insoluble oil was obtained which crystallized on cooling. The reaction mixture was filtered and the solid was washed with water and recrystallized from dilute ethanol to obtain 0.2 g. of 3-hydroxy-4-nitro-1,3,4-trimethylcyclohexanecarboxylic acid lactone as white needles, m.p. 112–113°.

Anal. Calcd. for $C_{10}H_{15}NO_4$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.64; H, 7.19; N, 6.65.

Method B. A suspension of 3 g. of lactone B (n_D^{25} 1.4692–1.4709) was refluxed 4 hr. in dilute nitric acid to obtain 1.45 g. (45% yield) of crude nitrolactone. Recrystallization of the product from dilute ethanol afforded 1 g. of white needles, m.p. 112–113° alone or mixed with the nitrolactone from lactone A. The infrared spectra (Nujol) of the nitrolactones were identical. Nitration of the mixed lactones A and B (n_D^{25} 1.4658) afforded crude nitrolactone in 58% yield, m.p. 99–105°.

Method C. Two grams of methyl 1,3,4-trimethyl-3-cyclohexenecarboxylate was refluxed for 2 hr. in a solution of 4 ml. of 70% nitric acid in 12 ml. of water. The cooled reaction mixture was filtered and the product was recrystallized from dilute ethanol to obtain white needles, m.p. 110.5–111.5°. The infrared spectrum of this product was identical to that of the above nitrolactone.

N-Cyclohexylmethacrylamide. Thirty grams of allene (0.75 mole) was allowed to react with 150 g. of cyclohexylamine (1.5 moles) and carbon monoxide at 135° and 1000 atm. pressure for 14 hr. in the presence of 2 g. of diruthenium nonacarbonyl catalyst. The dark fluid product (200 g.) was flash distilled to leave a residue of 70 g. which was not volatile at 170° (3 mm.). The distillate was redistilled to obtain 89 g. of colorless oil, b.p. 70–94° (1 mm.), n_D^{25} 1.4890–1.4912. The oil partially solidified on standing and was filtered to obtain about 14 g. of white solid. This product was recrystallized from methanol-water to obtain *N*-cyclohexylmethacrylamide as white needles, m.p. 109.5–110.5°. The infrared spectrum of the product is consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.74; H, 10.05.

Treatment of the filtrate with aqueous methanol afforded more of the crystalline methacrylamide, which was removed by filtration. There was finally obtained on distillation *N*-cyclohexylformamide, b.p. 143° (10 mm.), n_D^{25} 1.4846; reported[16] b.p. 140–142° (10 mm.), m.p. 39°. The infrared spectrum of the material is consistent with this structure.

3-Methyl-2-cyclopentenone. A mixture of 20 g. of allene (0.5 mole), 13 g. of acetylene (0.5 mole), 18 g. of water, 1 g. of ruthenium trichloride, and 1.2 g. of pyridine was heated to 130° in the presence of carbon monoxide at a final pressure of 1000 atm. The product (53 g.) was a dark red oil which was flash distilled at 25 mm. to obtain 35 g. of distillate. The distillate was extracted into ether and dried with calcium sulfate. Distillation afforded a 13-g. fraction of methacrylic acid and 2.5 g. of ketone fraction, b.p. 89–91° (25 mm.), n_D^{25} 1.4730. The ketone fraction was dissolved in ether and extracted with sodium carbonate solution to remove methacrylic acid and then dried over calcium sulfate. Removal of the ether by distillation afforded 3-methyl-2-cyclopentenone as a light yellow oil, n_D^{25} 1.4840, which was identified by infrared comparison with an authentic sample[17] (n_D^{25} 1.4855). The ketone afforded a semicarbazone, m.p. 210–211.5° dec. alone or on admixture with authentic 3-methyl-2-cyclopentenone semicarbazone, m.p. 212–213° dec. An orange red dinitrophenylhydrazone, m.p. 181° (from dilute acetic acid) was obtained which on admixture with authentic 3-methyl-2-cyclopentenone 2,4-dinitrophenylhydrazone, m. p. 179–180.5°, gave no melting point depression.

WILMINGTON 98, DEL.

(16) H. Wieland and E. Dorrer, *Chem. Ber.* **63**, 404 (1930).

(17) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Chemistry of Dimethylketene Dimer. II. Dehydration of *trans*-2,2,4,4-Tetramethyl-1,3-cyclobutanediol[1]

ROBERT H. HASEK, R. DONALD CLARK, AND JULIAN H. CHAUDET

Received December 21, 1960

trans-2,2,4,4-Tetramethyl-1,3-cyclobutanediol was cleaved easily when refluxed in dilute sulfuric acid, while the *cis* isomer was unaffected. The cleavage product was the expected 2,2,4-trimethyl-3-pentenal. The dehydration reaction is interpreted in terms of a concerted transannular elimination mechanism.

The acid-catalyzed dehydration of certain 1,3-diols results in a characteristic cleavage to olefinic and carbonyl moieties[2]:

$$R_2\underset{\mathrm{OH}}{\underset{|}{C}}CR_2\underset{\mathrm{OH}}{\underset{|}{C}}R_2 \longrightarrow H_2O + R_2C{=}CR_2 + R_2C{=}O$$

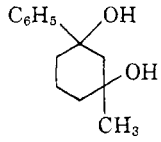
The steric effects of this reaction have been studied, and some pronounced differences in the rate or degree of cleavage have been noted for different isomers of acyclic glycols. There has been no similar study of the isomers of cyclic 1,3-diols. However, differences have been noted in susceptibility to cleavage of diols with differing ring size.[3,4] Thus, English and Brutcher[3] found an insignificant degree of acid-catalyzed cleavage of the cyclic glycol I, while Brutcher and Cenci[4] noted extensive cleavage of the indan derivative II. In neither instance was a comparison made of the behavior of *cis* and *trans* isomers of a particular cyclic glycol.

(1) First paper of this series: R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961).

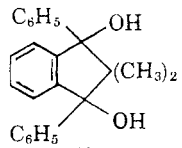
(2) For a review, see H. H. Wasserman in *Steric Effects in Organic Chemistry*, M. S. Newman, ed., Wiley, New York, 1956, p. 375.

(3) James English, Jr., and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **74**, 4279 (1952).

(4) F. V. Brutcher, Jr., and H. J. Cenci, *J. Org. Chem.*, **21**, 1543 (1956).

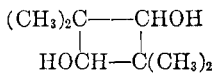


I



II

The catalytic hydrogenation of tetramethyl-1,3-cyclobutanedione to 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III) yields approximately equal quantities of the *cis* and *trans* isomers, which have been separated and identified.[1]



III
IIIa = *cis* isomer
IIIb = *trans* isomer

These isomers exhibit decidedly different properties when heated in dilute mineral acid. The *trans* isomer is dehydrated easily, with cleavage to 2,2,4-trimethyl-3-pentenal (IV), while the *cis* isomer is completely unreactive. The difference is striking: the *trans*-glycol IIIb was converted to the unsaturated aldehyde IV at a measurable rate by boiling aqueous sulfuric acid solution as dilute as 0.02*N*, while the *cis*-glycol IIIa was unaffected by boiling 20% aqueous sulfuric acid solution.

Treatment of a mixture of isomers of III with hot dilute acid, with provision for removal of the unsaturated aldehyde IV by steam distillation, left a residue of pure IIIa. Under these conditions, the unsaturated aldehyde IV was the principal product from the cleavage of IIIb. Prolonged refluxing of a mixture of the isomers of III with dilute acid, with retention of the cleavage products in the reaction mixture, led to more complex products, presumably through hydration of the aldehyde IV and formation of acetals.

The identity of IV was established by analysis, infrared spectroscopy, NMR spectroscopy, preparation and analysis of its 2,4-dinitrophenylhydrazone, and catalytic hydrogenation to a known compound.

Chemical shift peaks which defined the structure were found at −160 c.p.s. (−CHO), 0 c.p.s. (−C = CH), 131 c.p.s. (CH_3C = C−), 135 c.p.s. (CH_3C = C−), and 155 c.p.s. (CH_3—C—CH_3). The peak intensities indicate relative numbers of chemically different protons in accord with the 2,2,4-trimethyl-3-pentenal structure. (c.p.s. rel. to H_2O)

Spin-spin peaks resulting from the interactions between the olefinic proton and the protons of the methyl groups across the double bond were observed.

Catalytic hydrogenation of IV yielded 2,2,4-trimethyl-1-pentanol and established the structure of the carbon skeleton.

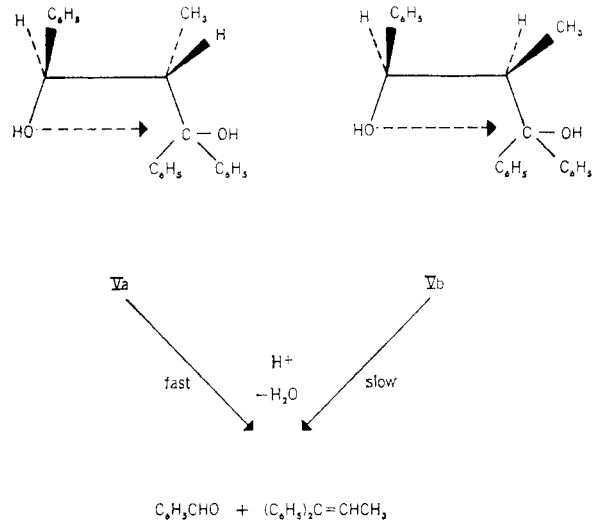
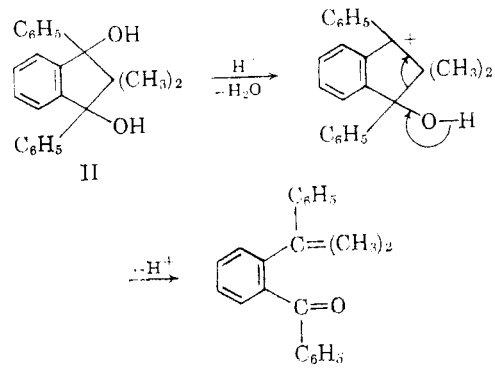


Figure 1

The mechanism of the acid-catalyzed cleavage of 1,3-diols has been explained in terms of carbonium ion intermediates[3,5] and by the use of concerted reactions with four-membered cyclic transition states.[6,7] The carbonium ion mechanism is an adequate explanation for the results of certain cleavage reactions. For example, carbonium ion formation from the glycol II[4] does not seem unlikely, particularly in view of the benzhydrol-type structure involved.



II

On the other hand, a carbonium ion mechanism does not account for the differences in rate of cleavage of the diastereoisomers of V.[8] A more likely explanation is a concerted mechanism requiring a specific orientation of the hydroxy groups in the transition state. The difference in ease of arrangement to the properly oriented intermediate thus explains the different rates of cleavage of these isomers.

(5) F. C. Whitmore and E. E. Stahly, *J. Am. Chem. Soc.*, **67**, 2158 (1945).
(6) A. Barbot, *Bull. Soc. Chim.*, [5] **2**, 1438 (1935).
(7) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2294 (1954).
(8) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2291 (1954).

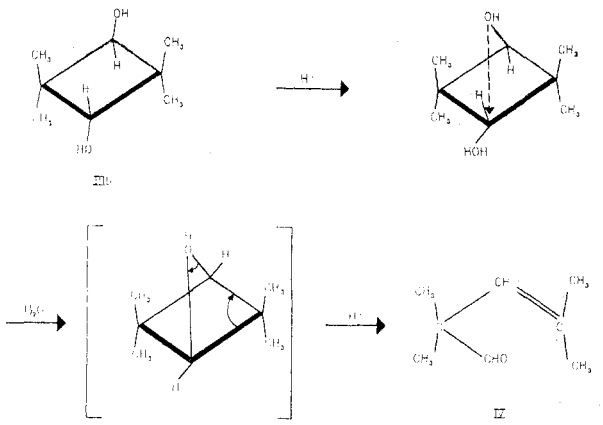


Figure 2

In the case of the cyclic glycol III, a cleavage reaction by a carbonium ion mechanism is obviously untenable in view of the large differences in behavior of the *cis* and *trans* isomers. Furthermore, a simple concerted mechanism, without participation of one hydroxy as a neighboring group in removal of the other hydroxy, does not provide an adequate explanation. A satisfactory mechanism requires a concerted transannular reaction, with formation of an intermediate bicyclic transition state.

The mechanism used by Zimmerman and English[8] to explain the different susceptibilities of acyclic glycols to cleavage thus provides an adequate explanation of the very large difference in the behavior of the isomers of III. The isomers of the acyclic glycol V differ only in the ease of orientation to the transition state configuration; in the case of the tetramethylcyclobutanediols, only the *trans* isomer can undergo cleavage by the corresponding transannular mechanism.

ADDED IN PROOF: In work reported since this paper was submitted, T. E. Maggio and J. English, Jr., *J. Am. Chem. Soc.*, **83**, 968 (1961), studied the cleavage of *cis* and *trans* isomers of cyclic 1,3-diols (one hydroxy group in a side chain). The mechanism proposed to accommodate their results does not provide an explanation for the difference in behavior of IIIa and IIIb.

EXPERIMENTAL

Dehydration of trans-2,2,4,4-tetramethyl-1,3-cyclobutanediol (IIIb). A solution of 100 ml. of concd. sulfuric acid (sp. gr. 1.84) in 2500 ml. of water was mixed with 1000 g. (6.94 moles) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III, a mixture of approximately equal amounts of *cis* and *trans* isomers[9,10]). The mixture was heated to boiling and the vapors were distilled into a continuous azeotrope separator. The solid glycol dissolved and the reaction mixture became homogeneous; as the reaction progressed, a crystalline solid gradually was deposited from the solution.[11] The mixture was heated until volatile organic material no longer evolved and collected in the azeotrope separator. After 72 hr. the amount of organic distillate was 427 g.

The residue, a mixture of solid and liquid, was cooled to room temperature and the solid was removed and dried. The yield of *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (IIIa), m.p. 158–163°, was 457 g. An additional 42 g. of IIIa, m.p. 162–163°, was obtained by making the filtrate slightly basic with sodium bicarbonate and then removing and drying the precipitate. The total yield of IIIa was 499 g. (100% based on an estimated content of 50% IIIa in the starting material).

The *cis*-glycol (IIIa) was dissolved in boiling toluene containing some solid sodium bicarbonate (to neutralize traces of occluded acid). Undissolved material was removed by filtration and the solution was cooled and allowed to stand. The recrystallized glycol (95% of the crude product) had a melting point of 162.5–163.5°, identical with that reported for pure IIIa.[1]

The liquid distillate (organic layer from the azeotrope separator) was dried with anhydrous magnesium sulfate, filtered, and distilled through a 1.8 × 25 cm. column filled with 0.16 × 0.16 in. protruded stainless steel packing. Fractions of 2,2,4-trimethyl-3-pentenal (IV), b.p. 81–83.5° (100 mm.), n_D^{20} 1.4357–1.4361, amounted to 218 g. (50%, based on an estimated content of 50% IIIb in the starting material). Strong absorption at 1735 cm.$^{-1}$ and 2700 cm.$^{-1}$; weak absorption at 1660 cm.$^{-1}$

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18; mol. wt., 126. Found: C, 76.11; H, 11.32; mol. wt., 119.

The NMR spectrum of IV was recorded with a Varian Associates Model V-4300-B high-resolution NMR instrument (40 mc.) equipped with a flux stabilizer. The chemical shift positions were determined relative to water as an external standard. Chemical shift peaks were observed at −160 c.p.s., 0 c.p.s., 131 c.p.s., 135 c.p.s., and 155 c.p.s. Spin-spin peaks (J = 1.5 c.p.s.) were observed in the resonance at 0 c.p.s. The resonances at 131 and 135 c.p.s. were each split into doublets by interaction with a single proton (J = 1.5 c.p.s.).

The 2,4-dinitrophenylhydrazone of IV was prepared and recrystallized from ethyl alcohol. It melted at 142–143°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.82; H, 5.75; N, 17.78.

Hydrogenation of 2,2,4-trimethyl-3-pentenal (IV). A mixture of 2,2,4-trimethyl-3-pentenal (66.3 g., 0.526 mole), 150 ml. of ethyl alcohol, and 5.0 g. of Raney nickel was heated and shaken in an autoclave at 150° under 1000 psi. pressure of hydrogen for 7 hr. The mixture was filtered to remove catalyst and the filtrate was distilled through a 1.8 × 18 cm. column packed with $^5/_{16}$-in. glass helices. The yield of 2,2,4-trimethyl-1-pentanol was 55.4 g. (81%), b.p. 164–166.5°, n_D^{20} 1.4292–1.4298. Brannock reported b.p. 166–166.5°, n_D^{20} 1.4300.[12] The infrared spectrum was identical with that of an authentic sample of 2,2,4-trimethyl-1-pentanol.

Stability of trans-2,2,4,4-tetramethyl-1,3-cyclobutanediol (IIIb). An equimolar mixture of the isomers of III was boiled with aqueous sulfuric acid solutions of increasing concentration. The rate of formation of IV was observed by collection of the condensate in a continuous azeotrope separator and measurement of the amount of organic distillate. The glycol III was unchanged after being heated in boiling water for 45 hr. A solution of 200 g. of III in 500 ml. of water containing 10 ml. of 0.1*N* sulfuric acid was also unchanged after being refluxed for 91 hr. After addition of 80 ml. more 0.1*N* sulfuric acid, further refluxing produced 2.4

(9) Available from Eastman Chemical Products, Inc., Kingsport, Tenn.

(10) R. H. Hasek and E. U. Elam, U. S. Pat. 2,936,324 (1960).

(11) The solid was *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (IIIa), which is less soluble in water than the mixture of isomers.

(12) K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).

g. of impure IV in 48 hr. Finally, after addition of 3 ml. of concd. sulfuric acid in 10 ml. of water, continued refluxing gave 72.3 g. more impure IV in 168 hr.

Stability of cis-2,2,4,4-tetramethyl-3-cyclobutanediol (IIIa). The *cis* isomer of III[1] (77.5 g.) was mixed with 500 ml. of water and 20 ml. of concd. sulfuric acid, and the solution was refluxed for 271 hr. in apparatus equipped with a continuous azeotrope separator. No IV was formed and apparently no change occurred. An additional 50 ml. of concd. sulfuric acid was added; again no IV was formed during 21 hr. of refluxing. The mixture was cooled and 180 ml. of concd. sulfuric acid was added. When heating was resumed, the solid glycol dissolved, the color of the reaction solution rapidly darkened, and tar gradually formed. After 41 hr., heating was stopped and the small amount of organic distillate in the azeotrope separator was examined. It was a complex mixture in which no IV could be found by distillation.

KINGSPORT, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Acenaphthene Chemistry. VII.[1,2] The Synthesis and Properties of an Acenaphthenequinolimide Acetate

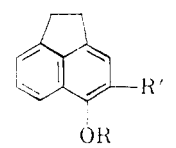
HENRY J. RICHTER AND WILLIAM C. FEIST[3]

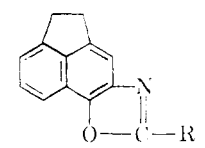
Received March 13, 1961

5-Acetoxyacenaphthene undergoes the Fries rearrangement to form 4-acetyl-5-acenaphthenol. The oxime of this ketone in acetic anhydride-acetic acid with hydrogen chloride formed 4,5-acenaphtho[*d*]2-methyloxazole. 4-Amino-5-acenaphthenol hydrochloride formed the same oxazole when treated with acetic anhydride followed by treatment of the product with concentrated hydrochloric acid. 4-Benzenesulfonamido-5-methoxyacenaphthene was oxidized to 4-benzenesulfonamido-5-methoxy-5-acenaphthenequinol acetate by lead tetraacetate. This quinol acetate is converted into 4,4′-dibenzenesulfonamido-5,5′-dimethoxy-2,1′-biacenaphthylidine when a suspension in acetic acid is treated with concentrated hydrochloric acid.

The preparation and characterization of 4,5-acenaphthenequinonedibenzenesulfonimide has been described.[4] In this work attention was directed toward a similar study of an acenaphthene compound with a quinonemonoimide structure. Quinonemonoimides with benzenoid and naphthenoid ring systems have been extensively investigated by R. Adams and his co-workers.[5]

In our work 5-acenaphthenol (I)[6] was treated with acetic anhydride to produce the acetate, II, which was found to undergo the Fries rearrangement on treatment with anhydrous aluminum chloride. The bright yellow product from this rearrangement, III, formed an oxime IV which was expected to produce 4-acetamido-5-acenaphthenol (V) when subjected to Beckmann rearrangement conditions.





I. R = H; R′ = H
II. R = $COCH_3$; R′ = H
III. R = H; R′ = $C(=N-OH)CH_3$
IV. R = H; R′ = $C(=N-OCOCH_3)CH_3$
V. R = H; R′ = $NHCOCH_3$
VI. R = H; R′ = $C(=N-CH_3)CH_3$

VII. R = CH_3
VIII. R = $CH{=}CHC_6H_5$

Two products were obtained. One separated from the reaction mixture in 26% yield and is believed to be the oxime acetate VI and the other obtained in 62% yield was precipitated as a tan solid m.p. 139–140°, VII, when the filtrate was poured into water. The anticipated acetamide V is reported[6] to melt at 165°. A comparison of the infrared spectra of our substance and that of V obtained from a sample kindly supplied by Professor H. Rapoport showed them to be different. The material melting at 139–140° exhibited strong absorption at 1580 cm.$^{-1}$ indicative of C=N.[7] Chemical analysis indicated $C_{14}H_{11}NO$ which corresponds to 4,5-acenaphtho[*d*]2-methyloxazole (VII). The literature[8–10] discloses the formation of oxazoles from

(1) Previous paper: H. J. Richter and W. C. Feist, *J. Org. Chem.*, **25**, 356 (1960).

(2) This work was supported by research grant CY-2997 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service and by a Monsanto Chemical Co. grant-in-aid.

(3) This paper and number VI of this series represent a portion of a thesis submitted by William C. Feist in partial fulfillment of the requirements for the Ph.D. degree at the University of Colorado, 1960. Presented at the 140th National Meeting of the American Chemical Society at Chicago in Sept. 1961.

(4) H. J. Richter and B. C. Weberg, *J. Am. Chem. Soc.*, **80**, 6446 (1958).

(5) R. Adams and W. Reifschneider, *Bull. Soc. Chim. France*, 23 (1958).

(6) H. Rapoport, T. P. King, and J. B. Lavigne, *J. Am. Chem. Soc.*, **73**, 2718 (1951).

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, N. Y., 1958, 2nd ed., (a) page 96, (b) page 179.

(8) J. Meisenheimer, *J. Pr. Chem.*, [11], 119, 315 (1928).

(9) A. H. Blatt, *J. Am. Chem. Soc.*, **60**, 205 (1938).

(10) J. Meisenheimer and R. Meis, *Ber.*, **57**, 289 (1924).