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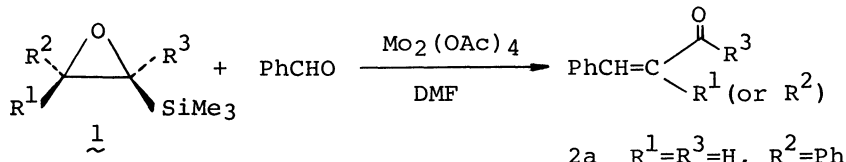
REGIOSPECIFIC RING CLEAVAGE OF α,β-EPOXYSILANES TO FORM TRANSITION METAL ENOLATE INTERMEDIATES

Toshikazu HIRAO, Yoshimi FUJIHARA, Shingo TSUNO,
Yoshiki OHSHIRO,* and Toshio AGAWA
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
2-1 Yamada-oka, Suita, Osaka 565

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 $Mo_2(OAc)_4$ or $Ti(OPr\text{-}i)_4$. Treatment of the α,β-epoxysilane 1 with 0.5 equiv. of $Mo_2(OAc)_4$ in the presence of 3 equiv. of benzaldehyde in DMF gave the α,β-unsaturated carbonyl compound 2.



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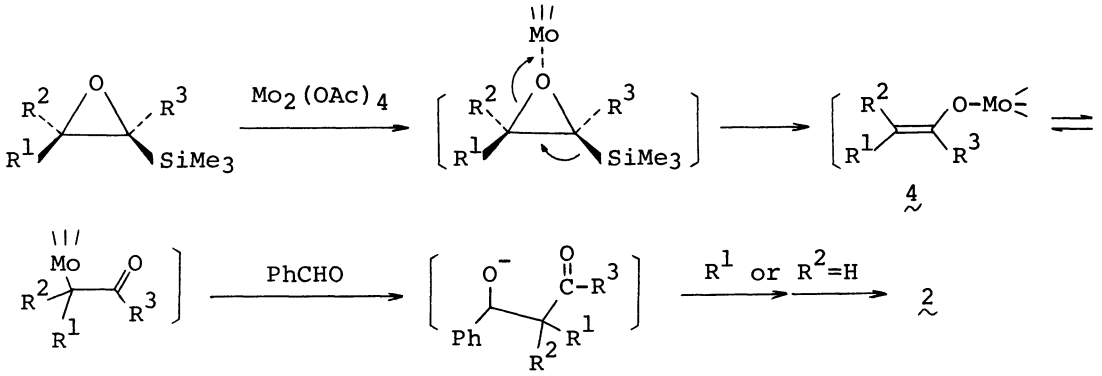
2a $R^1=R^3=H$, $R^2=Ph$ (100 °C, 7 h) 31%
b $R^1=R^2=H$, $R^3=Ph$ (100 °C, 10 h) 35%
c $R^1=n\text{-}Bu$, $R^2=R^3=H$ (80 °C, 15 h) 33%
d $R^1=R^2=R^3=H$ (100 °C, 8 h) 30%

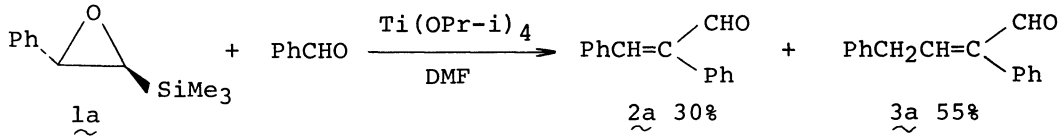
Acyclic α,β-epoxysilanes were converted to 2 with $Mo_2(OAc)_4$. In the reaction of (E)-β-phenylepoxyethyltrimethylsilane (1a), 2,4-diphenylcrotonaldehyde (3a, 34%) was produced together with the desired product, 2-phenylcinnamaldehyde (2a, 31%). The former corresponds to the self-condensation product 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 $Mo_2(OAc)_4$ as shown in the following scheme.[3]



$Ti(OPr\text{-}i)_4$ 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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