

THE NOVEL REACTION OF 1-CHLORO-2-( $\alpha$ -BROMOETHYL)HEXA-  
FLUOROCYCLOPENTENE-1 WITH GRIGNARD REAGENTS

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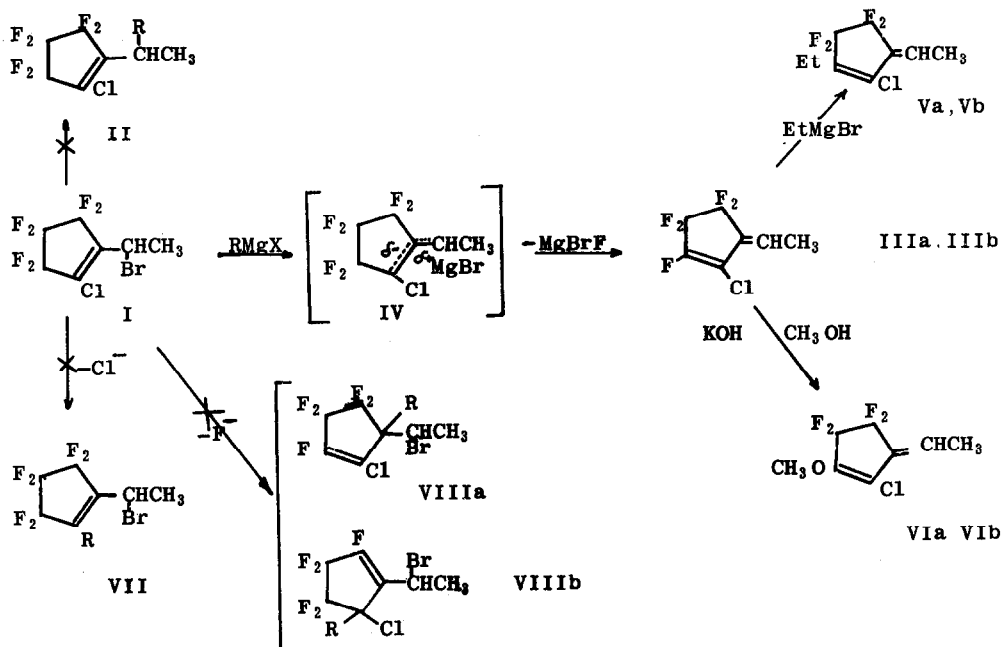
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The reactions of polyhalocycloalkenes with Grignard reagents<sup>1</sup> and organolithium compounds<sup>2</sup> generally lead to products whose origin can best be rationalized on the basis of nucleophilic displacement of vinylic ( $S_N2$ ) or allylic halide ( $S_N2'$ ) by the organic moiety of the organo-metallic reagent. Sullivan, et. al.<sup>3</sup> however, has reported that treatment of 1,2-dihalotetrafluorocyclobutenes with Grignard reagents led to the formation of relatively unstable cyclobutenylmagnesium halides when one of the vinylic halogens was bromine or iodine.

We would like to report a novel elimination reaction which arises from the reaction of Grignard reagents with 1-chloro-2-( $\alpha$ -bromoethyl)hexafluorocyclopentene-1 (I) and which apparently proceeds via a similar "halogen-metal exchange"<sup>3</sup>.

When I was treated with an equivalent amount of ethylmagnesium bromide in tetrahydrofuran at 28°C, the primary component of the mixture of compounds isolated was identified as a geometrical isomer of 2-chloro-3-ethylidenepentafluorocyclopentene-1 (IIIa). A similar result was obtained by either methylmagnesium chloride in THF or phenylmagnesium bromide in diethyl ether was employed in place of ethylmagnesium bromide in THF.

The structure of IIIa was based on spectrographic and chemical evidence. The proton NMR spectrum of IIIa exhibited a doublet at 7.92  $\tau$  ( $J=7.6$  cps) and a quartet at 3.78  $\tau$  ( $J=7.6$  cps). With integrated areas of 3:1, respectively,



the above spectrum is consistent with the assignment of 3 allylic and 1 vinylic proton. The infrared spectrum contained a strong absorption at  $1670 \text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$ ), a value consistent with the assigned structure. The above evidence, along with the elemental analysis obtained, argues conclusively against products arising from coupling of the allylic bromine of I with the Grignard reagents,<sup>‡</sup> vinylic displacement of chloride ion 1-alkyl-2-( $\alpha$ -bromoethyl)hexafluorocyclopentene 1 (VII), or  $\text{S}_{\text{N}}2'$  displacement of fluoride ion 2-chloro-3-alkyl-3-( $\alpha$ -bromoethyl)pentafluorocyclopentene-1 (VIIIa) 2-( $\alpha$ -bromoethyl)-3-

<sup>‡</sup>The product which would arise from coupling of the allylic bromine of I with ethylmagnesium bromide, 1-chloro-2-isobutylhexafluorocyclopentene-1, was synthesized independently by the method of Fonanelli utilizing<sup>1a</sup> 1,2-dichlorohexafluorocyclopentene-1 and isobutylmagnesium bromide.

chloro-3-alkylpentafluorocyclopentene-1 (VIIIb).

Calcd. for  $C_7H_4ClF_5$  : C, 38.64; H, 1.85; Cl, 15.85; F, 43.66.

Found: C, 38.54; H, 1.81; Cl, 16.45; F, 43.48.

Small quantities of cis- and trans-1-ethyl-2-chloro-3-ethylidenetetrafluorocyclopentene-1 (Va, Vb) were also isolated along with trace amounts of several other hydrocarbons which were not characterized.

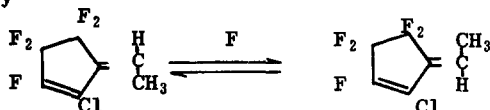
The formation of IIIa in preference to products resulting from coupling or nucleophilic displacement of halide ion can be explained on the basis of a competing Grignard exchange reaction similar in nature to that reported by Sullivan.<sup>3</sup> Formation of incipient 1-(2-chlorohexafluorocyclopentenyl)ethylmagnesium bromide (IV) results in a species in which the fluorocarbon portion presumably possesses a degree of allylic carbanion nature. This intermediate could then undergo a subsequent rearrangement with loss of magnesium bromofluoride leading to the observed products IIIa and IIIb. This explanation is in agreement with the observation that treatment of 1-chloro-2-alkylperfluorocycloalkenes with strong bases yields 1-substituted-2-chloro-3-alkylidenylperfluorocycloalkenes, a reaction believed to proceed via proton abstraction from the  $\alpha$ -carbon of the side chain by the attacking base resulting in a carbanionic intermediate (or transition state).<sup>4</sup>

The transitory nature of VI is evident since no 1-chloro-2-ethylhexafluorocyclopentene-1 was obtained from the addition of dilute hydrochloric acid to the reaction mixture shortly after the addition of the Grignard reagent to I.

Preliminary studies indicate that the ca.80:20 ratio of geometrical isomers obtained in the reaction of I with ethylmagnesium bromide in THF is relatively insensitive to changes in the Grignard species and/or solvent. The isomers have virtually identical physical properties and are separable only by careful preparative scale g.l.c.

Although slight differences<sup>‡</sup> have been detected in the proton NMR signals and the infrared spectrum of the two isomers, absolute assignment of geometrical structure is uncertain at present.

Since certain fluoride salts have been shown to effect isomerization of similar isomer pairs<sup>5</sup>, the relative amounts of IIIa and IIIb could result from an equilibrium mixture. However, no isomerization was detected when chromatographically



pure IIIa was relaxed in THF with the inorganic salts present in this reaction.

Treatment of a 95:5 mixture of IIIa/IIIb with methanolic potassium hydroxide at 0° C resulted in a rapid exothermic reaction yielding a 95:5 mixture of the geometrical isomers of 1-methoxy 2-chloro-3-ethylidenetetrafluorocyclopentene-1 (VIa, VIb). The identities of VIa and VIb were verified by comparison of infrared spectra with authentic samples obtained from an independent synthetic source.<sup>4</sup>

A highly exothermic reaction took place when an 80:20 mixture of IIIa/IIIb in THF was mixed with a solution of ethylmagnesium bromide in THF. Displacement of vinylic fluoride was effected in ca. 75% conversion to yield the geometrical isomers of 1-ethyl-2-chloro-3-ethylidenetetrafluorocyclopentene-1 (Va, Vb). The infrared spectra of these compounds were identical to those ob-

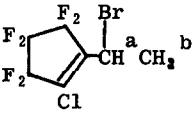
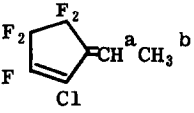
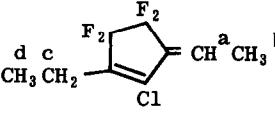
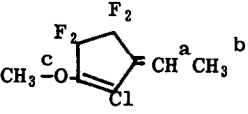
<sup>‡</sup>For example, the vinylic and allylic proton signals of VIb are centered at 4.05 and 7.89  $\tau$ , values, which are 0.04 and 0.12 downfield from the corresponding signals of VIa, respectively. The designation of VI"a" was arbitrarily assigned to the isomer with the shorter g.l.c. retention time.

(Carbowax 20M column).

tained in the direct reaction of I with an excess of ethylmagnesium bromide.

It is interesting to note that these displacement reactions proceed with retention of geometrical identity. Apparently, if carbanionic intermediates are involved in these reactions, subsequent loss of fluoride ion is more rapid than isomerization of the incipient allylic carbanion.<sup>7</sup>

Table I  
Representative Proton NMR Spectra of New Compounds

Compound	Signal	J (cps)		Assignment
I 	quartet doublet	5.09 8.06	7.2 7.2	H <sup>a</sup> H <sup>b</sup>
IIIa 	quartet doublet	3.78 7.92	7.6 7.6	H <sup>a</sup> H <sup>b</sup>
Va 	quartet doublet quartet triplet	3.83 7.93 7.54 8.79	7.7 7.7 7.7 7.7	H <sup>a</sup> H <sup>b</sup> H <sup>c</sup> H <sup>d</sup>
VIa 	quartet singlet doublet	4.09 5.93 8.01	7.5 - 7.5	H <sup>a</sup> H <sup>c</sup> H <sup>b</sup>

1-chloro-2-( $\alpha$ -bromoethyl)hexafluorocyclopentene-1 (I) was obtained from the reaction of 1-chloro-2-ethylhexafluorocyclopentene-1 with either N-bromosuccinimide in carbon tetrachloride or bromine in methylene chloride.

Further work is in progress concerning the scope and mechanistic implications of these reactions.

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References

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