

The Acid-catalyzed Dehydration of 2-(1-Cyclohexenyl)cyclohexanol

Fukumi HIRANO, Makato KAMEZAWA, and Hideto KAMEI

*Department of Chemistry, Faculty of Science, Okayama
College of Science, Okayama 700*

(Received September 16, 1976)

Synopsis. The dehydration of 2-(1-cyclohexenyl)cyclohexanol(**3**) gave cyclohexylcyclohexenes, cyclohexylidenecyclohexane, cyclohexylidenecyclohexene, cyclohexylcyclohexadienes, cyclohexenylcyclohexenes, phenylcyclohexane, and dodecahydrodibenzofurans. The product distribution was quite sensitive to the solvents and catalysts employed.

It is well known that the self-condensation of cyclohexanone(**1**) gives 2-(1-cyclohexenyl)cyclohexanone(**2**), along with a small amount of 2-cyclohexylidenecyclohexanone. A number of related papers have been reported.¹⁻¹¹ However, few paper of the derivatives has been reported. We attempted the condensation of **1** and found that the self-condensate is obtained by heating **1** in benzene in the presence of *p*-toluenesulfonic acid and removing the resulting water in a good yield (90%). The partial reduction of the condensate gave the corresponding unsaturated alcohol (**3**). NMR analysis showed that both condensate(**2**) and the alcohol(**3**) include a small amount of those of cyclohexylidene type. But GLC failed to show the presence of the minor component in the mixture of both condensate and the alcohol. As part of studies on the derivatives of the condensate, we wish to describe the dehydration of the alcohol(**3**) in the presence of acid catalyst.

2-(1-Cyclohexenyl)cyclohexanol(**3**) was treated with 40% aqueous sulfuric acid at 100°C for 4 hr. The gas chromatogram of the reaction mixture is shown in Figure 1. The mixture was found to contain seventeen components including the unreacted material (peak 15). Each product was isolated by the use of both fractional distillation under reduced pressure and preparative GLC.

Peaks 1, 2, and 3 were also obtained by the dehydration of 2-cyclohexylcyclohexanol(**15**) under the same conditions. Peaks 4, 5, 6, and 7 were hydrogenated at 83°C in the presence of Raney-Ni in ethanol under hydrogen pressure (20 kg/cm²

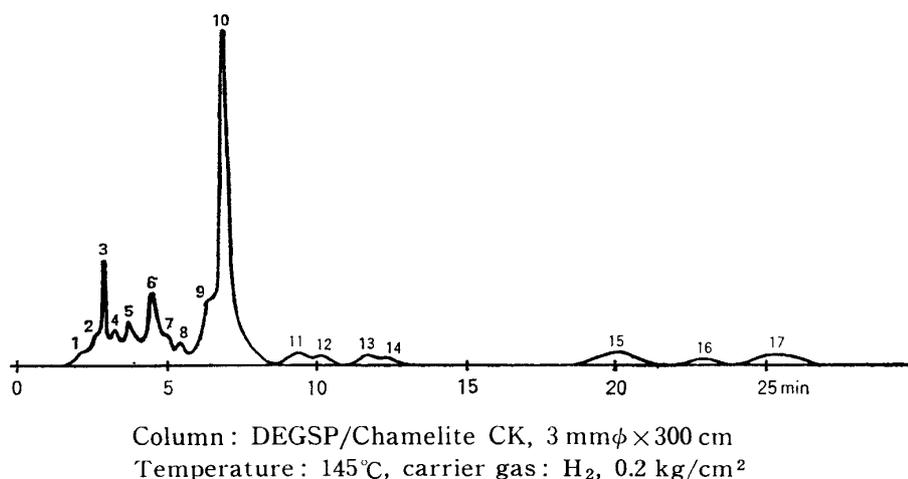
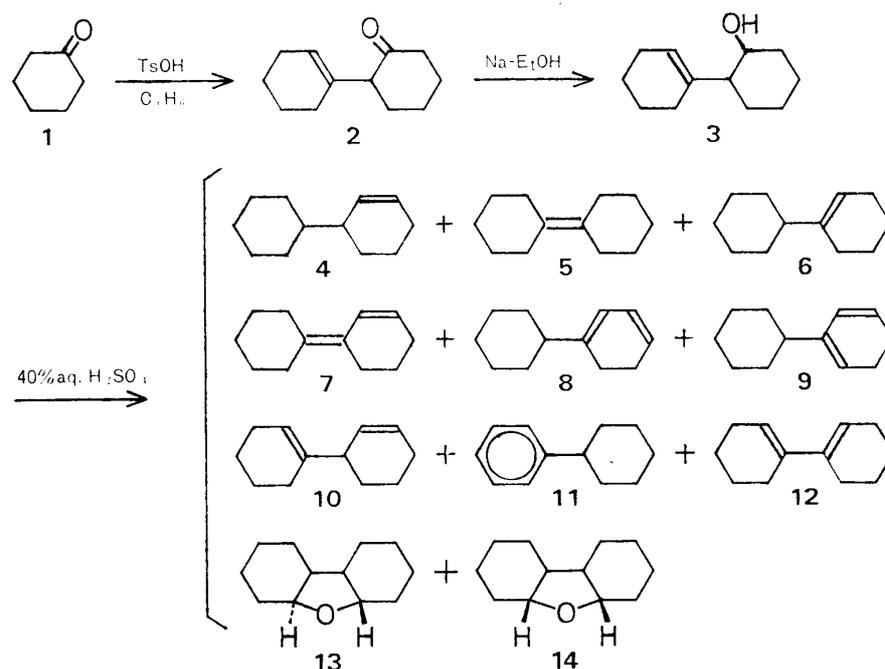


Figure 1. Gas chromatogram of dehydration products of 2-(1-cyclohexenyl)-cyclohexanol (**3**) (40% aq. H₂SO₄, 100°C, 4 hr)

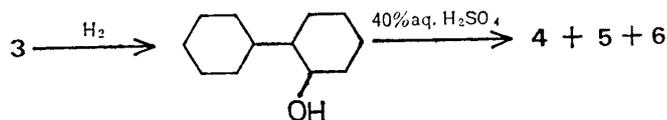
initial pressure). Analysis of the reaction mixture by GLC showed the quantitative formation of peak 3 as a main product and peak 1 as a minor product in a ratio of 3 : 2. Peaks 5, 6, and 10 added to maleic anhydride to form the crystalline adducts. Although peak 4 had the absorption for conjugated diene in UV spectrum, the compound did not react with maleic anhydride. The spectral data of peak 9 was consistent with those of the known compound, phenylcyclohexane.¹²⁾ The reaction of peak 10 with maleic anhydride gave a white crystal and the melting point coincided with that of bicyclohexenyl in literature.¹⁵⁾ On the basis of these results and the comparison of spectral patterns for individual peak, the structure of peaks 1—7, 9, and 10 were estimated; peak 1: 3-cyclohexylcyclohexene(**4**), peak 2: cyclohexylidenecyclohexane(**5**), peak 3: 1-cyclohexylcyclohexene(**6**), peak 4: 3-cyclohexylidenecyclohexene(**7**), peak 5: 1-cyclohexyl-1, 3-cyclohexadiene(**8**), peak 6: 2-cyclohexyl-1, 3-cyclohexadiene(**9**), peak 7: 1-(2-cyclohexenyl)cyclohexene (**10**), peak 9: phenylcyclohexane(**11**), and peak 10: 1-(1-cyclohexenyl)cyclohexene (**12**).

Peaks 11 and 13 are an isomer having a molecular formula C₁₂H₂₀O on the basis of elemental analysis. Their spectra were quite different from those of the products mentioned above and showed the presence of an ether bond which was suggested the structure of dodecahydrodibenzofuran derivatives. The *cis* and *trans* isomers of the compounds were assigned by the NMR spectrum, which indicated the characteristic signal of two methine protons adjacent to the ether bond in both isomers; peak 11: *trans*-dodecahydrodibenzofuran(**13**) and peak 13: the *cis* isomer (**14**). Peaks 8, 12, 14, 16, and 17 could not be isolated in the present work.



Scheme 1.

Products **4**, **5**, and **6** are assumed to be produced by the disproportionation during the dehydration of alcohol **3**, since the formation ratio of the products was in fair agreement with that of phenyl compound(**11**). A similar disproportionation would be expected to take place in the dehydration of 2-cyclohexylcyclohexanol (**15**). But the reaction of **15** gave mainly **6**, together with a small amount of **4** and **5**, and the phenomenon was not observed.



Scheme 2.

In order to obtain bicyclohexenyl(**12**) in a good yield, the dehydration of **3** was attempted in several reaction conditions. The results are given in Table 1. Optimum yield was obtained when the alcohol was heated in a 40% aqueous sulfuric acid solution. However, sulfuric acid in nonpolar solvents was markedly proceeded the polymerization of material. It is particularly interesting in this examination that the reaction in toluene in the presence of *p*-toluenesulfonic acid gave mainly **6**, but no bicyclohexenyl(**12**).

TABLE I. EFFECTS OF SOLVENT AND CATALYST IN DEHYDRATION OF 3

Material (mol)	Catalyst (mol)	Solvent (ml)	Reaction Condition Temp. (°C)	Time (hr.)	Formation Ratio in GLC (%)																
					Peak No																
					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
(0.0278)	H ₂ SO ₄ (0.0612)	H ₂ O (9)	100	4	0.3	1.7	6.1	2.1	2.4	3.9	1.7	1.5	8.0	46.8	5.1	2.8	3.1	0.8	4.8	0.7	4.3
"	" (")	Xylene (9)	"	"																	
"	" (0.0103)	Benzene (9)	83	"																	
(0.0278)	H ₃ PO ₄ (0.0612)	H ₂ O (9)	100	4	—	3.2	—	0.1	0.2	—	—	—	—	1.3	—	—	—	—	86.8	3.2	5.2
"	" (")	Benzene (9)	82	"	0.4	0.8	4.5	1.4	1.4	2.0	1.1	0.4	5.6	25.8	6.2	1.4	16.8	1.5	23.6	1.0	6.7
"	" (")	Toluene (9)	100	"	1.3	2.5	11.4	2.9	2.4	3.4	2.4	1.2	8.0	34.6	10.7	4.3	4.1	0.6	7.0	—	3.3
"	" (")	Xylene (9)	100	"	0.6	2.0	8.7	1.7	2.0	2.3	2.6	1.3	6.7	28.1	9.3	2.7	8.1	1.0	12.4	1.7	8.9
(0.0278)	(COOH) ₂ (0.0612)	H ₂ O (9)	100	4	—	0.7	2.0	trace	0.7	0.1	0.05	t	0.1	1.9	—	—	0.2	—	86.0	3.0	6.5
"	" (")	Benzene (9)	83	"	—	0.1	2.7	t	0.05	0.1	t	—	—	1.2	—	—	0.1	—	83.7	6.0	5.9
"	" (")	Toluene (9)	100	"	—	0.2	1.0	t	t	t	—	—	—	1.2	t	—	t	—	91.0	2.9	3.7
"	" (")	Xylene (9)	100	"	—	0.2	0.7	t	t	t	—	—	—	1.3	t	—	—	—	89.2	3.5	5.2
(0.0278)	TsOH (0.0612)	H ₂ O (9)	100	4	—	7.6	1.6	1.6	1.6	0.5	0.4	3.0	15.5	1.7	0.5	16.8	0.5	33.2	t	15.4	—
"	" (")	Benzene (9)	81	"	—	—	60.0	28.5	8.2	3.4	t	—	—	—	—	—	—	—	—	—	—
"	" (")	Toluene (9)	100	"	4.6	3.8	70.2	13.7	2.5	—	—	—	—	—	5.1	—	—	—	—	—	—
"	" (")	Xylene (9)	100	"	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
(0.0278)	ZnCl ₂ (0.0612)	Benzene (9)	170	1	—	12.4	17.8	33.2	10.0	4.4	2.9	2.1	0.6	5.1	0.4	—	—	—	11.1	—	—
"	" (")	Benzene (9)	80	4	0.2	0.5	9.5	6.9	0.5	0.4	0.2	t	t	0.1	7.2	1.4	17.3	1.4	44.9	0.2	9.2
(0.0278)	KHSO ₄ (0.0612)	Benzene (9)	180	1	—	3.2	4.2	3.3	6.5	4.2	1.6	1.5	4.6	10.1	2.2	1.3	4.1	2.1	31.2	4.1	16.0
"	" (")	Benzene (9)	80	4	—	—	2.5	0.2	0.1	0.2	t	—	t	1.4	—	—	—	—	83.9	4.7	7.1
(0.0278)	Phthalic anhyd. (0.0612)	Benzene (9)	80	4	—	—	0.3	t	t	t	—	—	—	2.5	—	—	—	—	87.7	4.7	4.7
(0.0278)	CF ₃ SO ₃ H (0.0612)	H ₂ O (9)	100	4	2.8	7.0	44.2	16.5	13.4	6.9	5.2	2.3	—	—	1.2	0.4	—	—	—	—	—

Experimental

IR spectra were recorded with a JASCO Model IR-2 spectrometer, and UV spectra with a Shimadzu Model UV-200 spectrometer in ethanol. NMR spectra were taken with a JEOL Model MH-60-II spectrometer in carbon tetrachloride containing TMS as an internal reference. Chemical shifts were recorded in δ unit, IR frequencies in cm^{-1} , and UV wavelengths in nm.

Self-condensation of Cyclohexanone(1). A mixture of 19.6 g (0.20 mol) of **1**, 20 ml of redistilled benzene and 0.76 g (4.0 mmol) of *p*-toluenesulfonic acid monohydrate was heated under reflux for 15 hr. The produced water was removed as an azeotrope with benzene. The reaction mixture was poured into 20 ml of water, neutralized with 5 % sodium carbonate and then extracted with two 50 ml portions of benzene. The benzene extracts were washed with water, dried over sodium sulfate and the benzene was evaporated. The residual oil was distilled to give 16.0 g (90 %) of 2-(1-cyclohexenyl)cyclohexanone(**2**) containing a small amount of 2-cyclohexylidenecyclohexanone: bp 110–112 °C/2 mmHg, d_4^{25} 1.0063, n_D^{25} 1.5049. The mixture showed a single, symmetrical peak in GLC and was not able to be isolated.

Preparation of 2-(1-Cyclohexenyl)cyclohexanol(3). To 17.8 g (0.10 mol) of **2** in 30 ml of ethanol was added 5.1 g (0.22 gramatom) of metallic sodium over a period of 3 hr. The temperature was maintained at 80–85 °C during the addition, and the refluxing was continued for a further 1 hr period. The solvent was evaporated and was treated as usual. Distillation gave a colorless oil (13.0 g, 72 %); bp 128 °C/8 mmHg, d_4^{25} 1.0020, n_D^{25} 1.5061.

Dehydration of 2-(1-Cyclohexenyl)cyclohexanol(3). A mixture of 50 g of **3** and 150 ml of 40 % aqueous sulfuric acid was heated at 100 °C under stirring for 4 hr. The reaction mixture was treated as usual. The fractional distillation gave 33.5 g (67 %) of a colorless liquid. GLC showed the distillate to contain seventeen components including unreacted alcohol, as shown in Figure 1. Each component was isolated by preparative GLC using a DEGS column at 130 and 150 °C.

3-Cyclohexylcyclohexene(4): d_4^{25} 0.8819, n_D^{25} 1.4849 (lit.,¹³) n_D^{20} 1.4941). MR : 53.29. Calcd for $\text{C}_{12}\text{H}_{20}$: 52.75. IR : 3037 (m), 1639 (w), 716 (w). NMR : 0.45–2.86 (m, 18 H), 5.07 (m, 2H).

Cyclohexylidenecyclohexane(5): d_4^{25} 0.8924, n_D^{25} 1.4852. MR : 52.68. Calcd for $\text{C}_{12}\text{H}_{20}$: 52.75. IR : 3040(w), 1622 (w). NMR : 0.80–1.69 (m, 12H), 1.88 (br. s, 8 H).

1-Cyclohexylcyclohexene(6): d_4^{25} 0.9025, n_D^{25} 1.4928 (lit.,¹⁴) n_D^{20} 1.4945). MR :

52.79. Calcd for $C_{12}H_{20}$: 52.75. IR: 3038 (m), 1653 (w), 798 (m). NMR: 0.78—2.71 (m, 19 H), 5.17 (br. s, 1 H).

3-Cyclohexylidenecyclohexene (**7**): d_4^{25} 0.9080, n_D^{25} 1.4922. MR: 51.69. Calcd for $C_{12}H_{18}$: 52.28. IR: 3005 (m), 1644 (w), 717 (m). NMR: 0.74—2.32 (m, 16 H), 5.47 (m, 2 H). UV: λ_{max} 259 (ϵ_{max} 8560).

1-Cyclohexyl-1,3-cyclohexadiene (**8**): d_4^{25} 0.9129, n_D^{25} 1.5069. MR: 52.80. Calcd for $C_{12}H_{18}$: 52.28. IR: 3016 (m), 1644 (w), 806 (m), 720 (m). NMR: 0.72—1.92 (m, 11 H), 2.01 (br. s, 4 H), 5.20 (m, 1 H), 5.37 (m, 1 H), 5.58 (br. s, 1 H). UV: λ_{max} 245 (ϵ_{max} 8700).

2-Cyclohexyl-1,3-cyclohexadiene (**9**): d_4^{25} 0.9210, n_D^{25} 1.5105. MR: 52.65. Calcd for $C_{12}H_{18}$: 52.28. IR: 3028 (m), 1644 (w), 688 (m). NMR: 0.88—1.94 (m, 11 H), 2.02 (br. s, 4 H), 5.12—5.82 (m, 3 H). UV: λ_{max} 257 (ϵ_{max} 7680).

1-(2-Cyclohexenyl)cyclohexene (**10**): IR: 3010 (m), 1678 (w), 1635 (w), 864 (m), 845 (m), 720 (m). NMR: 0.93—1.82 (m, 8 H), 1.82—2.88 (m, 7 H), 4.85—5.97 (m, 3H).

Phenylcyclohexane (**11**): d_4^{25} 0.9408, n_D^{25} 1.5297 (lit.,¹²) n_D^{20} 1.5258. MR: 52.51. Calcd for $C_{12}H_{16}$: 51.82. IR: 3054 (m), 3019 (m), 1600 (m), 1488 (m), 745 (s), 692 (s). NMR: 1.08—2.68 (m, 11 H), 6.96 (s, 5 H). UV: λ_{max} 247 (ϵ_{max} 42800).

1-(1-Cyclohexenyl)cyclohexene (**12**): d_4^{25} 0.9605, n_D^{25} 1.5330. MR: 52.34. Calcd for $C_{12}H_{18}$: 52.28. IR: 3043 (m), 1620 (w), 710 (m). NMR: 1.67 (m, 8 H), 2.15 (br. s, 8 H), 5.75 (br. s, 2 H). UV: λ_{max} 238 (ϵ_{max} 10500).

Found: C, 89.09; H, 11.18 %.

Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18 %.

trans-Dodecahydrodibenzofuran (**13**): d_4^{25} 1.0016, n_D^{25} 1.4941. MR: 52.32. Calcd for $C_{12}H_{20}O$: 52.66. IR: 1165(m), 1110 (m), 995 (s), 984 (s). NMR: 0.86—2.68 (m, 18 H), 4.18 (m, 2 H).

Found: C, 80.15; H, 11.23 %.

Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18 %.

cis-Dodecahydrodibenzofuran (**14**): d_4^{25} 1.0115, n_D^{25} 1.4943. MR: 51.83. Calcd for $C_{12}H_{20}O$: 52.66. IR: 1170 (s), 1150 (s), 955 (s). NMR: 0.80—2.45 (m, 18H), 3.50 (m, 1 H), 4.05 (m, 1 H).

Found: C, 80.17; H, 11.02 %.

Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18 %.

Reaction of the Dehydrates of 3 with Maleic Anhydride. The mixture of the dehydrates (1.0 g) with maleic anhydride (0.5 g) was heated at 100 °C for 4 hr with stirring. GLC analysis of the reaction mixture indicated the disappearance of

peak 5, 6, and 10 in Figure 1. The resulting crystal was recrystallized from benzene-cyclohexane (1 : 1) to obtain the adduct of diene **12**. Mp 122.0—122.5 °C (lit.,¹³) 122.5—123.5 °C). IR (in Nujol): 1850 (m), 1770 (s), 1220 (s), 1014 (m), 931 (s), 909 (s). NMR: 1.10—2.18 (m, 12 H), 2.18-2.90 (m, 6 H), 3.20 (m, 2 H).

Hydrogenation of the Dehydrates containing 7, 8, 9, 10, 11, and 12. In a 100 ml autoclave were placed 10 g of the dehydrates, 1.0 g of Raney-Ni, and 40 ml of ethanol. Hydrogen (20 kg/cm²) was changed after purging air twice with hydrogen and the mixture was stirred at 83°C for 10 hr. GLC analysis of the reaction mixture showed the formation of monoenes **4** and **6** in a ratio of 2 : 3 at 98 % conversion. Ethanol was removed by evaporation and the residue was distilled in vacuo to give 7.7 g of a mixture of **4** and **6**, bp 100—105 °C/30 mmHg.

Preparation of 2-Cyclohexylcyclohexanol (15). 2-(1-Cyclohexenyl)cyclohexanone (**2**) was hydrogenated over a Nickel catalyst (1.0 g) in n-hexane (50 ml) under hydrogen pressure (35 kg/cm²) at 150—160 °C for 8 hr. After the uptake of hydrogen ceased, the solution was filtered and the solvent was evaporated. The residue thus obtained was distilled under reduced pressure; **15** (39.4 g, 77 %) was thus obtained as a colorless oil. Bp 130—131 °C/8 mmHg, d_4^{25} 0.9769, n_D^{25} 1.4968.

Dehydration of 2-Cyclohexylcyclohexanol (15). By a similar way to the dehydration of **3**, **15** (5.0 g) was treated to give mainly 1-cyclohexylcyclohexene(**6**), along with a small amount of 3-cyclohexylcyclohexene(**4**) and cyclohexylidenecyclohexane(**5**) (4.2 g, 84 %).

The authors wish to thank Professor S. Wakabayashi for many helpful discussions and suggestions during this work.

References

- 1) O. Wallach, *Ber.*, **40**, 70 (1907).
- 2) A. Haller, *Ann. Chem.*, **1**, 295 (1924).
- 3) J. Reese, *Ber.*, **75**, 384 (1942).
- 4) M. H. Gault, L. Daltroff, and J. Eck-Tridom, *Bull. Soc. Chim. Fr.*, **12**, 952 (1945).
- 5) J. Stanek, *Chem. Listy*, **46**, 110 (1952).
- 6) J. Plesek, *Collection Czech. Chem. Commun.*, **21**, 375 (1956); *Chem. Listy*, **50**, 252 (1956).
- 7) E. Wenkert, S. K. Bhattacharya, and E. M. Willson, *J. Chem. Soc.*, **1964**, 5617.
- 8) D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, **1965**, 1662.
- 9) T. A. Favorskaya, A. S. Lozhenitsyna, G. A. Kalabin, and V. M. Vlasov, *Zh. Org. Khim.*, **2**, 739 (1966).
- 10) K. K. Kelly and J. S. Mathews, *J. Chem. Eng. Data*, **14**, 276 (1969).
- 11) H. Hayashi, H. Nishi, and T. Abe, *Nippon Kagaku Kaishi*, **1973**, 1392.

- 12) (a) C. J. Pouchert, "The Aldrich Library of Infrared Spectra" second edition, Aldrich Chemical Company, Inc., p 501 (1975). (b) C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra" Vol. IV, Aldrich Chemical Company, Inc., p 6 (1974).
- 13) R. A. Benkeser, R. K. Agnihotri, M. L. Burrous, E. M. Kaiser, J. M. Mallan, and P. W. Ryan, *J. Org. Chem.*, **29**, 1313 (1964).
- 14) F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).
- 15) E. E. Gruber and R. Adams, *J. Amer. Chem. Soc.*, **57**, 2555 (1935).