## A NOVEL SYNTHESIS OF HALOALKENES FROM ALDEHYDES WITH CARBON-CARBON COUPLING

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Key words: sulfoxide; 1-haloalkyl aryl sulfoxide; fluoroalkene; chloroalkene; ligand exchange reaction

Abstract: Treatment of  $\alpha$ -halo  $\beta$ -mesyloxy sulfoxides, easily synthesized from aldehydes and 1-haloalkyl aryl sulfoxides in two steps, with n-BuLi at -78 °C gives haloalkenes in good yields.

Haloalkenes are interesting compounds in organic chemistry.<sup>1</sup> In particular, fluoroalkenes have received much attention as non-hydrolizable amide isosters.<sup>2</sup>

Recently, we reported a new synthesis of  $\alpha$ -halo ketones from aldehydes and 1-haloalkyl aryl sulfoxides via ethylmagnesium bromide mediated desulfinylation of  $\alpha$ -halo  $\beta$ -keto sulfoxides.<sup>3</sup> This reaction was proved to take place by the attack of a carbanion to the sulfinyl group (ligand exchange reaction of sulfoxide<sup>4</sup>). We thought that a similar reaction would take place with  $\alpha$ -halo  $\beta$ -mesyloxy sulfoxides **2**. In this paper, we report the *n*-BuLi mediated desulfinylation of  $\alpha$ -halo  $\beta$ -mesyloxy sulfoxides **2**, easily derived from **1** and aldehydes, giving fluoroalkenes **3** (X=F) and chloroalkenes **3** (X=Cl) in high yields (Scheme 1).



Treatment of the carbanion of 1-fluorobutyl phenyl sulfoxide 1 (X=F, Ar=Ph, R<sup>1</sup>=CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sup>3</sup> with hydrocinnamaldehyde in THF at -78 °C gave the less polar adduct (L) and the more polar adduct (P)<sup>5</sup> in 20% and 77% yields, respectively. These adducts were mesylated (L: Ms<sub>2</sub>O-Et<sub>3</sub>N; P: MsCl-Et<sub>3</sub>N) to afford the  $\alpha$ -fluoro  $\beta$ -mesyloxy sulfoxides 2a-L (50%) and 2a-P (88%). Treatment of 2a-L in THF at -78 °C with 1.6 equivalents of *n*-BuLi gave cleanly the desired (*E*)-4 fluoro-1-phenyl-3-heptene (3a) as a single isomer in 70% yield. Interestingly, the same treatment of 2a-P gave a mixture of 3a (*E*/Z=70/30) in 86% yield. Corresponding chloride 2e (see Table 1) was treated with *n*-BuLi (1.2 equivalents) in ether to give the chloroalkene 3e in high yield. In this case striking *E*-specificity was observed from 2e-P. Representative examples for the synthesis of fluoroalkenes and chloroalkenes are summarized in Table 1. It is worth noting that the elimination of the sulfinyl group and the mesyloxy group of 2 took place quite smoothly to afford haloalkenes 3 in good to quantitative yields. Although the reason is obscure at present, one of the isomers shows *E*-specificity in the elemination.

The possible mechanism of these reactions can be proposed as shown in Scheme 1. The ligand exchange reaction occurs through the attack of butyl anion to the sulfinyl group to afford  $\beta$ -carbanion of the mesylate. Then,  $\beta$ -elimination of the mesyloxy group takes place to give the haloalkenes.

We are continuing to study the scope and limitation, and the synthetic uses of this procedure.

	1			Aldehyde	2	BuLi	3	
	Ar	x	$\mathbf{R}^1$	$R^2$	(Yield/%) <sup>a)</sup>	(equiv.) <sup>b)</sup>	Yield/% <sup>c)</sup>	(E/Z) <sup>d)</sup>
a	Ph	F	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub>	PhCH <sub>2</sub> CH <sub>2</sub>	$\frac{L^{e)}(10)}{P^{e)}(68)}$	3.0	<b>3a</b> 70 <b>3a</b> 86	(100/0) (70/30)
b	Ph	F	$CH_3(CH_2)_2$	$CH_3(CH_2)_8$	L (48) P (26)	3.0 2.5	3b 95 3b 70	(45/55) (75/25)
с	Ph	F	CH <sub>3</sub>	PhCH <sub>2</sub> CH <sub>2</sub>	(39) <sup>f)</sup>	4.0	<b>3c</b> 72	(41/59)
d	Ph	F	CH <sub>3</sub>	$CH_3(CH_2)_8$	(39) <sup>f)</sup>	3.0	<b>3d</b> 70	(57/43)
e	Tol	Cl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub>	$PhCH_2CH_2$	L (26) P (29)	1.2 1.2	<b>3e</b> 99 <b>3e</b> 79	(50/50) (98/2)
f	Tol	Cl	$CH_3(CH_2)_2$	$CH_3(CH_2)_8$	L (32) P (24)	2.0 2.0	3f 99 3f 96	(58/42) (100/0)
g	Tol	Cl	CH <sub>3</sub>	PhCH <sub>2</sub> CH <sub>2</sub>	L (22) P (29)	2.0 2.0	<b>3g</b> 92 <b>3g</b> 99	(73/27) (62/38)

Table 1. Synthesis of Haloalkenes 3 from 1 and Aldehydes via  $\alpha$ -Halo  $\beta$ -Mesyloxy Sulfoxides 2

a) Two-step overall yield from aldehyde and 1. b) The reaction was carried out in THF ( $\alpha$ -fluoro  $\beta$ -mesyloxy sulfoxide) and in ether ( $\alpha$ -chloro  $\beta$ -mesyloxy sulfoxide) at -78 °C. c) Isolated yield.

d) The E/Z-ratio was determined by <sup>1</sup>H NMR. e) See text. f) The isomers (L/P) were not separated.

## References and Notes

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