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The Hydrogenation of Pyran Derivatives. IV. The Skeletal Rearrangement in the Gas-phase Dehydration of Tetrahydropyran-2-methanol

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The gas-phase dehydration of tetrahydropyran-2-methanol (TPM), prepared by the hydrogenation of the acrolein thermal dimer (3,4-dihyro-2H-pyran-2-carboxaldehyde (AD)), was investigated over various catalysts under atmospheric pressure. In this reaction, some of the pyran ring was found to be rearranged rapidly to a seven- or five-membered ring. For example, the highly-purified and crystalline η-alumina without any carrier produced cyclopentanecarboxaldehyde (CPA) as the main product in the yield of 71% at 330°C. Over the commercial alumina catalyst, considerable amounts of 2,3,4,5-tetrahydrooxepine (THO) and oxepane (OXP) were produced as by-products, though CPA was the main product; in some cases, as much THO and OXP were produced as CPA. On the other hand, the use of a dehydrogenation catalyst resulted in THO as the main product and CPA as a by-product; in the case of the use of copper-chromium oxide supported on Kieselguhr, with hydrogen as a carrier gas at 430°C, the yields of THO and CPA were 44.8% and 4.7% respectively. In these skeletal rearrangements, the seven-membered carbonium ion compound produced by the Wagner-Meerwein-type rearrangement must be a reaction intermediate. From this intermediate, mainly CPA was produced over alumina, influencing the lone-electron pair of the ethereal oxygen. THO, on the contrary, was produced mainly over a dehydrogenation catalyst. Moreover, twice as high a yield of 1,6-hexanediol was obtained from the hydrogenation of the hydrated THO than from the hydrogenolysis of TPM or AD, as has been noted in a previous paper.

It is well known that dihydropyran is produced by the skeletal rearrangement during the dehydration of tetrahydrofurfuryl alcohol over an alumina catalyst. The reaction mechanism has been accurately established by many reports,[1,2] during the skeletal rearrangement, the carbonium ion, which is produced by the dehydroxylation of the side-chain alcohol at an acidic point on the surface of the alumina catalyst, may be rearranged to enlarge its ring *via* a step analogous to the Wagner-Meerwein rearrangement, followed by deprotonation. Accordingly, if such a reaction can be applied to the side-chain alcohol of a six-membered ring compound, the dehydration of tetrahydropyran-2-methanol (TPM) is likely to produce oxepine derivatives.

In only one patent[3] dealing with the dehydration of TPM, however, CPA has been reported as the main product; in this one case it was derived as an intermediate from the skeletal rearrangement of 2,3,4,5-tetrahydrooxepine (THO). If CPA was produced by the isomerization of THO, THO would be very unstable under the reaction conditions. However, it has been reported that the THO produced by the ring-closing dehydration of 1,6-hexanediol (1,6-D) is not changed at 250°C.[4] Therefore, the mechanism proposed by the patent is very doubtful.

In this paper, the skeletal rearrangement during the dehydration of TPM over various catalysts is accurately discussed on the basis of results concerning obtaining the unsaturated ring ether compound, THO, which is converted into 1,6-D in a good yield by hydration and by consecutive hydrogenation.

Experimental

Materials. *Acrolein Thermal Dimer (AD), 3,4-Dihydro-2H-pyran-2-methanol (DPM), and Tetrahydro-pyran-2-methanol (TPM).* These substances were shynthesized according to the methods described in previous papers,[5,6] except that the Diels-Alder reaction of acrolein was carried out under a 1—20 kg/cm^2 pressure of hydrogen instead of nitrogen, because then the yield of AD was increased a little compared with that under nitrogen.

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[1] C. L. Wilson, *J. Am. Chem. Soc.*, **69** 3004 (1947).

[2] R. L. Sawyer and D. W. Andrews, "Organic Syntheses," Coll. Vol. III, p. 276 (1954).

[3] R. R. Whetstone, (to Shell Development Co.) US 2480990 (1949).

[4] D. R. Larkin, *J. Org. Chem.*, **30** 335 (1965).

[5] A. Misono, T. Osa and Y. Sanami, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 1131 (1967).

[6] A. Misono, T. Osa and Y. Sanami, *ibid.*, **71** 137 (1968).

Cyclohexylcarbinol (CHC). This was also prepared according to the method described in a previous paper.7) All the other chemicals used in the present experiment were commercial compounds of the first grade.

Catalysts. The η-alumina catalyst without any carrier was prepared as follows. Fifty milliliters of an aqueous ammoniac solution was added to a saturated solution of 50 g of aluminum nitrate in water; the gel of aluminum hydroxide thus precipitated was rinsed with water five times and filtrated. The filtrated gel was dried in air for 10 hr at about 80°C and then sintered in air for 12 hr at about 600°C. The fine, white, sintered powder was tableted under a pressure of 150 kg/cm² and then crushed into particles 8—12 in mesh size. Commercial alumina catalysts, Neobead C (NC) (Al_2O_3: 100), Neobead D (ND) (Al_2O_3: 90, SiO_2: 10) and Neobead P (NP) (Al_2O_3: 88, SiO_2: 9, Na_2O: 3), were kindly supplied by the Mizusawa Chemical Co. Moreover, N631 (Al_2O_3: 15, SiO_2: 85), copper-chromium oxide (N208), copper-zinc oxide (N211), and nickel (N111), all except N631 supported on Kieselguhr were supplied by the Nikki Chemical Co.

Catalyst Activation. A catalyst was placed into the atmosphere of the feed and carrier gas for 3 hr at about 300°C, and then only a carrier gas, mostly hydrogen, was let flow through continuously until no water was formed. This pretreatment was carried out in all runs. The reaction over N111 was carried out as follows. The catalyst was renewed before each reaction, activated for 3 hr at about 450°C under the hydrogen carrier gas and at a constant flow rate of 10 m*l*/sec, and then placed in the atmosphere of the feed and nitrogen for 30 min.

The catalyst with tetrahydrofurfuryl alcohol (TFA) pretreated was prepared as follows; over an alumina catalyst TFA was passed by means of a nitrogen carrier for 20 min at about 300°C, and then nitrogen gas was allowed to flow through for 3 hr. The alumina catalyst obtained in this way was brown and was submitted to the reaction like other untreated aluminas.

Equipment and Methods. The dehydration reaction was carried out in the apparatus shown in Fig. 1. The reactor was equipped with a thermostat and was wrapped around with Nichrome heating wire. The reactor tube was packed with 15 m*l* of catalyst pellets, while the temperature was maintained at from 150°C to 500°C within ±3°C. The contact time was controlled by changing the rate of the material fed in. The majority of the product was condensed in a first trap cooled with methanol and dry ice at about −50°C, while the more volatile products were caught in a second trap cooled with methanol and dry ice below −60°C or, in some runs, with liquid nitrogen. The carrier gas was passed through the vaporizer to the reactor at a rate of from 5 to 35 m*l*/sec. As a carrier gas, hydrogen was generally used, because the selectivity of THO, as shown in Table 1, was slightly higher under the hydrogen carrier gas than under the nitrogen one. All the products except 1,6-hexanediol (1,6-D) were gas chromatographically analyzed using a 2 m×6 mm o.d. column containing silicon oil DC 550 on Diasolid M at 160°C. For the determination of 1,6-D and other compounds having higher boiling points, a column of 2 m×6 mm o.d. containing 10% polyphenyl ether and 2% Carbowax 20 M on Fruolopack 80 (60—80 mesh) was used at 170°C. 1,6-D recrystallyzed from a commercial product with carbon tetrachloride was used.

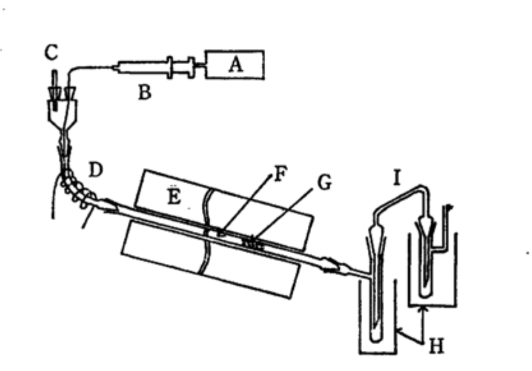

Fig. 1. Apparatus.

A	Extruder	F	Reaction tube
B	Injector	G	Catalyst
C	Gas inlet	H	Vessel with cooling material
D	Vaporizer		
E	Electric furnace	I	Trap

Identification of the Reaction Products. Pure samples of the reaction products were gas chromatographically isolated, or fractionally distilled, and identified by means of an IR spectrometer (Hitachi EPS-2) and an NMR spectrometer (Japan Electric Co. C-60). Both the preparative and analytical gas chromatographic work were carried out with a Kotaki-Superfractioner.

2,3,4,5-Tetrahydrooxepine (THO) ($C_6H_{10}O$): bp 112—114°C/760 mmHg, n_D^{25} 1.4509. IR (cm⁻¹); 2920, 2860, 1656(sh), 1650, 1302(sh), 1295, 1280(sh), 1125, 1080, and 740 (Fig. 2). NMR (ppm); multiplets at 8.3 (4 protons) and 7.95 (2 protons), a triplet at 6.15 (2 protons), a quadruplet at 5.35 (1 proton), and a doublet at 3.8 (1 proton).

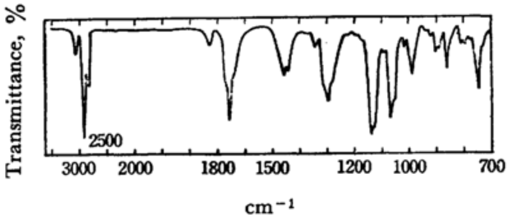

Fig. 2. IR spectrum of THO at NaCl plate.

Oxepane (OXP) ($C_6H_{12}O$): bp 124—126°C/760 mmHg, n_D^{25} 1.4349, IR (cm⁻¹); 2920, 2860, 1135, 1105, 995, and 970. NMR (ppm); a sharp peak at 8.35 (8 protons), and a peak like a triplet at 6.4 (4 protons).

2-Methyltetrahydropyran (MTHP) ($C_6H_{12}O$): bp 102—103°C/760 mmHg and n_D^{20} 1.4432 for MTHP of 96% purity. IR (cm⁻¹); 2960, 2920, 2860, 1380, 1215, 1095, 1085(sh), 1055, and 865.

6-Methyl-3,4-dihydro-2H-pyran (MDHP) ($C_6H_{10}O$): IR (cm⁻¹); 2960, 2850, 1730(sh), 1683, 1650(sh), 1450, 1390, 1300, 1240, 1170, 1095, 1070, 895, 820, and 765.

Cyclopentanecarboxaldehyde (CPA) ($C_6H_{10}O$): bp 87°C/78 mmHg and n_D^{25} 1.4379 for CPA of 98% purity. IR

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7) A. Misono, T. Osa and Y. Sanami, *ibid.*, **71** 680 (1968).

TABLE 1. EFFECT OF KINDS OF CARRIER GASES UPON SELECTIVITY[*1]

Gas	Temp. °C	Conversion, %	Selectivity, %						
			MCPE	CHE	MDHP	THO	OXP	CPA	CPEA
H_2[*2]	310	54.7	6.3	5.7	1.2	18.7	13.1	37.3	5.7
	330	62.1	7.1	5.5	2.1	17.3	11.3	41.2	7.4
	350	76.1	7.2	5.9	1.2	12.7	12.9	51.0	7.7
N_2[*2]	310	55.3	7.0	5.7	1.3	16.7	11.7	42.3	7.3
	330	63.2	7.2	5.3	1.4	16.9	10.1	43.7	7.9
	350	79.5	7.9	6.0	1.6	10.1	10.0	52.0	5.3
H_2[*3]	310	52.9	6.9	4.3	1.3	41.7	1.2	29.0	6.8
	330	68.7	7.6	7.1	1.6	39.4	1.3	28.9	6.7
	350	74.3	7.2	6.9	1.5	43.5	1.4	26.9	5.4
N_2[*3]	310	50.1	6.2	5.0	1.3	39.9	1.4	31.5	7.3
	330	67.3	7.1	5.1	1.2	40.1	1.3	30.8	6.9
	350	78.1	7.0	5.9	1.5	38.5	1.4	32.1	6.3

[*1] Feed rate of TPM and flow rate of carrier gas were constant at 10 m*l*/hr and 10 m*l*/sec, respectively. Length of catalyst bed was 7 cm.

[*2] Reactions over ND catalyst.

[*3] Reactions over NDF catalyst.

(cm^{-1}); 2930, 2850, 2820, 2720, 1725, and 1455. The 2,4-dinitrophenylhydrazone derivative was obtained as a yellow product, mp 158—162°C.

1-Cyclopentenecarboxaldehyde (CPEA) (C_6H_8O): IR (cm^{-1}); 2930, 2850, 2820(sh), 2720, 1720(sh), 1680, 1620, 1160, and 960 The 2,4-dinitrophenylhydrazone derivative was found to have a mp of 211—215°C

Cyclohexylidenemethane (CHYM) (C_7H_{12}): IR (cm^{-1}); 2920, 2850, 1655, 1450, and 890. NMR (ppm); a quintet peak at 8.45 (6 protons), a broad peak at 7.9 (4 protons), and a very sharp peak at 5.5 (2 protons).

1-Methylcyclohexene (MCHE) (C_7H_{12}): IR (cm^{-1}); 2920, 2860, 1455(sh), 1450, 1380, 1140, 915, 890, and 800.

Results and Discussion

In the gas-phase dehydration of tetrahydropyran-2-methanol (TPM), seven-membered compounds were detected using a catalyst other than the η-alumina catalyst, though a five-membered cyclopentanecarboxaldehyde (CPA) was mainly produced in the patent described above. Furthermore, there were many cases where an unsaturated ring ether compound, THO, was obtained in good yields. As the catalyst in this patent, there were employed one or more of the materials customarily referred to as dehydration catalysts, such oxides of the divalent or the polyvalent metals as alpha alumina, thorium oxide and titanium oxide. Catalysts with two functions, dehydration and hydrogenation, were also employed.

The results of the present investigation are illustrated in Table 2. Over the three commercial alumina catalysts, NC, ND and NP, the total amounts of the selectivities of THO and OXP were increased with a decrease in the acidity of a catalyst by analogy with its composition,[8] but that of CPA was decreased. The commercial alumina catalyst used is considered to participate with the reaction as in the dehydration of tetrahydrofurfuryl alcohol (TFA), and to produce seven-membered compounds. However, in the skeletal rearrangement during the dehydration of TPM, it might be a dominant characteristic that the selectivity of THO was higher over a catalyst used after the dehydration of TFA than over the same catalyst used directly.

The effect of pretreatment with an alumina catalyst with TFA upon the dehydration of alcohols has been little reported on; for example, the alumina catalyst pretreated with TFA decreased the rate of the dehydration of ethanol.[9] However, this effect, decreasing the selectivity of CPA and increasing that of THO, may result not only in a decrease in the dehydrating activity due to the occupation of the active points by TFA, but also in an essential change in a crystallinity of the catalyst. To elucidate these results, there is a need for further investigation of the effect of TFA on a catalyst. Therefore, the authors will report on this problem in a subsequent paper.

Over N631 as a silica-alumina catalyst, the selectivities of CPA, THO, and OXP decreased in all runs, but those of MCPE and CHE increased. MCPE and CHE are estimated to be derived from the decomposition of THO under the reaction conditions, because THO produced them selectively over N631 (Table 3).

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[8] H. Pines and J. Manassen, *Advance in Catalysis*, **16**, 53 (1966).

[9] C. H. Kline and J. Turkevich, *J. Am. Chem. Soc.*, **67**, 498 (1945).

TABLE 2. EFFECT OF REACTION CONDITIONS UPON SELECTIVITY[*1]

Catalyst[*2]	Temp. °C	Conversion, %	Selectivity, %						
			MCPE	CHE	MDHP	THO	OXP	CPA	CPEA
η	280	69.3	1.1	1.1	*t*[*3]	*t*	*t*	72.5	12.0
	300	73.9	2.3	2.0	1.0	*t*	*t*	72.5	5.3
	330	89.3	3.7	2.1	*t*	*t*	*t*	79.5	3.5
NC	310	42.1	3.2	1.8	2.1	12.5	13.2	49.5	7.6
	330	57.5	3.5	2.8	1.5	11.2	13.2	42.9	8.2
	350	78.2	3.5	3.0	1.3	7.5	12.1	50.2	8.2
ND	310	50.1	5.6	5.2	2.2	15.3	14.2	36.3	6.9
	330	53.6	5.6	5.1	1.7	10.3	11.1	40.2	7.9
	350	68.5	6.3	5.7	1.5	7.5	9.2	48.1	9.5
NDF	310	38.3	5.7	3.6	2.1	42.2	1.0	28.1	7.9
	330	63.2	7.8	6.2	2.0	37.3	1.3	26.3	6.7
	350	70.2	7.8	7.0	1.5	39.3	1.1	27.3	5.8
NP	310	41.2	3.2	2.1	9.7	16.5	12.7	30.1	17.5
	330	53.6	4.9	3.7	6.7	25.1	6.5	34.5	7.9
	350	71.2	5.8	4.3	3.2	23.7	7.2	37.2	8.2
NPF	310	32.1	2.5	1.2	2.4	48.1	4.8	27.1	14.2
	330	52.1	5.1	2.5	2.3	46.5	1.2	22.1	10.7
	350	79.5	5.2	3.1	1.0	42.5	*t*	36.0	6.2
N631	310	42.3	19.2	21.3	5.3	20.4	1.0	10.8	5.6
	330	54.3	11.3	14.3	9.7	24.1	*t*	17.1	6.1
	350	63.2	18.1	20.2	6.7	22.1	*t*	15.1	3.2
N208	390	53.9	6.3	4.2	10.5	39.1	*t*	5.2	14.3
	410	61.4	5.2	3.6	10.8	49.2	*t*	6.7	10.2
	430	82.1	2.3	6.3	8.3	52.4	*t*	5.4	7.7
N211	410	50.3	5.4	2.6	13.1	34.5	*t*	10.7	10.2
	430	61.3	7.3	5.3	12.1	39.3	*t*	11.6	8.9
	450	75.2	12.3	7.6	8.3	40.7	*t*	9.6	5.2
N111	410	47.2	4.3	23.2	7.4	32.5	*t*	1.0	3.9
	430	69.5	7.0	10.3	13.2	49.3	*t*	1.2	5.4
	450	97.4	5.2	11.0	12.3	50.2	*t*	1.0	2.5

[*1] Feed rate of TPM and flow rate of carrier gas were constant at 10 m*l*/hr and 10 m*l*/sec, respectively. Carrier gas was H_2 except in runs of N111 with N_2.

[*2] NDF and NPF were the catalysts pretreated with tetrahydrofurfuryl alcohol. Length of catalyst bed was 5 cm. In N111 runs, it was difficult to maintain the activity of the catalyst at constant, and therefore these data were the averages of the three kinds of reactions.

[*3] *t*=trace.

It has been reported[10)] that a dehydrogenation catalyst, for example, copper-chromium oxide, is applicable to the dehydration of some alcohols. Though such a catalyst, as was effected, decreased the conversion to some extent, it was used in the dehydration of TPM in order to study the reaction mechanism in more detail, for the activity of a dehydrogenation catalyst for isomerization during the dehydration of alcohols is markedly less than that of such a dehydration catalyst as an alumina. The results obtained are shown in Table 2. In all runs, only a trace of OXP was formed the main product being THO. Moreover, the amounts of MDHP increased with an increase in the reaction temperature, and also that of CPA decreased considerably, especially in N111 runs.

The behavior of THO and OXP under the present reaction conditions was also investigated. The results are shown in Table 3. As is shown in Table 3, in the use of the η-alumina catalyst, CPA

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10) J. Alagy, F. Defoor, S. Franckowiak, *Chem. Abstr.*, **62** 11701 (1964).

TABLE 3. BEHAVIOR OF THO AND OXP UNDER REACTION CONDITIONS*

Feed	Catalyst	Temp. °C	Conversion, %	Selectivity, % MCPE	CHE	CPA
THO	η	250	25	3	2	92
		290	46	3	7	87
		310	57	7	8	81
		330	72	12	11	72
	ND	290	16	42	53	*t*
		310	17	40	54	*t*
		350	18	41	53	*t*
	N631	290	23	41	51	3
		310	28	40	50	7
		350	35	45	46	2
	N208	450	13	44	43	2
	N111	450	7	41	42	2
					MTHP	
OXP	η	290	29		96	
		310	38		95	
		330	49		97	
		350	64		98	
	ND	350	7		*t*	
	N631	350	7		*t*	
	N208	460	7		*t*	
	N111	460	5		*t*	

* Carrier gas was H_2 except in N111 runs with N_2. Feed rate and flow rate of carrier gas were constant at 10 m*l*/hr and 10 m*l*/sec, respectively. Length of catalyst bed was 5 cm. *t*=trace.

TABLE 4. DEHYDRATION PRODUCTS OF CHC[*1]

Catalyst	Temp. °C	Conversion, %	Selectivity, % CHYM	MCHE	CHA[*2]
η	280	37.5	50.3	33.7	10.5
	310	53.2	48.3	38.6	7.5
	330	89.3	47.7	42.5	3.5
	350	94.2	46.5	44.8	4.1
ND	350	45.7	72.8	11.2	6.2
	370	57.5	70.5	13.2	5.1
	390	70.2	73.5	11.0	5.3
	410	85.5	74.6	10.6	6.2
N208	350	40.3	71.3	15.5	10.2
	370	59.6	72.6	18.4	3.5
	390	62.4	72.6	20.6	3.5
	410	75.4	71.8	21.5	1.0

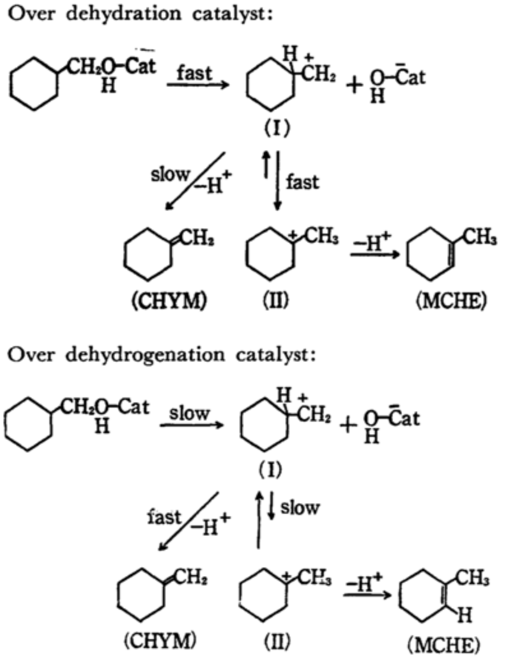
[*1] Carrier gas was H_2. Feed rate and flow rate were constant at 10 m*l*/hr and 10 m*l*/sec, respectively. Length of catalyst bed was 5 cm.

[*2] Cyclohexylcarboxaldehyde.

and MTHP were mainly obtained from the corresponding seven-membered compounds. However, over the other catalysts some skeletal rearrangement from seven to six or five occurred, though with difficulty.

In order to clarify the action of the catalyst in the dehydration of TPM, cyclohexyl carbinol (CHC), which is similar to TPM, was dehydrated over various catalysts. These results are shown in Table 4. It was seen that the dehydration occurred much faster over the η-alumina catalyst than over ND and N208 catalysts; that over the alumina catalyst the selectivity of CHYM was almost equal to that of MCHE; that the differences in between the selectivities of CHYM and MCHE lessened with an increase in the reaction temperature, and that, nevertheless, the differences were roughly constant until the reaction temperature over ND and N208 catalysts. Higher reaction temperatures were, moreover, required in runs with ND and N208 catalysts than in runs with the η-alumina catalyst.

The results obtained can be explained satisfactorily by the following general estimation.[8,11] The relative rate of carbonium-ion rearrangement in the dehydration mechanisms of several alcohols over alumina catalysts can be estimated from the relative stabilities of the carbonium ions involved; the stabilities are in the order: tertiary>secondary>primary. Therefore, rearrangements to olefines


Over dehydration catalyst:

Over dehydrogenation catalyst:

Fig. 3. Reaction pathway of dehydration of CHC.

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11) J. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

proceeding through primary carbonium ions are believed to occur at reasonably fast rates only on relatively strong acid sites, whereas those involving secondary and tertiary carbonium ions take place on both strong and weak acid centers.

Therefore, the reaction pathway of the dehydration of CHC may be concluded to be as shown in Fig. 3. Over a dehydration catalyst, such an alumina catalyst, the first step producing a carbonium ion (I) was very fast by virtue of its acidic sites,[8] so a large amount of I may exist in the reaction system. By the way, the deprotonation may change I into CHYM, or into MCHE *via* the methylcyclohexyl carbonium ion (II), which is produced by isomerizations and which rearranges its form to a more stable one under a high temperature. The faster the dehydration rate and the higher the reaction temperature, the smaller the difference in the selectivities between CHYM and MCHE may be. Over the dehydrogenation catalyst, on the contrary, the first dehydroxylation step producing an ionic structure (I) may be reasonably slow, and, moreover, the deprotonation may proceed extraordinarily fast as a result of the strong dehydrogenation activity of the catalyst.

Therefore, the reaction producing CHYM may be predominant, and a small quantity of MCHE may be produced by the deprotonation of the carbonium ion (II) rearranged from I.

Conclusion

The behavior of each catalyst has been clarified by elucidating the dehydration pathway of CHC. Over the dehydration catalyst, to put it simply, the rate of the dehydroxylation step is very fast, and that of the deprotonation step is very slow; therefore, the carbonium ion produced by the dehydroxylation migrates into the more stable form of the tertiary carbonium ion.[12] Over the dehydrogenation catalyst, it has been established that the deprotonation of the carbonium ion produced at the first step, contrary to the case of the dehydration catalyst, occurs faster than the migration of the primary carbonium ion to the tertiary one.

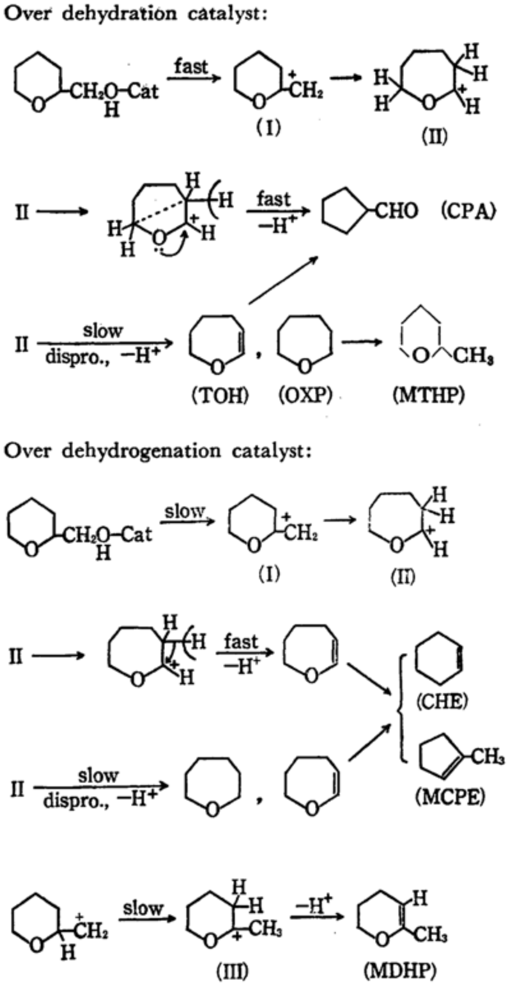

Fig. 4. Reaction pathway of dehydration of TPM.

Considering the results of the dehydration of CHC and the established reaction mechanism with respect to the dehydration of TFA, the skeletal rearrangement during the dehydration of TPM over various catalysts may be estimated to be as shown in Fig. 4. Over the dehydration catalyst, the carbonium ion (I) produced II by ring enlargement through a process analogous to the Wagner-Meerwein rearrangement, after which CPA was formed by ring-shrinking isomerization. In this step, the migration of the lone-electron pair of ring ethereal oxygen to the carbonium ion resulted in simultaneous deprotonation. As a result of the strong influence of the acidic sites of the catalysts on the lone-electron pair of ethereal oxygen, the electron transfer from the loosened electron pair to the carbonium ion may occur with ease; on the other hand, the weaker the acidity of the catalyst, the less may the lone pair of ethereal oxygen be affected. Therefore, over each Neobead catalyst having a weaker acidity on its surface than that of η-alumina, THO and OXP may be obtained from II by deprotonation and disproportionation; then THO may go through the step from II to CPA by means of protonation. On the other hand, though OXP can be isomerized to MTHP, its very slow reaction rate scarcely produced as much MTHP as was detected. Therefore, over the dehydration catalyst, the reaction pathway of I→II→CPA may be the main route.

On the contrary, over the dehydrogenation catalyst, the reaction step producing I was very slow and THO was the main product. Since the lone-electron pair of ethereal oxygen is not affected by the catalyst at all and may be very stable in itself,

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[12] H. Pines and W. O. Haag, *ibid.*, **83**, 2847 (1961).

it may be difficult for the electron transfer from ethereal oxygen to the carbonium ion to occur, resulting in the predominance of the deprotonation. Moreover, a small part of the THO and OXP was produced from II by disproportionation. Taking the affinity and the basisity of the catalyst for ethereal oxygen into account, the reaction pathway from I to III can be estimated over the dehydrogenation catalyst, wherein MDHP may be produced from III by deprotonation.

The affinity of each catalyst for the lone-electron pair may depend on its acidity, so alumina may be more active in responce to it than a nickel or copper-chromium oxide catalyst.

THO was obtained in the highest yield with a copper-chromium oxide catalyst 70 mm long under a 5 m*l*/sec flow of a hydrogen carrier and a TPM rate of 10 m*l*/hr at 430°C; therefore, the selectivity of THO was about 58%, and the conversion of TPM was about 87%. However, the patent literature regarding the dehydration of TPM, as has previously been mentioned, has touched upon THO only very briefly, treating it as a mere reaction intermediate, and has not isolated it from the reaction system at all. Consequently, the dehydration of TPM with the dehydrogenation catalyst may be considered to be a new and a more useful method by which THO was obtained in better yields than by the other reactions.

Therefore, a useful application of THO may be considered to be as follows; 5 m*l* of THO were added to 10 m*l* of a 0.01 N H_2SO_4 solution and the mixture was refluxed for 30 min at 90°C. Then the mixture was hydrogenated with 0.5 g (wet) of Raney Ni (W-2) at 100°C under an initial hydrogen pressure of 20 kg/cm^2 until no more hydrogen was absorbed. After the reaction product had then been filtrated, a vacuum distillation gave about 4.7 g of 1,6-D (84% yield. Moreover, 1,6-D was synthesized directly from TPM in a 42% yield by dehydration and subsequent hydrogenation *via* THO. This skeletal rearrangement during the dehydration of TPM may become a very useful reaction for synthesizing 1,6-D.

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