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Coupling of Fluoroalkyl Iodides¹

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ABSTRACT

The coupling of haloalkyl iodides by irradiation with ultraviolet light in the presence of mercury has been extended to fluorocarbons containing CHClI and CHFI 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 n. m. r. 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 was first reported by Haszeldine² in 1952. The reaction was initially applied to iodides containing the CFCII and CCl_2I groupings²⁻⁴ and was later extended to primary and secondary perfluoroalkyl iodides containing three or more carbon atoms⁵ and to compounds containing the $\text{CH}_2\text{CF}_2\text{I}$ ⁶ and CH_2CFI ⁷ groups. This reaction is of considerable interest in the preparation of high molecular weight, thermally stable liquids for use as hydraulic fluids, lubricants and plasticizers, and for the synthesis of a variety of symmetrical intermediate and long chain bifunctional fluorocarbons.

This paper extends the application of this reaction to compounds in which the reactive center is CHClI or CHF I . In both cases both meso and racemic isomers are produced in approximately equal amount.

2-Chloro-2-iodo-1,1,1-trifluoroethane was chosen as representative of the class of fluorocarbons bearing the CHClI structure. It 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.

Meso-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (b. p. 84.7°) containing about 10% of the racemic isomer was prepared by sulfur tetrafluoride fluorination of meso-2,3-dichlorosuccinic acid. The racemic isomer (b. p. 76.9°) containing less than 5% meso was similarly gotten from the racemic dichlorosuccinic acid. The two isomeric 2,3-dichloro-1,1,1,4,4,4-hexafluorobutanes were obtained in 99.9+% purity by preparative scale v. l. p. c.

Both isomers showed doublets in the F^{19} n. m. r. spectral region at -4.17 p. p. m. for the racemic isomer and at -7.50 p. p. m. for the meso isomer.⁸ The J values were 5.81 and 6.2 c. p. s., respectively. The racemic isomer showed a well defined quartet in the proton region at +0.25 p. p. m., but the corresponding resonance for the meso isomer at +0.50 p. p. m. was much more complex.

Treatment with bases under mild conditions resulted in removal of only one equivalent of hydrogen chloride. The 2-chloro-1,1,1,4,4,4-hexafluorobutene-2 thus produced from the meso isomer had a different infrared spectrum from that produced from the racemic isomer. Obviously

they were cis and trans olefins each apparently uncontaminated with the other. Assuming a trans elimination the meso butane would be expected to produce a cis butene while a trans butene would be expected from the racemic butane. Confirmation of these configurational assignments from the infrared spectra was not obvious. It is not surprising that the simple criteria which so readily allow assignment in simpler 1,2-disubstituted ethylenes should be less definitive when a third group of roughly comparable weight is introduced.

2,3-Dichloro-1,1,1,4,4,4-hexafluorobutane had been synthesized previously by Haszeldine⁹ 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 we repeated this work we obtained a mixture of racemic and meso isomers in nearly equal amounts. 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 CHF₂I 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 1) the shorter v.l.p.c. retention time, 2) the lower melting point, 3) the lower boiling point, 4) the lower heat of vaporization, and 5) the lower Trouton ratio. The n.m.r. spectra appeared to be in accord with this assignment. Both isomers showed typical A_2X_2 spectra. Coupling of the A_2X_2 grouping with CX_2 group was apparent, and the F^{19} spectra showed "nonequivalent" CF_2 s in both isomers. Neither isomer dehydrohalogenated readily.

Experimental¹⁰

Meso-2,3-dichloro-1,1,1,4,4,4-hexafluorobutane. A. From Coupling. — Into a Pyrex tube (18 mm. i.d. by 25 cm. long) was sealed 7.5 ml. of mercury and 5.53 g. (0.023 mole) of 2-chloro-2-iodo-1,1,1-trifluoroethane.¹¹ The tube was irradiated with ultraviolet light¹² at about 35° for 25 hr. during which time it was rotated at about 10 r.p.m. perpendicular to its major axis and with its major axis inclined about 30° from horizontal. The plane of rotation was about 6 in. from the light source. At the end of the irradiation period the tube was opened,¹³ and the volatile portion of its contents was distilled at room temperature and 10^{-5} atmospheres into a liquid-nitrogen-cooled trap. Mercury and its salts remained behind in the reaction vessel. The trap held 2.8 g. of colorless liquid, which 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./mole, Trouton ratio 20.6, m.p. about -90°, d_{22} 1.603 g./cc. Its vapor pressure over the

range from 300-800 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), 7.85 (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).

B. From SF₄ Fluorination of meso-2,3-Dichlorosuccinic Acid. - A 25 ml. stainless steel pressure vessel charged with 1.70 g. (0.01 mole) of meso-2,3-dichlorosuccinic acid (m.p. 221-224)¹⁴ and 0.05 mole of SF₄ was rocked in a Parr high pressure hydrogenation rocker¹⁵ at 140° for 6 hr. After cooling to room temperature the vessel was vented, and the liquid remaining in it was washed five times with 1 ml. portions of water then dried over anhydrous MgSO₄. V.l.p.c. on column A at 75° showed that the dried liquid which weighed 0.971 g. contained 76.3% meso-2,3-dichloro-1,1,1,4,4,4-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. A. 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./mole, Trouton ratio 19.6, d_{22} 1.615 g./cc. Its vapor pressure over the range from 300-800 mm. could be expressed by the equation $\log P_{\text{mm}} = 7.46791 - 1605.8/T_{\text{K}}$. 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).

B. From SF_4 Fluorination of dl-2,3-Dichlorosuccinic Acid. — The reaction was carried out in the same manner as with the meso isomer but starting with the dl acid (m. p. 168-172°).¹⁶ The washed and dried liquid residue weighed 0.75 g. and contained 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 either dichlorohexafluorobutane isomer through Ascarite in the manner previously described¹⁷ provided an essentially quantitative 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), 10.40 (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-trifluoroethane¹⁵ in the manner just described. 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./mole, Trouton ratio 21.3, d_{22} 1.563 g./cc., m. p. about -60°, molecular weight 234.9 (theory 235.0); meso; n. b. p. 96.1°, ΔH_{vap} 8016 cal./mole, Trouton ratio 21.7, d_{22} 1.602 g./cc., m. p. about -77°, molecular weight 236.2 (theory 235.0). The vapor pressure equations over the range from 300-800 mm. could be expressed as follows: racemic, $\log P_{\text{mm}} = 7.83248 - 1787.9/T_{\text{K}}$; meso, $\log P_{\text{mm}}$

$= 7.93120 - 1865.0/T_K$. 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).

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- (8) Proton chemical shifts were measured with respect to external water; F^{19} shifts with respect to external hexafluoroacetone. The author is indebted to James A. Happe for these measurements.
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- (10) The vapor pressure equations and constants derived therefrom were obtained in the manner described earlier [E. R. Bissell, J. Org. Chem., 26, 5100 (1961)]. 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 m. (for analysis) or 18.75 mm. o.d. by 6 m. (for prep.) copper tubing packed with 20 wt.% partitioning liquid on 42-60 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 (E. I. du Pont de Nemours and Co., Wilmington 98, Delaware). All three columns were used for

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checking the purity of each sample used for determination of physical properties. The carrier gas was He at a flow rate of 100 ml./min. The detector was of the thermal conductivity, tungsten filament type and was operated at the same temperature as the column.

- (11) E. R. Bissell, J. Org. Chem., 29, 252 (1964).
- (12) Ultraviolet light was supplied by a 360-w. Uviarc (with reflector) manufactured by George W. Gates and Co., Franklin Square, Long Island, N. Y.
- (13) 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.
- (14) Prepared by addition of chlorine to fumaryl chloride in the presence of ultraviolet light, followed by hydrolysis. Kirchoff [Ann., 280, 211 (1894)] reports a m.p. of 217-8°.
- (15) Series 4000, Parr Instrument Co., Moline, Ill.
- (16) Prepared by addition of chlorine to maleic anhydride in the presence of ultraviolet light, followed by hydrolysis. Van der Riet [Ann., 280, 219 (1894)] reports a m.p. of 175°.
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