

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-biphenyl)-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%; ¹⁹F-NMR (CDCl₃) 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

$$\text{RCH}_2\text{CClFSPH} \xrightarrow{\quad} \begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{R} & & \text{F} \end{array} + \text{RCH}_2\text{CHXY} \quad (1)$$

1 R=4-Ph-C₆H₄ 5 R=4-Ph-C₆H₄ a X,Y=F,Cl
2 R=1-naphthyl 6 R=1-naphthyl b X,Y=F,Br
3 R=Ph 7 R=Ph c X,Y=Cl,Br
4 R=PhCH₂CH₂



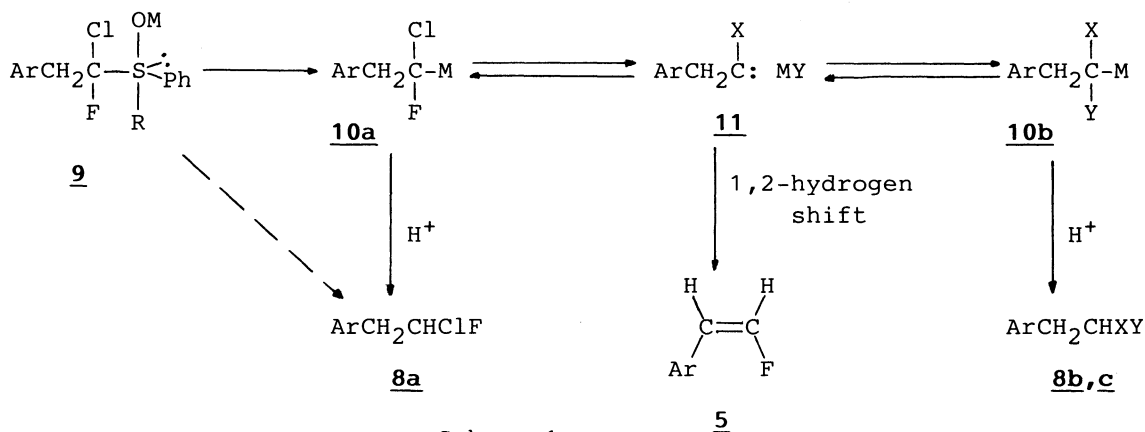
En-try	Nucleophile (equiv.)	Conditions ^{a)}		Yield/% ^{b)}		
		Additive (equiv.)	Temp	<u>1</u>	<u>5</u>	<u>8</u> (<u>a</u> : <u>b</u> : <u>c</u>) ^{c)}
1	PhMgBr (1)	none	-78 °C → r.t., 1 h	51	12	35 (6:10:1)
2	PhMgBr (1)	CuI (0.1)	-78 °C → r.t., 1 h	63	25	10 (6:9:1)
3	PhMgBr (2)	CuI (0.1)	-78 °C → r.t., 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-Biphenyl)hexenes ($^1\Delta\text{E}:^1\Delta\text{Z}:^2\Delta\text{E}:^2\Delta\text{Z} = 68:3:28:1$) 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 biphenylhexenes (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 vinylolithium,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 7¹¹⁾ (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



be clarified.

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