was then flushed with purified nitrogen and 4.94 ml. of ester solution was transferred to the conductivity cell with a calibrated pipet. Timing was started when one-half of the base was added from a 2.42-ml. fast delivery pipet. Zero-time resistance values, obtained before each run, were determined by carrying out the above procedure with the exclusion of ester. Infinity-time resistance values were obtained from independent measurements of standard solutions of sodium acetate. These values agreed within 2% for those reactions carried to infinite time.

Treatment of Kinetic Data.—The integrated second-order rate equation was used in calculating the rate constant

$$k_2 t = \frac{2.303}{C^0_{ester} - C^0_{NaOH}} \log \frac{C^0_{NaOH} C^t_{ester}}{C^0_{ester} C^t_{NaOH}} \quad (3)$$

where C^0_{ester} and C^t_{ester} are the concentrations of the ester at zero and time t, respectively; C^0_{NaOH} and C^t_{NaOH} are the concentration of sodium hydroxide at zero and time t, respectively. Term C^t_{NaOH} is calculated from the resistance $[C^t_{ester} = C^0_{ester} - (C^0_{NaOH} - C^t_{NaOH})]$. It is assumed that the reciprocal of the resistance is proportional to the concentration of dissolved electrolyte, where δ is a proportionality constant.

$$1/R = \delta_x C_x \quad (4)$$

In a solution containing sodium acetate and sodium hydroxide at any time, t

$$\frac{1}{R} = \delta_b C^t_{NaOAc} + \delta_a C^t_{NaOH} \quad (5)$$

where δ_b and δ_a are the proportionality constants calculated from the slope obtained from a plot of $1/R$ vs. concentration of sodium acetate and sodium hydroxide, respectively. Substitut-

ing the equality, $C^0_{NaOH} = C^t_{NaOH} + C^t_{NaOAc}$, in eq. 5, and after rearranging terms, eq. 6 was obtained.

$$C^t_{NaOH} = \frac{1}{ab}\left(\frac{1}{R} - \delta_b C^0_{NaOH}\right) \quad (6)$$

Thus the concentration of sodium hydroxide at any time during the run was calculated from the resistance.

Rates of Formation of 2-Methyl-2-pentenal by Treatment of Propionaldehyde, Cyclopropyl Acetate, and Cyclopropanol with Sodium Hydroxide Solution.—Standard solutions of propionaldehyde (cyclopropyl acetate, cyclopropanol) in water were prepared by weighing the material into S-shaped capillary tubes which were then dropped into volumetric flasks, filled to the mark with conductivity water, and crushed with a glass rod. After equilibration in an air-conditioned room at $20 + 2°$, aliquots of base and aldehyde (cyclopropyl acetate and cyclopropanol) were mixed, the timer was started, and a solution of the reaction mixture was transferred to a stoppered quartz Beckman cell. Absorbance of the solution from 3000 to 2000 Å. was recorded at various intervals on a Cary Model 14 recording spectrophotometer. The absorption maximum at 2355 (ϵ 17,700) was used to calculate the amount of 2-methyl-2-pentenal formed. Rate constants were subsequently calculated from this.

Reaction solutions containing high hydroxide concentration ($ca.$ 0.1 M) were diluted before obtaining the spectrum.

Infinity points were obtained by sealing aliquots of base and propionaldehyde (cyclopropyl acetate and cyclopropanol) in tubes and placing them in an 80° bath for 2 days. At the end of this period the tubes were opened, contents diluted, and spectra obtained. Approximately 80–85% of the theoretical yield of 2-methyl-2-pentenal was obtained as calculated from the absorption maximum at 2355 Å. 2-Methyl-2-pentenal was shown to be stable in 0.2 M sodium hydroxide under the above conditions.

Acid-Catalyzed Rearrangements of Medium Ring Cycloalkene Glycols[1]

BY JAMES G. TRAYNHAM AND PEGGY M. GREENE

Acid-catalyzed rearrangements of some medium ring cycloalkene glycols have been investigated with the intent of assessing the carbonium ion nature of intermediates formed in these reactions. Complex mixtures of products, resembling those formed in acid-catalyzed hydrolyses of cyclooctene oxides and strongly suggestive of a carbonium ion mechanism, are obtained from cis- and trans-cyclooctene glycols. Unlike cyclononene oxide and cyclodecene oxide, however, cis-cyclononene glycol and cis-cyclodecene glycol rearrange predominantly to the corresponding cycloalkanone (40 and 51% yields, respectively). Because nine- and ten-membered rings usually exhibit maximum tendencies for transannular processes in carbonium ion reactions, carbonium ion mechanisms are not believed to be of major importance in the pinacolic transformations of these glycols. The suggestion is made that (at least to the extent that ketone formation occurs) neighboring hydrogen migration coincides with departure of a water molecule from the protonated glycols, and substantial carbonium ion character never develops at the migration terminus.

Medium ring compounds exhibit a number of features which set them apart from other cyclic and acyclic compounds,[2] and we have found them useful in studies designed to unveil details of reaction mechanisms. Different kinds of intermediates (or transition states) can lead to different kinds of products to an extent seldom matched in other systems.[3] Reaction courses seem to be particularly sensitive to carbonium ion character in in-

termediates.[3] We have undertaken an extensive investigation of rearrangement reactions of 2-substituted cycloalkanols, which presumably could react through 2-hydroxycycloalkyl cations, and report here initial investigations of acid-catalyzed rearrangements (pinacolic transformations) of some cycloalkene glycols.

Pinacol (2,3-dimethyl-2,3-butanediol) undergoes acid-catalyzed rearrangement to pinacolone by a carbonium ion process,[4] and tertiary glycols in general appear to react in this fashion. Rearrangements of pinacols, olefin oxides, and amino alcohols of corresponding structure are presumed to be closely related processes.[5] In fact, the oxide, glycol, halohydrin, and amino alcohol derivatives of tetramethylethylene all give equivalent

(1) (a) We gratefully acknowledge the partial support of this research by Grant G14461 from the National Science Foundation. (b) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963. (c) Taken in part from the M.S. thesis submitted by P. M. G., Jan., 1964.

(2) For two recent reviews, see: (a) V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc.–Interscience Publishers, New York, N. Y., 1963, Chapter 9; (b) J. Sicher in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, London, 1962, Chapter 6.

(3) For example, see J. G. Traynham and W. C. Baird, Jr., J. Org. Chem., 27, 3189 (1962).

(4) C. A. Bunton, T. Hadwick, D. R. Llewellyn, and Y. Pocker, Chem. Ind. (London), 547 (1956); J. Chem. Soc., 403 (1958).

(5) Y. Pocker, ref. 2a, Chapter 1.

proportions of glycol (substitution) and ketone (rearrangement) products.[6] Such data have led to the claim that "the accepted mechanism for pinacolic transformation involves the prior formation of a carbonium ion intermediate."[5]

When hydrogen rather than alkyl or phenyl migrates in rearrangements of these olefin derivatives (for example, rearrangements of secondary glycols), evidence concerning the nature of the intermediate is far less extensive. Some data point to intermediates with little or no carbonium ion character in rearrangements of secondary glycols,[7] and different proportions of products have been reported for acid-catalyzed reactions of isobutylene oxide and glycol.[8] In the latter case, more carbonium ion character was attributed to the glycol reaction than to the epoxide one.

Although numerous examples of reactions involving hydrogen migration are known, evidence for migration *during departure of a leaving group* is meager. Even in some apparently ideally suited cases, neighboring hydrogen leads to small rate enhancements, and in some fast reactions involving hydrogen migration (for example, cyclodecyl tosylate acetolysis) anchimeric assistance has been shown to be absent.[9]

Acid-catalyzed hydrolyses of cycloalkene oxides led to the discovery of transannular processes.[2a,10] These reactions have the characteristics of carbonium ion processes and give transannular products extensively or exclusively. So well delineated are these reactions that their use in other investigations for diagnostic purposes seems particularly appropriate. The intermediate ion formed during solvolysis of cycloalkene oxide would be a 2-hydroxycycloalkyl cation, presumably the same one which would be formed in an ionizing process starting with the corresponding cycloalkene glycol. Formation of the same intermediate should be revealed by formation of the same (or at least highly similar) product mixtures. Conversely, formation of greatly different product mixtures can be taken as evidence that different intermediates intervened in reactions of the olefin oxides and glycols.[11] Particularly notable for our present considerations, the corresponding cycloalkanone is formed not at all or only in very small amount when medium ring cycloalkene oxides are subjected to solvolysis in acidic media.[2a]

In this first paper of what we expect to become a series on reactions of medium ring 2-substituted cycloalkanols, we describe acid-catalyzed rearrangements of *cis*- and *trans*-cyclooctene glycol, *cis*-cyclononene glycol, and *cis*-cyclodecene glycol. Because of the particular relevance of extensive formation of cycloalkanone and other relatively volatile products, and be-

cause the documentation concerning nonvicinal glycol products from olefin oxides is so thorough,[2a] our initial investigation has concentrated on the relatively volatile components of the product mixtures. Together with unconsumed starting glycols, these components account for 50–82% of the product mixtures.

Rearrangements of the glycols in hot dilute sulfuric acid led in every case to the formation of the corresponding cycloalkanone in substantial amounts, along with other products.[12] The most complex product mixtures were obtained from the cyclooctene glycols, and only in those cases was cycloalkanone not the major product.
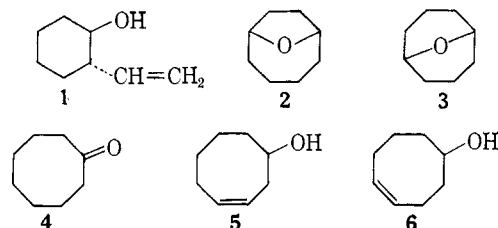
Cyclooctene Glycols.—Rearrangement of the two cyclooctene glycols gave very similar product mixtures: the components were essentially the same, with some difference in proportions. All of the products identified can be accounted for by transannular descriptions of the reactions, but the product mixtures are nonetheless quite different from those obtained in hydrolyses of cyclooctene oxides.[15]

The major product obtained from both cyclooctene glycols was a mixture of 1,4- and 1,5-epoxycyclooctane (2 and 3) (40% from *trans*-glycol, very largely 1,4-isomer; 20% from *cis*-glycol). *trans*-2-Vinylcyclohexanol (1), cyclooctanone, and 3-cyclooctenol (from *trans*-glycol) or a mixture of 3- and 4-cyclooctenol (from *cis*-glycol) were formed in intermediate and approximately equal amounts (5–9%). Several very minor products were detected by gas chromatography.

All of these products have been detected in rearrangements of the cyclooctene oxides,[15] but in quite different amounts from those found here. In the epoxide rearrangements, 3- and 4-cyclooctenols were major products, and *trans*-2-vinylcyclohexanol and 1,4- and 1,5-epoxycyclooctanes were formed in about 1% yields. The low yields of 5 and 6 and the high yields of 1, 2, and 3 in our mixture, together with the proposal that the latter compounds are formed in epoxide hydrolyses from 5 or 6,[15a] led us to suspect that 5 and 6, as primary reaction products, might be diverted to the other products in the hot sulfuric acid solutions which we em-

(6) Y. Pocker, *Chem. Ind.* (London), 332 (1959).

(7) (a) J. G. Traynham, *ibid.*, 1142 (1958); (b) W. B. Smith, R. E. Bowman, and T. J. Kmet, *J. Am. Chem. Soc.*, **81**, 997 (1959); (c) W. B. Smith, T. J. Kmet, and P. S. Rao, *ibid.*, **83**, 2190 (1961).

(8) B. J. Ley and C. A. Vernon, *Chem. Ind.* (London), 146 (1956); *J. Chem. Soc.*, 2387, 3256 (1957).

(9) V. Prelog and S. Borčić, unpublished work; see ref. 2a, p. 612.

(10) (a) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952); (b) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

(11) Product analysis has been designated as the most generally significant method for study of reaction mechanisms: J. F. Bunnett in "Technique of Organic Chemistry," Vol. VIII, 2nd Ed., S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., John Wiley and Sons, Inc.-Interscience Publishers, New York, N. Y., 1963, p. 271 (see also E. S. Lewis and C. E. Boozer, *ibid.*, p. 1412).

(12) The epoxide rearrangements were carried out in formic acid solutions,[10] but attempts to rearrange *cis*-cyclooctene glycol and *cis*-cyclodecene glycol under these conditions led only to esterification.[13] After saponification, the glycols were recovered in good yields. Even so, aqueous sulfuric acid should be about as good (or better) for carbonium ion processes as 90% formic acid.[14]

(13) The stability of *trans*-cyclooctene glycol under these conditions has already been reported; see ref. 15c.

(14) Reaction of cycloheptene oxide in formic acid leads to no transannular products (A. C. Cope and W. N. Baxter, *J. Am. Chem. Soc.*, **76**, 279 (1954)), but a small amount of 1,4-diol is formed during hydrolysis of that oxide in dilute hydrochloric acid (A. C. Cope, T. A. Liss, and G. W. Wood, *Chem. Ind.* (London), 823 (1956); *J. Am. Chem. Soc.*, **79**, 6287 (1957)).

(15) (a) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957); (b) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957); (c) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **81**, 1640 (1959).

ployed. When samples of 3- and 4-cyclooctenol were heated separately with dilute sulfuric acid solution, as were the glycols, rearrangements gave complex mixtures consisting mainly of **2** and **3** (chief product from **6**), **1** (chief product from **5**), and **4** (about seven times as much from **6** as from **5**). Similar rearrangements with different product proportions have been described for the solvolysis of 4-cyclooctenyl formate in formic acid.[16]

These results do not necessarily mean that all cyclooctanone formed in the glycol rearrangements is in fact a transannular product, but they do not require any other explanation. Since the other major products clearly arise from transannular processes, the entire cyclooctene glycol rearrangement may be pictured as an ionizing process leading to transannular products; that is, it is closely related to solvolysis of cyclooctene oxide.[15,17] Just as geometry played a small role in epoxide solvolysis (product distributions from cis- and trans-cyclooctene oxides were slightly different),[15] so the precise details in the cis- and trans-glycol rearrangements differ slightly. With respect to the epoxycyclooctanes and cyclooctenols formed, trans-cyclooctene glycol follows a reaction course more closely related to rearrangement of 3-cyclooctenol, while cis-cyclooctene glycol follows one more like that of 4-cyclooctenol.

cis-**Cyclononene Glycol and** cis-**Cyclodecene Glycol.** —The reaction products from cis-cyclononene glycol and cis-cyclodecene glycol are less complex, even though nine- and ten-membered rings usually exhibit maximum tendencies toward transannular processes and other medium-ring effects.[2] Some spectral evidence indicated that bicyclic ethers (transannular products) are probably among the minor reaction products, but cycloalkanone is by far the major product formed in these acid-catalyzed rearrangements (40% cyclononanone, 51% cyclodecanone). The contrast with solvolyses of the corresponding epoxides, in which little or no cycloalkanone is formed,[10b,18] is striking. Indeed, on the basis of published descriptions of these epoxide hydrolyses[10b,18] and the presumed similarity of reaction mechanism between epoxides and glycols,[5] the major product of the acid-catalyzed rearrangement of cis-cyclononene glycol and cis-cyclodecene glycol would have been predicted to be virtually absent.[12] We believe that descriptions of the glycol and epoxide rearrangements should reflect this difference.

If one accepts the carbonium ion description for the epoxide solvolyses, one can hardly infer that a 2-hydroxycycloalkyl cation is responsible for ketone formation in the glycol reactions. An alternative suggestion is that (at least to the extent that ketone formation occurs) neighboring hydrogen migration accompanies departure of water molecule from the protonated glycol, and substantial carbonium ion character never develops at the migration terminus. The geometry of the glycols as calculated from infrared data[19] is not unfavorable for such trans migration.

(16) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).
(17) But not identical: 2-methylcyclohexanecarboxaldehyde, a ring-contraction product which was formed during solvolysis of *trans*-cyclooctene oxide in 14% yield (25% of reaction product mixture),[15b] was not detected in our mixtures.
(18) V. Prelog, K. Schenker, and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).
(19) L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 4323 (1954). The torsion angles between OH groups in the olefin glycols were calculated to be: *cis*-cyclononene, 36°; *cis*-cyclodecene, 42°. These values lead to 156 and 162°, respectively, for the torsion angles between OH and *trans*-hydrogen on adjacent carbons.

Experimental

Gas chromatographic (g.c.) analyses were carried out with a Barber–Colman Model 20 instrument equipped with a hydrogen-flame detector and either a 200-ft. capillary column coated with Apiezon L (temperature 150°) or a 100-ft. capillary column coated with GE-96 silicone (temperature 100°). An Aerograph Autoprep Model A-700 instrument equipped with a $^3/_8$ in. × 20 ft. SE-30 silicone column or a $^3/_8$ in. × 10 ft. Carbowax 20-M column was used for preparative gas chromatography (g.c.). Melting points were obtained with a Thomas–Hoover apparatus and are uncorrected. Infrared spectra were obtained with a Beckman IR-5 spectrophotometer.

Preparation of Materials. cis-**Cycloalkenes.**—Cyclononene and cyclodecene were prepared through ring-enlargement reactions[20] starting with commercially available cis-cyclooctene. 9,9-Dibromobicyclo[6.1.0]nonane,[20a] b.p. 92–93.5° (0.9 mm.), formed in 72% yield from the reaction of bromoform and potassium *t*-butoxide with a 2 molar excess of cyclooctene,[20a] was converted in 80% yield to 1,2-cyclononadiene,[20a] b.p. 83–84.5° (36 mm.), by treatment with excess methyllithium in ether.[20] The allene was readily reduced, at 1–3 atm. pressure, with hydrogen and palladium-on-carbon or a nickel catalyst prepared by sodium borohydride reduction of nickel acetate.[21] At 3 atm. pressure, the rate of hydrogenation dropped sharply after about 15–25 min., but at 1 atm., 2–3 hr. was required for the reduction. Analysis (g.c.) indicated that little more than trace amounts of cyclononane and no trans-cyclononene[22] were formed along with the cis-cyclononene[18,22] (94% yield, 86–87° (50 mm.)).

Essentially the same procedure was used for **cyclodecene**, except that 1 molar excesses of bromoform and potassium *t*-butoxide (rather than excess cyclononene) were used. The products and yields obtained were: 10,10-dibromobicyclo[7.1.0]decane,[23,24] b.p. 97–101.5° (0.5 mm.), 22%; 1,2-cyclodecadiene,[23] b.p. 110–115° (40–42 mm.), 76%; and cis-cyclodecene,[25] b.p. 100–103° (42–44 mm.), 72%.

cis-**Cycloalkene Glycols.**—The cis-cycloalkenes were oxidized with basic permanganate in ice cold aqueous *t*-butyl alcohol solutions.[26] Cyclooctene and cyclononene decolorized the permanganate solution immediately, but cyclodecene required about 10 min. for complete reaction. The product glycols were extracted from the concentrated aqueous solutions with ether and subsequently purified by vacuum sublimation. The preparations were carried out with 0.05–0.10 mole of olefin; the products obtained are listed with m.p. and yield of sublimed material: cis-cyclooctene glycol,[10a] 76–77°, 56%; cis-cyclononene glycol,[18] 111–112°, 55%; cis-cyclodecene glycol,[25a] 136–137°, 30%.

cis-**Cyclooctene oxide**[10a] was prepared by treatment of cyclooctene with hydrogen peroxide in benzonitrile solution[27]; b.p. 96.5° (40 mm.), 77% yield. The epoxide was converted to trans-1,2-diol by refluxing for 25 hr. a solution of cis-cyclooctene oxide (0.22 mole), sodium acetate trihydrate (0.55 mole), and glacial acetic acid (140 g.).[15c,28] Most of the acetic acid was removed by distillation at reduced pressure, water was added to the residue, and the mixture was extracted with ether. After removal of ether solvent, the alcohol–ester mixture[28] was saponified with hot 10% sodium hydroxide solution (48 hr. reflux). Extraction with ether led to the isolation of trans-cyclooctene glycol[10a] in good yield, b.p. 101.5–102.5° (0.7 mm.), bisphenylurethan[10a] m.p. 174–175°. The glycol solidified[15a] when cooled overnight in a refrigerator.

(20) (a) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961); (b) T. D. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 636 (1948); (c) L. Skattebøl, *Tetrahedron Letters*, 167 (1961).
(21) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1003, 1005 (1963).
(22) W. R. Moore, *ibid.*, **84**, 3788 (1962).
(23) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961).
(24) Analysis (g.c.) of a sharp-boiling fraction indicated the presence of 3 components with almost equal peak areas; attempts to obtain a homogeneous sample were unsuccessful, but the material gave a good yield of cyclodecadiene. Multiple components may arise from pyrolysis of dibromide in the gas chromatograph.
(25) (a) V. Prelog, K. Schenker, and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (b) A. T. Blomquist, R. E. Burge, and A. C. Sucsy, *J. Am. Chem. Soc.*, **74**, 3636 (1952).
(26) K. B. Wiberg and K. A. Saegebarth, *ibid.*, **79**, 2824 (1957).
(27) G. B. Payne, *Tetrahedron*, **18**, 763 (1962).
(28) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1650 (1959).

Cyclooctenols.—3-Cyclooctenol[16] (b.p. 117° (34 mm.), n^{22}D 1.4994, phenylurethan[15a] m.p. 101.5–102.5°) and 4-cyclooctenol[16] (b.p. 115° (34 mm.), n^{22}D 1.4958, phenylurethan[15a] m.p. 91.8–93°, p-nitrobenzoate[15a] m.p. 85–86°) were obtained by lithium aluminum hydride reduction of 1,3-cyclooctadiene monoxide[16] and 1,5-cyclooctadiene monoxide,[29] respectively. Each monoxide was prepared by the addition during 30 min. of an ethyl acetate solution containing 1 equiv. of m-chloroperoxybenzoic acid[30] to a solution of diene[31] in ethyl acetate at 25°: 1,3-cyclooctadiene monoxide, b.p. 87–91° (40 mm.), $n^{23.5}$D 1.4871; 1,5-cyclooctadiene monoxide, b.p. 97–100° (40 mm.), n^{23}D 1.4937.

Infrared spectra of 5 and 6 are distinguishable by several absorption bands between 9.5 and 14.5 μ.

Treatment of Cycloalkanediols with Formic Acid.—Under much the same conditions as were used for studies of epoxide solvolyses,[10a,15a] small portions (1–2 g.) of cis-cyclooctene glycol and cis-cyclodecene glycol were treated separately with 90% formic acid (7–20 ml.). After being heated on a steam bath for 3 hr., the solutions were diluted with water and extracted several times with ether. Each organic residue remaining after removal of ether solvent was examined for the presence of ketone: it failed to form a precipitate with 2,4-dinitrophenylhydrazine reagent, and gas chromatograms contained no peaks attributable to ketone (cyclooctanone or cyclodecanone). The residues were separately saponified by refluxing with 30% sodium hydroxide solutions, and the starting glycols, which separated as solids from the alkaline solutions, were purified by vacuum sublimation. cis-Cyclooctene glycol, m.p. 76–78°, was recovered in 70% yield, and cis-cyclodecene glycol, m.p. 135–136.5°, in 86% yield.

Rearrangement of Cycloalkanediols in Dilute Sulfuric Acid.—A solution of glycol in 1 M sulfuric acid (about 50 ml. for 0.01 mole of glycol) was refluxed under a nitrogen atmosphere for 18–24 hr. Usually some oily material separated from the solution during this time. The mixture was extracted several times with ether, and the combined ether solution was dried over magnesium sulfate. After removal of the ether with a rotary evaporator, the crude residue was examined by g.c. and infrared spectroscopy. Identification of g.c. peaks was accomplished by comparison with authentic samples and by spectroscopic[32] and chemical examination of samples obtained by preparative scale g.c. Compositions of product mixtures were computed by comparison of g.c. responses with standard materials, both single compounds and mixtures. Ketone fractions were further identified by preparation of 2,4-dinitrophenylhydrazone derivatives: cyclooctanone 2,4-DNPH,[15a] m.p. 169–170.5°; cyclononanone 2,4-DNPH,[18] m.p. 139–140°; and cyclodecanone 2,4-DNPH,[10b,33] m.p. 161–163.5°. Melting points of these derivatives mixed with authentic samples were undepressed.

(29) K. Ziegler and H. Wilms, Ann., **567**, 1 (1950).

(30) Commercial sample obtained from FMC Corp. was used as supplied.

(31) We appreciate the gift of samples of 1,5-cyclooctadiene and 1,3-cyclooctadiene from Cities Service Research and Development Co.

(32) We greatly appreciate the helpful cooperation of Professor A. C. Cope, who lent us spectra of trans-2-vinylcyclohexanol, 1,4-epoxycyclooctane, and 1,5-epoxycyclooctane from his laboratory for comparison.

(33) V. Prelog, L. Frenkiel, M. Kobelt, and P. Barman, Helv. Chim. Acta, **30**, 1741 (1947).

Cyclooctene Glycols.—From both cis- and trans-cyclooctene glycol, trans-2-vinylcyclohexanol (1), 1,4- and 1,5-epoxycyclooctanes (2 and 3), cyclooctanone (4), and 3- and 4-cyclooctenols (5 and 6) were obtained as major products. Quantitative analyses of the crude reaction products with periodic acid[34] indicated that the mixture from trans-glycol contained 7% and that from cis-glycol 4–6% of the starting 1,2-diol. Some material in each mixture remained unaccounted for and may be nonvicinal diols. The actual yields, based on diol consumed (and, in parentheses, the percentage composition of the crude reaction mixtures as indicated by g.c. responses), are summarized here; the products are listed in order of increasing retention time in the gas chromatograph. From trans-cyclooctene glycol: an unsaturated hydrocarbon (3%); 1, 8.4% (10%); a mixture of 2 and 3 (mostly 2 on the basis of infrared spectrum), 34% (40%); 4, 4.5% (5%); and 5, 5.5% (6.5%). From cis-cyclooctene glycol: an unsaturated hydrocarbon (0.2%); 1, 4.9% (5.3%); a mixture of 2 and 3 (higher proportion of 3 than above), 18.5% (20.0%); 4, 7.7% (8.3%); and a mixture of 5 and 6 (mixture designation based on infrared spectrum), 8.6% (9.4%).

cis-**Cyclononene glycol** underwent rearrangement to form cyclononanone in 40% yield; 4–6 minor components, of shorter retention time than cyclononanone and yet unidentified accounted for about 12% of the total g.c. response area. A periodic acid titration[34] indicated that 19% of the starting glycol was present in the product mixture. Column chromatography of a portion of the mixture on Woelm alumina (neutral, Activity II) with petroleum ether and ethyl ether as developing solvents gave first a fraction (12% of the mixture introduced onto the column) whose infrared spectrum suggested a bicyclic ether, and then cyclononanone. (Diols present in the mixture were not eluted by ether solvent; about 65% of the mixture introduced onto the column was recovered.)

cis-**Cyclodecane glycol** rearranged to cyclodecanone in 51% yield; a periodic acid titration[34] indicated that 18% of the starting glycol remained in the product mixture. Analysis by g.c. further indicated that the product mixture contained 3 minor components (3.4% total) and an unidentified component (14%), all of shorter retention times than cyclodecanone. Preparative g.c. successfully separated cyclodecanone from the other components, but they could not be separated from each other. It was possible however to establish that these other components were not carbonyl-containing compounds.

Sulfuric Acid-Catalyzed Rearrangements of 3- and 4-Cyclooctenols.—Separate mixtures of 3- and 4-cyclooctenol and 1 M sulfuric acid (about 15 ml. of acid per gram of alcohol) were refluxed under nitrogen for 16–23 hr. Each of the two-phase mixtures was extracted three times with petroleum ether. Each combined organic solution was washed with water, dried over Drierite, concentrated by distillation, and examined with infrared spectroscopy and g.c. (both analytical and preparative) as described before. In addition to several minor components of short retention time, each product mixture contained 1, 2, 3, and 4. The proportions estimated from gas chromatograms are: from 5: 1, 41%; 2 and 3 (mostly 2), 30%; 4, 2.5%; and 5, 22%. From 6: 1, 2%; 2 and 3, 71%; 4, 22%; and 6, trace.

(34) S. Siggia, "Quantitative Organic Analysis via Functional Groups," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 39.

Photoisomerization of 1,3,5-Cyclooctatriene[1]

By O. L. Chapman, G. W. Borden,[2] R. W. King, and B. Winkler

Irradiation of 1,3,5-cyclooctatriene in ether gives the expected valence tautomer bicyclo[4.2.0]octa-2,7-diene (II) and a novel valence tautomer tricyclo[5.1.0.0⁴,⁸]oct-2-ene (VI). Nuclear magnetic double resonance experiments were prominent in the structure elucidation of VI.

Study of the photochemical transformations of cyclic and acyclic dienes and trienes has led to a

variety of interesting compounds and to useful syntheses of bicyclic systems.[3] Our interest in cyclic dienes[4]

(1) Part XIII of the photochemical transformations series. For Part XII see O. L. Chapman and G. W. Borden, Proc. Chem. Soc., 221 (1963). Portions of this manuscript were abstracted from theses submitted to Iowa State University by G. W. Borden, 1963, and B. Winkler, 1962.

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(3) For a review see O. L. Chapman in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Ed., John Wiley-Interscience Publishers, Inc., New York, N. Y., 1963.