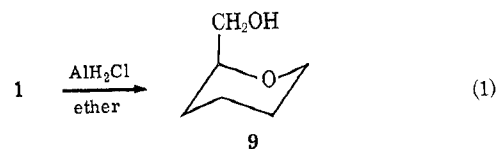


generate the bicyclic molecule **5** now containing the bromine atom in the α position. Both the exo and endo monobromo isomers are obtained. No firm decision could be made as to which path of reaction (A or B) is preferred or whether both routes are followed, one giving the exo and the other the endo monobromo isomer. However, path B was considered² to be the preferred route on the basis of the apparent greater ease of cleavage of the C-5-O-6 bond in the hydrolysis or alcoholysis of substituted bicyclic structures such as **1**.

Work on the hydrogenolysis of acetals and ketals by mixtures of LiAlH_4 and AlCl_3 in ether³ has indicated that, as is the case for the hydrolysis of acetals, the rate-controlling step of the hydrogenolysis reaction is the cleavage of the C-O bond, weakened by the association of its oxygen atom with the Lewis acid. However, the subsequent addition of the hydride ion to the resulting oxocarbenium ion is very fast and irreversible. Product analysis then provides clear evidence of the preferred route of bond cleavage.

We have subjected **1** to hydrogenolysis by AlH_2Cl , prepared from the appropriate quantities of LiAlH_4

and AlCl_3 ,⁴ and found that 2-hydroxymethyltetrahydropyran (**9**, eq 1) was produced in excellent yield.



No other product could be detected by gas-liquid chromatography (glc) of the reaction mixture. Since the model of **1** shows that both oxygen atoms are readily accessible to the Lewis acid (AlH_2Cl), this reaction provides evidence to support our view that acid-catalyzed bromination of **1** occurs by path B.

Experimental Section

To a stirred solution of lithium aluminum hydride (0.427 g, 0.01125 mol) in 10 ml of dry ether kept at 5° by an ice bath, was added dropwise 10 ml of ether solution of aluminum chloride (1.49 g, 0.01125 mol). After the addition, the solution was stirred at room temperature for 15 min. To this stirred mixture was then slowly added a solution of 1.71 g (0.015 mol) of 6,8-dioxabicyclo[3.2.1]octane (**1**) in 10 ml of dry ether. The mixture was then stirred at room temperature for 2 hr whereupon a 15% aqueous solution of potassium hydroxide was slowly added until no further reaction occurred. The solids were removed by filtration and washed with ether. The combined ether solutions were dried (Na_2SO_4) and freed from solvent. The residue was analyzed by glc with a column of 20% butanediol succinate on Chromosorb W 60-80 mesh. The compound 2-hydroxymethyltetrahydropyran was obtained in 93% yield as the only detectable product.

Registry No.—1, 280-16-0.

Acknowledgment. We thank the National Research Council of Canada for financial assistance in this work.

(4) U. E. Diner, H. A. Davis, and R. K. Brown, *ibid.*, **45**, 207 (1967).

Alumina-Catalyzed Dehydration of Substituted Cyclohexanones. Comments on the Mechanism of Hydrocarbon Formation

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Over the past several years, our investigations of alumina-catalyzed dienol dehydration^{1,2} have led us to investigate the formation and subsequent reactions of various 1,3-cyclohexadienes.³ Several workers^{4,5} have alluded to the possibility of the intermediacy of 1,3-cyclohexadiene in the alumina-catalyzed dehydration of cyclohexanone, even though it is found only as a minor product. Most of the reported product analyses, however, were incomplete, due mainly to difficulties in the separation of complex hydrocarbon mix-

(1) C. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

(2) C. Spangler, *ibid.*, **31**, 346 (1966).











(3) C. Spangler and R. Hennis, *ibid.*, **36**, 917 (1971).

(4) H. Adkins and S. Watkins, *J. Amer. Chem. Soc.*, **73**, 2184 (1951).

(5) G. Woods, *U. S. Dept. Com., Office Tech. Serv. AD 278,110*, 29 (1962).

(3) B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, **42**, 990 (1964); **43**, 1030 (1965).

TABLE I

Ketone, catalyst ^a (temp, °C, column length, cm)	% conversion ^b	% of total hydrocarbon ^c product						
								
2, A (400, 26)	45.5	0.0	27.5	34.4	2.3	8.8	7.5	11.9
2, A (300, 26)	20.2	0.0	32.0	67.3	Trace	0.6	0.1	0.0
2, A (300, 18)	1.5	0.0	28.8	66.7	Trace	1.7	Trace	2.8
2, A (400, 18)	26.4	0.0	37.2	57.6	1.3	3.0	0.6	0.3
2, B (300, 18)	8.9	0.0	28.0	72.0	0.0	0.0	0.0	0.0
2, B (400, 18)	38.6	Trace	36.3	53.1	0.2	3.8	4.6	0.1
2, C (300, 18)	13.5	0.0	30.0	69.9	0.0	0.0	0.0	0.0
2, C (400, 18)	36.6	0.0	33.6	57.3	2.2	3.5	0.2	2.6
3, A (300, 26)	40.0	98.7	0.0	0.0	0.4	0.0	0.0	0.9
3, A (400, 26)	60.3	81.0	0.0	0.0	2.1	5.0	4.6	6.0
3, A (300, 18)	36.0	99.8	0.0	0.0	0.2	0.0	0.0	0.0
3, A (400, 18)	58.3	95.0	0.0	0.0	2.6	0.5	0.9	1.0
3, B (300, 18)	12.4	99.9	0.0	0.0	0.1	0.0	0.0	0.0
3, B (400, 18)	42.0	91.5	Trace	2.7	1.1	1.8	0.1	1.9
3, C (300, 18)	25.5	99.9	0.0	0.0	0.1	0.0	0.0	0.0
3, C (400, 18)	37.0	80.0	Trace	16.3	0.2	0.4	0.6	2.0
  								
1, A (300, 26)	51.6	98.6	1.3	0.1				
1, A (400, 26)	78.2	90.0	8.2	1.8				
1, A (300, 18)	19.0	99.2	0.8	0.0				
1, A (400, 18)	42.2	96.0	2.8	0.6				
1, B (300, 18)	21.2	98.7	1.3	0.0				
1, B (400, 18)	55.4	95.4	4.1	0.5				
1, C (300, 18)	9.8	99.7	0.3	0.0				
1, C (400, 18)	49.0	97.0	2.8	0.2				

^a Catalyst A is KA 101 (Kaiser Chemicals); B is AL-0104 (Harshaw Chemical Co.); C is Houdry HA-100S (Houdry Process and Chemical Co.). ^b Expressed as percentage of original ketone converted to dehydration products, including phenolic material. ^c Methylene cyclohexene and unconjugated dienes make up the balance to equal 100% of total hydrocarbon content.

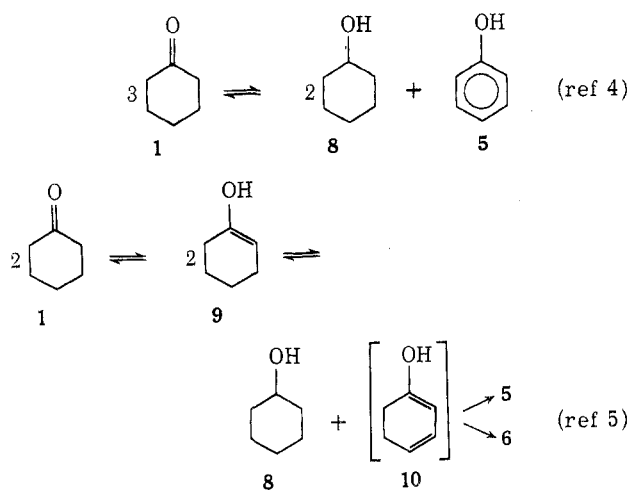
tures into their respective components. Our recent experience with such complex mixtures of this type prompted us to reinvestigate the dehydration of cyclohexanone and to extend our studies to include the methylcyclohexanones.

In the present study, cyclohexanone (1) was dehydrated over alumina at 300 and 400°. Three different alumina catalysts were utilized to determine the presence or absence of specific catalytic effect on our product distributions. Conversions of the cyclohexanone to products varied from 10 to 78%, enabling us to determine if product distributions varied significantly with percentage conversion. Gpc analysis of the lower temperature dehydration products showed them to be quite similar to those reported previously;^{4,5} however, dehydration at 400° produced much greater amounts of 1,3-cyclohexadiene than had been indicated earlier. Similarly, 2-methylcyclohexanone (2) and 4-methylcyclohexanone (3) were also dehydrated as described for 1. Product distributions (Table I) of both of these at 400° also revealed much greater concentrations of dienes than one would expect from the simple disproportionation mechanisms proposed earlier.^{4,5}

In Table I we have indicated only the product distribution for the hydrocarbon fraction. In all cases phenolic and, to a lesser extent, polymeric materials were also formed. As we did not intend to discuss this aspect of the mechanism, no effort was made to quantitatively determine the phenolic fraction of the total

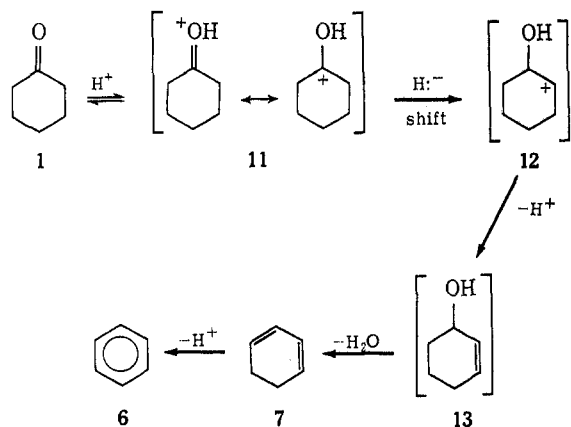
crude product. Thus dehydration of 1, 2, or 3 yields a mixture of hydrocarbons (see Table I), a phenol, traces of the corresponding cyclohexanol, and residual ketone, as reported previously.^{4,5} Table I emphasizes the make-up of the hydrocarbon fraction *only*.

Adkins and Watkins⁴ initially reported that alumina dehydration of cyclohexanone (1) yielded a mixture of cyclohexene (4), phenol (5), and unchanged 1. Woods,⁵ in a more detailed study, also confirmed the presence of both benzene (6) and 1,3-cyclohexadiene (7) in the product mixture, but was unable to obtain

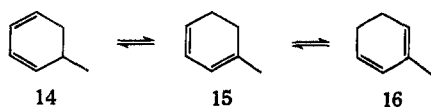


accurate quantitative product distributions. In both studies, however, the major products were cyclohexene and phenol. These results prompted the above workers to postulate disproportionation schemes for these reactions prior to catalytic dehydration. Thus, dehydration of **8** would yield **4**, the normal dehydration product, while either dehydration or dehydrogenation of **10** would yield **6** or **5**, respectively. Both the dehydration and dehydrogenation steps are well-known reactions over alumina at elevated temperature. Presumably, any 1,3-cyclohexadiene in the product would be formed by direct dehydration of **1**, probably *via* the enol **9**. Our results indicate that the Adkins-Watkins mechanism is probably the first step in the reaction, as only this pathway can account for the total quantity of hydrocarbons observed (theoretical limit is 67 mol% for 100% dehydration).

These observations raise the question of whether cyclohexanols are the precursors of all nonaromatic products, or if some pathway other than cyclohexanone disproportionation is operative. Corkern and Fry⁶ have recently reported the partial dehydration of both **1** and **2** over polyphosphoric acid at elevated temperature, obtaining benzene and toluene, respectively, although in low yield (3 and 5%). They postulate that dehydration occurs through rearrangement of an α -hydrogen or α -alkyl group to the conjugate acid of the carbonyl, followed by dehydration and dehydrogenation. This mechanism can easily be adapted to the production of a conjugated cyclic diene, proceeding *via* a 2-cyclohexen-1-ol.



Similarly, **2** and **3** would yield 2-methyl-1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene, respectively, as well as toluene. Under the conditions of methylcyclohexanone dehydration (300–400°), however, either of these dienes would rapidly isomerize either by thermal [1,5] sigmatropic migration of hydrogen or by acid-catalyzed routes,⁷ by which methylencyclohexene and the 1,4-dienes may also be obtained. The data in Table I clearly show that the dienes are more extensively isomerized at 400 than at 300°. This is in agreement with our previous work regarding thermal and acid-catalyzed isomerization of

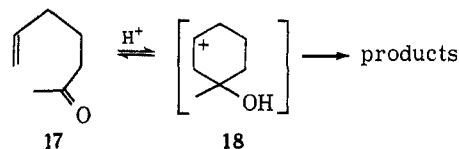


(6) W. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

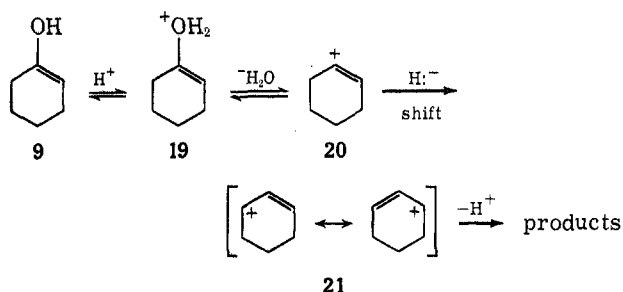
(7) R. Bates, E. Caldwell, and H. Klein, *J. Org. Chem.*, **34**, 2615 (1969).

methyl-1,3-cyclohexadiene mixtures in this temperature range.³

Similar intermediates have been postulated by Descotes, *et al.*,⁸ in the cyclodehydration of δ,ϵ -unsaturated ketones over both alumina and polyphosphoric acid, yielding product mixtures composed of aromatics, 1,3-cyclohexadienes, monoolefins, and some 1,4-cyclohexadienes.



An alternate pathway to the cyclic dienes might also occur through the enol (however, we feel that **20** would only form with great difficulty in the vapor phase) and is not as likely as a reaction proceeding through intermediates such as **12** or similar intermediates.



In order to eliminate the possibility that dienes were being formed by direct dehydrogenation of the monoolefins, 4-methyl-1-cyclohexene (**22**) was passed over all three of the catalysts employed in this study at 400°. No dienes or aromatic products were obtained, although between 2 and 5% of the olefin was isomerized to 1-methyl-1-cyclohexene. We conclude from our experiments that diene formation is a process totally unrelated to the disproportionation-dehydrogenation sequence yielding the monoolefins and phenolic products and, in fact, is much more important than any previous workers had indicated, especially under conditions of high conversion. It is probable that dienes result from an acid-catalyzed dehydration route similar to that proposed by Corkern and Fry,⁶ followed by isomerization *via* consecutive sigmatropic hydrogen shifts and/or acid-catalyzed isomerization.³

Experimental Section⁹

Nature of Catalysts.—The three catalysts employed in this study have different characteristics. Catalyst A (Kaiser Chemi-

(8) G. Descotes, M. Fournier, and R. Mugnier, *Bull. Soc. Chim. Fr.*, 382 (1968).

(9) Gas-liquid partition chromatography was performed with an Aerograph Model 202-1B dual-column instrument equipped with a Hewlett-Packard Model 3370A electronic integrator for peak area measurement; dual 15–15% TCEP on 60–80 mesh Chromosorb W columns were utilized for the analysis of the hydrocarbon fraction; dual 6 ft–15% Carbowax 20M on 60–80 mesh Chromosorb W columns were utilized for total analysis of the product mixtures. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202; nmr spectra were obtained with a Varian A60-A using TMS as an internal standard (CDCl₃ solvent). All compounds were identified by both uv and nmr spectra and glpc retention times, and comparison to authentic samples.

cals, KA-101)¹⁰ is a quasiamorphous alumina, as determined by X-ray diffraction,¹¹ which can be referred to as χ - ρ alumina. The X-ray pattern is diffuse and intermediate between amorphous ρ and the more crystalline χ , but distinct from each.¹¹ A minor phase (ca. 20–30%) which coexists with the above dominant phase resembles γ -alumina but is more diffuse. The catalyst is supplied as pellets, 8–14 mesh, with a surface area of 360 m²/g. Sodium content is 0.40%, expressed as Na₂O.

Catalyst C (Houdry HA-100S)¹² is a γ -alumina catalyst which has been described as essentially nonacidic,¹³ while catalyst B (Harshaw AL-0104)¹⁴ is also a γ -alumina, classed as weakly acidic. Both B and C have been utilized as dehydration catalysts in a large number of published examples by several different workers.¹³ C has a sodium content of 0.1–0.2%, while B has a content of 0.4% expressed as Na₂O.

Catalysts were prepared by heating at the dehydration temperature for a period of 1 hr under reduced pressure (20–25 mm). After this period they were used directly as described below.

Dehydration of Cyclohexanone (1).—Cyclohexanone¹⁵ (20 g, 0.21 mol) was added dropwise at a rate of 0.25 ml/min through a 22-mm Pyrex tube packed to a depth of either 18 or 26 cm with alumina and externally heated with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temperature, washed with water, filtered through anhydrous magnesium sulfate, and analyzed immediately by glpc (12.8 g, 72%).¹⁶ No attempt was made to maximize this yield, although we recognize that this method discriminates against isolating phenolic-type products. High-boiling materials were also condensed on the inside of the exit tube from the dehydration chamber. This was shown to consist mainly of phenolic material and higher-boiling residues. Since our main interest was in the hydrocarbon fraction, we made no further effort at a complete material balance for all products.

The dehydration products were identified by collecting each peak emanating from the chromatograph in glass V tubes immersed in cooling baths: (1) in isooctane for uv analysis, and (2) in CDCl₃ for nmr analysis. In each case, the product was identified by comparison of the uv, nmr, and glpc retention times to those of authentic samples in our laboratories.

Dehydration of 4-Methylcyclohexanone (3).—Methylcyclohexanone¹⁷ (20 g, 0.18 mol) was dehydrated at 400° as described above for cyclohexanone, yielding 14.9 g (87%)¹⁸ of the product, which was analyzed immediately by glpc.

Dehydration of 2-Methylcyclohexanone (2).—2-Methylcyclohexanone¹⁹ (15 g, 0.13 mol) was dehydrated at 400° as described above, yielding 9.3 g (73%)²⁰ of product, which was immediately analyzed by glpc.

Thermolysis of 4-Methyl-1-cyclohexene (22).—4-Methyl-1-cyclohexene (10 g) was thermolyzed by passage through an 18-cm column packed with either A, B, or C, at 400°. Immediate glpc of the recovered product (>95% in all three cases) revealed that the only new product was 1-methyl-1-cyclohexene (2–5%).

Registry No.—1, 108-94-1; 2, 583-60-8; 3, 589-92-4; alumina, 1344-28-1.

(10) Kaiser Chemicals, Division of Kaiser Aluminum and Chemical Corp.

(11) Private communication, Dr. Robert B. Emerson, Staff Research Associate, Chemical Aluminas, Kaiser Chemicals, Baton Rouge, La.

(12) Houdry Process and Chemical Co.

(13) See, for example, L. Klemm, J. Shabtai, and D. Taylor, *J. Org. Chem.*, **33**, 1480 (1968), and references therein.

(14) The Harshaw Chemical Co., Division of Kewanee Oil Co.

(15) J. T. Baker Chemical Co.

(16) For catalyst A (26-cm column) the following total product analysis was obtained: recovered **1**, 21.8%; total dehydration products, 78.2%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon content.

(17) Chemical Samples Co.

(18) For catalyst A (26-cm column) the following total product analysis was obtained: recovered **3**, 39.7%; total dehydration products, 60.3%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon present.

(19) Aldrich Chemical Co.

(20) For catalyst A (26-cm column) the following total product analysis was obtained: recovered **2**, 54.5%; total dehydration products; 45.5%. The hydrocarbon analysis is shown in Table I, recalculated on the basis of 100% total hydrocarbon present.

Mechanism of Redox Decomposition of Oxymercured *cis*-2-Butene in Aqueous Solution

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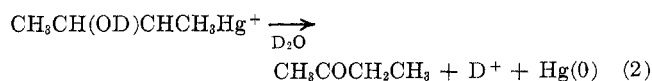
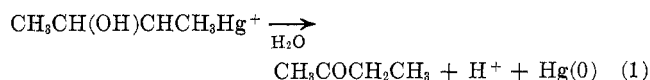
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Received October 1, 1971

Olefins are oxidized by mercuric ion in aqueous acid to yield unsaturated aldehydes,^{1–4} saturated aldehydes,^{2,3} allylic alcohols,⁴ or saturated ketones.⁵ Saturated ketones are obtained under milder conditions than unsaturated aldehydes or allylic alcohols. For example, acetone is obtained from propene at about 50° and methyl ethyl ketone from *trans*- or *cis*-2-butene below room temperature,⁶ whereas acrolein and crotonaldehyde are formed at about 80°¹ and allyl alcohol at 90°.⁴ These reactions proceed as the redox decomposition of hydroxymercured olefins,⁷ and their reaction rates are first order with respect to the mercurials,^{1,8} without depending on free mercuric ion in the case of ketone formation.⁸

Since hydroxymercured *cis*-2-butene is sufficiently stable at low temperatures, the reaction process can be pursued by nmr spectroscopy *in situ* after the temperature of the solution is raised abruptly. Time-sequential spectra following the redox decomposition of hydroxy- and deuterioxymercured *cis*-2-butene are shown in Figure 1.⁹

It is obvious in Figure 1 that methyl ethyl ketone is the sole product and, interestingly, no deuterium is incorporated into the product from the solvent D₂O. Therefore, reaction equations are presented as follows, where the mechanism of two electron transfer, *i.e.*, no association of free mercuric ion, is postulated on the basis of the reaction kinetics.⁸



The reaction product from the D₂O solution was analyzed by mass spectroscopy and the following deuterium distribution was obtained: $d_0 = 97.3\%$, $d_1 = 2.4\%$, $d_2 = 0.3\%$, $d_3 = d_4 = \dots = d_8 = 0.0\%$. Thus the result shown in eq 2 was confirmed unequivocally. A concerted mechanism is, therefore, suggested, whereby an intramolecular hydrogen shift occurs and

(1) B. C. Fielding and J. Roberts, *J. Chem. Soc. A*, 1627 (1966).

(2) J. C. Strini and J. Metzger, *Bull. Soc. Chim. Fr.*, 3145, 3150 (1966).

(3) B. Charavel and J. Metzger, *ibid.*, 4865 (1968).

(4) H. B. Tinker, *J. Organometal. Chem.*, **32**, C25 (1971).

(5) Y. Saito and M. Matsuo, *ibid.*, **10**, 527 (1967).

(6) Y. Saito, 1st Japan-U. S. S. R. Seminar on Catalysis, Novosibirsk, July 1971.

(7) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(8) M. Matsuo and Y. Saito, *Bull. Chem. Soc. Jap.*, **44**, 2889 (1971).

(9) Chemical shifts of α , β , γ , and β' protons of both hydroxy- and deuterioxymercured *cis*-2-butenes were δ 3.01, 3.86, 1.19, and 1.38, respectively, and their coupling constants for the sets of $\alpha\beta$, $\beta\gamma$, and $\alpha\beta'$ protons were 4.0, 6.0, and 7.6 Hz, respectively, where designation of α , β , β' , etc., was made from the mercured carbons.