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Coupling of Fluoroalkyl Iodides

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The coupling of haloalkyl iodides by irradiation with ultraviolet light in the presence of mercury has been extended to fluorocarbons containing the carbon, hydrogen, chlorine, and iodine and the carbon, hydrogen, fluorine, and iodine groupings as the reactive sites. Both meso and racemic isomers of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane and of 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane have been prepared in high purity and characterized by measurement of physical properties and infrared and NMR spectra.

COUPLING of fluoroalkyl iodides to fluorocarbons containing twice as many carbon atoms as the original iodide by irradiation with ultraviolet light in the presence of mercury has been extended to compounds in which the reactive center is CHClI or CHFI.

2-Chloro-2-iodo-1,1,1-trifluoroethane, representing the CHClI structure, coupled under the combined influence of mercury and ultraviolet light to afford an 81% yield of a mixture of isomers of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane, which could be separated by vapor-liquid phase chromatography (v.l.p.c.) into meso and racemic isomers. Identification of the isomers was made by independent synthesis.

Treatment of the dichlorohexafluorobutanes with bases under mild conditions resulted in removal of only one equivalent of hydrogen chloride. On the basis of a trans elimination, the 2-chloro-1,1,1,4,4,4-hexafluorobutene-2 derived from the meso butane was assigned the cis configuration; that from the racemic butane the trans configuration.

2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane had been synthesized previously by Haszeldine (*3*) by addition of chlorine to *trans*-1,1,1,4,4,4-hexafluorobutene-2 in the presence of ultraviolet light; the product was incompletely characterized, and no discussion of isomer distribution was presented. On the basis of the reported boiling point of 78°, it would appear that Haszeldine's material was primarily the racemic isomer (b.p. 76.9°). However, when the author repeated this work, a mixture of racemic and meso isomers in nearly equal amounts was obtained. This is not inconsistent with Haszeldine's reported boiling point because that measurement was made by the micro capillary method which tends to give the boiling point of the lowest boiling component of a mixture. The formation of both butane isomers from a single butene isomer indicates both stepwise addition of the two chlorine atoms and the existence of a planar intermediate at some point in the process. Both are expected in a free radical process.

1-Chloro-2-iodo-1,1,2-trifluoroethane was employed as a representative of the CHFI type of fluorocarbon iodide. It coupled less readily than 2-chloro-2-iodo-1,1,1-trifluoroethane but like it yielded both racemic and meso isomers, which were obtained in high purity by preparative scale v.l.p.c. The assignment of configuration was made on the basis of a comparison of physical properties of the two isomers with those of the two closely related 2,3-dichloro-1,1,1,4,4,4-hexafluorobutanes. In both cases, the racemic configuration was assigned to the isomer having the shorter v.l.p.c. retention time, the lower melting point, the lower boiling point, the lower heat of vaporization, and the lower Trouton ratio. The NMR spectra appeared to be in accord with this assignment.

EXPERIMENTAL

The vapor pressure equations and constants derived therefrom were obtained in the manner described earlier (*1*). Infrared absorption bands were measured in the vapor phase on a Perkin-Elmer Model 137 Infracord spectrometer and are reported in microns. Chromatography columns were 6.25 mm. o.d. by 4 meters (for analysis) or 18.75 mm. o.d. by 6 meters (for preparation) copper tubing packed with 20 wt.% partitioning liquid on 42 to 60 mesh GC-22 firebrick (untreated). The partitioning agents were: column A, di-*n*-decyl phthalate; column B, nonylphenoxy-(polyethoxy)ethanol; column C, Zonyl E-91. All three columns were used for checking the purity of each sample used for determination of physical properties. The carrier gas was He at a flow rate of 100 cc. per minute. The detector was of the thermal conductivity, tungsten filament-type and was operated at the same temperature as the column. Proton chemical shifts were measured with respect to external water; F^{19} shifts with respect to external hexafluoroacetone.

Caution: Normal precautions for handling sealed tubes should be observed. In addition, the crude reaction mixtures may contain highly toxic haloalkyl mercury compounds, which are detectable by their strong garlic-like odor.

***meso*-2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane.** From Coupling. 2-Chloro-2-iodo-1,1,1-trifluoroethane (*2*) was irradiated with ultraviolet light in the presence of mercury for 25 hours. The crude product was separated into several fractions by preparative v.l.p.c. on column A at 80°. The fraction containing the meso isomer was rechromatographed on column B at 50°. The yield of meso isomer was 42.6%. A 99.9 + % sample had the following physical constants: n.b.p. 84.7°, ΔH_{vap} 7357 cal. per mole, Trouton ratio 20.6, m.p. about −90°, d_{22} 1.603 g. per cc. Its vapor pressure over the range from 300 to 800 mm. could be expressed by the following equation $\log P_{\text{mm.}} = 7.67277 - 1715.2/T_{°\text{K.}}$ Major infrared absorption bands were found at 3.40 (w), 7.31 (m), 7.48 (m), 7.65 (s), 8.07 (vs), 8.29 (s), 8.43 (vs), 8.80 (vs), 9.50 (w), 11.20 (w), 11.38 (w), 11.90 (w), 12.20 (w), 12.52 (m), and 14.75 (w). The F^{19} NMR spectrum showed a doublet at −7.50 p.p.m. The *J* value was 6.2 c.p.s. The proton spectrum at +0.50 p.p.m. was quite complex.

From SF_4 Fluorination of *meso*-2,3-Dichlorosuccinic Acid. *meso*-2,3-Dichloro-succinic acid (m.p. 221–224°) was fluorinated with SF_4. V.l.p.c. on column A at 75° showed that the crude reaction mixture contained 76.3% *meso*-2,3-dichlorol,1,1,4,4,4-hexafluorobutane (31.6% yield) and 8.3% of the racemic isomer (3.4% yield). The small amount of racemic impurity probably arose from racemic impurity in the starting material. The meso isomer, separated by v.l.p.c. was identical with that obtained from the coupling experiments.

***dl*-2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane.** From Coupling. This isomer was obtained from the same experiments that lead to the meso isomer. The yield of racemic isomer was 38.4%. A 99.9 + % sample had the following physical constants: n.b.p. 76.9°, ΔH_{vap} 6877 cal. per mole, Trouton ratio 19.6, d_{22} 1.615 g. per cc. Its vapor pressure over the range from 300 to 800 mm. could be expressed by the equation $P_{\text{mm.}} = 7.46791 - 1605.8/T_{°\text{K}}$. Major infrared absorption bands were found at 3.40 (w), 7.30 (w), 7.55 (m), 7.80 (s), 7.93 (s), 8.11 (m), 8.43 (s), 8.70 (s), 8.88 (m), 9.52 (w), 11.28 (m), 12.05 (w), 12.55 (w), 13.50 (w), and 14.00 (w). The F^{19} NMR spectrum showed a doublet at −4.17 p.p.m. with a *J* value of 5.81 c.p.s. The proton spectrum showed a well defined quartet at +0.25 p.p.m.

From SF_4 Fluorination of *dl*-2,3-Dichlorosuccinic Acid. SF_4 fluorination of the *dl* acid (m.p. 168–172°) yielded a crude product containing 61.1% of *dl*-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (19.5% yield). Only a trace of the meso isomer was present. The purified racemic isomer was identical with that obtained from the coupling experiments.

Dehydrochlorination of *dl*- and *meso*-2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane. Passage of the vapors of either dichlorohexafluorobutane isomer through Ascarite provided an essentially quantative yield of 2-chloro-1,1,1,4,4,4-hexafluorobutene-2. The butene derived from the racemic butane (presumably trans) showed major infrared absorption bands at 6.03 (w), 7.60 (m), 7.80 (s), 7.95 (s), 8.43 (s), 8.60 (s), 10.40 (w), 11.60 (w), and 12.00 (w). The butene from the meso butane (presumably cis) had bands at 6.08 (m), 7.40 (m), 7.60 (m), 7.85 (s), 8.43 (s), 8.60 (s), 8.70 (sh), 10.39 (m), 11.60 (m), and 14.80 (m). The CH band in the 3μ region for both isomers was extremely weak.

***dl*- and *meso*-1,4-Dichloro-1,1,2,3,4,4-hexafluorobutane.** These isomers were prepared in 23.2 and 23.4% yields by coupling of 1-chloro-2-iodo-1,1,2-trifluoroethane (*2*). Samples purified by v.l.p.c. in the same way as the 2,3-dichloro isomers showed the following properties: racemic—n.b.p. 87.9°, ΔH_{vap} 7674 cal. per mole, Trouton ratio 21.3, d_{22} 1.563 g. per cc., m.p. about −60°, molecular weight 234.9 (theory 235.0); meso—n.b.p. 96.1°, ΔH_{vap} 8016 cal. per mole, Trouton ratio 21.7, d_{22} 1.602 g. per cc., m.p. about −77°, molecular weight 236.2 (theory 235.0). The vapor pressure equations over the range from 300 to 800 mm. could be expressed as follows: racemic, $\log P_{\text{mm.}} = 7.83248 - 1787.9/T_{°\text{K.}}$; meso, $\log P_{\text{mm.}} = 7.93120 - 1865.0/T_{°\text{K.}}$. Major infrared absorption bands for the racemic mixture were found at 3.35 (w), 7.55 (s), 7.87 (s), 8.58 (vs), 9.05 (s), 9.40 (s), 9.78 (s), 10.10 (s), 12.00 (m), 12.38 (m), 13.17 (m), 13.90 (s), and 14.12 (s). For the meso isomer they were at 3.38 (w), 7.38 (m), 7.66 (s), 8.00 (s), 8.12 (s), 8.36 (s), 8.75 (vs), 9.40 (s),9.89 (s), 10.10 (s), 10.85 (m), 12.00 (m), 12.30 (m), 12.80 (m), 13.22 (m), 13.63 (m), and 14.40 (m). Both isomers showed NMR spectra consistent with the assigned structures. Neither isomer dehydrohalogenated readily.

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