Reaction of Hexafluoropropene Dimers with Organomagnesium and -lithium Reagents

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Nucleophilic reactions of *F*-2-methyl-2-pentene (**1**) and (*E*)-*F*-4-methyl-2-pentene (**2**), the dimers of hexafluoropropene, with organomagnesium and -lithium reagents were investigated. The reaction of **1** proceeded readily, giving two alkyl- or aryl-substituted polyfluoroalkenes which resulted from α- and γ-fluorine elimination, respectively. Only phenyllithium reacted with **2**, giving also α- and γ-fluorine eliminated phenylpolyfluoroalkenes. The reaction mechanism of γ-elimination was postulated in relation to the electropositive property of the organo group and to Mg–F or Li–F bond formation.

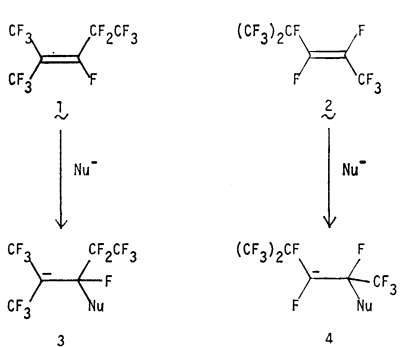
In our continuing studies on the chemistry of hexafluoropropene oligomers,[1)] we have reported a number of reactions of the oligomers with various nucleophiles except those with C-nucleophiles such as organomagnesium or organolithium reagents. Although some reactions between terminal perfluoroalkenes and organometallic reagents of this type have been investigated,[2)] none of reports on those of non-cyclized inner perfluoroalkenes have appeared in the literature.

In this paper we wish to reveal an interesting behavior of the dimers of hexafluoropropene, a typical inner perfluoroalkene, towards organomagnesium and organolithium reagents.

Results and Discussion

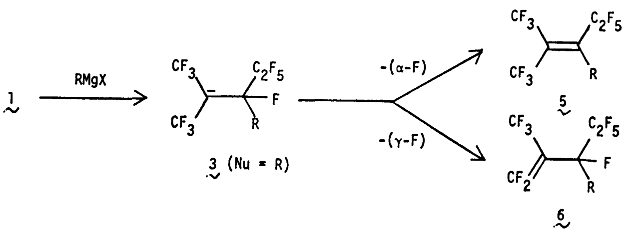
It is well known that two kinds of perfluoroalkenes are obtained by the anionic dimerization of hexafluoropropene:[1)] *F*-2-methyl-2-pentene (**1**) and (*E*)-*F*-4-methyl-2-pentene (**2**).

The perfluoroalkene **1** is thermodynamically more stable than the other isomer **2**, and, nevertheless, **1** is much more reactive to O-, N- and S-nucleophiles than **2**.[3)] This is ascribed to the higher stability of the carbanion (**3**) formed from **1** and a nucleophile, compared with the carbanion (**4**) derived from **2**, owing to the two electron-withdrawing trifluoromethyl groups attached to the anionic carbon atom.[3)]

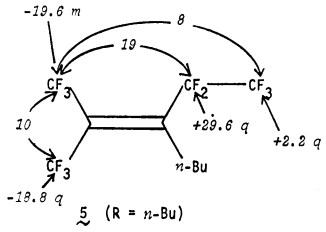


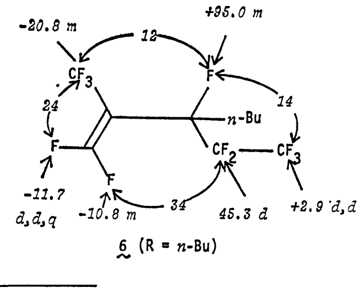
In a course of studies on the reactions of these dimers with organo-magnesium and -lithium reagents, we observed a similar tendency. The reaction of **1** was instantaneous and highly exothermic for all Grignard reagents except aryl one, while the less reactive isomer **2** with Grignard reagents, for example butylmagnesium bromide, did not produce any significant amount of products.

The products obtained by the reactions between **1** and alkylmagnesium halides were, however, always a mixture of two isomeric compounds which resulted from α- and γ-elimination of a fluoride ion from the intermediate carbanion **3** (Nu=R).



All the reactions were carried out in diethyl ether using about twice molar amounts of the Grignard reagents to ensure fast reaction. Although the two isomeric compounds in the products were not separable, the combined yield was over 70% (from ^{19}F NMR), and the structure of each isomer was readily established by careful checking of the ^{19}F NMR spectra. For example, the chemical shifts and coupling constants for the compound **5** and **6** (R=*n*-Bu) were as follows:[†]





[†] All the ^{19}F chemical shifts throughout this article are shown in δ ppm upfield from external CF$_3$CO$_2$H. The coupling constants are given in Hz.

Table 1. Reaction of *F*-2-methyl-2-pentene (**1**) with Grignard reagents

$$\underset{\mathbf{1}}{(CF_3)_2C{=}CFCF_2CF_3} \xrightarrow[Et_2O]{RMgX} \underset{\mathbf{5}}{(CF_3)_2C{=}C(R)CF_2CF_3} + \underset{\mathbf{6}}{CF_2{=}C(CF_3)CF(R)CF_2CF_3}$$

Run	RX	RX/**1** mol/mol	Et_2O/RX ml/mmol	Temp °C a)	Time min	Product, **5**+**6**			Found (Calcd) (%)	
						Yield b) %	Ratio **6**/**5**	Bp °C/mmHg d)	C	H
1	EtI	2.3	0.7	0	5	91	1.9	102—103/760	30.69 (30.98)	1.60 (1.63)
2	EtI	2.2	0.8	0	30	76	1.9			
3	EtBr	2.1	0.8	0	5	85	2.0			
4	EtBr	2.3	0.8	0	30	74	2.1			
5	*n*-PrI	2.4	0.7	0	5	87	1.3	54—55/72	33.51 (33.35)	2.24 (2.18)
6	*n*-PrBr	2.6	2.0	0	8	75	1.6			
7	*n*-PrBr	2.5	0.7	−45	8	75	1.0			
8	*n*-PrBr	2.4	0.7	0	60	78	1.4			
9	*n*-PrBr	2.2	0.8	+35	60	75	1.7			
10	*n*-BuBr	1.8	0.8	0	20	78	1.2	131—133/760	35.23 (35.50)	2.68 (2.68)
11	*n*-BuBr	1.2	2.5	+8	180	70 c)	1.4			
12	*n*-$C_8H_{17}Br$	2.0	0.6	0	30	87 c)	1.1	95—96/18	42.89 (42.60)	4.46 (4.35)
13	*c*-$C_6H_{11}CH_2Br$	2.7	0.8	0	7	88	1.0	83—85/22	41.58 (41.28)	3.54 (3.46)
14	$PhCH_2Br$	2.3	0.7	0	4	90	4.0	85—86/25	42.00 (41.95)	1.92 (1.90)
15	*i*-PrBr	2.4	0.7	0	4	77	7.4	42—43/40	33.09 (33.35)	2.18 (2.18)
16	PhBr	2.4	1.3	+23	60	46 c)	0.13	101—103/97	40.42 (40.24)	1.47 (1.41)
17	*p*-MeC_6H_4Br	2.4	0.8	+23	60	59	0.12	80—82/21	41.73 (41.95)	1.86 (1.90)

a) Deviation in the range of ±3 °C was allowed. b) Based on the ^{19}F NMR signal intensities unless otherwise noted. c) Isolated yield. d) 1 mmHg≈133.322 Pa.

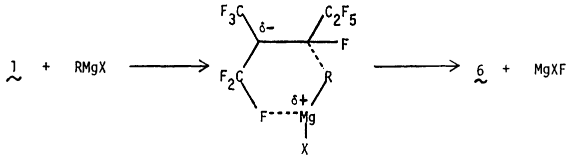
Although no evidence was found for isomerization of **6** into thermodynamically more stable **5** in the reaction system, and also in the post-treatment of the reaction mixture, the conversion was ascertained by the ^{19}F NMR to be realized readily by adding triethylamine in a polar solvent such as acetonitrile or *N*,*N*-dimethylformamide within 5 min, assisting confirmation of the structures.

The ratios of isomeric products in reaction mixtures, **6** *vs.* **5** or γ-elimination *vs.* α-elimination varied with the organo group of the reagents, reaction temperature, and other reaction conditions.

Thus, from Table 1, the order of percentage for γ-elimination forming **6** in ethereal solution was *i*-Pr> $PhCH_2$≫*n*-alkyl>aryl which is correlated to the relative reactivities of Grignard reagents, *i*-Pr>*s*-Bu>$PhCH_2$> *n*-alkyl.[4,5] Also the reactivity of Grignard reagents is correlated to the electropositivity of their identifying organo group[6] and, in fact, the order listed above shows a general, if imperfect, similarity to that of the electropositivities of organo groups, *i.e.* $PhCH_2$>*i*-Pr>*n*-alkyl>aryl.[7]

Regarding the mechanism of the reaction of **1** with Grignard reagents, α-elimination of a fluoride ion from the carbanion **3** resulting in a substituted product **5** is quite natural, and this type of reaction is frequently observed in the normal reactions of **1** with O- and N-nucleophiles.[1]

However, the formation of the rather unstable terminal alkene **6** resulted from γ-elimination is unusual. The elimination of a fluoride ion from the terminal trifluoromethyl group should be assisted by an electron donating group on one side and a fluoride ion-pulling group on another side. Thus we postulate that the magnesium behaves as a strong fluoride ion acceptor, as it can occupy a very close position to the fluorine atoms of CF_3, and as the Mg–F bond is thermodynamically very strong (462 kJ mol^{-1}).[8]



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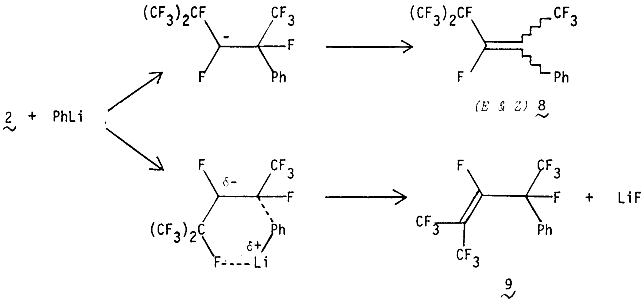
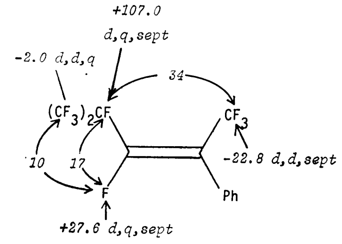
This kind of γ-elimination has been also observed in the reactions of **1** with thiols[9] and with ortho-difunctional benzenes.[10] The experimental fact mentioned above revealed that the more electropositive the organo group of the Grignard reagent is, the more γ-elimination becomes dominant. This is quite reasonable because an electropositive group will make the electron density more localized on a $^{-}C(CF_3)$ group, and will make magnesium more "metallic," and both effects will render it easy to release a fluoride ion from the trifluoromethyl group. This assumption would be also supported by the difference in values **6**/**5** for RMgBr and RMgI. The more metallic organomagnesium bromide slightly prefers γ-elimination than organomagnesium iodide does. However, a fluoride ion elimination from a trifluoromethyl group is a process demanding higher energy because of a stronger carbon-fluorine bond in CF_3. So that it is natural that the reactions at higher temperatures enhanced the γ-elimination.

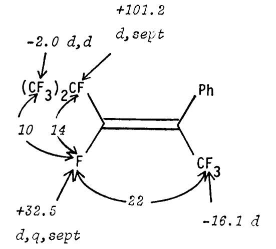
Similar reactions of another dimer, (*E*)-*F*-4-methyl-2-pentene, **2**, were sluggish and practically no products were formed with Grignard reagents. Phenyllithium, however, reacted with **2** and gave a significant amount of γ-elimination product (**9**) together with normal α-elimination product (**8**) in a ratio **9**/**8**=0.6.



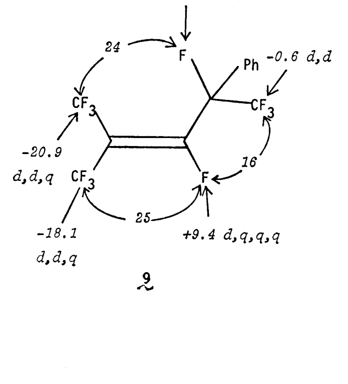
This value seems rather high because probability of γ-elimination for **2** should be one sixth of that for **1**. However, it should be understandable by considering that the Li–F bond is very strong (577 kJ mol^{-1})[8] and the tertiary fluorine atom would be released easily to give a stable perfluoro inner alkene. The structures of these isomers were also established by careful cheking of the ^{19}F NMR spectra for the mixture though it was unable to separate them from each other. The ratio of **8** to **9** was 5 : 3, of which **8** containing (*E*) and (*Z*) form (1 : 6.5). The chemical shifts and coupling constants were assigned to all fluorine atoms of the isomers as above:



(*E*) **8**



(*Z*) **8**



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Experimental

Grignard Reactions of F-2-Methyl-2-pentene (1). Grignard reagents were prepared in a dried apparatus with air replaced by argon. Magnesium turnings and mild heating were used to initiate the reaction; in no case were chemical initiators necessary. The Grignard reagents in diethyl ether were very clear, almost colorless solution, except for aryl reagents which were dark brown. After formation of the Grignard reagent, the solution was brought to a specified temperature, and **1** was added with magnetic stirring. The addition was highly exothermic, and vigorous shaking of the bath was required to keep the temperature under control. Addition of the requisite amount of perfluoroalkene generally took about 5 min, after which the mixture was quenched by 2% HCl. Typical procedures are as follows.

Determination of Isomer Ratio. To the Grignard reagent prepared from magnesium turning (0.28 g, 11.5 mmol) and propyl bromide (1.51 g, 12.3 mmol) in dry diethyl ether (9 ml) was added **1** (purity over 95%, 1.62 g, 5.13 mmol) over 10 min at 0±3 °C. After stirring for 50 min at that temperature, the remaining Grignard reagent was quenched by the addition of dilute hydrochloric acid (2%, 2 ml). To the homogeneous ethereal solution, fluorobenzene (0.3784 g, 3.94 mmol) was added as internal standard. The ^{19}F NMR spectrum for this solution showed that the ratio of **6** to **5** (R=Pr) was 1.4, in a combined yield of 78%.

Isolation. To the Grignard reagent prepared from magnesium turning (2.65 g, 110 mmol) and octyl bromide (17.3 g, 90 mmol) in dry diethyl ether (55 ml) was added **1** (13 g, 41 mmol) at 0 °C. After 30 min the reaction was quenched by the addition of dilute hydrochloric acid (2%, 10 ml). The mixture was extracted with ether, washed with brine and dried over $MgSO_4$. After removing the solvent, distillation gave a mixture (15.2 g) of **5** and **6** ($R=n\text{-}C_8H_{17}$). The yield was 89%.

Isomerization of 6 to 5. To a mixture of **5** and **6** (R=alkyl) was added an approximately equal volume amount of acetonitrile in an NMR tube. It was ascertained by ^{19}F NMR that no isomerization occurred until a drop of triethylamine was added, upon which complete conversion of **6** to **5** occurred with 1 or 2 min. *N*,*N*-Dimethylformamide in the presence of triethylamine also effected the isomerization of **6** to **5** quantitatively.

Reaction with Phenyllithium. Into a solution of **1** (3.00 g, 10.0 mmol) in dry diethyl ether (20 ml), a solution of phenyllithium in diethyl ether (1.3 M (1 M=1 mol dm^{-3}), 10 ml) was dropped under nitrogen atmosphere at −60 °C, controlling the temperature with Dry Ice–acetone bath. The reaction mixture was stirred for 2 h allowing the temperature to rise up to room temperature. After additional stirring for 1 h at room temperature, the reaction was quenched by the addition of dilute hydrochloric acid and ethereal layer was washed with water and dried over $MgSO_4$. The solvent was removed and the residue was subjected to distillation *in vacuo* yielding a mixture of **5** and **6** (R=Ph) (2.25 g, 63%, **6**/**5**=0.16), bp 101—103 °C/97 mmHg. Found: C, 40.42; H, 1.47%. Calcd for $C_{12}H_5F_{11}$: C, 40.24; H, 1.41%.

In a similar manner, **2** (3.00 g, 10.0 mmol) and phenyllithium–diethyl ether solution (1.0 M, 20 ml) were allowed to react for 1 h at −70 °C. The reaction mixture was worked up as mentioned above and distillation under reduced pressure gave a mixture of **8** and **9** (2.80 g, 78%, **9**/**8**=0.6, (*Z*)**8**/(*E*)**8**=

6.5), bp 98—102 °C/115 mmHg. Found:C,40.04; H,1.48%. Calcd for $C_{12}H_5F_{11}$: C, 40.24; H, 1.41%.

References

1) Review: N. Ishikawa and M. Maruta, *Yuki Gosei Kagaku Kyokai Shi*, **39**, 51 (1981).

2) For example, L. A. Rozov, L. S. German, Yu. V. Zeifman, Ya. A. Cheburkov. and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1974**, 741; L. F. Rybakova, E. M. Panov, and K. A. Kocheshkov, *Zh. Org. Khim.*, **11**, 2576 (1975).

3) N. Ishikawa and A. Nagashima, *Bull. Chem. Soc. Jpn.*, **49**, 502 (1976).

4) T. Holm, *Acta Chem. Scand.*, **28** (Ser. B), 809 (1974).

5) W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 4945 (1974).

6) M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

7) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

8) CRC, "Handbook of Chemistry and Physics," 59th ed, (1978—1979), p. F 219.

9) M. Maruta and N. Ishikawa, *J. Fluorine Chem.*, **13**, 111 (1979).

10) M. Maruta, S. Kubota, N. Yoshimura, T. Kitazume, and N. Ishikawa, *J. Fluorine Chem.*, **16**, 75 (1980).