[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Bicyclic Olefin from *cis,trans,trans*-Cyclododecatriene and Sulfuric Acid[1]

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Treatment of *cis,trans,trans*-1,5,9-cyclododecatriene with 80% sulfuric acid produces a mixture of hydrocarbons containing $\Delta^{1,6}$-bicyclo[4.6.0]dodecene. The structure of the monoölefin is indicated by ozonolysis to a diketone, 1,6-cyclododecadione, oximation of the diketone, Beckmann rearrangement, and hydrolysis to a mixture containing δ-aminovaleric acid and ψ-aminoenanthic acid, identified by paper chromatography. The structures are confirmed by comparison of the diketone with a sample produced from benzocycloöctene by Birch reduction to $\Delta^{1,6}$-bicyclo[4.6.0]dodecene and ozonolysis of the latter.

A carbonium ion formed by protonation of one of the double bonds of cyclododecatriene (I), the easily available trimer of butadiene,[3] would be expected to generate a bicyclic carbonium ion as the result of interaction between the initially formed ionic center and one of the remaining double bonds. The present work is an examination of some of the products obtained by a treatment of the triolefin with strong sulfuric acid under conditions similar to those employed in the hydration of simple olefins.

When *cis,trans,trans*-1,5,9-cyclododecatriene[4] was treated with cold 80% sulfuric acid and the mixture was stirred for some time at 15°, then diluted with ice, slowly warmed, and finally steam distilled, a volatile hydrocarbon fraction resulted, amounting to about 20% of the triolefin employed. Analyses of redistilled samples of this substance indicated it to have the formula $C_{12}H_{20}$, richer in hydrogen by two atoms than the triolefin. The substance was not hydrogenated by Adams' catalyst in ethyl acetate or acetic acid under conditions (1 to 3 atm.) that effected rapid hydrogenation of the triolefin, and the infrared spectrum did not reveal absorption in the 1650 cm.$^{-1}$ region. However, the samples did give positive tests for unsaturation with bromine and with potassium permanganate, and a titration by the modified Hanus method[5] indicated 1.1 double bonds per molecule. These observations suggest a structure containing one double bond common to two rings, presumably of a conformation that interferes with interaction between the double bond and the hydrogenation catalyst. Oxidation of a compound of this structure should lead to a diketone.

Ozonolysis of the new hydrocarbon produced a crystalline substance, of the composition $C_{12}H_{20}O_2$, having the properties of a diketone (reactions with carbonyl reagents, infrared absorption at 1708 cm.$^{-1}$). The derivatives obtained with *p*-nitrophenylhydrazine and with hydroxylamine were solids of quite narrow melting range and of the expected compositions; nevertheless, as indicated below, the oximation product must contain two of the three possible *syn-anti* forms. The structure of the diketone was investigated by subjection of the oximation product to the Beckmann rearrangement, hydrolysis of the dilactams so formed, and analysis of the resulting amino acids by paper chromatography. Spots resulting from the amino acids in the mixture (R_f values, 0.44 to 0.47 and 0.61 to 0.65) agreed closely with those measured on known samples of δ-aminovaleric acid (0.42 to 0.46) and ω-aminoenanthic acid (0.65) in identical experiments, and differed significantly from that (0.50–0.52) measured on ϵ-aminocaproic acid. Evidence for the presence of 1,6-diaminohexane was observed in a spot (R_f 0.24 to 0.25, as compared to 0.24 to 0.29 for the known compound), but no indication of 1,4-diaminobutane was seen.

The results of the paper chromatography are those expected if the diketone has the structure III, and if the dioxime contains two of the three possible isomers (IV and V). A diketone derived from an isomer of II having two seven-membered rings or a combination of five- and nine-membered rings could give only ϵ-aminocaproic acid or a mixture of γ-aminobutyric and ω-aminoöctanoic acid. The probability that the unknown material had the structure II thus seemed great enough to justify the synthesis of II and III for comparison.

Benzocycloöctene was synthesized by a modification of the method of Huisgen and Rapp.[6] When this hydrocarbon was treated with lithium and ethylamine under the conditions of the Birch[7] reduction, it yielded a product of the composition $C_{12}H_{20}$ which was very similar in properties to the unknown hydrocarbon; differences, such as those in the infrared spectra, could be attributed to the higher purity of the synthetic specimen. Ozonolysis yielded the crystalline diketone, identical in in-

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[2] Graduate Research Assistant, 1957–58, on a grant provided by Phillips Petroleum Company.

[3] G. Wilke, *Angew. Chem.*, **69**, 397 (1957); *J. Polymer Science*, **38**, 45 (1959).

[4] Kindly supplied by Esso Research and Engineering Co.; stabilized with 0.1% of *t*-butylcatechol.

[5] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 33.

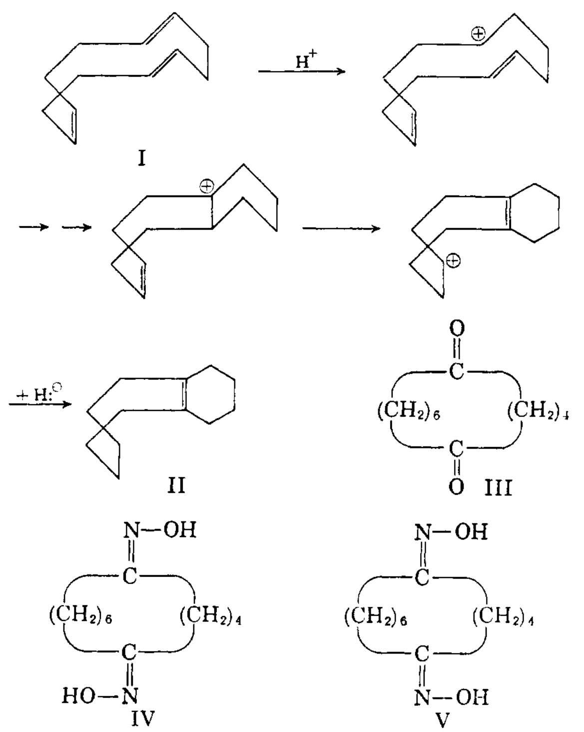
[6] R. Huisgen and W. Rapp, *Ber.*, **85**, 826 (1952).

[7] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

frared spectrum, melting point, and mixed melting point with the sample prepared from the unknown. The *p*-nitrophenylhydrazones and oximes of the two samples also were identical as determined by melting points and mixed melting points.

The formation of the bicyclic ring system in II can be explained readily on the basis of protonation, transannular attack of the carbonium ion so formed on a second double bond within the system, hydride shift, and deprotonation, the final step generating the double bond common to the two rings. This series would produce a diolefin, rather than a monoölefin, however. It is possible that instead of the last suggested step, or following it, a proton is transferred to the remaining disubstituted double bond, and that the unsaturated carbonium ion so formed abstracts a hydride ion from another molecule in the reaction mixture to generate the monoölefin, this step being similar to that occurring in the alkylation of paraffins by olefins,[8] and producing a more highly unsaturated product which may have polymerized (as much as 65% of the triolefin was converted to nonvolatile materials). Such a possible path is shown in the accompanying scheme.

Recently disclosed studies report the action of cyclododecatriene with carbon monoxide and strong acids,[9] alone or in the presence of alcohols, to give mixtures of C_{13} acids and their esters, which, because of the absence of infrared absorption attributable to olefinic groups, are regarded as saturated polycyclic compounds. Some of these products may have the carbon skeleton of II.



EXPERIMENTAL[10]

Treatment of cis,trans,trans-1,5,9-cyclododecatriene with 80% sulfuric acid. To 66 ml. of stirred 80% sulfuric acid, cooled in ice salt, was added over 30 min. 16.2 g. of the cyclododecatriene. The ice salt bath was replaced by an ice bath and the mixture was stirred 3 hr. at 15°. Ice (250 g.) was added, and the mixture was stirred until it had come to room temperature. It was then slowly warmed to 60°, and finally subjected to steam distillation in order to separate volatile materials from tars and other nonvolatile products. The distillate, *ca.* 3 l., was saturated with sodium chloride and extracted with 800 ml. of ether in four portions. After being washed with sodium bicarbonate solution and with water, the solution was dried over magnesium sulfate and concentrated at low temperature. A typical fractional distillation of the light yellow oil through a 0.8 × 16 cm. Vigreux column yielded about 3.3 g. of colorless liquid boiling in the range 62–68° (1 mm.); n^{25}_{D} 1.4960–1.5000. Analytical samples were obtained by repeated redistillation from a micro still; b.p. 34–35° (0.2–0.3 mm.), n^{25}_{D} 1.4995.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.28. Found: C, 87.64; H, 12.40.

Ozonolysis. Ozonized oxygen (5% ozone) was passed for *ca.* 2.5 hr. through a solution of 1.52 g. of the above product in 200 ml. of methanol at −5°. The solvent was removed at low temperature *in vacuo* behind a shield, and 70 ml. of 40% acetic acid was added to the residue. The mixture was cautiously warmed to 50° and then allowed to stand in the room overnight before the addition of 1.5 g. of sodium sulfite. Salt was added, and the mixture was extracted with 120 ml. of ether in four portions. After washings with bicarbonate solution and water and drying over magnesium sulfate the solution was concentrated *in vacuo* to give 0.74 g. of a white solid of m.p. 79–89°. A second crop (0.36 g., m.p. 82–90°) was obtained from the combined aqueous acetic acid solution and aqueous washings by neutralization with potassium bicarbonate, extraction with ether, etc. Crystallization from petroleum ether (b.p. 30–60°) raised the m.p. to 91–95°, and sublimation increased it to 94–95°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.27. Found: C, 73.25; H, 10.18.

The substance gave a derivative with 2,4-dinitrophenylhydrazine (m.p. 257–260°), but a solvent for recrystallization was not found. The *p*-nitrophenylhydrazone[11] (m.p. 203–207°) was crystallized from ethanol.

Anal. Calcd. for $C_{24}H_{30}N_6O_4$: C, 61.78; H, 6.48. Found: C, 61.12; H, 6.47.

The oxime(s), prepared in pyridine[11] and recrystallized from ethanol, melted at 233–235.5°.

Anal. Calcd. for $C_{12}H_{22}O_2N_2$: C, 63.68; H, 9.80; N, 12.38. Found: C, 63.44; H, 9.63; N, 12.22.

Beckmann rearrangement of the dioximes and hydrolysis of the lactams. A mixture of 9.2 mg. of the oximes above and 1 ml. of 85% sulfuric acid was gently heated over a small flame for a few minutes (until white vapors formed). It was then cooled, diluted with 25 ml. of water, and refluxed for 3 hr. After cooling it was neutralized with 50% aqueous

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[8] P. Bartlett, F. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1534 (1944).

[9] Belgian Patent **567,112** (April 25, 1958) to Studiengesellschaft Kohle.

[10] Melting points were determined on a Kofler microstage apparatus, and are uncorrected. Microanalyses were performed by Mr. Josef Nemeth and his associates. Infrared spectra were measured by Mr. Paul McMahon and his associates.

[11] This and other carbonyl derivatives were prepared by procedures described by R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1956.

sodium hydroxide and refluxed 3 hr. Samples of the cooled solution were spotted on strips of filter paper, along with known solutions (*ca.* 3 mg. per ml.) of 1,6-diaminohexane, δ-aminocaproic acid, and ε-aminovaleric acid, individually and mixed together. ω-Aminoenanthic acid was spotted on identical paper, but at a later date because of the unavailability of a sample at the time. The strips were developed by descending paper chromatography for 12 hr., with an eluant prepared by thoroughly mixing 1-butanol, glacial acetic acid, and water in the ratio 40:10:50 and discarding the lower layer. The strips were air-dried for 4 hr., sprayed with 0.25% alcoholic ninhydrin, and dried for 30 min. The R_f values calculated[12] were those listed above. Similar results were obtained when the Beckmann rearrangement was initiated with phosphorus pentachloride.

Birch reduction of benzocycloöctene. $\Delta^{1,6}$-*Bicyclo[4.6.0]-dodecene.* Benzocycloöctene was prepared by the method of Huisgen and Rapp,[6] except that methyl acid adipate (Eastman Kodak Co.), was employed instead of the ethyl ester. The hydrocarbon (1.6 g., b.p. 95–100°/5 mm., n_D^{25} 1.5376 to 1.5380, lit.[6] n_D^{21} 1.5392) was added dropwise to a stirred mixture of 0.7 g. of clean lithium wire and 50 ml. of dry ethylamine, under an atmosphere of nitrogen in an apparatus fitted with a Dry Ice cooled condenser, at such a rate that the blue color of the solution was not discharged. At the end of the addition more (0.15 g.) lithium was introduced and stirring was continued 2 hr. The unchanged lithium was removed and the solution was concentrated at room temperature. About 50 ml. of water was added with cooling and the solution was extracted with 80 ml. of ether in four portions. The extracts were washed with dilute hydrochloric acid and water, and dried over sodium sulfate. Removal of the solvent gave 1.34 g. of an oil (b.p. 45–46°, 0.15–0.2 mm.; n_D^{25} 1.5024) which was twice redistilled from a micro still. The fraction analyzed boiled at 42° (0.1 mm.); n_D^{25} 1.5022.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.28. Found: C, 87.75; H, 12.28.

The infrared spectrum of this substance was very similar to that of the $C_{12}H_{20}$ product obtained from cyclododecatriene, the peaks being sharper in the Birch reduction product presumably as the result of higher purity.

1,6-Cyclododecadione. The ozonolysis of 0.534 g. of the above olefin in 75 ml. of carbon tetrachloride was conducted with 4% ozonized oxygen at 0° for 2 hr. The product, isolated as described above, melted at 91–94° after one crystallization from petroleum ether (b.p. 00–00°), and at 94–95° after sublimation, undepressed by admixture with the sample described above. The infrared spectra of the two samples were indistinguishable.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.27. Found: C, 73.27; H, 10.23.

The dioxime melted at 240°.

Anal. Calcd. for $C_{12}H_{22}O_2N_2$: C, 63.68: H, 9.80. Found: C, 63.92; H, 9.87.

The di-*p*-nitrophenylhydrazone[11] melted at 203–206°, undepressed by admixture of the derivative (m.p. 203–207°) described above, but the analyses of this sample indicated incomplete removal of solvent. No depression of melting point occurred when the (unanalyzed) disemicarbazones[11] from the two samples of diketone were mixed; in this instance the derivative of the diketone prepared from the triolefin melted higher (212° dec., *vs.* 202–205° dec.). The bisdinitrophenylhydrazone[11] (unanalyzed) melted at 266–267° dec.

URBANA, ILL.

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[12] E. Lederer and M. Lederer, "Chromatography," Elsevier Publishing Co., New York, N. Y., 1957, p. 115.

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

Preparation and Acid-Catalyzed Solvolysis of 6-Tosyloxyisophorone

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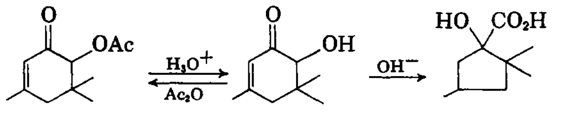
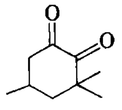
6-Tosyloxyisophorone (I) in dioxane-hydrochloric acid undergoes loss of *p*-toluenesulfonic acid to give 3,4,5-trimethylphenol. In methanolic hydrogen chloride I gives 3,4,5-trimethylanisole.

6-Tosyloxyisophorone (I) has been prepared in three steps from isophorone. Some acid-catalyzed solvolysis reactions have been examined briefly and are reported here.

Isophorone was acetoxylated with lead tetraacetate to give a fair yield of an acetoxyisophorone which has been assigned structure II on the basis of its conversion to III and IV. The ketol III, obtained by hydrolysis of II, was oxidized by Fehlings solution and also gave a positive acyloin test.[1] Acetylation of the ketol gave back II. The structure of III was established by its conversion to the known compound, 1-hydroxy-2,2,4-trimethylcyclopentanecarboxylic acid (IV), by the action of hot alcoholic alkali. The transformation of III to IV undoubtedly proceeds through the α-diketone V, which, however, was not isolated in the present work. The rearrangement of III to V has a fairly close analogy in the conversion of 2-hydroxypulegone to diosphenol in hot aqueous alkali.[2] It has been shown that V is converted into IV in hot alkali.[3]



II III IV



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[1] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[2] R. H. Reitsema, *J. Am. Chem. Soc.*, 79, 4465 (1957).

[3] M. Qudrat-I-Khuda and S. K. Ghosh, *J. Ind. Chem. Soc.*, 16, 287 (1939).