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# Regioselective Reduction of α,β-Unsaturated Carbonyl Compounds to Allylic Alcohols by Vapor Phase Hydrogen Transfer Reaction over $MgO\text{-}B_2O_3$ Catalyst

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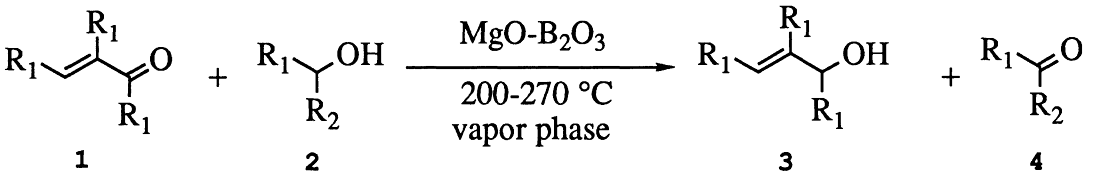
Regioselective reduction of α,β-unsaturated carbonyl compounds to the corresponding allylic alcohols was performed effectively by vapor phase hydrogen-transfer reaction over $MgO\text{-}B_2O_3$ (Mg / B = 100 / 2) catalyst using secondary alcohols as a hydrogen donor.

It is known that the catalytic regioselective reduction of α,β-unsaturated carbonyl compounds to the corresponding allylic alcohols is difficult to be performed in the conventional hydrogenation with hydrogen, since the olefinic bond usually is more preferentially reduced than the carbonyl group. For example, the direct hydrogenation of acrolein to allyl alcohol in the presence of $Ag\text{-}MnO_2$ system catalyst in the liquid phase has been reported.1) However, the selectivity was not high (around 50 mol%). The Meerwein-ponndorf-Verley reaction is a well-known selective reduction of a carbonyl compound to a corresponding alcohol. On the other hand, only a few examples regarding to the hydrogen-transfer reaction in vapor phase between saturated or unsaturated carbonyl compounds and alcohols using MgO and MgO-ZnO catalysts have been reported.2-4) The efficiencies of these reactions were not so high.

Recently we found that the vapor phase hydrogen-transfer reaction between α,β-unsaturated carbonyl compounds (**1**) and alcohols (**2**) could be performed with high catalytic activities and selectivities by use of $MgO\text{-}B_2O_3$ catalyst of which acidity and basicity were controlled to be weak. In this paper we report the regioselective reduction of **1** to the corresponding allylic alcohols (**3**) over $MgO\text{-}B_2O_3$, as well as the correlation between catalytic activity and electron donating power of **2**.



$R_1 = H, CH_3$
$R_2 = CH_3, C_2H_5, C_3H_7, Ph, PhCH_2$

The MgO-$B_2O_3$ catalyst was prepared as follows. A mixture of $Mg(OH)_2$ (29.0 g) and $B_2O_3$ (0.35 g) was suspended in 200 ml of deionized water and dried at 120 °C under air. The dried mass was pulverized (9 to 16 mesh) and calcined at 600 °C for 2 hours under air. Atomic ratio of the catalyst prepared was Mg / B = 100 / 2. From the results of measurement of the acid and base strengths of this catalyst by Hammett indicator method[5)], the $H_0$ value was in the range of +4.0 to +7.0 and the $H_-$ value was in the range of +7.0 to +12.2.

The hydrogen-transfer reactions were carried out as follows. 5 ml of a catalyst was filled up in a reaction tube (10 mm inside diameter). A reaction gas mixture comprising of an $\alpha,\beta$-unsaturated carbonyl compound, an alcohol, and nitrogen in volume ratio of 5 : 25 : 70 was passed through the tube at a space velocity of 1,500 $h^{-1}$ (STP) and continuously reacted, and products were analyzed by gas chromatography.

The results of the hydrogen-transfer reaction at 270 °C between methacrolein [MAL ; $CH_2$=CH($CH_3$)CHO] and various alcohols over MgO-$B_2O_3$ are shown in Table 1. The main product was methallyl alcohol (MAA), and a small amount of isobutyl alcohol (i-BuOH) and isobutyl aldehyde (i-BuAL) were formed as a by-product by hydrogenation of MAL and MAA. Ethyl alcohol (EtOH), propyl alcohol (n-PrOH), butyl alcohol (n-BuOH), isopropyl alcohol (i-PrOH), benzyl alcohol ($PhCH_2OH$) and phenyl ethyl alcohol ($PhCH_2CH_2OH$) which acted as hydrogen donors were dehydrogenated to the corresponding aldehyde or ketone (**4**), respectively. The other compounds such as ethers and olefinic compounds from alcohols were not observed. The consumptions of alcohols in these reactions were closed to the total amounts of MAA, i-BuAL and twice of i-BuOH formed. The selectivity to **4** from **2** were almost 100 %.

Table 1. Hydrogen-transfer between MAL and Various Alcohols

| | Conversion / mol% | Selectivity / mol% | | |
|---|---|---|---|---|
| Alcohols | MAL | MAA | i-BuOH | i-BuAL |
| EtOH | 58.1 | 85.1 | 11.9 | 3.0 |
| n-PrOH | 59.3 | 85.3 | 11.8 | 2.9 |
| n-BuOH | 66.0 | 87.0 | 10.4 | 2.6 |
| i-PrOH | 91.2 | 89.9 | 8.1 | 2.0 |
| $PhCH_2OH$ | 76.0 | 90.1 | 8.0 | 1.9 |
| $PhCH_2CH_2OH$ | 82.9 | 92.4 | 5.9 | 1.7 |

The i-PrOH, $PhCH_2OH$ and $PhCH_2CH_2OH$ are excellent hydrogen donors, and they showed the high conversion and high selectivity. In particular, in the case of i-PrOH, the highest conversion was observed. The order of the reactivities of various aliphatic alcohols as hydrogen donors to MAL is as follows; EtOH < n-PrOH < n-BuOH << i-PrOH. This tendency corresponds to the results of Brauman and his co-workers in which the order of acidity of aliphatic alcohols in vapor phase is EtOH < n-PrOH < n-BuOH, according to the measurement by ion cyclotron resonance spectroscopy.6) The $PhCH_2OH$ and $PhCH_2CH_2OH$ showed relatively higher conversion than that of primary aliphatic alcohols. Since the degree of dissociation of proton in vapor phase has been known to depend on polarizability of alcohols,6) it may be concluded that the order of reactivity of alcohols corresponds to the order of polarizability of the alcohols.

The hydrogen-transfer reaction between **1** and i-PrOH over $MgO\text{-}B_2O_3$ ( Mg / B = 100 / 2) were performed in order to examine the reactivities as shown in Table 2. The reactions were carried out at 200 °C due to higher activity of i-PrOH. The products were the **3**, acetone, saturated alcohols, saturated aldehydes and a small amount of unknown compounds.

The selectivities to allyl alcohol and methallyl alcohol were extremely high, but the selectivities to crotyl alcohol and 3-buten-2-ol were not so high due to increasing the formation of saturated alcohols and saturated aldehydes. This means olefinic bonds of these reactants or products were easily hydrogenated.

Table 2. Hydrogen-transfer between Carbonyl Compounds and Isopropyl alcohol

| a,b-Unsaturated carbonyl compound 1 | Allylic alcohol 3 | By-product a) | Conversion /mol% 1 | Selectivity / mol% | |
|---|---|---|---|---|---|
| | | | | 3 | By-pro. |
| methacrolein | methallyl alcohol | isobutyl alcohol | 65.4 | 93.1 | 5.7 |
| | | (isobutyl aldehyde) | | | (1.2) |
| acrolein | allyl alcohol | propyl alcohol | 78.8 | 92.9 | 5.4 |
| | | (propyl aldehyde) | | | (1.7) |
| methyl vinyl ketone | 3-buten-2-ol | 2-butyl alcohol | 100.0 | 68.6 | 23.3 |
| | | (2-butyl aldehyde+unknown) | | | (8.1) |
| croton aldehyde | crotyl alcohol | butyl alcohol | 93.6 | 56.5 | 28.1 |
| | | (butyl aldehyde+unknown) | | | (15.4) |

a) Except acetone from i-PrOH.

The saturated aliphatic alcohols in these reaction are formed by consecutive hydrogenation of allylic alcohols and by direct hydrogenation of $\alpha,\beta$–unsaturated aldehydes via $\alpha,\beta$-saturated aldehydes. Therefore it seems that the $MgO\text{-}B_2O_3$ catalyst effectively controls these consecutive hydrogenation of allylic alcohols and direct hydrogenation of $\alpha,\beta$-unsaturated aldehydes and shows the high catalytic activity and selectivity to allylic alcohols.

## References

1) Y. Nagase, H. Muramatu, and T. Sato, *Chem. Lett.*, **1988**, 1695.
2) S. A. Ballard, H. D. Finch, and D. E. Winkler, *Adv. Catal.*, **9**, 754 (1957).
3) H. Niiyama and E. Echigoya, *Bull. Chem. Soc. Jpn.*, **45**, 938 (1972).
4) Y. Okamoto, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **45**, 3207 (1972).
5) K. Tanabe, " Solid Acids and Bases," Kodansha, Tokyo (1970), p. 6.
6) J. I. Brauman and L. K. Blain, *J. Am. Chem. Soc.* **92**, 5986 (1970).

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