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Catalytic Conversion of Alcohols

V. Selectivity Properties of Y_2O_3

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Yttria was active for both dehydrogenation and dehydration of alcohols; it was more selective for dehydration of acyclic alcohols than for cyclic alcohols. The dehydration selectivity increased with increasing temperature and with increasing time-on-stream. The temperature coefficients for dehydration and dehydrogenation for both cyclic and acyclic alcohols were similar to those obtained with an alumina catalyst. Yttria was very selective in forming 1-alkenes from 2-ols. *Cis*- or *trans*-2-methylcyclohexanol was isomerized to the equilibrium *cis/trans* composition more rapidly than the combined dehydration–dehydrogenation reaction. It appears that the major pathway for the elimination of water from 2-methylcyclohexanol was an anti mechanism.

INTRODUCTION

Alcohol conversion provides a dehydrogenation/dehydration selectivity as well as a selectivity for alkene formation. These selectivities have been used to characterize metal oxide catalysts (*1*). Alumina has been a popular catalyst for the conversion of alcohols, and in recent years many studies have been concerned with alkene selectivities from a variety of alcohols (*2*). Less work has been done in defining the selectivities of other pure metal oxide catalysts.

Sharf *et al.* (*3*) found that yttria was selective for the formation of 1-alkene from 2-pentanol and that the catalyst was 1.6 times more selective for dehydration than dehydrogenation at 280°C. Spitsyn and co-workers (*4*) have examined yttria as an alcohol conversion catalyst in their studies on the effects of radiation on catalytic selectivity and activity and found that the selectivity for dehydrogenation varied with temperature.

EXPERIMENTAL

Catalysts. A 20-fold excess of concentrated ammonium hydroxide was dumped into a rapidly stirred, approximately 0.1 *M* yttrium nitrate solution. The gel was collected by filtration and was washed to the point of peptization by repeated redispersion–filtration cycles. The gel was dried at 120°C, then heated to 500°C in flowing oxygen and then in flowing hydrogen at 500°C. The BET surface area was 42.2 m^2/g. (The area was determined with a Quantasorb Sorption System by Mr. Barry Rosovsky of Quantachrome Corp.).

After each reaction run, the catalyst was cooled to room temperature and flushed with air at room temperature prior to heating to 250°C in air. After about 3 hr at 250°C, the temperature was increased to 500°C in air, after 1 hr the air was replaced by an oxygen flow, and after 3 hr, the oxygen was replaced by hydrogen and the catalyst was held at 500°C in

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hydrogen for 4 to 7 hr. The catalyst was cooled to the reaction temperature in flowing hydrogen. For the few cases where results are given for the oxygen pretreated catalyst, the above procedure was followed except for omitting the final hydrogen pretreatment.

Alcohols. Alcohols were purchased from commercial sources. Most alcohols contained less than 1% ketone, and in many cases it was much less than this. However, 2-octanol contained approximately 1.5% 2-octanone. The pure *cis*- or *trans*-2-methylcyclohexanol contained less than 0.5% of the other isomer.

Procedure and analyses. The reactor system was of conventional design with a motor-driven syringe liquid feed, an electrically heated plug flow reactor, and a liquid sample collector. The alcohol was pumped over the catalyst at atmospheric pressure without added carrier gas. The LHSV was varied from 0.4 to 12 in order to obtain a conversion of less than 30% in most cases. The liquid products were collected at intervals and analyzed for conversion by temperature-programmed gas chromatography (gc) using a Carbowax 20M column. The alkene fraction was analyzed by operating the gc column (Carbowax 20M, β,β'-oxydipropionitrile, or Ucon) appropriate for the alkenes isothermally at a temperature where the alkenes were separated and the retention time for the ketone and alcohol was very long so that several samples could be analyzed before the ketone or alcohol eluted. The (*cis* + *trans*)-2-methylcyclohexanols were analyzed using a diglycerol gc column at 100°C.

RESULTS

In Table 1 we present the dehydration–dehydrogenation selectivity for the conversion of several alcohols over yttria. This selectivity changes with time-on-stream and, as shown by the representative data presented in Fig. 1, the change is always to a more selective dehydration catalyst. The selectivity also changes with tempera-

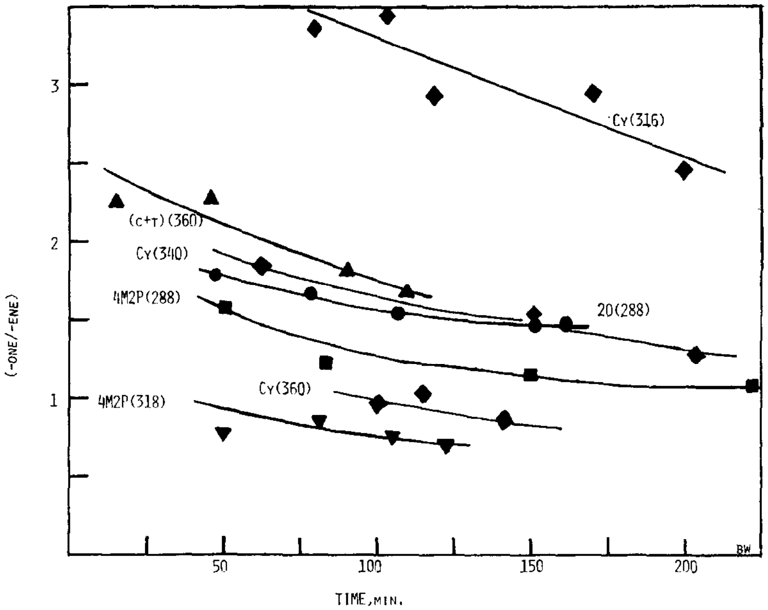

FIG. 1. Representative dehydrogenation/dehydration selectivity change with time-on-stream. The numbers in parentheses are the reaction temperatures. Alcohols are: Cy, cyclohexanol; (C + T), *cis*-2- plus *trans*-2-methylcyclohexanol; 4M2P, 4-methyl-2-pentanol; 2O, 2-octanol.

TABLE 1

The Dehydration–Dehydrogenation Selectivity for Alcohol Conversion over Y_2O_3 Pretreated with Hydrogen

Alcohol	Temperature (°C)	Conversion range (mol%)	Length of run (min)	–one/–ene[a]
2-Octanol (O_2 pretreatment)	240	19–6[b]	375	9.4–8.4
2-Octanol	288	23–22	475	1.8–1.5
	314	28–29	225	0.9–0.7
	345	30–23	165	0.4–0.5
4-Methyl-2-pentanol	250	7–6	255	4.5–2.8
	288	22–15	253	1.6–1.1
	318	31–26	115	0.8–0.7
	340	30–22	98	0.8–0.4
2-Hexanol	300	43–35	253	1.6–1.3
3-Pentanol	310	39–28	190	17–7.4
2-Pentanol	258	16–11	300	10–5.6
	284	14–15	340	2.8–2.8
	316	27–23	316	3.2–2.3
4,4-Dimethyl-2-pentanol	345	18–15	85	0.4–0.2
(*cis* + *trans*)-2-Methylcyclohexanol	295	27–22	290	9.2–5.4
	330	32–23	215	3.6–2.1
	360	32–29	110	2.3–1.6
cis-2-Methylcyclohexanol	285	22–24	130	9.2–9.4
trans-2-Methylcyclohexanol	299	27–22	150	9.7–7.3
Cyclohexanol	316	14–9	200	3.3–2.6
	340	17–16	210	1.8–1.3
	362	21–20	265	1.0–0.9

[a] The first number is for the first sample and the second number is for the last sample collected.

[b] The flow rate was adjusted to give the conversion shown for each temperature.

ture as presented in Figs. 1 and 2. With increasing temperature, yttria becomes a more selective dehydration catalyst and may become more selective for dehydration than dehydrogenation.

In general, for a particular temperature the dehydrogenation/dehydration selectivity, S, is higher for the cyclic alcohols than for the acyclic alcohols. However, as can be seen in Table 2 the selectivity, S, for the acyclic 2-ols varies slightly with the groups attached to the carbinol carbon. The data in Table 2 indicate that the selectivity, S, changes in the direction expected by a linear free energy relationship.

In Table 3 alkene distributions are presented for the conversion of 2-ols over yttria at various temperatures. The catalyst is a very selective catalyst for the formation of the 1-alkene from all of the 2-ols tested. The selectivity for 1-alkene is slightly higher at the lowest temperature. *Cis*- and *trans*-2-alkenes are formed in

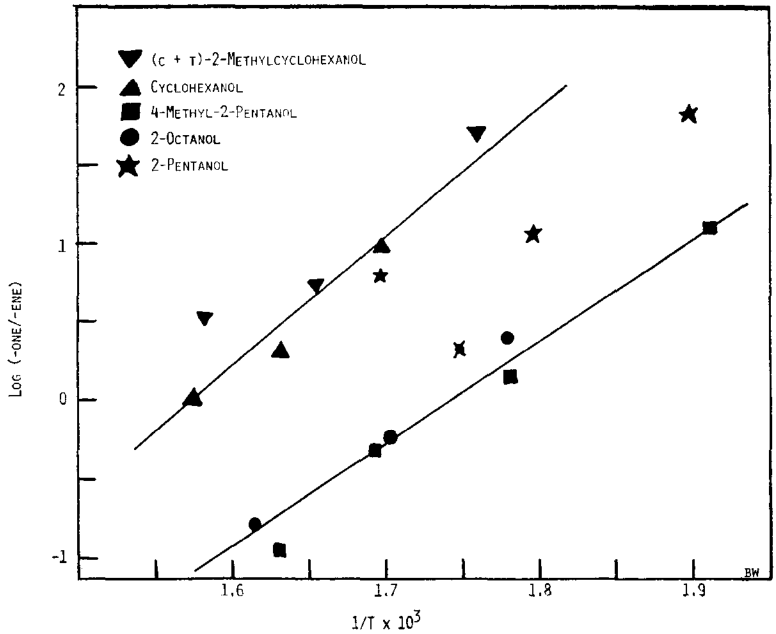

FIG. 2. Log (dehydrogenation/dehydration selectivity) *vs* the reciprocal temperature. The selectivities are for later time-on-stream.

about equal amounts from all of the 2-ols tested. The *trans*-2-isomer elutes from the column on the tail of the 1-alkene peak, and the observation of a slightly higher amount of the *trans*-isomer is probably due to this.

The alkene distribution does not change appreciably during the course of a run; the slight change is such that for 2-ols the catalyst becomes more selective for 1-alkene formation.

The data in Table 4 shows that the dehydrogenation reaction has a lower temperature coefficient than the dehydration reaction. The temperature coefficient for dehydration for the acyclic alcohols is about 10 kcal/mol lower than for the cyclic alcohol but the temperature coefficient for dehydrogenation is about the same for both the cyclic and acyclic 2-ols. The rates used in these calculations were arbitrary ones obtained by correcting all conversions to the lowest flow rate. A zero order was assumed for all alcohols and was confirmed for 2-octanol at 0.5 and 1-atm pressure.

TABLE 2

Selectivity and Steric and Polar Parameters for 2-ols

Alcohol	*R*	E_s	σ^*	ln (-one/-ene)
2-Pentanol	C_2H_5	−0.07	−0.10	−0.16
4-Methyl-2-pentanol	i-C_3H_7	−0.47	−0.19	−1.0
4,4-Dimethyl-2-pentanol	t-C_4H_9	−1.54	−0.30	−1.6
2-Hexanol	*n*-C_3H_7	−0.36	−0.115	−0.6
2-Octanol	*n*-C_5H_{10}	—	—	−0.75

The results for the conversion of two tertiary 2-ols are presented in Table 5. The 1- 2-alkene ratio from amyl alcohol is in line with what we find for other catalysts at this temperature and agrees well with those from the acetate pyrolysis (*5*). The 1-alkene isomer does not dominate for either tertiary 2-ol as it did for the secondary 2-ol. The *cis*-2-isomer was formed in a larger amount than the *trans*-2-isomer in contrast to the formation of nearly equal amounts of the two isomers from secondary 2-ols.

TABLE 3

Alkene Distribution from the Conversion of 2-ols over Yttria

Alcohol	Temperature (°C)	Time-on-stream (min)	Alkene (mol%)		
			1–	*trans*-2	*cis*-2
2-Pentanol	255	230	92.7	3.3	4.0
		300	92.6	3.1	4.4
	284	295	93.4	3.2	3.4
		340	93.5	2.8	3.8
	316	125	88.0	4.6	7.4
		130	91.7	4.3	4.0
2-Hexanol	300	165	79.0	12.7	8.3
		255	83.4	10.2	6.4
4-Methyl-2-pentanol	248	185	96.4	3.6	
		255	94.9	5.1	
	288		94.8	5.2	
			94.9	5.1	
	318		93.9	6.1	
	340	90	93.5	6.5	
		98	93.9	5.2	
4,4-Dimethyl-2-pentanol	345	74	87.2	5.89	5.05
		85	96.0	3.97	tr
2-Octanol (O_2 pretreatment)	240	120	74.6	14.6	10.8
		156	69.7	18.1	12.2
2-Octanol (H_2)	288	455	89.7	6.7	3.7
		475	89.8	6.1	4.1
	314	190	89.4	7.3	3.4
		225	87.9	6.9	4.2
	345	145	88.9	6.4	4.7
		165	88.1	6.4	5.5

The results from the conversion of *cis*- and of *trans*-2-methylcyclohexanol over yttria show that the *cis–trans* isomerization of the alcohol is more rapid than the dehydration reaction (Table 6). The same *cis–trans*-alcohol ratio was obtained whether the reactant was pure *cis*, pure *trans*, or a mixture of *cis*- and *trans*-alcohol; hence, it appears that an alcohol composition of 33% *cis*–67% *trans*-2-methylcyclohexanol represents the equilibrium composition at 290–300°C. The amount of *cis*-alcohol present at equilibrium increased slightly with increasing temperature. The alkene distribution obtained from the *cis*- and the *trans*-alcohol isomer was different. With the *trans*-2- charge more of the 3-methylcyclohexene was formed than the 1-methyl isomer; with the *cis*-alcohol the 1-methylcyclohexene isomer dominated. The alkene composition from the conversion of a mixture of the *cis*- and *trans*-alcohols is between the values for the conversion of the pure isomeric alcohols.

The data in Table 7 show a wide variation in alkene composition from the conversion of three pentanols. With the 2-pentanol the 1-isomer dominated with about equal

TABLE 4

Temperature Coefficient for the Conversion of Cyclic and Acyclic 2-ols over Yttria

Alcohol	Temperature range (°C)	Temperature coefficient (kcal/mol)	
		Dehydration	Dehydrogenation
Cyclohexanol	320–360	39.0	15.1
(*cis* + *trans*)-2-Methylcyclohexanol	250–330	37.6	19.6
2-Pentanol	260–315	29.6	18.6
2-Octanol	240–345	32.2	18.4
4-Methyl-2-pentanol	250–340	29.3	18.4

amounts of the *cis*- and *trans*-2-pentene being formed in small amounts. With 3-pentanol the *trans*-2-/*cis*-2-pentene isomer ratio is about two rather than one which was obtained from 2-pentanol. The absence of the 1-isomer from 3-pentanol shows that positional isomerization does not occur and the equal amounts of *cis*- and *trans*-2-pentene suggest that geometric isomerization does not make a significant contribution in determining the ultimate alkene distribution from acyclic alcohols. Replacing the carbinol hydrogen in 3-pentanol with a methyl group alters the alkene product distribution. The *trans*-2-/*cis*-2- ratio changed from 2 for 3-pentanol to 0.6 for the 3-methyl-3-pentanol. 3-Methyl-3-pentanol may also be viewed as a 2-butanol in which the carbinol hydrogen has been replaced by an ethyl group; the selectivity for 1-alkene (Hoffman elimination) is much lower than for the unsubstituted 2-ol. In all considerations of alkenes in this paragraph we are only considering alkene isomers formed by a β elimination.

DISCUSSION

In agreement with Spitsyn *et al.* (*4*) and Sharf *et al.* (*3*), we find that the dehydration selectivity of yttria is temperature dependent and that the catalyst becomes a more selective dehydration catalyst with increasing temperature. The change in selectivity shows a reasonably good log S vs $(1/T)$ relationship as would be expected for competitive reactions with

TABLE 5

Conversion of Tertiary Alcohols over Yttria

Alcohol	Temperature (°C)	Time (min)	Conversion (mol%)	Alkene[a]		
				1–	2–	
t-Amyl alcohol	245	42	14	46.9	53.1	
		55	12	46.0	54.0	
				1–	*t*–2	*c*–2
3-Methyl-3-pentanol	245	93	13	18.7	30.6	50.7
		106	12	19.9	29.8	50.3
		116	11	21.0	31.3	47.6

[a] The alkenes from *t*-amyl alcohol are 1– and 2-methyl-1-butene and 1- and 2-methyl-2-butene; from 3. methyl-3-pentanol; 1- and 2-ethyl-1-butene. *t*-2 = *trans*-3-methyl-2-pentene; *c*-2, = *cis*-3-methyl-2-pentene-

different activation energies. At a given temperature, the catalyst is about an order of magnitude less selective for dehydration for the cyclic alcohol than for the acyclic alcohol.

With alumina, Drause and co-workers found a linear free energy relationship (LFER) for substitution at the methylene β-carbon of 2-ols with the general formula $R{-}CH_2{-}CHOH{-}CH_3$ (*6*). Kibby and Hall found a correlation of the rate of dehydration for 15 acyclic alcohols over "nonstoichiometric" hydroxyapatite with Taft σ^* constants for substitution at the α-carbon, and it appeared that the necessary requirement was a sufficiently acidic hydroxyl group at the surface (*7*). We did not obtain the LFER for the overall reaction rate or for the individual dehydration or dehydration reaction rate.

As seen in Table 2, the dehydrogenation/dehydration selectivity, at a given temperature, decreased slightly as the R group attached to the methylene β-carbon provided a larger steric effect. These results are suggestive but are not of sufficient accuracy to allow a definitive conclusion. Even with a good LFER plot there is still a question as to the validity of distinguishing between a steric effect and a polar effect with alkyl groups. For alkyl groups, the polar effect, σ^*, usually lies between 0 and -0.3, and it has been possible to obtain a good linear relationship between E_s, the steric factor, and σ^* (*8*). If this is the case, either effect would give a linear plot with the selectivity.

Yttria is a very selective catalyst for the formation of 1-alkenes from 2-alcohols. About equal amounts of *cis*- and *trans*-2-alkene are formed from 2-ols. Our selectiv-

TABLE 6

Conversion of 2-Methylcyclohexanols over Y_2O_3 Catalysts

Charge	Temperature (°C)	Time-on-stream (min)	Total conversion (mol%)	Alcohol (mol%)		Cyclohexene[a] (mol%)	
				cis	*trans*	3-methyl-	1-methyl-
cis-2-	285	64	22	33	67	39	61
		129	24	32	68	40	60
trans-2-	300	117	22	32	68	58	42
		150	22	34	66	60	40
cis + *trans*[b]	250	130	5.8	33	67	—	—
		195	4.8	34	66	—	—
cis + *trans*[b]	295	225	21	33	67	52	48
		290	22	33	67	52	48
cis + *trans*[b]	330[c]	190	22	36	64	51	49
		215	23	—	—	49	51
cis + *trans*[b]	360[c]	90	31	37	63	53	47
		110	29	38	62	—	—

[a] Less than 5 mol% of 4-methylcyclohexene and methylenecyclohexene were present.

[b] Charge (*cis* + *trans*) was 53.07 mol% *cis* and 46.93 mol% *trans*.

[c] Flow rate varied as well as the temperature.

ity for the 2-ols are in excellent agreement with those of Sharf *et al.* (*3*) who observed that 2-pentanol yielded 90% of the 1-pentene isomer.

In contrast, the tertiary alcohol, 2-methyl-2-butanol, was not selectively converted to the 1-alkene, even though the statistical factor would favor the 1-alkene even more in this case than for the 2-ols. In fact, the alkenes from 2-methyl-2-butanol were in line with the general trend for a number of catalysts we have tested and found to be in line with an extension of the alkene selectivity for the acetate ester prolysis (*5*).

We obtained a temperature coefficient for acyclic alcohols of 29–32 kcal/mol for dehydration and 19 kcal/mol for dehydrogenation. The values Spitsyn *et al.* obtained for isopropanol with Y_2O_3, 19.4 kcal/mol for dehydration and 11.0 kcal/mol for dehydrogenation, are considerably lower than the ones we obtained. However, our values for dehydration are similar to those obtained for alumina (*9*, *10*). The cyclic alcohols gave a higher temperature coefficient of 38–39 kcal/mol for dehydration, but the 15–20 kcal/mol for dehydrogenation is in line with that of the acyclic alcohols. With the rather limited data, it appears that the temperature coefficient for dehydrogenation of all alcohols is similar while the coefficient for dehydration of cyclic alcohols is about 1.5 times that of the acyclic alcohols.

The alkene distributions from 3-methyl-3-pentanol and 2- and 3-pentanol do not appear to follow a consistent trend. With the 2-isomer we observe a very strong selectivity for the 1-alkene isomer and about equal amounts of the *cis*- and *trans*-isomer. In going to 3-pentanol we find that the *trans*-2-alkene isomer is favored over the *cis*-2-isomer in about a 2:1 ratio. The 3-methyl-3-pantanol alkene products do not resemble those from 3-pentanol since 50% of the total alkenes were the *cis*-isomer; likewise, it does not resemble the distribution expected from a 2-ol since only 20% of the alkenes are the 1-isomer.

TABLE 7

Alkene Distribution from the Conversion of Pentanols over Yttria

Alcohol	Pentenes (mol%)[a]		
	1–	*trans*-2-	*cis*-2-
2-Pentanol	92	4	4
3-Pentanol	1	64.6	34.4
3-Methyl-3-pentanol	20	30	50

[a] 1– is for 2-ethyl-1-butene, and *trans*-2- and *cis*-2- represent the *cis* and *trans* isomers of 3-methyl-2-butene.

The alkene distribution from 2-methylcyclohexanol is inconclusive because of the *cis–trans* isomerization of the alcohol. The same alcohol composition in the liquid product when starting with pure *cis*, *pure trans*, or a *cis–trans* mixture indicates that the equilibrium alcohol composition was reached. There is only a small increase in the *cis*-alcohol as the temperature was increased; since Chiurdoglu and Masschlein (*11*) found $\Delta F_{\mathrm{cis,trans}}$ to be 479 cal/mol we would not expect a strong temperature dependence. In making their measurements, Chiurdoglu and Masschlein used the hydrogenation of 2-methylcyclohexanone in the temperature range 110–170°C and found 63–66% *trans*-alcohol after 20 hr. In our study, the liquid product composition from the conversion of the *cis*-alcohol required that the conversion of the reactant alcohol to the *trans*-alcohol be about three times as great as the conversion to the alkene plus ketone. This requires the isomerization reaction to be at least three times as rapid as dehydrogenation plus dehydration; since the equilibrium alcohol composition was obtained, it may be many times greater. In any event, it appears that yttria would be a good catalyst to use to determine the *cis–trans* equilibrium for substituted cycloalkanols.

A *trans* elimination mechanism for the methylcyclohexanols would lead to 3-methylcyclohexene from *trans*-2-methylcyclohexanol and a predominance of 1-methylcyclohexene from the *cis*-alcohol isomer. With the *trans*-alcohol, about 60% of the alkene fraction was the 3-methyl isomer; with the *cis*-alcohol only about 40% of the alkene fraction was the 3-methyl isomer. In both cases the alkene fraction is far from the equilibrium composition where only about 15% of the 3-methyl isomer would be present. Thus, it appears that the alkene isomerization is not extensive under our conditions. The alkene distribution suggests that a major dehydration pathway for 2-methylcyclohexanol is an anti-elimination mechanism.

The selectivity, *S*, for many oxides varied depending on whether a hydrogen or oxygen pretreatment was used (*12*). A hydrogen-pretreated sample, in most cases, was more selective for dehydration than an oxygen-pretreated sample. Arias and Selwood (*13*) found that treating Y_2O_3 with hydrogen in the 550–700°C range generated Y^{2+} ions in the surface. It seems reasonable to attribute the increase in selectivity for dehydration with increasing temperatures and with time-on-stream to such a surface reduction.

As an alcohol conversion catalyst, yttria resembles thoria (*14*, *15*, *16*) much more than alumina. The *cis–trans* isomerization of 2-methylcyclohexanol shows that the "dehydrogenation–hydrogenation" is faster than desorption of the ketone.[1] It seems reasonable that a similar situation should apply for the acyclic alcohols. It also would appear likely that a similar dehydrogenation equilibrium could occur with the hydrogen of the methyl group in 2-ols and exchange in the β-CH_3 has recently been reported (*17*).

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[1] A referee suggested that the isomerization reaction occurs as a hydrogen transfer from the C_α of the alcohol to a ketone [as examples, see Refs. (*15*) and (*16*)]. We do not wish to restrict the mechanism for the isomerization and believe that a carbanion intermediate could be involved in the isomerization as well as dehydrogenation of the alcohol C_α by the catalyst rather than by the alcohol.

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