Tetrahedron Letters, Vol.32, No.28, pp 3385-3386, 1991
Printed in Great Britain

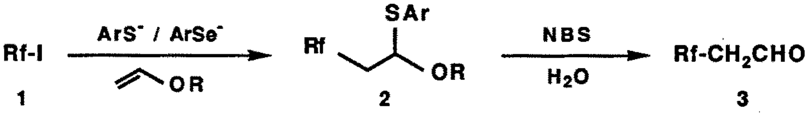
0040-4039/91 $3.00 + .00
Pergamon Press plc

ARENESELENOLATE-MEDIATED PERFLUOROALKYL-SULFENYLATION OF ENOL ETHERS

Kenji Uneyama* and Kouichi Kitagawa
Department of Applied Chemistry, Faculty of Engineering,
Okayama University, Okayama 700, Japan

Summary; Areneselenolate-mediated perfluoroalkyl-sulfenylation of enol ethers has been performed by the reaction of sodium arenethiolates, a catalytic amount of sodium areneselenolates, perfluoroalkyl iodides, and olefins where ArSeNa initiates a chain reaction via an electron transfer mechanism.

Metal-catalyzed perfluoroalkyl-iodination of olefins is a well known process. Some anions or radical anions mediate radical perfluoroalkyl-iodinations and the related reactions of olefins1), but very few are incorporated into olefins instead of iodine2). Perfluoroalkyl-sulfenylation has never appeared in literatures although Wakselman3) demonstrated that trifluoromethylation of arenethiolates proceeds via a radical process which is initiated by an electron-transfer from the thiolates to trifluoromethyl bromide. As an extension of perfluoroalkyl-selenation of olefins4), we describe a novel areneselenolate-mediated perfluoroalkyl-sulfenylation of enol ethers whose products are transformed into perfluoroalkyl-2H, 2H-aldehydes(3).



Into an ether suspension of p-$MeOC_6H_4SH$ (0.6 mmol) and NaH (1.2 mmol), PhSeNa prepared from $(PhSe)_2$ (0.03 mmol) and $NaBH_4$ (0.15 mmol) in dry EtOH (0.05 ml) and dry ether (0.6 ml), and isobutyl vinyl ether (1.8 mmol) were added under N_2. Then, $C_8F_{17}I$ (0.72 mmol) was added with stirring and the mixture was refluxed for 2 hr, affording **2a** (88%). The results are summarized in Table 15). The reactions are complete in 1~2 hr in most cases. The yields of **2** are dependent on the electron-donating nature of substituents of ArSNa and satisfactory for ArSNa [p-MeO (86%), H (92%), p-Cl (88%)] even if the selenolate ($ArSe^-$) is not used. However, in the absence of the selenolate, both sodium p-methoxythiophenoxide and thiophenoxide reacted slowly, affording **2a** and **2d** in 25% and 35% yields for 2 hr, respectively, and p-nitrothiophenoxide was recovered intact after 12 hr. The initial electron-transfer process may be a rate-determining step and the intermediate radicals **4** can react even with less reactive p-nitrothiophenoxide. In contrast to perfluoroalkyl-selenation4), 1-octene gives none of the desired **2**, but 1-perfluoroalkyl-1-octene in 55% yield, which may arise from base-catalyzed dehydroiodination of the corresponding iodide6). The intermediate radicals 4 may react competitively with thiolate and RfI. The relative reactivities of 4 would be intensively affected with electronic and steric natures of substituents(R') and the electron-transfer reagents. The selenolate would mediate perfluoroalkyl-alkylation and the related functionalization of olefins which are under investigation.

The acetals(**2**) can be transformed into perfluoroalkyl-2H,2H-aldehydes(**3**) within 10 min. by the NBS-catalyzed oxidative desulfenylation in ice-cooled aqueous acetonitrile in reasonable yields [C_4F_9 (87%), C_6F_{13} (83%), C_8F_{17} (90%)]7).

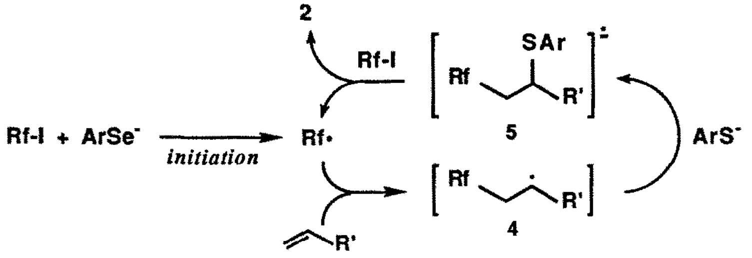
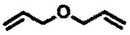


Table 1. Areneselenolate-mediated Perfluoroalkyl-sulfenylations

Entry	p-XC_6H_4SNa	p-YC_6H_4SeNa	RfI	Time(h)	Olefins	Yield(%)[a]	
1	X=MeO	none[b]	$C_8F_{17}I$	6		***2a***	86
2		Y=H		2			88
3			$C_6F_{13}I$	2		***2b***	93
4			C_4F_9I	2		***2c***	87
5	H	none[b]	$C_8F_{17}I$	6		***2d***	92
6		Y=MeO		1			80
7	Cl	none[b]	$C_8F_{17}I$	8		***2e***	88
8		Y=MeO		2			80
9	NO_2	none[b]	$C_8F_{17}I$	12		***2f***	trace
10		Y=H		2			45
11	H	MeO	$C_8F_{17}I$	2		***2g***	39[c]
12	H	MeO	$C_8F_{17}I$	3		***2h***	40[d]
13	H	MeO	$C_8F_{17}I$	4		***2i***	0[e]

a) Isolated yields based on ArSNa. b) In the absence of ArSeNa. c) Diastereomeric mixture trans/cis=71: 29 d) 

e) $C_8F_{17}CH{=}CHC_6H_{13}$ was obtained (55%).

References and notes

1) A. E. Feiring, *J. Fluorine Chem.*, **24**, 191 (1984); idem., *J. Org. Chem.*, **50**, 3269 (1985); W. Y. Huang, *J. Fluorine Chem.*, **32**, 179 (1986); G-B. Rong and R. Keese, *Tetrahedron Lett.*, **31**, 5615 (1990).

2) A. E. Feiring, *J. Org. Chem.*, **48**, 347 (1983); Q-Y. Chen and Z-M. Qiu, *J. Fluorine Chem.*, **31**, 301 (1986); idem., *ibid.*, **35**, 343 (1987); C. P. Andrieux, L. Gelis, and J-M. Saveant, *Tetrahedron Lett.*, **30**, 4961 (1989).

3) C. Wakselman and M. Tordeux, *J. Chem. Soc., Chem. Commun.*, 793 (1984).

4) K. Uneyama and K. Kitagawa, *Tetrahedron Lett.*, **32**, 375 (1991).

5) Perfluoroalkyl-selenated compounds (**2**, SeAr instead of SAr) were obtained (5~8%) as by-products.

6) The control experiment of the iodide prepared separately gave the olefins in the same conditions.

7) The yields of the aldehydes(**3**) were obtained as the corresponding crystalline 2,4-dinitrophenylhydrazones. Preparation of **3** (44~53%) from perfluoroalkylated-vinyl ethers; S. V. Pazenok, E. A. Chaika, I. I. Gerus, and L. M. Yagupolskii, *Zh. Org. Khim.*, **25**, 1376 (1989).

(Received in Japan 14 February 1991)