REGIOSPECIFIC RING CLEAVAGE OF α , β -EPOXYSILANES TO FORM TRANSITION METAL ENOLATE INTERMEDIATES

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Molybdenum(II) acetate dimer or titanium(IV) i-propoxide induced regiospecific ring cleavage of α , β -epoxysilanes to form the enolate intermediates, which reacted with aldehydes to give the corresponding α , β -unsaturated carbonyl compounds.

 α,β -Epoxysilanes are useful synthetic reagents because they are easily converted to β -hydroxysilanes or β -ketosilanes stereospecifically and/or regiospecifically on treatment with electrophiles or nucleophiles.¹⁾ These transformations result from the bond fission between oxygen and α -carbon (α -cleavage). Although β -cleavage is expected due to the stabilization effect of β -cations by silicon, no studies on regiospecific β -cleavage have been known. The previous paper demonstrated its possibility by using palladium(II) salts to afford α,β unsaturated aldehydes and ketones stereoselectively.²

Now we wish to report the novel formation of enolate intermediates by regiospecific ring opening of α,β -epoxysilanes with Mo₂(OAc)₄ or Ti(OPr-i)₄. Treatment of the α,β -epoxysilane 1 with 0.5 equiv. of Mo₂(OAc)₄ in the presence of 3 equiv. of benzaldehyde in DMF gave the α,β -unsaturated carbonyl compound 2.

 $R^{2} \xrightarrow{0}_{R^{1}} R^{3} + PhCHO \xrightarrow{MO_{2}(OAC)_{4}}_{DMF} PhCH=C \xrightarrow{0}_{R^{3}} R^{1} (or R^{2})$ $2a R^{1}=R^{3}=H, R^{2}=Ph (100 °C, 7 h) 31\%$ $b R^{1}=R^{2}=H, R^{3}=Ph (100 °C, 10 h) 35\%$ $c R^{1}=n-Bu, R^{2}=R^{3}=H (80 °C, 15 h) 33\%$ $d R^{1}=R^{2}=R^{3}=H (100 °C, 8 h) 30\%$

Acyclic α,β -epoxysilanes were converted to 2 with Mo₂(OAc)₄. In the reaction of (E)- β -phenylepoxyethyltrimethylsilane (1a), 2,4-diphenylcrotonaldehyde (3a, 34%) was produced together with the desired product, 2-phenylcinnamaldehyde (2a, 31%). The former corresponds to the self-condensation product of 1a. In the absence of benzaldehyde, 3a was formed in 31% yield. In the other cases, the similar type of the self-condensation compound was not detected, and 2 was the only isolable main product. The reaction of 1a with 3-phenylpropionaldehyde gave the desired α,β -

unsaturated aldehyde and 3a in 21% and 1% yields, respectively, with a small amount of 2-benzyl-5-phenyl-2-pentenal. 1-Trimethylsilyl-1-cyclohexene oxide resisted ring opening under the conditions employed above.

Since the carbonyl group appeared regiospecifically at the α -carbon of 1, 2 is considered to arise from the condensation reaction of the enolate complex 4 with benzaldehyde. Although the reaction mechanism has not been certain, the formation of the complex 4 is assumed to depend on regiospecific β -cleavage of the α,β -epoxysilane 1 induced by Mo₂(OAc)₄ as shown in the following scheme.³⁾



Ti(OPr-i)₄ was found to be workable in the present transformation, and the reaction of 1a with benzaldehyde proceeded even at room temperature for 60 h to give 2a and 3a in comparable yields. Starting from (Z)-1-trimethylsilyl-1-hexene oxide (1c), 2c was produced in 57% yield (80 °C, 13 h).



The present reaction provides a novel method for the regiospecific ring cleavage of α,β -epoxysilanes. This regiospecific ring opening gives the molybdenum and titanium enolate complexes which are revealed to be capable of reacting with aldehydes.

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References

- 1) E. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), p. 83.
- 2) T. Hirao, N. Yamada, Y. Ohshiro, and T. Agawa, Chem. Lett., 1982, 1997.
- 3) Another path might be explained by intermediacy of silyl enol ethers or enol acetates derived by α -cleavage with acetate or siloxide and subsequent elimination, but the corresponding intermediates were not detected when the reaction was followed by GLC.

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