If the polymer which is formed early in the reaction should undergo a change during later stages of conversion, anomalous results might be obtained. For example, the reciprocal of the instantaneous molecular weight, $1/M$, which is given by equation (6), is equal to dN/dW. If it should be found at some stage of the polymerization that dN/dW were negative, one would have a proof of cross-linking. Obviously a negative molecular weight would be meaningless, but a negative value for dN/dW would be very meaningful. Cross-linking and branching might also affect "increment" intrinsic viscosities in an unusual but significant manner. Compositional analyses, however, should be free from any such anomalous effects.

Summary

Equations are derived by means of which "average" polymer data known as functions of conversion can be analyzed to give the properties of polymer increments forming at different stages of conversion. Suggestions are given as to the types of data which can be so studied and to possible interpretations of anomalous results.

URBANA, ILLINOIS RECEIVED AUGUST 8, 1945

[CONTRIBUTION FROM THE IPATIEFF HIGH-PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, AND UNIVERSAL OIL PRODUCTS CO.]

Studies in the Terpene Series. IV.[1] Method for the Determination of Rings in Bicyclic Dihydroterpenes. Isomerization of Pinane in the Presence of Dilute Aqueous Salt Solutions

BY V. N. IPATIEFF AND HERMAN PINES

The study of the structure of bicyclic dihydroterpenic hydrocarbons could be greatly facilitated if the relative size of the various rings could be established. This has now been achieved by treating the various dihydroterpenic hydrocarbons with dilute aqueous acid-acting salt solutions at elevated temperatures and pressures, using experimental conditions given in a previous paper of this series.[2] From the present study of the action of 1–2% aqueous magnesium chloride solution upon cyclofenchene, pinane, isobornylane and isocamphane, it has been shown that the most stable bicyclic hydrocarbons are those containing a five-membered within a six-membered ring; less stable are those having a four-membered ring and the most reactive are those having a three-membered ring.

It was found that the cyclopropane ring in *cyclofenchene* underwent scission when this hydrocarbon reacted with aqueous magnesium chloride solution at 280°. Bicyclic olefinic hydrocarbons were formed which on hydrogenation yielded dihydrodicyclic hydrocarbons. The hydrocarbons, according to their properties and analysis, had the formula $C_{10}H_{18}$ and contained at least one five-membered ring.

Isocamphane when heated with the same catalyst to 400° underwent partial dehydrogenation; no rupture of the rings occurred. The product of the reaction on hydrogenation at 50° formed the original isocamphane, m. p. 62°.

Isobornylane was heated at 425° for several hours but remained without change.

It was found that in *pinane* the cyclobutane ring underwent rupture when it was heated at 350°, under pressure in the presence of an equal volume of a 2% aqueous solution of magnesium chloride. Under these conditions, the pinane did not yield the expected methylisopropylcyclohexene but underwent, mostly, isomerization into an unsaturated hydrocarbon containing a five-membered ring consisting, probably, of 1-ethyl-2-isopropylcyclopentene. The product of the reaction was distilled on a 45-plate column and the distillation curve (Fig. 1) showed a plateau at 157° corresponding to the five-membered-ring hydrocarbon and a plateau at 165°. The preliminary investigation showed that the higher product consisted mainly of unreacted pinane admixed with unsaturated monocyclic hydrocarbons, the structure of which we intend to study.

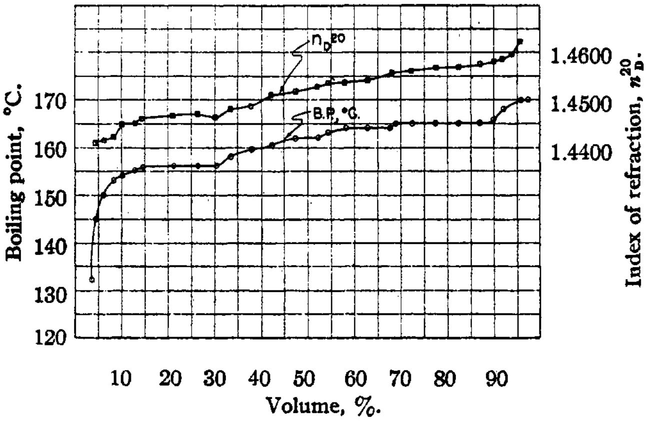

Fig. 1.

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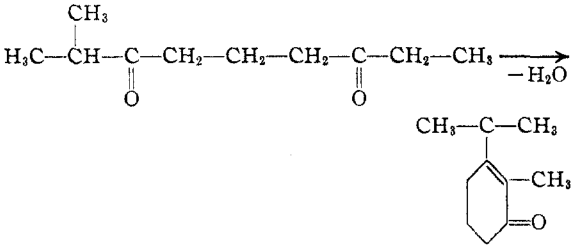
(1) For paper III of this series see V. N. Ipatieff and H. Pines, THIS JOURNAL, **67**, 1226 (1945).

(2) V. N. Ipatieff and H. Pines, *ibid.*, **66**, 1120 (1944).

The presence of a cyclopentane ring was suggested by the fact that the product, after hydrogenation by the usual method, did not undergo dehydrogenation to aromatic hydrocarbons when passed over platinized alumina at 300°. It has been demonstrated that cycloalkanes containing six-membered rings, including those in which two hydrogen atoms on the same carbon atom are substituted, yielded under similar conditions, aromatic hydrocarbons.

The products, obtained from the treatment of pinane, absorbed on hydrogenation one mole of hydrogen per mole of hydrocarbons. Unlike other olefins[3] the alkylcyclopentene produced did not react with benzene, using sulfuric acid as catalyst, which suggests the existence of a sterically hindered ethylene bond.

The product on ozonization yielded 15% of a keto acid and about 60% of a diketone, the latter being characterized by means of semicarbazone melting at 183° and 2,5-dinitrophenylhydrazone, melting at 169°. The diketone gave a negative iodoform test. On refluxing with alcoholic potassium hydroxide it underwent cyclization, resulting in the formation of a monoketone which was characterized by means of dinitrophenylhydrazone melting at 156–158°. The compound formed, probably, according to the equation:

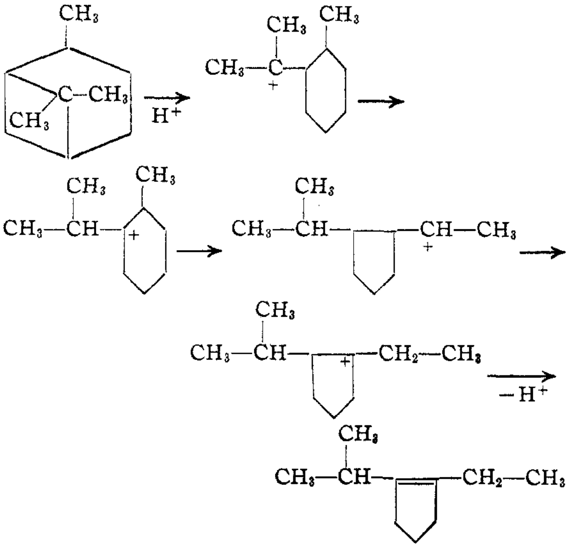


The properties of the diketone produced and the analysis of the dinitrophenylhydrazone and semicarbazone indicate that the product was of the formula $C_{10}H_{18}O_2$; however, the elementary analysis of the diketone, although repeated several times, did not agree with the values calculated. Since no active hydrogen was present in the molecule as determined by the Zerewitinoff–Tschugaeff methylmagnesium bromide test, the low carbon value could not be attributed to a hydrated form of the diketone.

The diketone on hydrogenation yielded a cyclic ether, probably a substituted pyrane; the formation of the latter is due to cyclic dehydration of the glycol formed. This type of hydrogenation has been reported to occur with 1,4- and 1,5-diketones. Part of the diketone did not react and was recovered unchanged. It showed, on analysis, carbon and hydrogen values corresponding to $C_{10}H_{18}O_2$; the dinitrophenylhydrazone was identical with that of the original diketone. It seems that on hydrogenation some of the "impurity" responsible for the low carbon analysis was removed.

The keto acid produced by the ozonolysis of the cycloalkene corresponded according to elementary analysis and to neutralization equivalent to $C_{10}H_{18}O_3$. It showed a negative iodoform test.

The formation of 1-ethyl-2-isopropylcyclopentene from pinane can be explained on the assumption that the first product of reaction was 1-methyl-2-isopropylcyclohexene which through a ring contraction underwent further isomerization according to the scheme



In order to prove conclusively that the main product obtained from the isomerization of pinane is 1-ethyl-2-isopropyl-cyclopentene, synthesis of this product or of the product resulting from its oxidation is contemplated.

The higher-boiling hydrocarbons consisted of unreacted pinane and small amounts of cyclic olefins, the structure of which was not studied.

Experimental

Material

Isocamphane was prepared from isoborneol according to the method described previously by us[2]; it melted at 62°.

Isobornylane was obtained by hydrogenating fenchyl alcohol by means of alumina–nickel catalyst.[4]

Pinane was prepared by hydrogenating α-pinene dissolved in an equal volume of *n*-pentane in the presence of a nickel–kieselguhr catalyst at 60° and under an initial hydrogen pressure of 100 atmospheres measured at 20°. The pinane obtained distilled at 165–166°, $n^{20}D$ 1.4605.

Cyclofenchene was obtained by dehydration of fenchyl alcohol in the presence of activated alumina. It distilled at 143–144°, $n^{20}D$ 1.4513.

Procedure

Cyclofenchene, 24 g., was heated in the presence of an equal volume of a 2% aqueous solution of magnesium chloride, in a rotating autoclave at 280° for three hours. Eleven grams of unsaturated hydrocarbons boiling at 145–

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(3) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253, references (1940).

(4) The product formed was originally reported by V. N. Ipatieff (*Ber.*, **45**, 3205 (1912), to be fenchane; but it has been shown that isobornylane was the hydrocarbon produced (J. L. Simonsen, "The Terpenes," Vol. II, Cambridge Univresity Press, 1932, p. 435).

160° was separated on distillation, the remainder consisted of high-boiling polymers. This distillate was hydrogenated at 62°; it absorbed one mole of hydrogen per 1 mole of product charged. The hydrogenated material, boiling at 145–165°, $n^{20}D$ 1.4462, contained a small amount of aromatic hydrocarbons. The latter was removed by treating the product with sulfuric acid containing 15% sulfur trioxide. The treated product distilled at 155–157°, $n^{20}D$ 1.445.

Anal.[5] Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.61; H, 13.19.

Isocamphane, 60 g., was heated at 400° with aqueous magnesium chloride solution for four hours, as described above. The product consisted of 55 g. of a liquid and 1500 cc. of a gas containing 80% hydrogen. The liquid product (b. p. 162–170°) on hydrogenation at 50° yielded a completely saturated hydrocarbon corresponding to isocamphane (b. p. 166–167°, m. p. 62–63°).

Isobornylane, 50 g., was heated at 425° for three hours in the presence of the above-described catalyst. The product, after distillation and analysis was shown to be the original isobornylane with the same freezing point (−15–−18°).

Pinane.—A mixture consisting of 138 g. (1 mole) of pinane and 150 cc. of an aqueous solution containing 2% by weight of magnesium chloride was heated at 350° for two hours in a rotating autoclave of 850-cc. capacity. The maximum pressure reached was 255–260 atmospheres. The autoclave was cooled, hydrocarbons were separated from the water layer, washed and dried. A composite of several experiments was combined and distilled on a 45-plate distilling column. The results of the distillation and the index of refraction of the various fractions are given in Fig. 1.

Investigation of fraction; b. p. 157–158°, $n^{20}D$ 1.4472, d^{20}_4 0.8003.

Hydrogenation.—Sixteen grams (0.12 mole) of the product was hydrogenated in a 125-cc. capacity rotating autoclave in the presence of 2 g. of nickel–kieselguhr catalyst at 60°. The initial hydrogen pressure was 125 atmospheres. One mole of hydrogen was absorbed per 1 mole of hydrocarbon used. The product after hydrogenation distilled at 159–161°, and had $n^{20}D$ 1.4330, and d^{20}_4 0.7889.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.77; H, 14.04.

Dehydrogenation.—Three cc. of the hydrogenated product was passed over platinized alumina at 305° according to the procedure described previously.[6] Dehydrogenation did not take place, although the catalyst showed high activity toward dehydrogenation of *p*-menthane.

Ozonization.—The ozonization was carried out in three portions; in each case 10.3 g. (0.075 *M*) of the unsaturated hydrocarbons was dissolved in 100 cc. of carbon tetrachloride and ozonized at 0°; two to three hours were required to complete the ozonization. The ozonide was decomposed by adding it to 40 cc. of solution consisting of equal volumes of 30% hydrogen peroxide and 10% aqueous sodium carbonate and heating it at 60° for three hours with constant stirring. The composite of the three experiments was steam distilled. The lower, carbon tetrachloride layer which contained the neutral product, was separated. The water layer was extracted twice with carbon tetrachloride and the extract was combined with the original lower layer, dried with anhydrous sodium sulfate and distilled (A).

The product remaining in the flask, from the steam distillation and containing sodium salts of the organic acid produced, was acidified with hydrochloric acid, extracted twice with ether, dried with sodium sulfate and distilled (B).

Neutral Product (A).—The product after the removal of the carbon tetrachloride was distilled at 3.5 mm. pressure: (1) 53–57°, 11.9 g., $n^{20}D$ 1.4466; (2) 57–59°, 9.6 g., $n^{20}D$ 1.4476; (3) bottoms, 1.6 g. The density of the combined fractions 1 and 2 was d^{20}_4 1.0125.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59, mol. wt., 170. Found: C, 65.67; H, 9.58, mol. wt., 163.

The following derivatives of the combined fractions 1 and 2 were prepared:

2,5-Dinitrophenylhydrazone.—The yield was almost quantitative. This derivative was only slightly soluble in hot ethanol and was crystallized from a boiling ethanol–chloroform solution; m. p. 169° (cor.).

Anal. Calcd. for $C_{22}H_{26}O_8N_8$: C, 49.80; H, 4.91; N, 21.13. Found: C, 49.68; H, 4.82; N, 21.08.

The semicarbazone was prepared according to the procedure described by Shriner and Fuson.[7] It was crystallized from a 50% ethanol, melting point, 183°.

Anal. Calcd. for $C_{12}H_{24}O_2N_6$: C, 50.70; H, 8.45. Found: C, 50.56; H, 8.18.

Treatment with Alkali.—Two cc. of the neutral product, boiling point 53–59° at 3.5 mm., was refluxed for six hours with 25 cc. of ethanol containing 0.15 g. of potassium hydroxide. The product was diluted with water, extracted with ether, and the ether evaporated.

2,5-Dinitrophenylhydrazone of the alkali-treated product was prepared. After crystallization from hot alcohol it melted at 156–158°. The mixed melting point of this dinitrophenylhydrazone with that obtained from the original diketone (m. p. 169°) was 140–142°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: N, 16.85. Found: N, 17.10.

Hydrogenation of Diketone.—Four cc. of the diketone was dissolved in 10 cc. of *n*-pentane and hydrogenated at 50–75° in the presence of 1 g. of nickel–kieselguhr catalyst and under 100 atm. initial hydrogen pressure. The hydrogenated product distilled as follows: (1) 72–77° at 27 mm., 1.9 cc., $n^{20}D$ 1.4395; (2) 77–110°, 15 mm. 0.1 cc.; (3) 100° at 13 mm., 1.3 cc., $n^{20}D$ 1.4441.

Cuts 1 and 3 did not contain an active hydrogen; hydroxy groups were absent; it was soluble in dilute sulfuric acid.

Anal. of Cut 3: Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.92; H, 10.38.

Cut 1 did not react with dinitrophenylhydrazine, indicating the absence of ketone.

Cut 3 formed a 3,5-dinitrophenylhydrazone melting at 168° which did not show a depression in melting point when mixed with the dinitrophenylhydrazone of the original diketone.

Acidic Product (B).—The organic acids obtained from the ozonolysis distilled at 134–137° at 3.5 mm., 6.3 g., $n^{20}D$ 1.4575.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.52; H, 9.68; neut. equiv., 186; iodoform test, negative. Found: C, 64.10; H, 9.13; mol. wt., 180.

Summary

A method of distinguishing terpene hydrocarbons containing three-, four- and five-membered rings within a six-membered ring was described.

A rupture of the three-membered ring in cyclofenchene and of the four-membered ring in pinane occurs when these hydrocarbons are heated with a 2% aqueous solution of magnesium chloride at 280 and 350°, respectively, under pressure. The lower-boiling hydrocarbons obtained from the treatment of pinane and amounting to 20% of the total product, consisted probably of 1-ethyl-2-isopropylcyclopentene.

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(5) Microanalysis by Dr. T. S. Ma, University of Chicago.

(6) H. Pines and V. N. Ipatieff, THIS JOURNAL, 61, 1076 (1939).

(7) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 145.

Isobornylane is stable toward the treatment with aqueous magnesium chloride at 425°.

When isocamphane is heated at 400° with aqueous magnesium chloride it retains the dicyclic ring structure; part of the isocamphane undergoes dehydrogenation.

EVANSTON, ILLINOIS
RIVERSIDE, ILLINOIS RECEIVED JULY 13, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Formation of 5-Hydroxymethylfurfural from D-Glucose in Aqueous Solution[1]

BY BARRETT L. SCALLET WITH JOHN H. GARDNER[2]

The literature pertaining to the decomposition of D-glucose during heating in aqueous solution reveals that, in each case studied, some other substance besides glucose and water was present. Decomposition in the presence of amino acids with the production of colored compounds has been extensively studied,[3,4,5] and the action of oxygen on hot aqueous glucose solutions has been noted in the presence and absence of amino acids.[6] In these cases, extent of reaction was judged by amount of color formation or oxygen consumption. Alkaline reagents such as 5% sodium phosphate,[7] dilute potassium hydroxide,[8] and dilute sodium carbonate[9] lead to formation of small quantities of methylglyoxal from glucose, while dilute acids yield 5-hydroxymethylfurfural.[10]

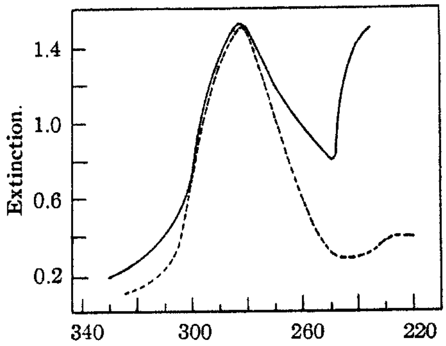

Fig. 1.—Ultraviolet absorption curves: full line, 16.7% glucose solution heated seven hours, diluted 1:4; broken line, benzene extract of a heated glucose solution.

However, no one has attempted to follow the decomposition of glucose in pure aqueous solution. It has now been found that heating such a solution leads to formation of 5-hydroxymethylfurfural in small quantity. The reaction can be followed by measuring the ultraviolet absorption of the solution (Fig. 1, full curve), since 5-hydroxymethylfurfural shows a characteristic, intense absorption band in the ultraviolet (Fig. 2). This permits its determination in very low concentrations such as are present when glucose is decomposed under relatively mild conditions. A glucose solution (16.7%), heated for one hour in boiling water, yielded 6 parts of 5-hydroxymethylfurfural per million parts of glucose and showed no color. Solutions heated two and one-half and seven hours contained 15 and 170 p. p. m., respectively, and the latter was highly colored.

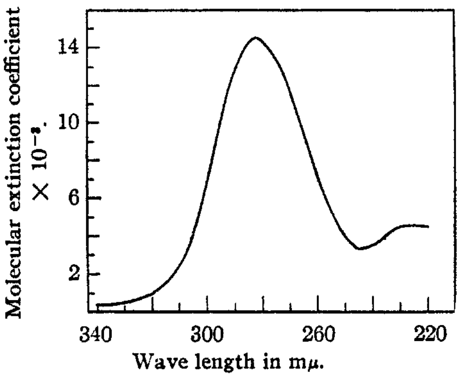

Fig. 2.—Ultraviolet absorption curve for 5-hydroxymethylfurfural.

The presence of the reactive aldehyde and hydroxyl groups in 5-hydroxymethylfurfural suggests that this compound may easily polymerize to give long-chain molecules. Joslyn[11] has indicated that this reaction does take place, yielding brown pigments. Undoubtedly some of the color produced during heating of glucose solutions is due to this reaction. When a heated glucose solution is extracted with benzene the color decreases markedly, but the extracted material, which is nearly pure 5-hydroxymethylfurfural (Fig. 1, broken curve), is almost colorless. In one run, a glucose solution heated overnight in boiling water had a pronounced color. During subsequent extraction with benzene the color decreased about 25%. On evaporation of the benzene, 5-hydroxymethylfurfural, colored a pale

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(1) Part of a dissertation presented to the Board of Graduate Studies of Washington University by Barrett L. Scallet in partial fulfillment of the requirements for the degree of Master of Science, 1943.

(2) Present address, J. T. Baker Chemical Co., Phillipsburg, N. J.

(3) Maillard, *Compt. rend.*, **153**, 1078 (1911).

(4) Ruckdeschel, *Z. ges. Brauw.*, **37**, 430 (1914).

(5) Ambler, *Ind. Eng. Chem.*, **21**, 47 (1929).

(6) Lieben and Bauminger, *Biochem. Z.*, **292**, 371 (1937).

(7) Dakin and Dudley, *J. Biol. Chem.*, **15**, 127 (1913).

(8) Evans, Edgar and Hoff, THIS JOURNAL, **48**, 2665 (1926).

(9) Fischler and Lindner, *Z. physiol. Chem.*, **175**, 237 (1928).

(10) Alberda van Ekenstein and Blanksma, *Chem. Weekblad*, **6**, 217 (1909); *Ber.*, **43**, 2355 (1910).

(11) Joslyn, *Ind. Eng. Chem.*, **33**, 308 (1941).