6 min.), with the area ratio of 1.42:1. The starting material under these conditions was eluted after 6.3 min. The compounds responsible for the peaks at 2.7 min. and at 5.6 min. gave identical mass-spectrographic spectra, but different infrared spectra and melting points. The first compound eluted, m.p. 21–23°; the second compound eluted failed to crystallize even at −80°.

Coupling of I *with mercury under ultraviolet irradiation.* 4,4-Dihydro-3-iodoperfluoroheptane (I) (40.00 g., 0.087 mole) was sealed with mercury (12.8 ml., 0.87 mole) under nitrogen atmosphere in a Vycor tube. The resulting mixture was shaken over a period of 48 hr. while irradiated with a Hanovia ultraviolet lamp. At the end of this period some mercury was still observed, but the bulk of material consisted of black and red solid admixed with a colorless liquid. The tube was opened and the contents were extracted with ether (300 ml.). The ether was removed by distillation *via* a short column. The residue (26.23 g.) was distilled at reduced pressure affording IV, 21.60 g. (74.5%), b.p. 67–68° (5 mm.), n^{25}_D 1.3022. Gas chromatography of this material using a 5-ft. column packed with Monoplex S-70 on Chromosorb-B gave two well separated peaks with an area ratio of 1.54:1. The two compounds were found to be identical with those obtained in the preceding experiment.

Coupling of XV with mercury under ultraviolet irradiation. 2,2-Dihydro-3-iodoperfluoropentane (XV) (32.63 g., 0.0906 mole) was treated with mercury (14.9 ml., 1.01 moles) while irradiated with a Hanovia ultraviolet lamp following the procedure described above in the preparation of IV. The residue (17.46 g.), obtained after removal of ether (used to extract the product), was distilled at reduced pressure yielding 3,4-diperfluoroethyl-2,2,5,5-tetrahydroperfluorohexane, 16.01 g. (75.7%), b.p. 71.5–72.5° (40 mm.), n^{25}_D 1.3044.

Anal. Calcd. for $C_{10}H_4F_{18}$: C, 25.76; H, 0.865; F, 73.37. Found: C, 25.94; H, 0.75; F, 73.68.

Gas chromatography of this material using a 5-ft. column packed with Monoplex S-70 on Chromosorb-B at 62°, helium flow 0.2 std. cu. ft. per hr., gave two well separated peaks (the first after 2.8 min., the second after 8.2 min.) with an area ratio of 1.93:1 (under these conditions XV was eluted after 5.6 min.). The two compounds had distinctly different infrared spectra and melting points. The first compound eluted, m.p. 7–8°; the second compound eluted, m.p. 30–31°.

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(10) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

(11) Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. The infrared spectra were taken on Baird Model B, double beam, infrared spectrophotometer by Mrs. Mildred Lewis of Wyandotte Chemicals Corporation.

Treatment of VIII *with trifluoroiodomethane using thermal free-radical initiation.* 1,1-Dihydroperfluorobutene-1 (VIII) (15.0 g., 0.0915 mole) and trifluoroiodomethane (29.9 g., 0.152 mole) were sealed *in vacuo* in a heavy-wall glass tube. Subsequently, the tube was placed in an autoclave cushioned with glass wool and mineral oil. Nitrogen gas, 190 p.s.i., was introduced, and the autoclave was heated gradually to 200°, it was kept at this temperature for 12 hr. The autoclave was allowed then to cool overnight. A red liquid with some iodine particles was present in the reaction tube. Distillation at atmospheric pressure *via* a 12-cm. column packed with glass helices (bath temperature −22 to 23°) afforded 38 g. of material believed to consist mainly of the starting materials admixed with a small quantity of the olefin XIII, as indicated by an infrared band at 5.79 μ. During the transfer operations some of the low-boiling material was lost; therefore only 38 g. of material was collected. Only 2.6 g., n^{25}D 1.3365, of a material boiling above 25° was obtained. This material was distilled under reduced pressure *via* a 5-cm. column packed with glass helices. The separation achieved was very poor. Some of the material boiling at *ca.* 40° (70 mm.) was subsequently purified by gas chromatography using a 100 cm. column packed with Silicone Oil-550 (Dow Corning Corp.) on Chromosorb-B (at 77°, helium pressure 8 p.s.i.). 2,2-Dihydro-3-iodoperfluoropentane (XV) was one of the compounds separated (elution time 3.0 min.). It was identified by comparison of its infrared spectrum with that of an authentic sample. Another constituent (elution time 1.3 min.) was also isolated by gas chromatography, n^{25}D 1.310; its elemental analysis, boiling point and infrared spectrum indicated compound XVI.

Anal. Calcd. for $C_9H_5F_{15}$: C, 27.14; H, 1.26; F, 71.57. Found: C, 27.59; H, 1.26; F, 68.06.

2,2,4,4-Tetrahydro-3-perfluoroethyl-5-iodoperfluoroheptane (IX) was also separated and identified by comparison of its infrared spectrum with that of an authentic sample. However, the bulk of material appeared to consist of higher telomers than compounds XVI and IX.

2,2-Dihydro-3-iodoperfluoropentane (XV). 1,1-Dihydroperfluorobutene-1 (VIII) (7.8 g., 0.0476 mole) distilled (*in vacuo*) over Ascarite and anhydrous calcium chloride was sealed with similarly treated trifluoroiodomethane (18.8 g., 0.0959 mole) in a Vycor tube. The tube was then placed 10 cm. from a Hanovia ultraviolet lamp (with the liquid portion sheltered with aluminum foil) and was left under irradiation for 14 days. During this period some iodine was deposited on the walls of the tube. The tube was opened *in vacuo* while cooled in liquid nitrogen. The volatile material (12.3 g.) was distilled at atmospheric pressure as described in the previous experiment. The higher-boiling material (above 25°, 10.99 g.) was distilled at reduced pressure and the fraction, b.p. 51.5–52° (110 mm.), n^{25}D 1.3552, 9.32 g. (54.4%) was found to be XV.

Anal. Calcd. for $C_5H_2F_9I$: C, 16.68; H, 0.56; F, 47.50; I, 35.26. Found: C, 16.89; H, 0.55; F, 47.28; I, 35.20.

2,2,4,4-Tetrahydro-3-perfluoroethyl-5-iodoperfluoroheptane (IX). 2,2-Dihydro-3-iodoperfluoropentane (XV) (7.30 g., 0.0203 mole) and 1,1-dihydroperfluorobutene-1 (VIII) (1.6 g., 0.00976 mole) were sealed *in vacuo* in a heavy-wall glass tube. Subsequently the tube was placed in an autoclave cushioned with glass wool and mineral oil. Nitrogen gas, 190 p.s.i., was introduced and the autoclave was heated at 185° for 26 hr. On opening, very little of low-boiling material was found; some iodine (0.15 g.) was deposited. The material was then distilled under reduced pressure and the fraction, b.p. 57–57.5° (10 mm.), n^{25}D 1.3474, 1.83 g. (36%) was the desired product (IX).

Anal. Calcd. for $C_9H_4F_{15}I$: C, 20.63; H, 0.77; F, 54.38; I, 24.22. Found: C, 20.88; H, 0.52; F, 53.93; I, 24.26.

Gas chromatography of IX using a 5-ft. column packed with Monoplex S-70 on Chromosorb-B at 90°, helium flow 0.2 std. cu. ft. per hr., gave two well separated peaks (the first after 11.9 min., the second after 17.3 min.), with an area ratio of 2:1. These compounds gave identical mass-spectrographic spectra but different infrared spectra.

The first eluted compound and the second eluted compound when treated with an equimolar quantity of triethylamine, afforded 86 and 81% respectively of 2,2,4-trihydro-3-perfluoroethyl-4-perfluoroheptene (XVIII) as identified by comparison of infrared spectra of the dehydrohalogenated products with that of an authentic sample.

2,2,4-Trihydro-3-perfluoroethyl-4-perfluoroheptene (XVIII). A solution of IX (13.80 g., 0.02633 mole) and triethylamine (3.00 g., 0.0296 mole) after standing overnight at room temperature was heated under reflux at 75° for 6 hr. A copious precipitate was observed in the dark-brown solution. Glass wool was introduced and the liquid was distilled at room temperature at 1.5–0.9 mm. The product (9.0 g., n^{2}D 1.3077) was collected in a Dry Ice cooled receiver (based on the iodide ion in the residue, the dehydroiodination yield was 86%). Subsequent distillation *via* a 6-cm. column packed with glass helices yielded 7.10 g. (68.0%) of XVIII, b.p. 59–60° (90 mm.), n^{3}D 1.3044. This was followed by further purification using gas chromatography (Silicone Oil-550 on Chromosorb-B); the purified material had n^{3}D 1.3035. It was apparent from gas chromatography that the simple distillation resulted in 90% pure material. The infrared spectra supported the postulated structure.

Anal. Calcd. for $C_9H_3F_{15}$: C, 27.29; H, 0.76; F, 71.95. Found: C, 27.39; H, 0.89; F, 71.67.

2,4-Dihydro-3-perfluoroethyl-2,4-perfluoroheptadiene (X). To (XVIII) (3.90 g., 0.00985 mole) in a round-bottom flask was added powdered potassium hydroxide (2.83 g., 0.0505 mole), then a reflux condenser was attached and the mixture was left standing at room temperature. In *ca.* 8 min. a vigorous reaction commenced, which subsided, however, when the flask was cooled in an ice bath. This was followed by 2 hr. at room temperature. Finally the contents were heated at 110° for 24 hr. Black solid admixed with some liquid resulted. Vacuum distillation at room temperature afforded 2.08 g. of a product which was collected in a Dry Ice cooled receiver. This material was dried over anhydrous magnesium sulfate. Its infrared spectrum indicated the presence of the desired diene admixed with some starting material. This mixture was purified by gas chromatography (at 30°, helium pressure 15 psi.) using a 15-ft. column packed with Silicone Oil-550 on Chromosorb-B. A total of 7 peaks was observed, the largest peak (retention time 17 min.) was found to consist of the desired product X.

Anal. Calcd. for $C_9H_2F_{14}$: C, 28.74; H, 0.53; F, 70.72. Found: C, 29.21; H, 0.72; F, 70.38.

Ultraviolet spectrum was determined in cyclohexane, λ_{max} 214 mμ, log ϵ = 3.675.[12]

Treatment of XVIII with an equimolar quantity of triethylamine at 89° for 96 hr., followed by washing with dilute hydrochloric acid and water, gave a mixture of XVIII and X which could not be separated by ordinary column distillation. Again gas chromatography had to be employed.

WYANDOTTE, MICH.

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(12) We are indebted to Dr. J. M. Vandenbelt of Parke, Davis and Co. for furnishing and interpreting the ultraviolet spectrum.