Butadiene Formation from Ethanol over Silica-Magnesia Catalysts

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Butadiene formation reaction from ethanol over various kinds of silica-magnesia having different MgO contents were studied from the standpoint of its acid-base catalysis. Maximum acidity was obtained at 50% MgO, while basicity increased with the MgO content. Silica-magnesia (85% MgO) having adequate acidity and basicity gave the maximum activity. The reaction mechanism and the roles of acidic and basic sites are discussed. The rate controlling step is the acetaldehyde formation catalyzed by basic sites.

Many investigations have been carried out on the reaction of butadiene formation from ethanol.[1,2,3] It was reported that active catalysts should have activities for both dehydration and dehydrogenation reactions. However, the roles of active sites were not clarified. In a previous paper,[4] dehydration and dehydrogenation of alcohols over acid-base bifunctional catalysts were described. It was concluded that the former took place on acidic and the latter on basic sites.

Since butadiene formation reaction includes dehydration and dehydrogenation reactions, acid-base properties of catalysts would be essential. In this paper, the correlations between acidity and/or basicity and the activity of SiO_2-MgO catalysts are given.

Experimental

Catalysts. SiO_2-MgO; A settled amount of magnesium hydroxide (Wako Pure Chem. Co.) and colloidal silica (Nissan Chem. Co.) was kneaded for 3 hr. The gel obtained was dried for 24 hr at 100°C in an oven and then calcined in an electric furnace at 600°C for 3 hr.

SiO_2; Colloidal silica was heated over a water bath. The obtained gel was dried in an oven and then was calcined at 600°C for 3 hr.

MgO; Magnesium hydroxide was calcined at 600°C for 3 hr.

Acidity measurements. Titration (Benesi's method) and gravimetric measurement of pyridine adsorption were used.

Titration was carried out as follows. Samples of the catalysts were calcined at 550°C for 1 hr and then degassed at 300°C under 10^{-5} mmHg. 0.1～0.5 g of the samples were taken in flasks containing water-free benzene. A known amount of *n*-butylamine in benzene solution (0.02N) was added. After four days, Hammett indicators were added and the color of the samples were compared visually with each other.

Adsorption of pyridine was carried out as follows. 0.15～0.3 g of the catalyst was taken in a basket made of quartz and evacuated *in situ* under 10^{-5} mmHg for 3 hr at 350°C. Pyridine was then introduced to the system up to 25 mmHg at 200°C. After adsorption equilibrium had been established (after 1～1.5 hr), desorption was started at the same temperature by trapping the remaining pyridine in the gas phase. The adsorbed amount was determined with a spring balance (sensitivity 10 μg/div.)

Basicity measurements. Titration by benzoic acid using phenolphtalein and nitroaniline[5] as indicators was carried out in order to measure the basicity. Some catalysts, however, showed abnormal color change, making the values obtained unreliable. In this study, the adsorbed amount of boron trifluoride was measured by the gravimetric method and was taken as the index of basicity. Pretreatments and procedures were almost the same as in the acidity measurements.

Infrared spectroscopy. A thin wafer, 1.2×2.0 cm, was prepared by compressing 0.02～0.03 g of the catalyst under 300 kg/cm^2. The infrared cell used was similar to that used by Little.[6] The cell could be attached to the conventional vacuum system and heated *in situ*. The infrared spectra were recorded on a Shimadzu IR spectrometer.

Reaction. Catalytic activities in butadiene formation from ethanol were measured by a conventional flow method. Ethanol and/or other reactants were stored in evaporators maintained at a constant temperature. They were introduced into the reactor with hydrogen, carrier gas. Vaporous products were taken out with a sampling tube and analyzed by gas chromatography.

Results and Discussions

Ethylene, ether, acetaldehyde, butadiene and water were found in the products when SiO_2-MgO catalysts were used. In the case of MgO catalyst, crotonaldehyde and other unknown products were also obtained. SiO_2-MgO catalyst (75 mol% MgO) was used in order to clarify the reaction mechanism.

The effects of contact time on the conversion to all the products were studied. A typical example is given in Fig. 1. Acetaldehyde formation decreased with increase of the contact time, while butadiene formation showed an induction period.[7] This suggests that acetaldehyde is an intermediate product and butadiene a final one in the consecutive reaction.

Several reactants considered[8] to be intermediate products were tested to confirm the reaction mechanism. The results are given in Table 1 and a typical example

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[1] W. M. Quattlebaum, W. J. Toussaint, and J. T. Dunn, *J. Amer. Chem. Soc.*, **69**, 593 (1947).

[2] Yu. A. Gorin, *J. Gen. Chem. USSR*, **16**, 283 (1946), *C.A.*, **41**, 685 (1947), *Zhur. Obshchei Khim.*, **19**, 664 (1949), *C.A.*, **44**, 1006 (1950).

[3] M. Ya. Kagan, G. D. Lyubarskii, and O. M. Poduroskaya, *Bull. Acad. Sci. USSR Classe Sci. Chim.*, (1947), *C.A.*, **42**, 4515 (1948).

[4] H. Niiyama and E. Echigoya, This Bulletin, **44**, 1739 (1971).

[5] J. Take, S. Kikuchi, and Y. Yoneda, *Syokubai (Catalyst)*, **10**, 127 (1968).

[6] L. H. Little, "Infrared Spectra of Adsorbed Species", Academic Press, New York and London (1966) p. 31.

[7] The induction period is not shown so clearly in this figure, but it was more apparent in the case of SiO_2-MgO catalysts (25 or 50 mol % MgO).

[8] M. E. Winfield, "Catalysis Vol. 7" ed. by P. H. Emmett, Reinhold Pub. Co., New York (1960), p. 109.

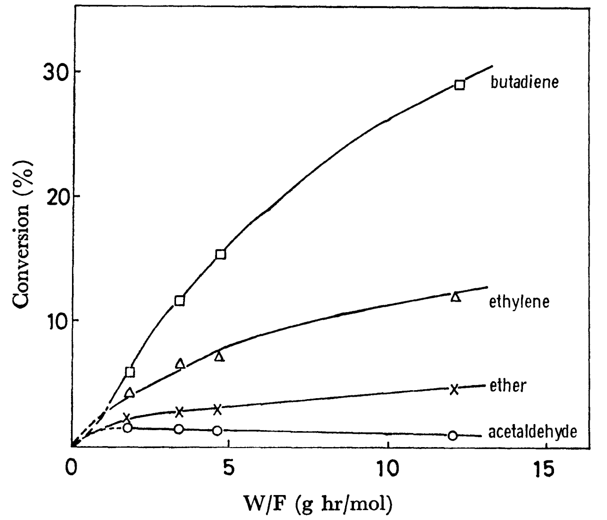


Fig. 1 The effects of contact time on the conversion to all the products. temperature; 380°C, pressure of ethanol; 0.1 atm, catalyst; SiO_2-MgO (75 mol% MgO)

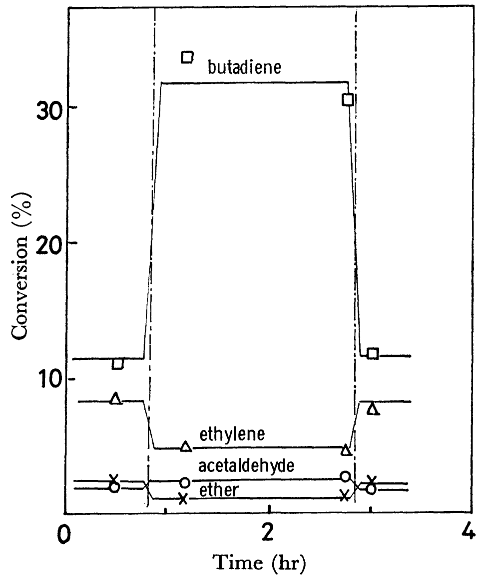


Fig. 2 The effects of acetaldehyde additon. (Reaction conditions were given in table 1)

in Fig. 2. Though neither acetaldehyde nor crotonaldehyde was converted into butadiene, butadiene was readily produced when either of them was fed with ethanol. Moreover, with *n*-propanol or isopropanol instead of ethanol, each produced butadiene with the corresponding dehydrogenated products (propionaldehyde or acetone). Under such reaction conditions, no acetone was found in the products when isopropanol alone was fed. It was also found that any combination of alcohols and ketones or aldehydes brings about hydrogen transfer reaction.[9]

TABLE 1. BUTADIENE FORMATION FROM VARIOUS KINDS OF REACTANTS.

Reaction Conditions;
Catalyst; SiO_2-MgO (75 mol% MgO) 1.0 g
Reaction temperature; 380°C
Carrier gas; H_2 100 m*l*/min stp

run No.	Reactants	Partial Preseure	Conversion to butadiene	By-products
1	ethanol	0.1	0.11	
2	acetaldehyde	0.1	trace	crotonaldehyde
3	crotonaldehyde	0.01	trace	
4	1,3-butanediol	0.01	trace	
5	ethanol acetaldehyde	0.1 0.01	0.31[a]	
6	ethanol crotonaldehyde	0.1 0.01	0.36[a]	
7	1-propanol crotonaldehyde	0.1 0.01	0.18[b]	propionaldehyde
8	2-propanol acetaldehyde	0.1 0.01	0.08[c]	acetone

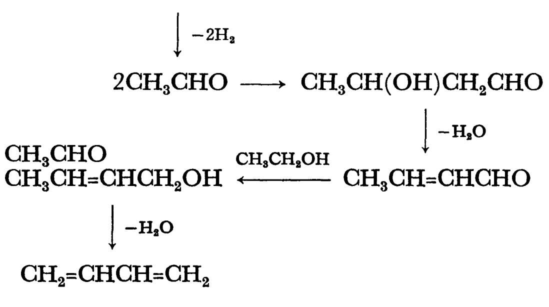
a) $\dfrac{\text{butadiene produced}\times 2}{\text{ethanol fed}}$

b) $\dfrac{\text{butadiene produced}\times 2}{n\text{-propanol fed}}$

c) $\dfrac{\text{butadiene produced}\times 2}{iso\text{-propanol fed}}$

Various mechanisms have been proposed for butadiene formation reaction. Most investigators considered acetaldehyde as a first intermediate product. Kagan[3] postulated that two acetaldehyde underwent an aldol condensation to form crotonaldehyde. Crotyl alcohol was then produced by the reduction of crotonaldehyde and converted into butadiene. The hydrogen atoms derived from the dehydrogenation of ethanol took part in the reduction. On the other hand, Quattlebaum *et al.* postulated[1] that the hydrogenolysis of crotonaldehyde took place *via* hydrogen transfer from ethanol to crotonaldehyde. 1-hydroxybutene or 1,3-butanediol produced from acetaldehyde and ethanol was also postulated as an intermediate product.[8]

Our results indicate that 1,3-butanediol can not be intermediate product (Table 1, run 4). 1-hydroxybutene is not appropriate, because acetaldehyde and isopropanol gave butadiene instead of isoprene or pentadiene. The mechanisms postulated by Kagan[3] could be rejected because isopropanol gave no dehydrogenated products under the reaction conditions. It was thus concluded that the mechanisms postulated by Quattlebaum *et al.*[1] is valid for this catalyst. This is schematically shown as follows.



$$\begin{array}{l}
2CH_3CH_2OH \\
\quad\downarrow{-2H_2} \\
2CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO \\
\qquad\qquad\qquad\qquad\qquad\downarrow{-H_2O} \\
\begin{matrix}CH_3CHO\\ CH_3CH{=}CHCH_2OH\end{matrix} \xleftarrow{CH_3CH_2OH} CH_3CH{=}CHCHO \\
\quad\downarrow{-H_2O} \\
CH_2{=}CHCH{=}CH_2
\end{array}$$

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[9] H. Niiyama and E. Echigoya, This Bulletin, **45**, 938 (1972).

TABLE 2. EXPECTED CONVERSION BASED ON THE ASSUMPTION THAT THE FIRST DEHYDROGENATION STEP IS RATE DETERMING

reactants	partial pressure	calculated conversion of alcohol	experimental value	run No. in Table 1
ethanol acetaldehyde	0.1 0.01	$0.11+0.10+\sum_{i=1}^{\infty}0.1\times2^{-i}=0.31$	0.31	5
ethanol crotonaldehyde	0.1 0.01	$0.11+0.10\times2+\sum_{i=1}^{\infty}0.1\times2^{-i}=0.41$	0.36	6
1-propanol crotonaldehyde	0.1 0.01	$0.10\times2=0.20$	0.18	7
2-propanol acetaldehyde	0.1 0.01	0.10	0.08	8

Determination of the rate controlling step. On the basis of this scheme and assuming that acetaldehyde formation is the rate controlling step, we can expect the conversion for run 5, taken as an example, in the following way. A mixture of acetaldehyde and ethanol (0.1: 1) was fed. The relative amount of butadiene derived from ethanol independently of acetaldehyde addition was 0.11 (*cf.* run 1). Since the process after the dehydrogenation of ethanol was assumed to be very fast, all the added acetaldehyde was converted into butadiene. The amount of butadiene from the added acetaldehyde was thus 0.10. Hydrogen transfer between crotonaldehyde and ethanol took place and acetaldehyde was produced again. The secondary acetaldehyde formation was repeated infinitely. Thus the amount of butadiene derived from secondary produced acetaldehyde was $\sum_{i=1}^{\infty}0.1\times2^{-i}$, where i is the cycle number. The expected conversion was calculated as follows.

$$0.11 + 0.10 + \sum_{i=1}^{\infty}0.1 \times 2^{-i} = 0.31$$

The results for runs 5, 6, 7, and 8 are summarized in Table 2. There is a good agreement between the results and the calculated values.

Correlations between catalytic activity and acidity and/or basicity. The acidic properties determined by the Benesi's method and pyridine adsorption method, both of which show a similar tendency, are given in Table 3. The basicity is also given in the table.

The maximum acidity was obtained when MgO content reached 50%, while basicity increased with MgO content. Specific rates of butadiene formation increased with the MgO content up to 85%, but pure MgO showed little activity. This aspect was quite different from that of acidity and also of basicity.

Since the rate controlling step of this reaction was the dehydrogenation of ethanol catalyzed by basic sites,[4] the rate was expected to increase with the MgO content. This, however, was not the case. When MgO catalyst was used, crotonaldehyde was found in the products. This indicates that MgO has a catalytic activity in the aldol condensation reaction.[10] More-

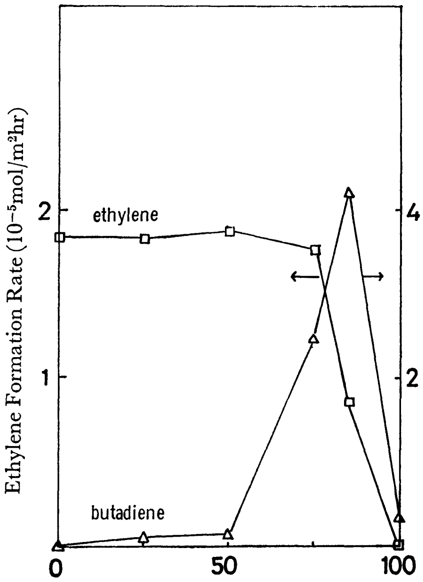

Fig. 3 Rate of production of butadiene or ethylene against MgO contents. temperature; 380°C, pressure of ethanol; 0.1 atm

TABLE 3. ACIDITY AND BASICITY OF THE CATALYSTS

Catalyst	Acidity			Basicity BF adsorption at 300°C 10^{-6} eq/m²
	Benesi's method		Pyridine adsorption at 200°C 10^{-6} eq/m²	
	Acidity $H_0>3.3$ 10^{-6} eq/m²	maximum acid strength H_0		
SiO_2	—	—	0.09±0.02	0.8±0.2
SiO_2-MgO 25% MgO	1.29±0.1	+1.5	0.68±0.1	4.0±0.5
50% MgO	2.14±0.1	−3.0	0.94±0.1	4.2±0.5
75% MgO	2.14±0.2	+1.5	0.74±0.1	6.2±0.5
85% MgO	1.31±0.2	+1.5	0.28±0.05	7.2±0.5
MgO	—	—	0	15.0±2

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10) S. Malinowski and S. Basinski, *J. Catalysis*, **2**, 203 (1963).

over, it showed considerable activity in the hydrogen transfer reaction.[9] Poor activity of MgO catalyst in the reaction could be attributed to the small dehydration activity for the final step catalyzed by acidic sites. It is thus concluded that both acidic and basic sites are necessary to increase the yield of butadiene.

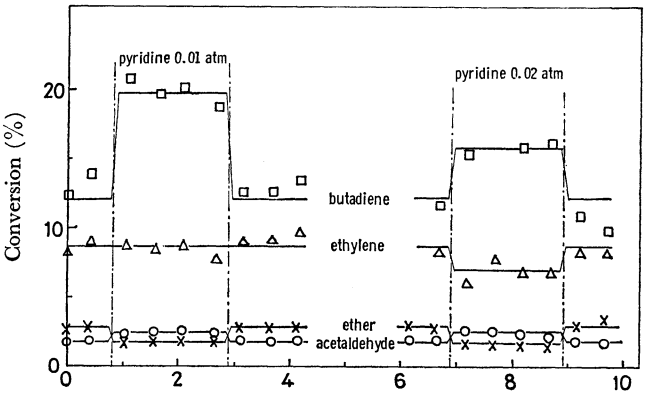

Fig. 4 The effects of pyridine addition. temperature; 380°C, pressure of ethanol; 0.1 atm, W/F=3.4 g hr/mol

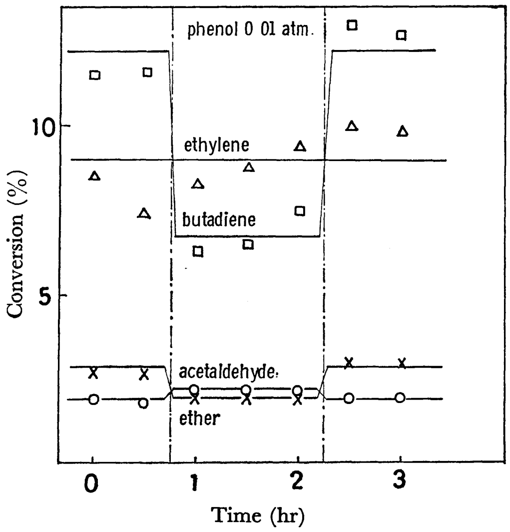

Fig. 5 The effects of phenol addition. temperature; 380°C, pressure of ethanol; 0.1 atm W/F=3.4 g hr/mol

Addition of acidic and basic materials. Pyridine and phenol were introduced into the reaction system in order to poison acidic and basic sites, respectively. The results are shown in Figs. 4 and 5. The addition of phenol brought a marked decrease in butadiene formation, but ethylene formation remained constant. Since the rate controlling step in butadiene formation is the first dehydrogenation catalyzed by basic sites, the effects of phenol are rational.

On the other hand, pyridine had a "promoter action" in butadiene formation. To understand the "promoter action" of pyridine the behavior of surface hydroxyl group was studied by infrared spectroscopy. As is shown in Fig. 6, four absorption bands were observed in 3400—4000 cm^{-1} region. They were assinged to OH stretching vibration bands since they could be exchanged with D_2O. Generally speaking, a hydroxyl group with higher stretching frequency has a basic nature.[11] It was observed that the bands around 3840 cm^{-1} and 3720 cm^{-1} remain while the band around 3650 cm^{-1} readily disappeared in contact with D_2O vapor. Since acidic OH is expected to undergo ex-

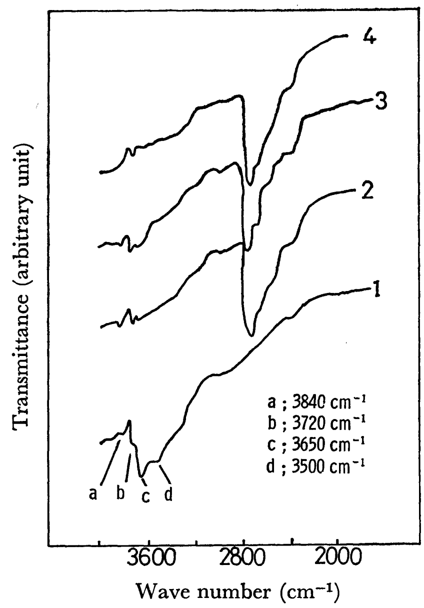

Fig. 6 IR spectra of surface hydroxyl group.

1. evacuated at 350°C for 6 hr.
2. exchanged with D_2O at 350°C for 1 hr and then evacuated at 350°C for 1 hr.
3. exchanged with D_2O again at 350°C for 1 hr and then evacuated at 350°C for 1 hr.
4. exchanged with D_2O again at 350°C for 1 hr and then evacuated at 350°C for 3 hr.

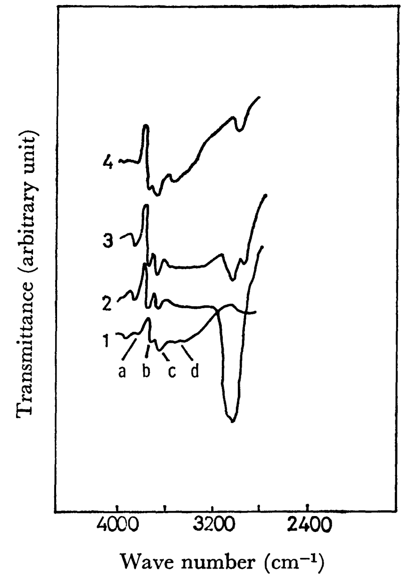

Fig. 7 The effects of pyridine adsorption on surface hydroxyl group.

1. evacuated at 340°C for 3 hr.
2. rehydrated by traces of water under atmosphere of pyridine
3. evacuated again at room temperature for 0.5 hr.
4. evacuated at 100°C for 0.5 hr.

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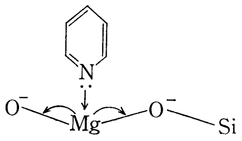
[11] J. D. S. Goulden, *Spectrochim. Acta*, **6**, 129 (1954).

change more readily than neutral or basic OH, the band around 3650 cm^{-1} should refer to acidic OH. In other words, bands around 3840 cm^{-1} and 3720 cm^{-1} could be considered to have a basic nature as compared with 3650 cm^{-1} band.

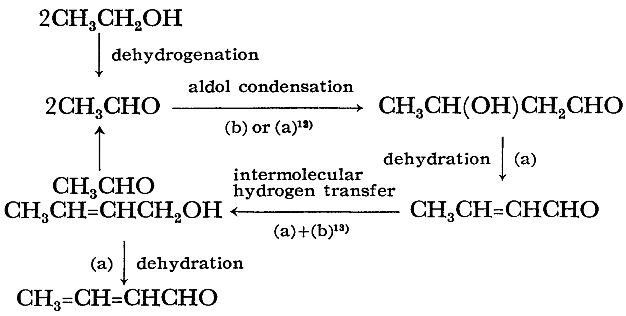
The effects of pyridine on the behavior of these surface hydroxyl group are shown in Fig. 7. Rehydration of the evacuated sample by traces of water (0.03 meq) made little change in the higher frequency bands. In the presence of pyridine, however, rehydration made the intensity of these bands increase. Evacuation at 100°C gave rise to the decrease of the intensity of these bands, with an accompanying decrease of a band around 2900 cm^{-1} assigned to CH stretching of pyridine. This suggests that basic sites are produced by adsorption of pyridine. This would be caused by the inductive effects of adsorbed pyridine.



When pyridine is adsorbed on acidic sites, the nearest oxide ions become rich in electron density. This will produce new basic sites available to catalyze the dehydrogenation of ethanol. A small amount of pyridine thus increases basicity accompanied with the increase of dehydrogenation activity. By excess addition, however, pyridine occupies more of the acidic sites than is necessary and makes the "promoter action" retarded.

Conclusion

The reaction mechanism and roles of acidic and basic sites in butadiene formation over silica-magnesia catalysts can be written as follows.



(a) and (b) represent acidic and basic sites, respectively. The rate controlling step over silica-magnesia catalysts is the dehydrogenation of ethanol catalyzed by basic sites. Thus activity increases with basicity. Over magnesia catalyst which has great basicity but no acidity, however, dehydration of crotyl alcohol hardly takes place and the activity is low. It is important to control the acidity and basicity in order to increase the yield of butadiene.

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12) Both (a) and (b) are available in this step.14)

13) This step was considered to take place in an acid-base concerted mechanism.8)

14) Y. Ogata, "Yuuki Hannoron (Organic Reactions)" Maruzene, Tokyo (1967) p. 279.