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A Novel Generation and Behavior of Alkylfluorocarbenoids from α,α-Chlorofluoroalkyl Sulfoxides

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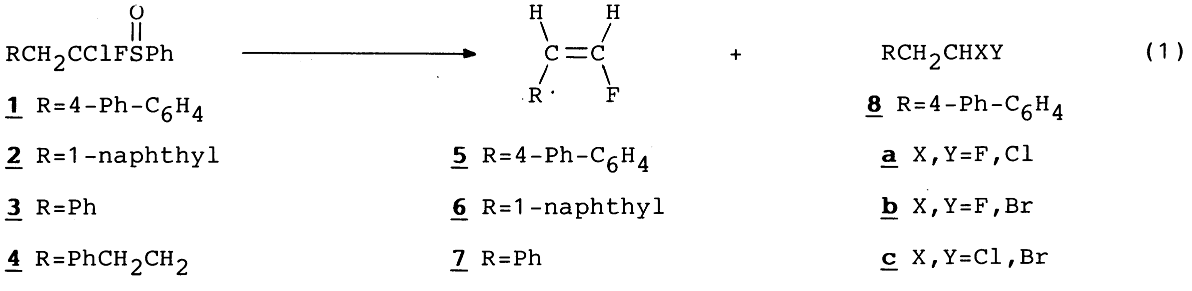
α,α-Chlorofluoroalkyl sulfoxides undergo nucleophilic desulfinylation with a Grignard reagent to give alkylfluorocarbenoids which collapse into cis-fluoroalkenes in the presence of copper(I) iodide.

In recent years, there has been considerable attention directed toward an elucidation of the mechanistic details involved in the 1,2-hydrogen migration of carbenes to olefins.1) However, little has been known about the behavior of alkylfluorocarbenes, even though a precursor such as 3-fluoro-3-alkyldiazirines is now available by the diazirine exchange reaction.2) From synthetic points of view, the 1,2-hydrogen shift of fluorocarbenes will become a useful preparative method for fluoroalkenes if the stereochemical control is well documented.3) Herein we report our findings that alkylfluorocarbenoids derived from the nucleophilic desulfinylation reaction of α,α-chlorofluoroalkyl sulfoxides are subject to 1,2-hydrogen shift, giving cis fluoroolefins in a highly stereoselective manner.

Nucleophilic desulfinylation4) of 2-(4-biphenylyl)-1-chloro-1-fluoroethyl phenyl sulfoxide (**1**)5) was carried out under the conditions listed in Table (Eq 1). Treatment of the sulfoxide **1** with 1 equiv. of phenylmagnesium bromide gave the cis-β-fluorostyrene **5** (12%; ^{19}F-NMR ($CDCl_3$) δ -122.2, J_{FH}=82.7 and 44.9 Hz), the dihalogeno derivatives **8** (35%; **a**:**b**:**c**=6:10:1 estimated by NMR), and a large amount of starting material **1** (51%) (entry 1). In the presence of a catalytic amount of CuI, the fluoroolefin **5** was formed in preference to the dihalogeno derivatives **8**, although the conversion was unsatisfactory yet. When 3 equiv. of the Grignard reagent were employed, the starting sulfoxide was entirely consumed (entry 4). These results can be rationalized by assuming a competitive consumption of the Grignard reagent by diphenyl sulfoxide produced during the course of the reaction, because biphenyl and diphenyl sulfide were major side products isolated from the reaction mixtures.[6] Stereoselectivity of the formation of the fluorostyrene **5** was confirmed to be cis/trans=33/1 by ^{19}F-NMR analysis of the reaction mixture (entry 4). Changing the nucleophile to organolithiums altered



$$\mathrm{RCH_2CClF\overset{\overset{O}{\|}}{S}Ph} \longrightarrow \mathrm{(R)(H)C{=}C(H)(F)} + \mathrm{RCH_2CHXY} \qquad (1)$$

1 R=4-Ph-C_6H_4
2 R=1-naphthyl
3 R=Ph
4 R=$PhCH_2CH_2$

5 R=4-Ph-C_6H_4
6 R=1-naphthyl
7 R=Ph

8 R=4-Ph-C_6H_4
a X,Y=F,Cl
b X,Y=F,Br
c X,Y=Cl,Br

$PhCH_2CH_2CH_2COPh$
12

$PhCH_2CH_2CH{=}CHPh$
13

Table 1. Nucleophilic Desulfinylation of **1**

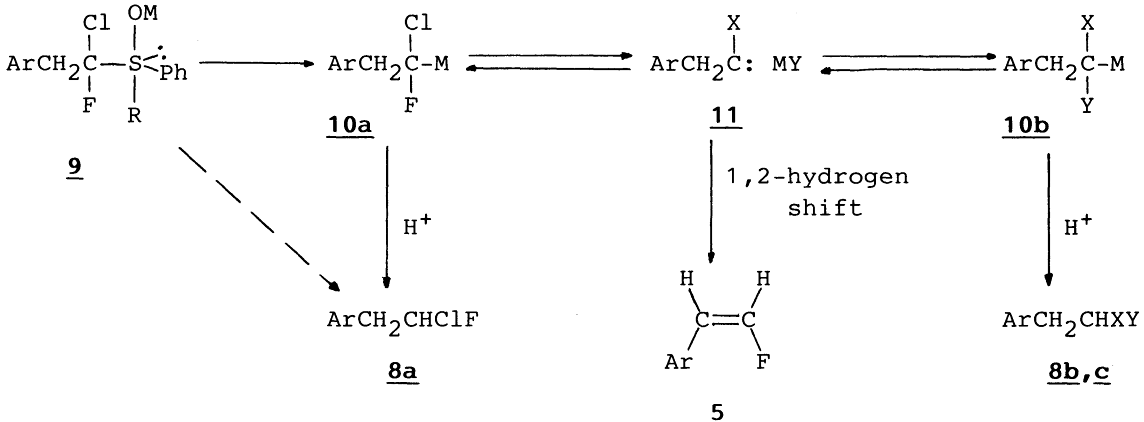
Entry	Nucleophile (equiv.)	Conditions[a)] Additive (equiv.)	Temp	Yield/%[b)] **1**	**5**	**8** (**a**:**b**:**c**)[c)]
1	PhMgBr (1)	none	-78 °C → r.t., 1 h	51	12	35 (6:10:1)
2	PhMgBr (1)	CuI (0.1)	-78 °C → r.t., 1 h	63	25	10 (6:9:1)
3	PhMgBr (2)	CuI (0.1)	-78 °C → r.t., 1 h	16	33	5 (1:2:1)
4	PhMgBr (3)	CuI (0.1)	-78 °C → r.t., 1 h	-	54	10 (1:2:1)
5	PhMgBr (3)	CuI (0.3)	-78 °C → r.t., 1 h	-	40	13 (3:5:1)
6	PhLi-LiBr (1)	none	-78 °C → -30 °C, 1 h	44	trace	27 (8:1:0)
7	PhLi-LiBr (1)	none	-78 °C, 1 h	36	trace	51 (9:1:0)
8	n-BuLi (1)	none	-78 °C, 1 h	42	trace	27 (1:0:0)[d)]

a) All reactions were carried out on a 0.3-mmol scale. b) Isolated yield by column chromatography on silica-gel using hexane as an eluant. c) Determined by NMR. d) 1-(4-Biphenylyl)hexenes ($^1\Delta\underline{E}:{}^1\Delta\underline{Z}:{}^2\Delta\underline{E}:{}^2\Delta\underline{Z}$ = 68:3:28:1) were obtained in 7% yield.

the product distribution. Thus, the reaction of **1** with PhLi-LiBr gave a 51% yield of **8** together with a trace amount of the fluorostyrene **5** (entry 7), while the reaction with n-BuLi afforded 4-(2-chloro-2-fluoroethyl)biphenyl (**8a**) (27%) and biphenylylhexenes (7%). The isomeric ratios of the latter product depended on the quenching mode of the allyl anions generated in the strongly basic media. The incorporation of butyl group may be attributed to stronger nucleophilicity and/or higher aggregation of n-BuLi than PhLi.7)

The product variations observed in reactions with the Grignard reagent and with organolithiums are well understood by taking account of an equilibrium between the carbenoid **11** and the carbanionoid intermediates **10** (Scheme 1). As a trigonal bipyramidal sulfurane derived from the reaction of a vinyl sulfoxide with t-butyllithium was suggested to decompose to a vinyl compound without intermediacy of a vinyllithium,8) the chlorofluoro derivative **8a** might be directly formed from the sulfurane **9** in the case of organolithium. Moreover, if the carbanionoid **10a** (M=Li) would be generated, halide exchange reaction of the lithium carbenoids **11** with coordinated lithium bromide9) would be less significant than that of magnesium carbenoids. Thus, the chlorofluoro derivative **8a** was dominantly obtained in reactions with organolithiums. Presence of CuI favored the formation of the carbenoid **11**, and led to **5** via 1,2-hydrogen shift of **11**. The high cis stereoselectivity realized in the formation of **5** would be due to a sterically small contribution of fluorine atom in the transition state of the 1,2-hydrogen shift.10)

Similar reactions of sulfoxides **2** and **3** with PhMgBr (3 equiv.) in the presence of CuI gave also cis-fluoroolefins **6** (26%) and **7**11) (11%) as the respective main products, whereas the reaction of **4** gave the ketone **12** (12%) and the olefin **13** (7%) as the only isolable products. This remarkable contrast remains to



Scheme 1.

be clarified.

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5) α,α-Chlorofluoroalkyl sulfoxides were prepared in 45-75% yields from the reaction of the respective halides with lithiated chlorofluoromethyl phenylsulfoxide (MeLi-LiBr, -90 °C, 1 h), which in turn was obtained in good yields by oxidation of the corresponding sulfide with MCPBA.

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