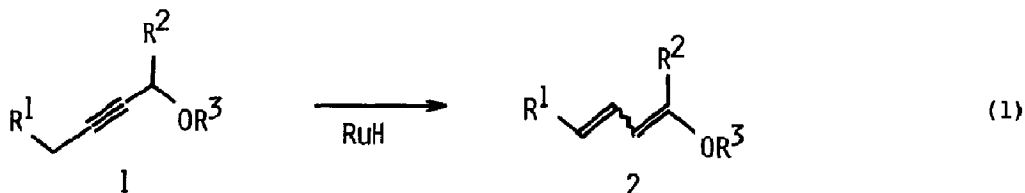


CATALYTIC ISOMERIZATION OF ACETYLENIC SILYL ETHERS TO DIENOL SILYL ETHERS  
BY RUTHENIUM HYDRIDE COMPLEXES

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**Abstract:** Acetylenic silyl ethers are converted catalytically to the corresponding conjugated dienol silyl ethers by ruthenium hydride complexes.

The double bond migration of olefins catalyzed by transition metal complexes has been investigated in detail for a long time.<sup>1)</sup> However, the reaction usually affords isomeric mixture of products, and accordingly, has scarcely utilized for organic synthesis. In the previous paper, we reported a catalytic isomerization of allyl silyl ethers to silyl enol ethers using a ruthenium dihydride complex.<sup>2)</sup> The reaction gives a sole product to offer a useful preparation method of silyl enol ethers from allyl alcohols. We have further applied the reaction to an isomerization of acetylenic silyl ethers to dienol silyl ethers which are easily converted to acetals,  $\alpha,\beta$ -unsaturated ketones, and 1,4-dicarbonyl compounds.



Isomerization of acetylenic ethers 1 to the corresponding dienol ethers 2 proceeds facily by heating of 1 at 150-180°C in benzene containing a catalytic

amount of ruthenium hydride complexes. Practically, a mixture of acetylenic silyl ether 1a (5mmol) and the catalyst  $\text{RuH}(\text{Cl})(\text{PPh}_3)_3\text{Tol}$  (Tol; toluene, ca 5  $\mu\text{mol}$ ) in dry benzene (5 ml) was sealed in Pyrex tube and heated at 150°C for 5 hrs. After cooling, removal of solvent left a colorless oily liquid of 1,4-bis(trimethylsiloxy)-1,3-butadiene (2a)<sup>3)</sup> as a 1 : 1 mixture of (Z,Z) and (Z,E) stereo isomers in a quantitative yield. The reaction is specific for acetylenic ethers and the results of the isomerization of the other acetylenic ethers are shown in Table 1.<sup>4)</sup> When R<sup>2</sup> was hydrogen, 1 was converted almost quantitatively to the corresponding diene but substitution of R<sup>2</sup> by an alkyl group decreased the yield of 2. The reaction was not applicable to terminal acetylenes and the reactants having a hydroxy group which deactivated the ruthenium hydride catalysts.

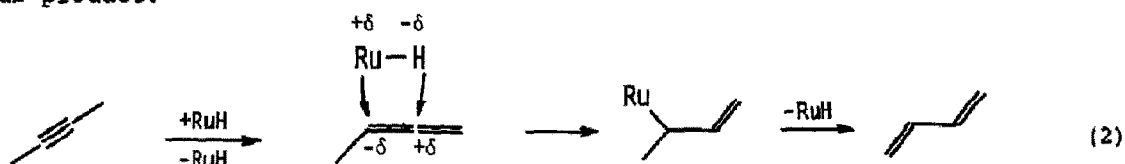
Although isomerization of acetylene by transition metal complexes has scarcely reported, base-catalyzed isomerizations have been reported by several authors.<sup>5)</sup> The base-catalyzed reaction gives usually 1,2-diene<sup>6)</sup> but this reaction affords 1,3-diene selectively. The difference of the isomerized

Table 1. Isomerization of acetylenic silyl ethers to dienol silyl ethers catalyzed by ruthenium hydride complexes. a)

Entry	Acetylenic ether ( <u>1</u> )			Reaction conditions			Dienol ether ( <u>2</u> ) Yield (%)	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Cat <sup>b)</sup>	Temp(°C)	Time(hr)		
1	<u>1a</u>	OSiMe <sub>3</sub>	H	SiMe <sub>3</sub>	a	150	5	100
2	<u>1b</u>	OMe	Me	SiMe <sub>3</sub>	b	180	48	65
3	<u>1c</u>	OMe	Et	SiMe <sub>3</sub>	b	180	48	60
4	<u>1d</u>	n-Pr	H	SiMe <sub>3</sub>	a	180	120	100
5	<u>1e</u>	n-Pr	Me	SiMe <sub>3</sub>	a	180	24	63
6	<u>1f</u>	n-Pent	Me	SiMe <sub>3</sub>	a	180	24	51
7	<u>1g</u>	Me	H	Me	a	180	24	70

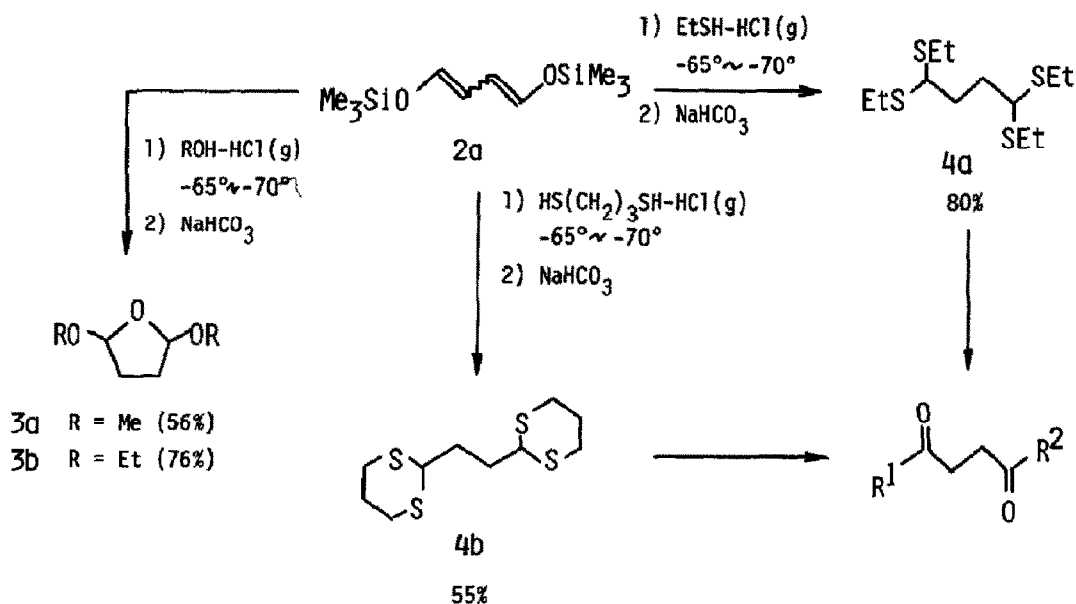
a) The usual scale was as follows; 1 (5 mmol) and the catalyst (50  $\mu\text{mol}$ ) in ml of dry benzene. b) Catalyst; a,  $\text{RuH}(\text{Cl})(\text{PPh}_3)_3\text{Tol}$ . b,  $\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3$   
 c) The yield was determined by glc and nmr spectra. Recovered material other than 1,3-diene was only the starting acetylenic silyl ether except entry 7 where a small amount of the Diels-Alder reaction product between 1 and 2 was observed.

products is well explained by the mechanism involving addition and elimination of ruthenium hydride (eq. 2), which has been established in the double bond migration of olefins.<sup>7)</sup> Allene derivatives may be formed first and the consecutive addition of hydride to the central carbon of 1,2-diene and ruthenium metal to the terminal one causes further migration of double bond to form 1,3-diene derivatives as the final product.



The utility of the isomerized products is demonstrated by the conversions of silyl dienol ethers to various synthetic intermediates.  $\gamma$ -Ketoaldehydes and  $\alpha,\beta$ -unsaturated ketones were easily obtained by the hydrolysis of 2 in alcoholic acid and base, respectively. Utilization of the product 2a is depicted in Scheme 1. Desilylation of 2a by alcoholic HCl yields acetals 3.<sup>8)</sup> Thioacetals 4 were prepared by the treatment of 2a with gaseous HCl in RSH. Diene 2 thus provides a general synthetic method of 1,4-dicarbonyl compounds, useful precursors of cyclopentenones, by the alkylation of thioacetals 4 followed by hydrolysis.<sup>9)</sup>

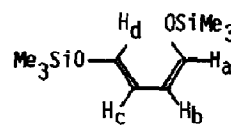
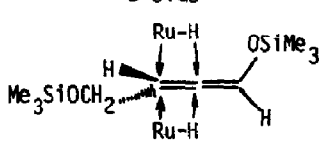
Scheme 1



Acknowledgement

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References and Notes

- For example, isomerization catalyzed by ruthenium complexes;
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- 2a; Mixture of (Z,Z) and (Z,E) stereo isomers. (Z,Z)/(Z,E) = 1 : 1 based the  $^1\text{H}$  nmr spectroscopy.  $^1\text{H}$  nmr ( $\text{CCl}_4$ , TMS); (Z,Z) isomer,  $\delta$  0.12(s, 18H), 5.34(dd,  $J=4$ , 1Hz, 2H), 5.88(dd,  $J=4$ , 1Hz, 2H). (Z,E) isomer, 0.12(s, 18H), 4.77(d,  $H_d$ ,  $J_{dc}=5\text{Hz}$ ), 4.94(d,  $H_c$ ,  $J_{cd}=5\text{Hz}$ ), 5.17(d,  $H_a$ ,  $J_{ab}=12\text{Hz}$ ), 6.44(d,  $H_b$ ,  $J_{ba}=12\text{Hz}$ ).  
 Formation of (Z,Z) and (Z,E) isomers of 2a is explained by a stereoselective addition of ruthenium hydride to the allene intermediate from A-side (less hindered) in the figure.
 
- Satisfactory analytical and spectral data were obtained for dienol silyl ethers 2b-2g.
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- It was reported that 1,4-bis(diamino)-2-butyne was rearranged to 1,4-bis(diamino)-1,3-butadiene by sodium sand catalyst. However, the rearrangement was limited to only 1,4-diamino-2-butyne derivatives.
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- 3a, 3b; Both were mixture of cis- and trans-isomers. Analytical and spectral data were satisfactory for either 3a or 3b.
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