JOURNAL OF CATALYSIS 74, 24–30 (1982)

Catalytic Conversion of Alcohols

XVIII. Comparison of *cis–trans* Isomerization of 2-Methylcyclohexanol Isomers and the Corresponding Methyl Ethers

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Received June 8, 1981; revised October 26, 1981

Methoxymethylcyclohexane did not undergo *cis–trans* isomerization over three oxide catalysts under conditions where the corresponding alcohol undergoes isomerization to the *cis–trans* equilibrium composition. The ether underwent elimination to form an alkene to about the same extent as the corresponding alcohol. The ketone formed from the alcohol but not from the ether.

INTRODUCTION

The stereochemistry of elimination reactions from cyclic systems provides much of the basis for the current view of the elimination mechanism (*1*). It has recently been recognized that the amount of Hoffman (i.e., anti-Saytzeff) elimination may be determined by base size as well as base strength (*2a–d*). A larger base favors the Hoffman product.

An important consideration in heterogeneous catalysis is the elucidation of the geometry of the catalytic site. Since instrumental techniques are unavailable for complete characterization of the site, recourse must be made to indirect methods. One such approach is to use well-characterized, stereochemically demanding organic reactions and to infer the nature of the site by analogy with the homogeneous case.

Alumina catalyzes the dehydration of each 2-methylcyclohexanol isomer with a high degree of stereoselectivity and without *cis–trans* isomerization of the alcohol reactant. On the other hand, yttria, india, and zirconia catalyze both dehydration and dehydrogenation as well as *cis–trans* isomerization; they do not exhibit the stereochemical selectivity of alumina. In the case of india, it has been speculated that an enol mechanism, with intermediates analogous to those well established in homogeneous exchange and elimination chemistry, may account for the observed preference for the Hoffman olefin as well as for the dehydration–dehydrogenation selectivity and facile *cis–trans* isomerization (*3a–c*). In this paper we report results from studies of the ether analog of 2-methylcyclohexanol with catalysts that exhibit *cis–trans* isomerization activity; the enol form should not be a reaction intermediate in the case of the ether reactant.

EXPERIMENTAL

The catalysts were prepared by precipitation from a nitrate solution by the rapid addition of concentrated ammonium hydroxide (*3a, 4–6*). The catalyst, activated at 500°C in flowing air prior to use, was placed in a plug flow reactor with glass beads above the catalyst to serve as a preheater. The reactant was fed by a syringe pump, and liquid products were collected at intervals.

The liquid products were analyzed for degree of conversion by gas chromatography (GC) using a 10% Carbowax 20M column, 6 ft in length with temperature programming. The alkene composition was determined by isothermal GC with an OV-1

0021-9517/82/030024-07$02.00/0

column. A diglycerol column, at 95°C, was used to measure the amount of *cis*- and *trans*-2-methylcyclohexanol in the liquid products. *cis*- and *trans*-1-methoxy-2-methylcyclohexane did not separate using the above GC columns. Carbon-13 NMR spectra of the two isomers (Fig. 1) are sufficiently different to permit a determination of the relative amount of the two isomers. The peaks at 16.2 and 21.8 ppm, corresponding to ring position 4 and 5 carbons, were used to estimate the amount of the *trans* isomer; the peaks at 25.0 and 25.6 ppm, corresponding to the same ring carbons, were used for the *cis* isomer. The ^{13}C ring assignments are by analogy with the corresponding alcohol isomer (Sadtler Catalogue Spectra).

Pure (>99%) *cis*- and *trans*-2-methylcyclohexanols were purchased from Chem Samples Company. Each pure isomeric alcohol was converted, by a stereospecific methanation with sodium hydride and methyl iodide, to the corresponding methoxymethylcyclohexane (*7*).

RESULTS

The conversion of 2-methylcyclohexanol over the four catalysts was followed by collecting a series of samples at increasing time on stream. Thus, the analytical data for each sample in Tables 1–3 represent an average integral conversion during the time between the collection of two samples.

The three catalysts listed in Table 1, yttria, india, and zirconia, were active for the interconversion of *cis*- and *trans*-2-methylcyclohexanol. Earlier work with yttria catalysts has shown that the pure *cis*-, pure *trans*-, and *cis*–*trans* mixtures of 2-methylcyclohexanol yield the same alcohol composition (33% *cis*-2-methylcyclohexanol) in the product (*4*). Chiurdoglu and Masschelein (*8*) found $\Delta G_{cis,\ trans}$ to be 479 cal/mole; thus, there should be little change in the equilibrium composition with temperature.

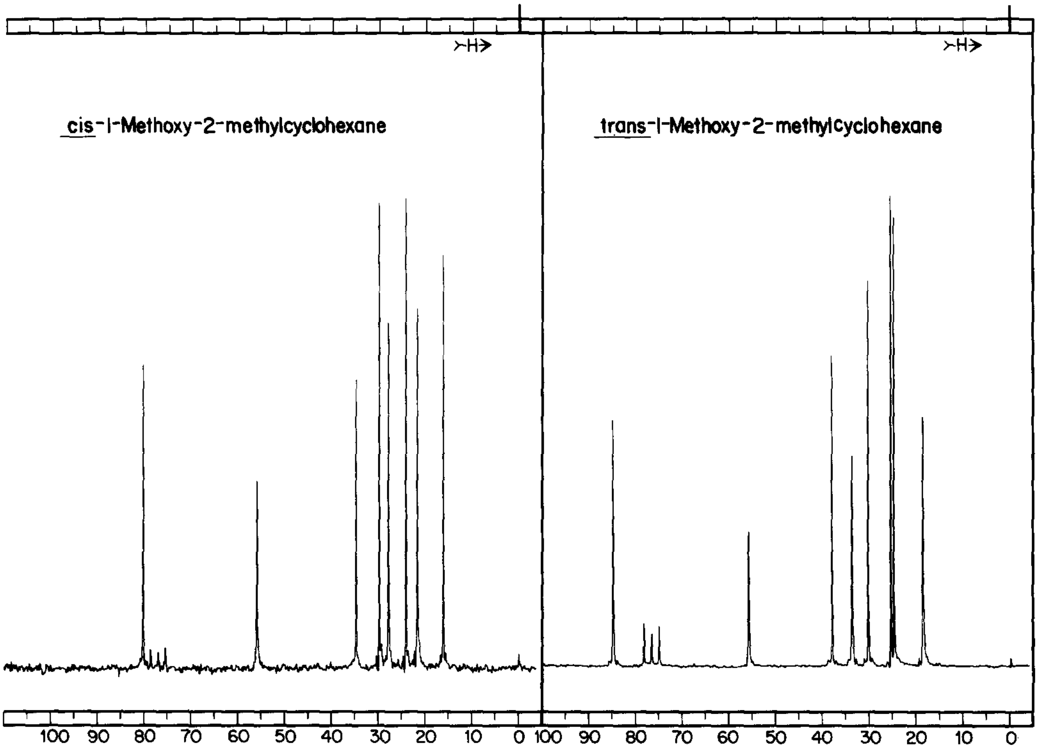

FIG. 1. ^{13}C nuclear magnetic resonance spectra for *cis*- and *trans*-1-methoxy-2-methylcyclohexane.

TABLE 1

Reaction Products from the Conversion of 2-Methylcyclohexanol and 1-Methoxy-2-methylcyclohexane over India, Zirconia, and Yttria Catalysts (250°C; Reactant Pressure, 1 atm)

Reactant	Time (min)	Alkenes	Ketone	Unconverted alcohol		Methylcyclohexene	
				cis	*trans*	3-	1-
			India				
trans-2-Methylcyclohexanol	11	3.0	54	26	74		
	26	2.7	56	29	71	74	26
	34	2.1	54	27	73		
	49	1.8	56	29	71	72	28
cis + *trans*-Methylcyclohexanol	15	3.7	54	31	69	65	34
	27	2.6	56	32	68	75	25
	33	2.4	56	31	69	75	25
	47	2.6	54	32	68	76	24
trans-1-Methoxy-2-methylcyclohexane	18	2.3	2.5 (1.4)[a]	—	100	50	50
	27	2.0	1.5 (0.4)[a]	—	100	38	62
	36	2.0	1.5 (0.5)[a]	—	100	38	62
	47	2.0	1.3 (0.2)[a]	—	100	40	60
			Yttria				
cis-2-Methylcyclohexanol[b]	64	4	18	33	67	39	61
	129	5	19	32	68	40	60
trans-2-Methylcyclohexanol[b]	117	4	18	32	68	58	42
	150	5	17	34	66	60	40
cis-1-Methoxy-2-methylcyclohexane	28	16.1	0.07	100	—	19	81
	64	10.6	0.4	100	—	21	79
	113	5.8	0.6	100	—	34	76
trans-2-Methylcyclohexanol	31	6.6	20.7	23	77	33	77
	70	2.2	9.4	28	72	36	64
	100	2.0	5.6	34	66	42	58
			Zirconia				
cis-2-Methylcyclohexanol[a]	105 (5)[d]	4.4	6.6	64	36	52	48
trans-2-Methylcyclohexanol[c]	175 (5)[d]	4.4	4.4	9.9	90	57	43
trans-1-Methoxy-2-methylcyclohexane	92	14.7	—	—	100	56	43
	175	9.2	—	—	100	54	46
	230	11.5	—	—	100	50	50
cis-1-Methoxy-2-methylcyclohexane	84	43	—	100	—	32	68
	195	39	—	100	—	33	67
	200	36	—	100	—	34	66
	254	28	—	100	—	32	68

[a] Number in parentheses is the amount of 2-methylcyclohexanol.

[b] Data from Ref. (*4*) for hydrogen-pretreated yttria, reactor temperature 285–300°C.

[c] Data from Ref. (*5*) for air-pretreated catalyst; flow rate, and hence the conversion, was not the same for the alcohol and ether runs.

[d] Number in parentheses is the number of samples collected to this time.

TABLE 2

Conversion Products from Equimolar Mixture of Cyclohexanone and *trans*-2-Methylcyclohexanol or *trans*-1-Methoxy-2-methylcyclohexane over Yttria (250°C; Reactant Pressure, 1 atm)

Reactant	Time (min)	Methylcyclohexene			Reactant	
		3-	1-	Percentage formed	*cis*	*trans*
trans-2-Methylcyclohexanol	22			3	38	62
	37	34	66	1.5	37	63
	95	33	67	1	40	60
trans-1-Methoxy-2-methylcyclohexane	20	49	51	2.5	—	100
	50	41	59	0.5	—	100
	90	41	59	0.5	—	100
	140	43	57	0.4	—	100

The alcohol composition we obtained at 290–300°C is essentially the same as that obtained by Chiurdoglu and Masschelein for the hydrogenation of 2-methylcyclohexanone (33–37% *cis* alcohol). This means that under the reaction conditions used, all three catalysts give near-equilibrium alcohol mixtures.

cis- and/or *trans*-1-methoxy-2-methylcyclohexane were passed over the three catalysts employing reaction conditions where methylcyclohexanol had previously been observed to undergo dehydration, dehydrogenation, and *cis–trans* isomerization (*4*). *cis–trans* Isomerization of the methoxymethylcyclohexane isomer was insignificant in all three cases. This is true even for the india catalyst where a minor quantity of 1-methoxy-2-methylcyclohexane was converted to 2-methylcyclohexanone and 2-methylcyclohexanol.

Three of the catalysts used in this study catalyze both dehydrogenation of the alcohol to the ketone and dehydration to alkenes. To determine the role of a ketone in the isomerization, an equimolar mixture of a ketone, cyclohexanone, and *trans*-1-methoxy-2-methylcyclohexane (or *trans*-2-methylcyclohexanol) was passed over the yttria catalyst. The cyclohexanone, in the presence of the alcohol or the ether, underwent condensation to higher-molecular-weight ketones. Thus, there is no doubt that some of the ketone was absorbed on the catalyst surface. However, even in the presence of the high ketone concentration, the *trans*-1-methoxy-2-methylcyclohexane did not undergo detectable *cis–trans* isomerization (less than 1 mole% conversion).

Alumina catalyzes the Meerwein–Ponndorff–Verley reaction (*9*, *10*) in the temperature range used in the present study. A mixture of 2-butanone and *cis*-2-methylcyclohexanol was converted over an acidic alumina at 180°C. The formation of 2-buta-

TABLE 3

Conversion Products from *cis*-2-Methylcyclohexanol for a Mixture of 2-Butanone (45.5%) and *cis*-2-Methylcyclohexanol (54%) with an Alumina Catalyst (180°C, 1 atm Total Pressure without Diluent, LHSV = 24)

Time (min)	Methylcyclohexene[a]		2-Methylcyclohexanone[a]	Methylcyclohexanol[a]		(Dehydrogenation/Isomerization)[b]
	3-	1-		*cis*	*trans*	
3	Discard					
7	16 (28)[c]	40	15	23	5.4	2.8
12	16 (29)[c]	39	17	23	4.5	3.8
24	12 (26)[c]	34	13	38	3.8	3.3
34	9.6 (22)[c]	33	11	43	2.9	3.9

[a] Weight percentage based on alcohol charged.

[b] Based on formation of 2-methylcyclohexanone and *trans*-2-methylcyclohexanol.

[c] Percentage of 3-methylcyclohexene is in parentheses.

nol and 2-methylcyclohexanone verified that the Meerwin–Pondorff–Verley reaction did take place. 2-Methylcyclohexanone formation was 26–31% relative to the amount of dehydration to methylcyclohexenes. The corresponding amount of *trans*-2-methylcyclohexanol formed was 7 to 12% of the amount of methylcyclohexenes formed. The amount of dehydrogenation by hydrogen transfer was about three times as great as the isomerization of the *cis*-2-methylcyclohexanol. Thus, both dehydration and hydrogen transfer are more rapid than the alcohol isomerization.

Under similar reaction conditions the alcohol and the corresponding methyl ether behave similarly in regard to the degree of dehydration to alkenes. This observation is somewhat qualitative since catalyst aging is a factor; the rate of aging may depend on catalyst activation, etc., so that a quantitative comparison may not be possible. The ratio of the alkenes formed from *trans*-2-methylcyclohexanol with or without the cyclohexanone present over a ytteria catalyst is independent of the concentration of added ketone.

DISCUSSION

The conversion of 1-methoxy-2-methylcyclohexane isomers differs from that of the corresponding alcohols in two important respects: (1) a ketone is a major product from the alcohol but not from the ether and (2) *cis–trans* isomerization is a relatively rapid reaction with the alcohol but not with the ether.

Had the methoxymethylcyclohexane undergone isomerization analogous to the isomeric alcohol, the result would have been definitive in showing that the hydroxyl hydrogen was not directly involved in the *cis–trans* isomerization. Obtaining this definitive result would show that a carbanion-like structure was the intermediate for *cis–trans* isomerization and, by analogy, probably for dehydrogenation. However, this definitive result was not obtained since no *cis–trans* isomerization occurred with the ether. An alkoxide, or strongly hydrogen bonded alcohol, is apparently required if *cis–trans* isomerization is to occur at a rate competitive with elimination. The absence of *cis–trans* isomerization with methoxymethylcyclohexane indicates that the hydroxyl hydrogen plays a role in this reaction. Clearly, abstraction of the hydrogen from the hydroxyl carbon (as hydride) with readdition from the opposite side of this carbon does not occur.

The *cis–trans* isomerization reaction of alcohols may be bimolecular and resemble, in the extreme case, a Meerwein–Pondorff–Verley reaction (*9*, *10*). Accompanying considerable *cis–trans* alcohol isomerization, dehydrogenation to the ketone occurred. Since the ketone was not formed in significant amounts from 1-methoxy-2-methylcyclohexane, it could be postulated that *cis–trans* isomerization failed to occur with the ether reactant because of the absence of ketone. However, passing an equimolar mixture of ketone and ether over yttria did not result in *cis–trans* isomerization of the ether compound. The corresponding 2-methylcyclohexanol isomer underwent isomerization to an equilibrium mixture when passed over yttria with or without added ketone. Thus, it does not appear that the *cis–trans* isomerization is a bimolecular reaction requiring a ketone acceptor for hydrogen transfer with dehydrogenation catalysts.

We found that *trans*-2-methylcyclohexanol was converted more rapidly than *cis*-2-methylcyclohexanol with alumina (*11*); this agrees with other workers (*12*). Also the dehydration is stereospecific with *trans*-2-methylcyclohexanol producing 78–82% 3-methylcyclohexene and *trans*-2-methylcyclohexanol producing 18–22% of the 3-methylcyclohexene isomer (*11*); this also agrees with the results of others (*12*). The alkene distribution obtained from dehydration of *cis*-2-methylcyclohexanol mixed with 2-butanone (Table 3) is similar to that obtained from dehydration of the pure alcohol. This result shows that dehydration of the *trans*-2-methylcyclohexanol formed during conversion of the alcohol–ketone mixture did not undergo an appreciable amount of dehydration as a secondary reaction. Neither the pure *cis*- nor *trans*-2-methylcyclohexanol underwent isomerization or dehydrogenation when converted using an alumina catalyst. The presence of about two times as many moles of ketone as alcohol did cause some *cis–trans* isomerization; however, it was still less than 10% of the total alcohol conversion. Thus, the results suggest that isomerization is about three times slower than hydrogen transfer and about ten times slower than dehydration.[1]

Infrared studies show that many alcohols form alkoxides on metal oxides that catalyze dehydration (e.g., alumina (*13*)). Alkoxide intermediates have also been well characterized in instances where dehydrogenation and *cis–trans* reactions are effectively catalyzed [e.g., ZnO (*14a, b*) and thoria (*15a–c*)]. For the three catalysts used in this study, 1-methoxy-2-methylcyclohexane undergoes elimination to about the same extent as do the 2-methylcyclohexanol isomers. In contrast, the alcohol, but not the ether, undergoes dehydrogenation and *cis–trans* isomerizaiton. The same alkoxide would be formed from both the alcohol and the ether so, if this intermediate formed, both reactants should yield the same products. The fact that the two reactants produce the same amount of elimination products at the same space velocity suggests a similar elimination pathway for the two reactants. Therefore, an alkoxide is not likely to be the intermediate that leads to elimination.

The data are consistent with a common intermediate for dehydrogenation and *cis–trans* isomerization. This intermediate may differ from that leading to elimination products. This implies that the catalytic site is multicentered. Complex interactions that may include both geometrical (steric) and basicity factors must be involved in the alcohol conversions. The dehydration–dehydrogenation (and *cis–trans* isomerization) selectivity would be determined by the relative extent of the C–OH and CO–H bond weakening (or full ionization) perhaps in concert with appropriate weakening of the other bonds involved in the elimination.

When we undertook the investigation of alcohol conversion with a large number of metal oxides, it was with the view of using the alkene and dehydration selectivity, by analogy with the well-founded homogeneous elimination, to arrange metal oxide catalysts in order of base strength. The alkene and dehydration selectivity from the conversion of 2-methylcyclohexanol, with a demanding steric requirement for *syn* and *anti* elimination, do show a catalyst sensitivity (*5, 14–18*). However, much more work, including detailed tracer studies, are needed before this reaction can be used to define in detail the catalytic site.

REFERENCES

1. Ingold, C. K., "Structure and Mechanism in Organic Chemistry." Cornell Univ. Press, Ithaca, N.Y., 1953.

2. (*a*) Bartsch, R. A., Pruss, G. M., Bushaw, B. A., and Wiegers, K. E., *J. Amer. Chem. Soc.* **95,** 3405 (1973). (*b*) Bartsch, R. A., Wiegers, K. E., and Gurize, D. M., *J. Amer. Chem. Soc.* **96,** 430 (1974). (*c*) Bartsch, R. A., *Acc. Chem. Res.* **8,** 239 (1975). (*d*) Baciocchi, E., *Acc. Chem. Res.* **12,** 430 (1979).

3. (*a*) Davis, B. H., *J. Catal.* **52,** 435 (1978). (*b*) Venatasubramanian, N., and Karuppannasamy, S., *J. Catal.* **65,** 238 (1980). (*c*) Davis, B. H., *J. Catal.* **65,** 241 (1980).

4. Davis, B. H., *J. Catal.* **52,** 176 (1978).

5. Davis, B. H., and Ganesan, P., *Ind. Eng. Chem. Prod. Res. Dev.* **18,** 199 (1979).

6. Davis, B. H., *J. Org. Chem.* **37,** 1240 (1972).

7. Brown, C. A., Barton, D., and Sivaram, S., *Synthesis,* 434 (1974).

8. Chiurdoglu, G., and Masschelein, W., *Bull. Soc. Chim. Belg.* **70,** 782 (1961).

9. Kibby, C. L., and Hall, W. K., *J. Catal.* **29,** 144 (1973).

10. Gutsche, C. D., and Pasto, D. J., "Fundamentals of Organic Chemistry," p. 659. Prentice–Hall, Englewood Cliffs, N.J., 1975.

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[1] The conversion of the ketone–alcohol mixture was prompted by a reviewer's comment.

11. Davis, B. H., *Acta Chim. Soc.* (*Hungary*), in press.

12. Blanc, E. J., and Pines, H., *J. Org. Chem.* **33,** 2035 (1968).

13. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).

14. (*a*) Nagao, M., and Morimoto, T., *J. Phys. Chem.* **84,** 2054 (1980). (*b*) Davis, B. H., unpublished results.

15. (*a*) Siegel, H., Schoolner, R., Dombrowski, D., and Wendt, G., *Z. Anorg. Allg. Chem.* **441,** 252 (1978). (*b*) Canessen, P., and Blanchard, M., *J. Catal.* **42,** 205 (1976). (*c*) Canessen, P., Gonolonfoun, F. N., and Blanchard, M., *Bull. Soc. Chim. Fr.*, 2839 (1973); 3308 (1971).

16. Pines, H., and Marassen, J., *in* "Advances in Catalysis and Related Subjects," Vol. 16, p. 49. Academic Press, New York/ London, 1966.

17. Kibby, C. L., Lande, S. S., and Hall, W. K., *J. Amer. Chem. Soc.* **94,** 214 (1972).

18. Davis, B. H., unpublished results.