ethanol solution was concentrated, diluted with diethyl ether, and filtered. The solution was again concentrated, diluted, and filtered. The ether was removed and the remaining liquid was distilled under reduced pressure, bp 101–115° (0.03 mm), to yield 24.8 g of a yellow liquid. Another sample prepared similarly was stripped of some low-boiling contaminants by vacuum distillation in a spinning-band apparatus, and an analytical sample was separated from two lower boiling impurities by vpc using column C: $[\alpha]^{22}\mathrm{D} = -39.3°$ (c 3.1 in $CHCl_3$); $\nu_{\max}^{\mathrm{neat}}$ 5.91 μ (C=O); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.1–6.4 (multiplet, 2 H, CH), 6.8–7.0 (multiplet, 4 H, $-CH_2-$), 7.67 (singlet, 6 H, $-COCH_3$), 8.69 (singlet, 6 H, $C(CH_3)_2$).

Anal. Calcd for $C_{11}H_{18}O_4S_2$: C, 47.46; H, 6.52; S, 23.04. Found: C, 48.11; H, 6.60; S, 22.58.

2,3-*O*-Isopropylidene-1,4-dithio-$\mathrm{L_g}$-threitol (12).—To a solution of 14 mg of sodium in 40 ml of dry methanol was added 24.7 g of **11**. Methanol and methyl acetate vapors (bp 54–56°) were slowly removed through an 8-cm Vigreux column during 8 hr. The reaction was followed by the disappearance of the infrared carbonyl absorption (5.91 μ) of **11**. An additional 15 ml of methanol containing 16 mg of dissolved sodium was added and the distillation was continued for 4 hr. Removal of the remaining solvent and direct distillation of the liquid residue yielded 17.3 g (quantitative yield) of colorless liquid: bp 60° (0.15 mm); $[\alpha]^{23°}\mathrm{D}$ −13.0° (c 3.2 in $CHCl_3$); $\nu_{\max}^{\mathrm{neat}}$ 3.87 (S–H), 7.39 and 7.44 μ (doublet, $C(CH_3)_2$); $\tau_{\mathrm{TMS}}^{\mathrm{neat}}$ 5.95–6.17 (multiplet, 2 H, CH), 7.08–7.37 (multiplet, 4 H, $-CH_2-$), 8.25 (triplet, J = 8 cps, 2 H, –SH), 8.64 (singlet, 6 *H*, $C(CH_3)_2$). Injection of 10 μl or larger samples into the vpc instrument resulted in some thermal decomposition to a hydroxylic material with both columns A and B.

(4*R*,5*R*)(+)-4,5-Isopropylidenedioxy-1,2-dithiane (13).—Oxygen gas was bubbled for 30 hr through a solution of 2.97 g of **12** and 1.80 g of potassium hydroxide in 50 ml of methanol and 20 ml of water. Some crystalline solid precipitated during this period. Addition of 40 ml of water and chilling overnight in the refrigerator caused the separation of 2.14 g (72%) of the cyclic disulfide ketal (**13**), mp 69.4–70.2° after drying in a desiccator with Drierite for 48 hr. Another sample, mp 69.4–70.8°, twice sublimed onto a cold finger under 0.05 mm at room temperature, showed the following properties: $[\alpha]^{22°}\mathrm{D}$ +237° (c 2.3 in $CHCl_3$); $\lambda_{\max}^{\mathrm{isooctane}}$ 287 mμ (ε 335) and 238 mμ (ε 179).

Anal. Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.91; H, 6.17; S, 33.27.

(2*R*,3*R*)(−)-1,4-Dithiothreitol = (−)-1,4-Dithio-$\mathrm{L_g}$-threitol (2).—A solution of 4.15 g of the ketal dithiol (**12**) in 60 ml of 0.1 *N* hydrochloric acid–methanol (1:1) was heated under reflux for 4 hr with stirring. The solution was then diluted with 50 ml of water and continuously extracted with ethyl ether for 7 hr. Concentration of the ether extracts under reduced pressure and distillation at 84–97° (0.03 mm) yielded 2.65 g (80%) of product which slowly crystallized to a colorless, waxy solid.

Compound **2** was also prepared by hydrolysis of **11** in refluxing 2 *N* hydrochloric acid–methanol (2:1) for 1.5 hr under nitrogen. Neutralization of most of the acid, continuous extraction, and distillation as above gave comparable yields of liquid product, much of which solidified on seeding. Three sublimations of this latter material at 41° (0.02 mm) gave crystals which softened at 43° and melted at 45.0–47.0°; $[\alpha]^{22°}\mathrm{D}$ −11.7 (c 2.4 in $CHCl_3$). Two recrystallizations from ethyl ether yielded needles, mp 48.2–49-8°.

Anal. Calcd for $C_4H_{10}O_2S_2$: C, 31.14; H, 6.54; S, 41.57. Found: C, 31.23; H, 6.67; S, 41.71.

(4*R*,5*R*)(+)-4,5-Dihydroxy-1,2-dithiane (3).—A mixture of 0.60 g of the dithiane ketal (**13**) in 35 ml of 0.1 *N* hydrochloric acid–methanol (4:3) become homogeneous after being stirred for 5 hr at room temperature. The resulting solution was extracted continuously with ethyl ether for 2 hr, after which the ether extracts were concentrated to dryness under reduced pressure. The crude product, mp 115–117°, was sublimed during 3 hr at 85° (0.01 mm), yielding 0.44 g (93%) of crystalline diol. Recrystallization from chloroform yielded a product melting at 116.2–117.8°: $[\alpha]^{23°}\mathrm{D}$ +260 (c 0.32 in $CHCl_3$); $\lambda_{\max}^{\mathrm{H_2O}}$ 281 mμ (ε 326) (the literature[2a] value for the racemic compound is $\lambda_{\max}^{\mathrm{H_2O}}$ 283 mμ (α_{m} 273).

Anal. Calcd for $C_4H_8O_2S_2$: C, 31.57; H, 5.30; S, 42.14. Found: C, 31.63; 31.68; H, 4.80, 4.99; S, 42.20.

Registry No.—**2**, 16096-97-2; **3**, 16096-99-4; **11**, 16096-98-3; **12**, 16097-00-0; **13**, 16097-01-1.

Phenylmagnesium Bromide Induced S_N2' Reaction and Migrations of Fluorine in 1,1-Di(chlorodifluoromethyl)ethylene

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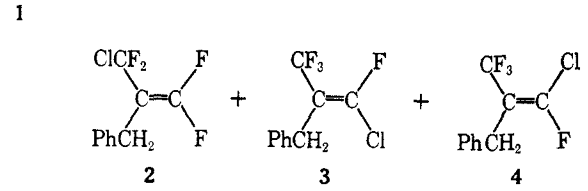
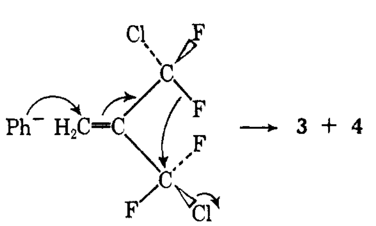
The S_N2' rearrangement[2] of highly fluorinated olefins of the type $H_2C=C(CF_2X)_2$ with lithium aluminum hydride or alkyl Grignard reagents has been previously reported as a general method for the preparation of terminal perfluoromethylene[3] olefins of the type $F_2C=C(CF_2X)R$, where X is F, Cl, or H and R is an alkyl group.

In this work 1,1-di(chlorodifluoromethyl)ethylene, **1**, was treated with phenylmagnesium bromide at approximately −20°. This led to a mixture of products from which the following compounds were isolated: 1,1-difluoro-2-chlorodifluoromethyl-3-phenylpropene, **2**, and the *cis* (**3**) and *trans* (**4**) isomers of 1-chloro-1-fluoro-2-trifluoromethyl-3-phenylpropene. An indication that the above reaction is more complicated than when alkyl Grignards or hydride ions are used as the nucleophilic species[3] is borne out by the presence of **3** and **4** whose combined yields were 25%, based on **1**. Other materials were also observed in the reaction mixture but they were not characterized because they were either present in small quantities or were intractable residues.



Formation of **2** can be easily rationalized with an S_N2' reaction.[4] Formation of **3** and **4** can be rationalized by a concerted nucleophilic attack on the $=CH_2$ group and an intramolecular substitution of chlorine by a fluorine atom to form the $-CF_3$ group. An inter-



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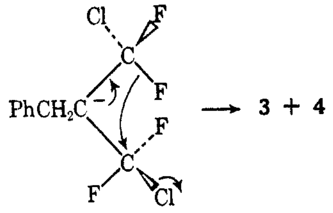
[2] R. E. Kepner, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **71**, 115 (1949).

[3] M. H. Kaufman, J. D. Braun, and J. G. Shdo, *J. Org. Chem.*, **32**, 2749 (1967).

[4] Substitution of a chlorine atom by a fluorine atom has been previously observed in single substituted reactions of fluoride ions (in $CHCl_3$, CH_2Cl_2, and in acetone) with chlorine-containing olefins. See, for instance, W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).

mediate carbanion ensued by an intramolecular rearrangement would also lead to **3** and **4**. Thermal isomerization of **2** to **3** and **4** seems unlikely. A 95% pure sample of **2** was heated to 200–203° for 2 hr with no change in the infrared absorption band characteristic of $=CF_2$ groups at 1740 cm^{-1}. Further heating at 200–203° over added KF did not produce any noticeable change in this absorption band.

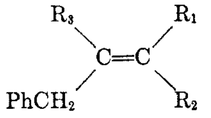


Initially **2**, **3**, and **4** were isolated as a mixture by simple distillation from the reaction flask. This mixture was further fractionated by vapor phase chromatography (vpc) which gave **2** (95% pure with 5% **3** and **4**, by F^{19} nmr) and a mixture of the *cis* (**3**) and *trans* (**4**) isomers. Attempts at separating the *cis* from the *trans* isomer by vpc were unsuccessful presumably due to closeness in their boiling points. Hence **3** and **4** were characterized as a mixture.

Structure assignments of the isomeric reaction products were made on the basis of their nuclear magnetic resonance (nmr) spectra. The H^1 nmr spectrum demonstrated that **2**, **3**, and **4** contained the benzyl group (one peak for the phenyl protons at τ 2.83 and overlapping multiplet for the $-CH_2-$ protons at τ 6.53). Table I gives F^{19} nmr data for **2**, **3**, and **4**.

TABLE I

FLUORINE NUCLEAR MAGNETIC RESONANCE[a]



2, $R_1 = F; R_2 = F; R_3 = CF_2Cl$
3, $R_1 = F; R_2 = Cl; R_3 = CF_3$
4, $R_1 = Cl; R_2 = F; R_3 = CF_3$

Compound	Group	Chemical shift,[b] ppm	Multiplicity
2	$-CF_2Cl$	47.1	Pair of doublets
	$=CF_2$	76.0	Pair of triplets[c]
	$=CF_2$	82.8	Pair of triplets[c]
3	$-CF_3$	60.8	Doublet
	$=CFCl$	67.3	Quartet
4	$-CF_3$	60.1	Doublet[c]
	$=CFCl$	65.4	Quartet[c]

[a] The data were originally taken with a mixture of 40% **2**, 27% **3**, and 33% **4** before an isolation procedure had been established to separate **2** from **3** and **4**. The expected nmr spectra were later obtained with the purified substances. [b] See ref 5. [c] Plus additional weak proton splitting.

Interestingly, treatment of **1** with phenylmagnesium bromide at 33° resulted in a distillable mixture of products containing 84% of the *cis* and *trans* compounds. Also a very small fraction, about 6%, was obtained from the vpc of the distillate. This fraction has an infrared spectrum similar to analytically pure **2**, but was not further characterized.

Experimental Section[5]

1,1-Difluoro-2-chlorodifluoromethyl-3-phenylpropene (2) and a Mixture of *cis* and *trans* 3 and 4, Respectively.—To 53.1 g (0.3 mol) of 1,1-di(chlorodifluoromethyl)ethylene (**1**) kept at approximately −20° by external cooling was added 100 ml of a 3 *M* (0.3 mol) ether solution of phenylmagnesium bromide. The Grignard reagent was added dropwise over a period of 50 min and the reaction mixture was stirred during the addition. Stirring was continued for an additional period of 0.5 hr at −20°. The reaction mixture was allowed to warm to room temperature and to stand for 2 days for settling of the solids which were subsequently filtered under nitrogen. The filtrate was distilled through a simple one-step distillation apparatus and the fraction which distilled between 71 and 88° at 10 mm was collected, yield 40 g, 59% based on the substitution of a chlorine atom by a phenyl group. To remove all traces of carried-over solids this fraction was redistilled at atmospheric pressure through a short column packed with Teflon wool, bp 200–203°. The distillate was made up of 50% **2**, the rest being **3** and **4**. This distillate was fractionated by means of vpc[6a] which yielded **2** (>95% pure by F^{19} nmr) and the mixture of the *cis* and *trans* isomers. The F^{19} nmr pattern of the mixture of **3** and **4** indicated the *trans* isomer to be more abundant than the *cis* isomer, a ratio of *trans*/*cis* = 11/9 was obtained. The infrared spectrum of **2** had absorption bands at 2850–3050 (CH medium), 1740 ($=CF_2$, strong), 690–710 (Ph, very strong), and 760 cm^{-1} ($=CH$, medium).

Anal. Calcd for **2** ($C_{10}H_7F_4Cl$): C, 50.33; H, 2.96; F, 31.84; Cl, 14.86. Found: C, 50.25; H, 2.82; F, 31.62; Cl, 14.91.

1-Chloro-1-fluoro-2-trifluoromethyl-3-phenylpropene, 3 and 4.—To 98.0 g (0.5 mol) of **1** was added 175 ml of a 3 *M* (0.5 mol) ether solution of phenylmagnesium bromide. After adding the first few milliliters of the Grignard solution the reaction mixture was heated to 33° and stirred. After addition was completed, 1.5 hr, the mixture was kept at 33° overnight. The resulting solids were filtered the filtrate was stripped of low-boiling substances. Distillation at ambient pressure gave approximately 50 ml of a high-boiling liquid made up of mostly **3** and **4**. The liquid was redistilled and a center cut of the fraction boiling at 70° and 10 mm was fractionated by means of vpc.[6b] The major constituent was the mixture of **3** and **4** which made up 84% of the chromatographed liquid.

Anal. Calcd for mixture of **3** and **4**: C, 50.33; H, 2.96; F, 31.84; Cl, 14.86. Found: C, 50.60; H, 3.16; F, 31.73; Cl, 15.09.

Acknowledgment.—The authors wish to acknowledge helpful and stimulating discussions with Dr. R. T. Merrow, and to thank Dr. Wayne Carpenter for the helpful discussions regarding vpc separation of the isomers.

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[5] All reaction and distillations were carried out under a helium or nitrogen atmosphere although **2**, **3**, and **4** appear stable toward the atmosphere. All boiling points are uncorrected. Proton and fluorine nmr spectra were taken on Varian A-60 and DP-60 instruments, respectively. The internal standard used for H^1 nmr spectra was $(CH_3)_4Si$ and for the F^{19} nmr spectra CF_3Cl.

[6] (a) A $^3/_8$ in. × 10 ft aluminum column packed with Chromosorb impregnated with Dowfax-200 was used. (b) A $^3/_8$ in. × 20 ft aluminum column packed with Chromosorb impregnated with SE-30 was used.