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HYDROGEN TRANSFER REACTION OF ALLYLIC ALCOHOLS CATALYZED BY A MOLYBDENUM COMPLEX

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Summary

Allylic alcohols undergo hydrogen transfer reactions in the presence of a catalytic amount of the dinitrogen complex *trans*-$Mo(N_2)_2(dppe)_2$ (dppe = Ph_2PCH_2-CH_2PPh_2). From the acyclic allylic alcohols, saturated carbonyl compounds were obtained as the main products whereas from the cyclic allylic alcohols, unsaturated ketones and saturated alcohols were formed predominantly. Accompanying the hydrogen transfer reaction, a decarbonylation reaction occurred simultaneously to give a molybdenum carbonyl complex, *cis*-$Mo(CO)_2(dppe)_2$ as well as the hydrocarbon in certain cases. The mechanisms of both reactions are discussed.

Introduction

There are many studies on the transfer hydrogenation of ketones or olefins with Group VIII transition metal catalysts [1]. Recently, Tatsumi et al. studied hydrogen transfer from alcohols to ketones and olefins using molybdenum complexes as the catalyst, which is the first example of a Group VI metal catalyst known to be active in the hydrogen transfer reaction [2,3]. We now wish to report the results of the hydrogen transfer reaction of allylic alcohols, which contain both a hydrogen donor and a hydrogen acceptor in the same molecule, catalyzed by a molybdenum dinitrogen complex, *trans*-$Mo(N_2)_2(dppe)_2$ (I).

Results and discussion

The allylic alcohols shown in Table 1 were refluxed for 0.5–3 hours in benzene or xylene under nitrogen using I as the catalyst. The products of the reactions were separated and characterized by preparative GLC, GC-MS, and IR and NMR

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* Guixin Lei participated in part of this work.

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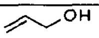
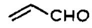
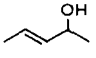
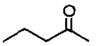
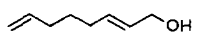
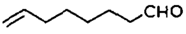
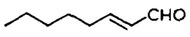
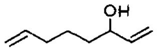
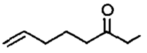
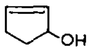
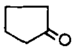
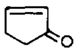
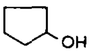
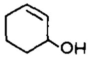
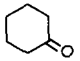
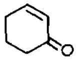
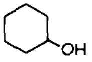
TABLE 1

HYDROGEN TRANSFER REACTION OF ALLYLIC ALCOHOLS CATALYZED BY *trans*-$Mo(N_2)_2(dppe)_2$ [a]

Reactant		Product[b] A	Product[b] B	Product[b] C	Conversion[b] (%)
II		 (5)	 (1)	 (1)	90-95[c]
III			–	–	98-100
IV				isomerized product	90-95[c]
V			–	–	98-100
VI		 (1)	 (2)	 (2)	95-98
VII		 (1-1·5)	 (1)	 (3)	90-95

[a] Reaction condition: reactant : catalyst = 5 : 1, reflux in benzene for 3 hours. [b] The conversion and selectivity were determined by gas chromatography and NMR spectra. Figures in parentheses represent the ratio of components A, B and C. [c] For the primary alcohols, $Mo(CO)_2(dppe)_2$ was formed in 60% yield (calculated from I).

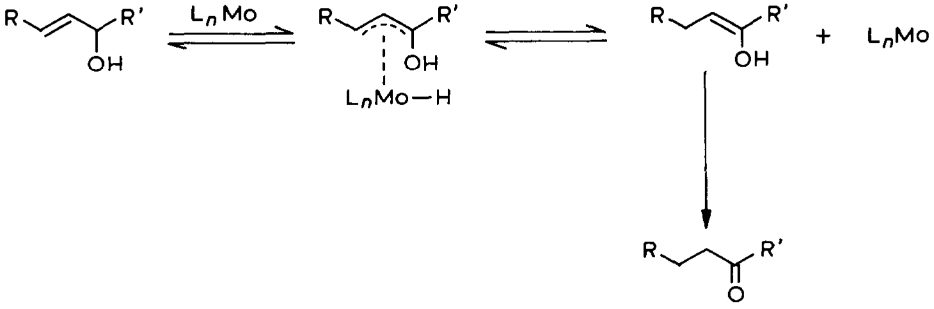
spectra and the yields of each fraction were estimated by gas chromatography or NMR spectra. From Table 1, it is shown that all the allylic alcohols used were transformed into the corresponding aldehydes or ketones with high conversions, but the selectivity varied for different types of allylic alcohols.

Tatsumi et al. [3] reported that a secondary alcohol was more active than a primary alcohol in the hydrogen transfer reaction. We found that the secondary allylic alcohols were more reactive than the primary alcohols. When penten-3-ol-2 (III) or octadien-1,7-ol-3 (V) was refluxed in benzene or xylene in the presence of I, the corresponding ketone, pentanone-2 or octen-7-one-3 was obtained respectively in 95% selectivity at 98% conversion. For primary alcohols, the reaction proceeded with a slightly lower conversion and a mixture of products was formed. For example, from allyl alcohol (II), were obtained propionaldehyde, acrylaldehyde and propanol in a ratio of 5 : 1 : 1. A complex mixture of products was formed from the reaction of octadien-2,7-ol-1 (IV). In addition to octen-7-al-1 and octen-2-al-1, the products with isomerized double bonds were also indicated in GC-MS.

For the cyclic secondary alcohols, for example, from cyclopenten-2-ol-1 (VI), besides the expected cyclopentanone, cyclopenten-2-one-1 and cyclopentanol were formed predominantly. Similarly, from cyclohexen-2-ol-1 (VII), cyclohexanone, cyclohexen-2-one-1 and cyclohexanol were formed.

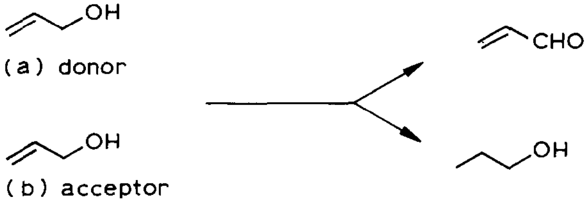
The mechanism of the hydrogen transfer reaction of allylic alcohols seems to be slightly different from the hydrogen transfer reaction of saturated alcohols to olefins

[1,2]. A 1,3-hydrogen shift mechanism which was suggested for hydrogen transfer reaction of allylic alcohols catalyzed by iron pentacarbonyl [4] seems applicable here to elucidate the results of our reaction as shown below:



It is possible that molybdenum coordinates at first to the allylic alcohol to form the π-allyl hydrido complex by hydride abstraction. The complex then dissociates to the vinyl alcohol which is further isomerized to the saturated carbonyl compound as shown in column A of Table 1. Thus, for octadien-1,7-ol-3 (V) and octadien-2,7-ol-1 (IV), only the β,γ-double bond was hydrogenated while the terminal double bond remained intact. For compound IV, there is a possibility of forming a π-allyl complex by abstracting hydrogen from another carbon atom. In this case, isomerization of the double bond may occur in the reaction of a long chain allylic alcohol.

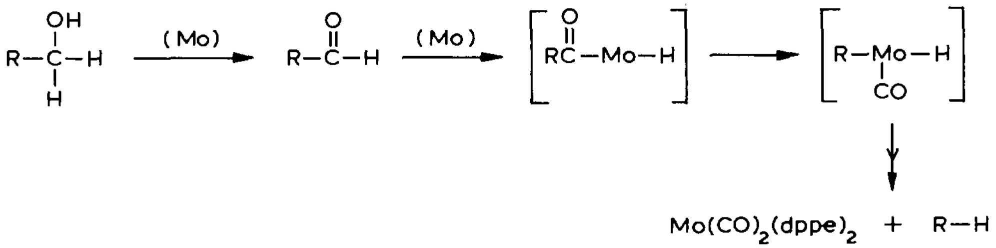
Besides the intramolecular 1,3-shift mechanism, an intermolecular hydrogen transfer reaction may also occur to form the products in columns B and C. Here, the allylic alcohol can act not only as a hydrogen donor but also as a hydrogen acceptor:



Thus, molecule a of allyl alcohol may donate hydrogen atoms to molecule b of allyl alcohol to form acrylaldehyde and molecule b of allyl alcohol accepts hydrogen atoms to form propanol-1. For cyclic allylic alcohols, the intermolecular reaction proceeded predominantly to form the compounds shown in columns B and C.

After careful study of the reaction mixtures, we found that a decarbonylation reaction occurred simultaneously with the hydrogen transfer reaction. We not only isolated molybdenum dicarbonyl complexes from the reaction mixture of primary alcohols, but also identified the hydrocarbon formed in the reaction. In benzene, a mixture of *cis*-$Mo(CO)_2(dppe)_2$ and *trans*-$Mo(CO)_2(dppe)_2$ was identified, while in xylene only *cis*-$Mo(CO)_2(dppe)_2$ was isolated. This is reasonable because the complex *trans*-$Mo(CO)_2(dppe)_2$ will transform into the *cis*-form at a high temperature [5].

As regards the mechanism of the decarbonylation reaction, we assume that aldehydes are first formed in the reaction and then decarbonylated to give the carbonyl complex and hydrocarbons as shown below:



Thus, from compound IV, *cis*-$Mo(CO)_2(dppe)_2$ was isolated and heptene-1 was identified by gas chromatography and NMR spectra. Owing to the inertness of *cis*-$Mo(CO)_2(dppe)_2$ as a catalyst towards hydrogen transfer reaction [2,3], the rate of hydrogen transfer reaction decreased as the carbonyl complex gradually formed. The greater the rate of decarbonylation reaction for primary alcohol, the lower would be the conversion of hydrogen transfer reaction.

For cyclic alcohols, however, no carbonyl complex could be detected in the reaction mixture. A yellow complex having an IR absorption at 1730 cm^{-1} was indeed isolated from the reaction mixture of VI. It had a similar IR and mass spectra to those of the complex formed by the reaction of isopropanol and I as mentioned by Tatsumi [6] and was proposed to be the molybdenum hydride species [7]. Thus, for cyclic allylic alcohols, the reaction seems to proceed in a similar way to that reported by Tatsumi [3,6].

Experimental

All reactions were carried out under prepurified nitrogen using Schlenk technique. The complex *trans*-$Mo(N_2)_2(dppe)_2$ was prepared by George's method [8]. Octadien-2,7-ol-1 (IV) and octadien-1,7-ol-3 (V) were prepared from the telomerization of butadiene [9]. All solvents and organic compounds were distilled under nitrogen before use. ^1H NMR spectra were recorded on a Varian EM 360 spectrometer. Infrared spectra were taken as liquid films for liquid samples and as KBr pellets for the complexes using a SPECORP 75 IR spectrometer. GC-MS was performed on a Finnigen 4021 GC/MS/DS instruments using a column of 10% Carbowax 20M on Chromosorb W (60–80 mesh).

Example of hydrogen transfer reaction of allylic alcohols

A solution of octadien-1,7-ol-3 (V) (0.25 ml) and trans-$Mo(N_2)_2(dppe)_2$ (361.3 mg, 0.38 mmol) in benzene (0.7 ml) was refluxed for 3 h. After cooling, the conversion was determined by GLC to be nearly quantitative. After separation from the catalyst by distillation, a colorless liquid was obtained. Infrared spectra indicated the presence of absorptions at 1645, 990 and 910 ($\rangle C{=}CH_2$) and 1715 cm^{-1} ($\rangle C{=}O$). ^1H NMR(benzene solution): $\delta = 0.80$ (3 H, t), 1.1(2 H, m), 1.2–1.8(6 H, m), 4.5–5.1(2 H, m), 5.1–5.4 ppm(1 H, m); GC-MS, m/z: 126(M^+), 97($M^+ - C_2H_5$), 69($M^+ - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}C_2H_5$), 57($\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}C_2H_5$), 55(). The compound was characterized as octen-7-one-3.

If necessary, the reaction mixture was separated by preparative gas chromatography and NMR, IR and mass spectra were determined.

Example of isolation of a molybdenum complex, cis-$Mo(CO)_2(dppe)_2$

A solution of octadien-2,7-ol-1 (IV) (0.6 ml, 4.10 mmol) and *trans*-$Mo(N_2)_2(dppe)_2$ (412.3 mg, 0.434 mmol) in benzene (0.7 ml) was refluxed for 3 h. After cooling and standing, the precipitated yellow solid was separated, washed with benzene, and characterized as *cis*-$Mo(CO)_2(dppe)_2$ by IR (ν(C≡O) 1780, 1850 cm^{-1}) and mass spectra (M^+ 950, M^+-CO 922) by comparison with an authentic sample. Yield: 60% (calculated from I).

On caraful distillation of the residual liquid from the low boiling point portion was obtained a fraction which proved to be heptene-1 by IR, GC and NMR.

Example of isolation of the molybdenum hydride species

A solution of cyclopenten-2-ol-1 (0.15 ml) and *trans*-$Mo(N_2)_2(dppe)_2$ (199.4 mg) in benzene (0.5 ml) was refluxed for 3 h. After cooling and standing, the pale yellow precipitate was collected, washed with benzene, and dried. Its IR spectra indicated the absence of carbonyl absorptions but the presence of Mo–H at 1730 cm^{-1}. The complex was proposed to be the molybdenum hydride species by IR and mass spectra.

Acknowledgements

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