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A HIGHLY REGIOSELECTIVE REACTION OF ALLYLIC ACETATES WITH SILYLATED CARBON NUCLEOPHILES DIRECTED BY A SULFENYL GROUP

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Summary : (α-Sulfenylmethyl)allyl acetates reacted with silylated carbon nucleophiles in the presence of a catalytic amount of a Lewis acid to give mainly α-adducts at the sulfenylmethyl group in moderate to good yields with high regioselectivity. The reaction may proceed *via* episulfonium ion intermediates.

Episulfonium ions, which are generated either by the addition of sulfenyl cation to alkenes or by the neighboring group participation of a β-sulfenyl group toward cationic centers, are common intermediates in organic reactions, and have appeared in some functionalization reactions.1) Meanwhile, there have been only a few studies on synthetically important carbon-carbon bond forming reactions *via* an episulfonium ion.2) In connection with the above-memtioned reaction, we have recently reported the *anti*-Cram selective aldol reaction of α-sulfenyl acetals with silylated carbon nucleophiles,3) and have tried to extend this intermediate to another selective reaction. In this communication, we report regioselective carbon-carbon bond formation of allylic electrophiles.

In order to make an episulfonium ion, (α-sulfenylmethyl)allyl acetate was designed as a substrate. We first examined the reaction of (*E*)-2-acetoxy-1-phenylthio-3-pentene4) with trimethylsilyl enol ether of diisopropyl ketone in the presence of titanium(IV) chloride, and found that the adduct was obtained in 61% yield as a 93 : 7 mixture of regioisomers. Main isomer was proved to be an α-adduct at the sulfenylmethyl group.

After screening several reaction conditions, generality of this reaction was tested with a couple of substrates and nucleophiles as in Table 1. Run 7 indicates that the reaction proceeds with complete retention of configuration, suggesting the intermediacy of an episulfonium ion.

A control reaction was performed for (*E*)-4-acetoxy-2-octene with trimethylsilyl enol ether of diisopropyl ketone. In this case, both the regioselectivity (α : γ = 35 : 65) and the yield (29%) were much poorer. That is to say, the sulfur function in the substrate not only stabilizes the cationic intermediate but also directs the reaction course.

The general procedure is as follows: To a stirred solution of (α-sulfenylmethyl)allyl acetate (0.5 mmol) and silylated carbon nucleophile (0.6 mmol) in dichloromethane (4 ml) was added a dichloromethane solution of trimethylsilyl trifluoromethanesulfonate (0.05 mmol) at -78 °C under an argon atmosphere. The resulting solution was stirred for 2 h at ambient temperature. Then, saturated aqueous sodium hydrogencarbonate (5 ml) was added, and the aqueous layer was extracted with dichloromethane (2 x 5 ml). After drying the combined organic layer over sodium sulfate, the solvent was removed. Purification by preparative tlc gave a mixture of α- and γ-adducts. The product ratio was determined by capillary gas chromatography.

Recently, the regioselective carbon-carbon bond formation of an allylic electrophile was achieved with some organometallic reagents.5) On the other hand, the Lewis acid-mediated reaction of such a substrate is known to be affected only by steric factors, namely, a nucleophile always attacks at less hindered site of the allylic system.6) So, if both ends of an allyl cation are secondary, low regioselectivity is observed (*vide supra*). Our method provides a new way for differentiating two termini of such an allyl cation.

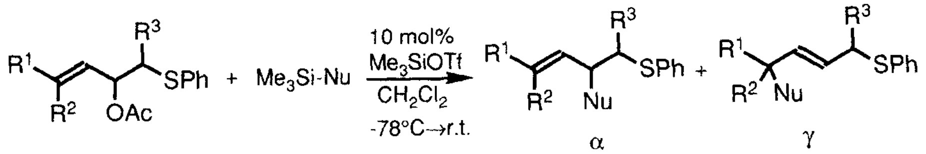
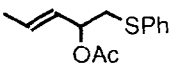
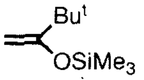
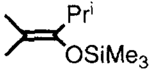
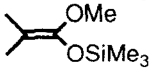
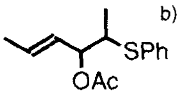
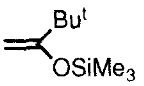
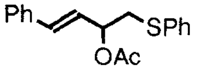
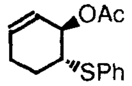


Table 1. Reaction of (α-Sulfenylmethyl)allyl Acetates with Various Nucleophiles[a)]

Run	Substrate	Nucleophile	Yield / %	α : γ
1			68	94 : 6
2			82	89 : 11
3			78	91 : 9
4			59	91 : 9
5			49	$82^{b)}$: $18^{b)}$
6			80	92 : 8
7			67	$100^{c)}$: 0

a) All products gave satisfactory ir and ^{1}H-nmr spectra. b) A 1 : 1 mixture of diastereomers.
c) Only the *trans* isomer was obtained.

Mechanistic aspects of this reaction and other selective reactions using an episulfonium ion are now under investigation in this laboratory.

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3) K. Saigo, K. Kudo, Y. Hashimoto, H. Kimoto, and M. Hasegawa, Chem. Lett., 941 (1990).
4) This compound was easily synthesized in one-pot reaction [(1) Thioanisole, *n*-BuLi, TMEDA, THF, 0 °C (2) crotonaldehyde, -78 °C (3) acetyl chloride, 0 °C; 56 % yield].
5) For example, B. M. Trost and M.-H. Hung, J. Am. Chem. Soc., **106**, 6837 (1984); E. Nakamura, K. Sekiya, M. Arai, S. Aoki, J. Am. Chem. Soc., **111**, 3091 (1989); J. E. Bäckvall, M. Sellén, and B. Grant, J. Am. Chem. Soc., **112**, 6615 (1990); and references cited therein.
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