hr. on a steam bath. The solvent was removed and the n.m.r. spectrum of the residue (solid), determined in deuteriochloroform, was found to be identical to *trans* XI.

Similar experiments were carried out using a mixture of XI (*cis* and *trans*) and X. The n.m.r. spectrum of the product was identical to that of the starting mixture.

Attempted Thermal Decomposition of X and XI.—A mixture (0.25 g.) of X and XI (*cis* and *trans*) was heated in a nitrogen atmosphere for 2.5 hr. at 175–176°. The n.m.r. spectrum of the residue was identical to that of the starting mixture and showed no absorption characteristic for the aldehyde XII. The infrared spectrum of the product was identical to that of the starting mixture and showed no absorption at 1712 cm.$^{-1}$ characteristic for XII.

Isomerization of XI to X.—A mixture (80 mg.) of XI (*cis* and *trans*) and X was dissolved in 0.6 ml. of a cold (10°) solution prepared by mixing acetic anhydride (2 ml.), acetic acid (0.5 ml.), and sulfuric acid (1 drop). The resulting solution was placed in an n.m.r. tube and stored for about 1 hr. at Dry Ice–acetone temperature after sealing under vacuum. A blank solution was prepared in the same manner, but the sulfuric acid was omitted. Each solution was warmed to approximately 20° and the n.m.r. spectra were determined. The blank solution showed absorption bands characteristic for the CH_2 and $-\underset{|}{CH}-OCO-$ groups for all three components (the $O{=}\overset{|}{C}-CH_3$ groups were masked by the solvent). The solution containing the acid showed absence of XI (*cis* and *trans*) and increased concentration of X.

Acknowledgment.—Helpful discussions related to this study with Professor R. M. Dodson are gratefully acknowledged.

The Pinacol Rearrangement of Cyclopentylcyclohexane-1,1′-diol

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When cyclopentylcyclohexane-1,1′-diol is heated with dilute acid, the major product is the diene, 1-(1-cyclopentenyl)cyclohexene; spiro[5.5]undecan-1-one and spiro[4.6]undecan-6-one, with the former predominating, are minor products.

The pinacols of several cycloalkanes have been reported and converted to a mixture of a spiro ketone and a diene[1–3] (Table I). The purpose of this investigation was to uncover some of the factors that influence the course of these reactions.

TABLE I

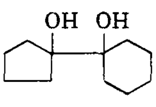
PINACOL REARRANGEMENT OF ALICYCLIC GLYCOLS

Glycol	% Spiro ketone[a]	% Diene
Bicyclobutyl-1,1′-diol	100[b]	
Bicyclopentyl-1,1′-diol (II)	86[c]	10–15[d]
Bicyclohexyl-1,1′-diol (III)	12.7[e]	88[g]
Bicycloheptyl-1,1′-diol	1.25[f]	98.75
Bicyclooctyl-1,1′-diol	1.83[f]	98.17

[a] All per cents represent composition of product mixtures isolated; per cent yields are less. [b] Diene not reported.[1] [c] See ref. 4. [d] Isolated as maleic anhydride adduct.[2] [e] Isolated as semicarbazone.[3] [f] See ref. 2. [g] E. deB. Barnette and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

Cyclopentylcyclohexane-1,1′-diol (I) was chosen for this purpose because it is capable of giving two rearrangement products as well as a diene. Structural features that influence the rearrangement would be indicated by determining which of the two possible rearrangement products is formed in greater quantity.

Preparation of the glycol I was accomplished by pinacol reduction of a mixture of cyclopentanone and cyclohexanone. Since the product proved to be an inseparable mixture of I, II, and III, rearrangement was carried out by refluxing the impure glycol with 25% sulfuric acid. Seven products were obtained (Table II).



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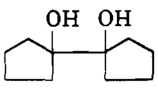

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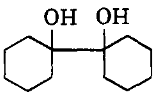


III

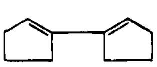
TABLE II

PINACOL REARRANGEMENT OF CYCLOPENTYLCYCLOHEXANE-1,1′-DIOL

Product	Per cent from Impure I[a]	Pure I[b]	Pure II[b,c]	Pure III[b,c]
IV	3.0		15.2	
V	16.8		84.8	
VI	40.3	80.2		
VII	1.3	2.6		
VIII	8.7	17.2		
IX	4.0			13.5
X	25.6			86.5

[a] These per cents represent the composition of the 60 g. of product mixture obtained from 100 g. of the glycol. They were determined by weighing the peaks obtained in the gas chromatographic analysis of the mixture. [b] Calculated from the percentages determined for the impure glycol. [c] The agreement with the reported values in Table I is confirmation of the reliability of the analytical method.

The composition of the product mixture was determined by gas chromatography. The components of the mixture were identified by comparison with authentic



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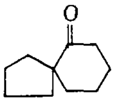

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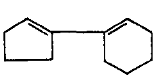

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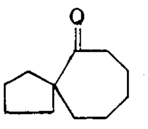

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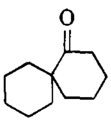

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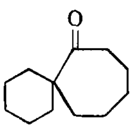

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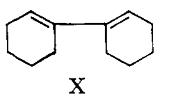

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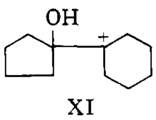

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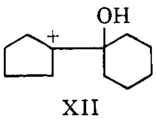

XII

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(1) E. Vogel, *Chem. Ber.*, **85**, 25 (1952).

(2) D. S. Greidinger and D. Ginsberg, *J. Org. Chem.*, **22**, 1406 (1957).

(3) Qudrat-i-Khuda, *J. Indian Chem. Soc.*, **16**, 525 (1939).

(4) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 2753 (1954).

materials and by chromatographic isolation with an Aerograph A-700 Autoprep. The only product that has not been reported is VI, which was characterized by its maleic anhydride adduct.

The results in Table II clearly indicate that VIII is the preferred rearrangement product of I. Since it is known that a carbonium ion is more easily formed (and more stable once formed) on a five- than on a six-membered ring,[5] XII is the more likely of the two carbonium ions possible in the reaction of I with dilute acid. Furthermore, since XII leads to the minor rearrangement product VII, the ring expansion products do not reflect the relative ease of formation or stabilities of the carbonium ions.[6] The product composition found is the result of a competition between ring expansion and proton loss involving the internal strains[7] of the two reversibly formed carbonium ions XI and XII.

In the more easily formed carbonium ion XII, both rings are strainless. Even though there is some expansion of the strainless six-membered ring, to give a small amount of VII, proton loss, followed by loss of water to give VI, is the major course of the reaction involving carbonium ion XII.

In the more difficultly formed carbonium ion XI both rings are strained. Relief of the strain of both rings is available through expansion to VIII; relief of the strain of the six-membered ring only is available through proton loss, a route which leads to VI after loss of water. Ring expansion with XI is more important than with XII because both rings of XI are strained.

Although ring size does not influence the degree of ring expansion in many reactions, and is not the only factor involved in many other reactions,[8] it is certainly important in the reaction of alicyclic glycols with dilute acid. The preference for ring expansion in the strained four- and five-membered rings, because both rings of the intermediate carbonium ion are strained, and the preference for diene formation in the strainless six-, seven-, and eight-membered rings, because only one ring of the intermediate carbonium ion is strained, is seen in Table I.

Experimental

Preparation of Cyclopentylcyclohexane-1,1′-diol.—A solution of 62 g. of mercuric chloride in a mixture of 316 ml. (300 g., 3.57 moles) of cyclopentanone and 370 ml. (350 g., 3.57 moles) of cyclohexanone was slowly added to a boiling mixture of 800 ml. of benzene and 132 g. of aluminum dust. The mixture was refluxed for 3 hr. after the completion of the addition, hydrolyzed by the addition of 500 ml. of water and another 800 ml. of benzene and then refluxed another 2 hr. The mixture was filtered while hot, the residue was washed with benzene, and the benzene was removed from the filtrate by distillation. Recrystallization of the cooled residue from ligroin (60–90°) gave 153 g. (23%) of the impure glycol, m.p. 100–101°.

Rearrangement of Cyclopentylcyclohexane-1,1′-diol.—The impure glycol, 100 g., was refluxed with 25% sulfuric acid for 2 hr. Ether extraction was followed by bicarbonate and water washings of the extract and drying of the ether solution over magnesium sulfate. Evaporation of the ether under reduced pressure gave 60 g. of residue.

Preparation of Reference Compounds.—The spiro ketones V and IX as well as the dienes IV and X were prepared by rearrangement of the appropriate glycols II and III. The ketones were isolated as the semicarbazones, leaving the dienes; the ketones were obtained from the semicarbazones by hydrolysis. The spiro ketones VII and VIII were obtained by the method of Mousseron, Jacquier, and Christol.[9]

Analysis of the Reaction Mixture.—The rearrangement mixture was analyzed by gas chromatography using a 6-ft. column of Dow-Corning silicone stopcock grease on Johns-Manville Chromosorb. The separation of VII and VIII was accomplished with a Perkin-Elmer vapor fractometer Model 154, using column R, polypropylene glycol. The identification of the compounds was done on the reaction mixture, the reaction mixture after the dienes had been removed with maleic anhydride, and on the ketones regenerated from the semicarbazones. Further proof of the identity of the reaction products was accomplished by isolation with an Aerograph A-700 Autoprep and comparison with the known compounds.

Compound VI, after the chromatographic separation, was a colorless liquid boiling at 87° (4 mm.), $n^{22}D$ 1.5289; maleic anhydride adduct had m.p. 110–111°.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 89.18; H, 10.70. Calcd. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.32. Found: C, 73.09; H, 7.29.

The per cent composition of the reaction mixture was determined by weighing the peaks in the chromatographic analysis. The reliability of this method of analysis is confirmed by the agreement of the values for the rearrangements of II and III shown in Table II compared with the previously reported values shown in Table I.

The per cent of VIII relative to VII only varied between 85 and 90 over a range of sulfuric acid concentrations from 5 to 50%. Wolff–Kishner reduction of the semicarbazones from the rearrangement mixture gave hydrocarbons that show the same relative per cents. Extended refluxing of either the reaction mixture or the regenerated ketones alone with 25% sulfuric acid left the relative per cents of VIII and VII essentially unchanged.

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[5] H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

[6] This is in agreement with the fact that the initial ionization in the pinacol rearrangement is reversible: M. Stiles and R. P. Mayer, *ibid.*, **81**, 1498 (1959); C. J. Collins, *Quart. Rev.* (London), **14**, 357 (1960).

[7] Either angle- or bond opposition-type I strain.

[8] P. A. S. Smith and D. R. Baer, *Org. Reactions*, **11**, 181 (1960).

[9] M. Mousseron, R. Jacquier, and H. Christol, *Compt. rend.*, **239**, 1805 (1954).