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SOME COMPOUNDS RELATED TO BICYCLO(3,2,1)OCTANE

A THESIS

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the Faculty of the Graduate Division
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Master of Science in Chemistry

By
William Elmore Gardner

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SOME COMPOUNDS RELATED TO

BICYCLO(3,2,1)OCTANE

Approved : _____

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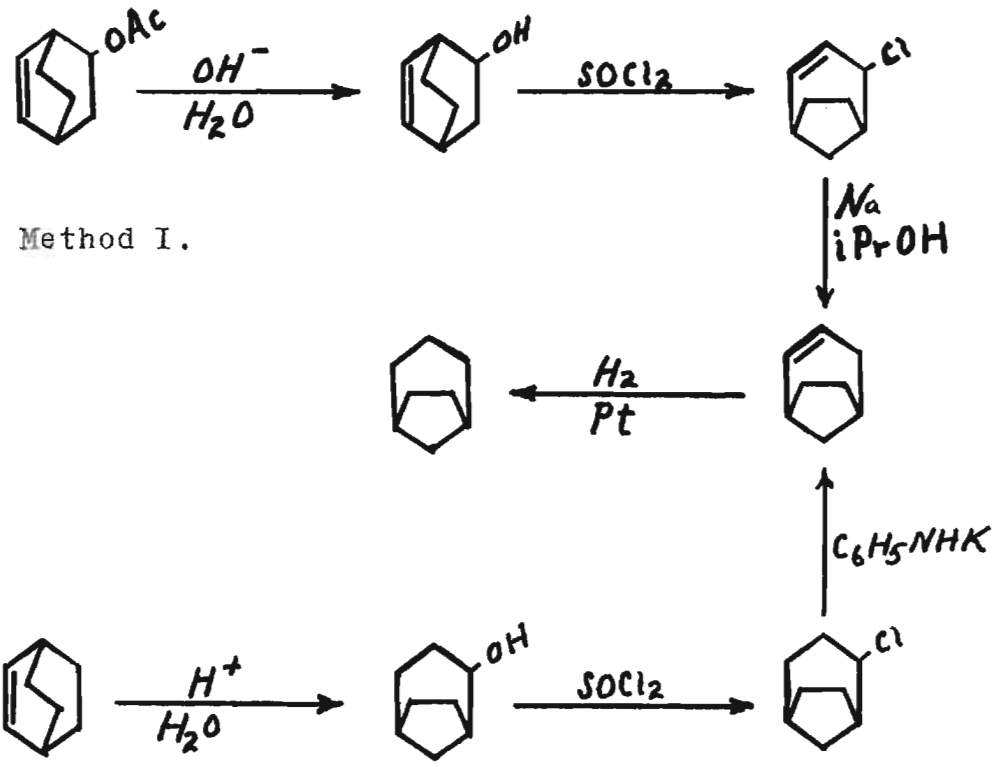
INTRODUCTION

Certain bicyclo(2,2,2)octane compounds undergo reactions which transform them to bicyclo(3,2,1)octane compounds. This investigation proposes to determine whether such rearrangements offer a sound method of preparation of the bicyclo(3,2,1)octane series. Two series of reactions were chosen which should lead to rearrangement of the (2,2,2) compounds producing the (3,2,1) compounds. They are schematically outlined below:



Method I.

Method II.

In both of the methods there is a critical step which first invokes the formation of a carbonium ion and is then followed by rearrangement to the (3,2,1) series. However, the

reaction could proceed by the normal route and in so doing produce the unrearranged products. If the two reaction mechanisms are in competition with each other, mixtures of (3,2,1) and (2,2,2) compounds will result. If this should happen to any great extent the foreseeable difficulty of separating the isomers might well render the method impractical for the synthesis of bicyclo(3,2,1)octane compounds. The thermodynamic and stereochemical considerations favor the formation of the bicyclo(3,2,1)octane compounds.

DISCUSSION

While the literature offers several references relating to the synthesis of cyclohexene dibromide (1), all of them involve diluents along with the cyclohexene. For our experiments cyclohexene was chilled and brominated with elemental bromine in a fashion similar to that described in Organic Synthesis (2). It was found that about ten ml of acetic acid aided in the bromination due to its polar characteristics and was in small enough quantities so as not to cause a serious problem in separation. In order to learn the physical properties of the pure material, some very pure cyclohexene dibromide was made by a modification of the same general scheme of synthesis.

It was necessary to find a good method of preparing 1,3-cyclohexadiene because its cost was prohibitive. It is the diene used in the Diels-Alder condensation which allows an entry to the bicyclo(2,2,2)octane system.

The method of Calingaert and co-workers involving the passage of cyclohexene dibromide vapors over hot calcium oxide was not entertained because it produced too many impurities which could not be separated (3). The addition of cyclohexene

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(1) A. Baeyer, Ann., 278, 108 (1894); L. Fortey, J. Chem. Soc., 73, 948 (1898); W. Markownikoff, Ann., 302, 29 (1898); K. Ziegler, et al, Ann., 551, 110 (1942).

(2) A. H. Blatt, Organic Synthesis, Collective Volume II, John Wiley and Sons, Inc., New York, 1950, p. 171.

(3) G. Calingaert, H. Soroos, H. Shapiro, Industrial Engineering Chemistry, 36, 1055 (1944).

dibromide to hot triethanolamine was tried and did produce some diene. However, the diene was contaminated with too much benzene and cyclohexene to be of any real value. The diene content was only about 30 to 40 per cent as determined by refractive index and infrared spectra.

The best method found was the addition of the dibromide to hot (around 210°C) mono sodium salt of ethylene glycol. The temperature of the reaction vessel was maintained as close to 210°C as possible and the take-off temperature was kept around 70° to 85°C in order to prevent distillation of organic bromides. It was found that a definite excess of the base was conducive to higher yields.

Variations of the reaction conditions were tried. Procedure I, in the experimental section, uses a temperature of around 160°C which did not produce a good yield. It is believed that lower temperatures are not conducive to E2 type reactions which is desired in this case. In Procedure III the temperature is about 210°C which did improve the yield. This was taken as the optimum operating temperature since temperatures much higher cause decomposition of the glycol. The use of nitrogen in the system gave no noticable improvement. The addition rate of the dibromide was slowed but this did not markedly improve the yield. The extra time needed to improve the yield slightly poses the rhetorical question of whether the use of the time validates itself. Large scale methods to make 1,3-cyclohexadiene have been worked out in

this laboratory (4) using larger equipment and greater quantities of chemicals.

The yellow crude diene, after drying over calcium chloride, was distilled through efficient columns to produce a clear product of 80 to 85 per cent purity and leave a yellow residue in the distilling vessel. Distillation data suggest the composition of the yellow residual liquid was mainly 3-bromocyclohexene and 1-bromocyclohexene.

The diene thus prepared was used to synthesize the bicyclo(2,2,2)octane derivatives by two different reaction series. Both series involve the rearrangement of certain bicyclo(2,2,2)octane compounds to the (3,2,1) series. The first series of reactions, as proposed in the introduction, present one critical step where rearrangement takes place. It is the rearrangement of 2-hydroxybicyclo(2,2,2)-5-octene (prepared by the method of Wildman and Saunders (5)) to 2-chlorobicyclo(3,2,1)-3-octene which occurs when the alcohol is treated with thionyl chloride. One can consider the formation of the allylic carbonium ion as a powerful driving force towards the production of the allylic chloride. Any driving forces towards the production of 2-chlorobicyclo-(3,2,1)-6-octene are not apparent but its formation is theoretically possible. Wildman and Saunders report the rearrangement of 2-aminobicyclo(2,2,2)-5-octene, upon treatment with

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(4) J. Hine, et al, J. Am. Chem. Soc., 77, 594 (1955).

(5) W. C. Wildman and D. R. Saunders, J. Org. Chem., 19, 381 (1954).

nitrous acid, to 2-hydroxybicyclo(3,2,1)-3-octene (6). Their reaction is analogous to the one here presented. The allylic carbonium ion is fairly stable and the reaction media is polar enough to permit its existence as an intermediate.

The chloride was treated with sodium in isopropanol to yield bicyclo(3,2,1)-2-octene. Fractionation of the olefin did not definitely produce two olefins but the first few drops of material which were collected (at 132°C) remained a liquid. Zalkow reports the bicyclo(3,2,1)-2-octene as being a liquid (7). After these few drops came over the rest of the distillate began to solidify into slush that looked half liquid and half solid. This material was undoubtedly a mixture of the (3,2,1) and the (2,2,2) olefins. The bicyclo(2,2,2)-2-octene is a solid with a melting point of 113-114°C (8). Hine and co-workers (4) report 110-113°C while Doering and co-workers (9) report 143-144°C but perhaps intended to say 113-114°C. All investigations of the (2,2,2) olefin definitely indicate it is a solid at room temperature. The information on bicyclo(3,2,1)-2-octene is not well established. All indications from this laboratory point to the olefin as being

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(6) W. C. Wildman and D. R. Saunders, J. Am. Chem. Soc., 76, 946 (1954).

(7) L. H. Zalkow, Ph. D. Thesis, Georgia Institute of Technology, 1955, p. 119.

(8) R. Seka and O. Tramposch, Ber., 75B, 1379 (1942).

(9) W. von E. Doering, et al, J. Am. Chem. Soc., 74, 4370 (1952).

a liquid at room temperatures which boils around 132°C. Zalkow synthesized this (3,2,1) olefin in an entirely different fashion and his results indicate the compound is a liquid (7). J. von Braun reports bicyclo(3,2,1)-2-octene as being a liquid which boils at 132°C (10). However, his work presents a great element of doubt due to the fact that his synthesis also leads to the formation of bicyclo(3,3,0)-octene isomers along with the expected (3,2,1) derivative.

The infrared spectra of this olefin mixture definitely indicates there is a mixture of the (3,2,1) and the (2,2,2) olefin.

The saturated hydrocarbons, as obtained from the hydrogenation of the olefin mixture, gave a melting point range of 125-133°C indicating mixtures. Recrystallization of this material (or any of the other mixtures mentioned in this discussion) will produce materials or higher melting points. Invariably, the (2,2,2) constituent is the higher melting component which means that recrystallization enriches the mixture in the (2,2,2) compound which is undesirable for our purposes of investigating the (3,2,1) compounds. The upper melting point of 133°C corresponds to the same value reported in the literature (11) (12) for bicyclo(3,2,1)octane. The melting

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(10) J. von Braun, Ber., 74, 273 (1941).

(11) G. Komppa, Ann., 521, 242 (1936).

(12) J. W. Barrett and R. P. Linstead, J. Chem. Soc., 611 (1936).

point of bicyclo(3,2,1)octane was also reported at 141°C (13) (14). The melting points of bicyclo(2,2,2)octane reported in the literature are 169.5-170.5°C (9), 168-169°C (15), 175-176°C (8). In any case, it can be seen that the (2,2,2) hydrocarbon melts higher than the (3,2,1) isomer.

The infrared spectra of this mixture definitely indicates the presence of both the (3,2,1) and the (2,2,2) hydrocarbons.

Carbon-hydrogen analysis by the Clark Microanalytical Laboratory[1] gave the results of:

	Calc.	Found	"Found"
Carbon	88.82	87.61	88.86
Hydrogen	11.18	10.97	11.13

for bicyclo(3,2,1)-2-octene. The results for bicyclo(3,2,1)-octane were:

	Calc.	Found	"Found"
Carbon	87.10	86.78	87.05
Hydrogen	12.89	12.91	12.95

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(13) K. Alder and E. Windermuth, Ber., 71, 2404 (1938).

(14) W. von E. Doering and M. Farber, J. Am. Chem. Soc., 71, 1515 (1949).

(15) P. D. Bartlett and G. F. Woods, ibid, 62, 2933 (1940).

[1]Clark Microanalytical Laboratory, 104½ West Main Street, Urbana, Illinois.

Since both of the hydrocarbons are quite volatile, the fact that the analysis reported by Clark adds up to less than 100 per cent suggests loss by volatilization. On this assumption, the analysis were recalculated so as to total 100 per cent with the results listed under "Found". Volatility losses were easily noticed in this laboratory during weighing processes.

The second method mentioned in the introduction proposes the rearrangement of bicyclo(2,2,2)-2-octene to 2-hydroxybicyclo(3,2,1)octane.

Walborsky (16) proposes a mechanism which explains the rearrangement of the (2,2,2) olefin to the (3,2,1) alcohol. The first essential step in his proposition is the addition of a proton to the olefin which produces a normal carbonium ion. The second step is the rearrangement of this classic carbonium ion to a non-classic carbonium ion which has, in essence, a dispersed positive charge over a given area of the carbon skeleton. The third step is the attack of the nucleophilic species on the charged portion of the non-classic ion. This attack might be expected to proceed in such a manner as to produce the most stable product which in this case would be 2-hydroxybicyclo(3,2,1)octane. In the (3,2,1) system, one can draw the molecules in such a way as to show that six of the carbon atoms will form a cyclohexane ring which can take the more strainless "chair" form. This can not

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(16) H. M. Walborsky, Experientia, 9, 209 (1953).

be done in the bicyclo(2,2,2)octane system. It is believed the sulfuric acid-water mixture, the media of the reaction, is a very important factor in several ways. It is a polar solution which is necessary for sustaining the life of the carbonium ion intermediate. It also is a rich source of protons.

If the reaction proceeds according to the above mentioned mechanism the (3,2,1) alcohol will be the product. However, there is the possibility that the reaction could proceed in another fashion. The neucleophilic species could attack the original carbonium ion before it rearranges to the non-classic carbonium ion. This would result in the formation of 2-hydroxybicyclo(2,2,2)octane, the product one might normally expect from the hydration of the double bond.

Newman and Yu (17) report the rearrangement of bicyclo(2,2,2)-2-octene to 2-hydroxybicyclo(3,2,1)octane. On the other hand, Walborsky (16) found no rearrangement when he treated the same olefin with HBr, HCl, acetic acid or, thioacetic acid. He obtained the unrearranged (2,2,2) products. It would appear that the media of the reaction and the ability of the media to furnish protons are very important. Doering and Farber (14) have effected the transformation of the silver salt of 2-carboxybicyclo(2,2,2)octane to 2-bromobicyclo(3,2,1)octane by treatment of the salt with bromine

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(17) M. S. Newman and Y. T. Yu, J. Am. Chem. Soc., 74, 507 (1952).

and silver bromide. This reaction probably goes through the non-classic carbonium ion intermediate to produce the (3,2,1) species.

The bicyclo(2,2,2)-2-octene used in this investigation was prepared by Brown and Zalkow according to the methods worked out by these investigators (4). The hydration of this material was carried out according to the methods of Newman and Yu (17). This essentially amounts to the treatment of the olefin with a mixture of sulfuric acid and water. The mixture is stirred, at room temperature, for two to three days until all of the bicyclo(2,2,2)-2-octene dissolves. Steam distillation of this mixture produces the alcohols 2-hydroxybicyclo(2,2,2)octane and 2-hydroxybicyclo(3,2,1)-octane as white waxy crystals. The alcohols are separated from the water and recrystallized from the hydrocarbon solvents to yield a white powder that melts over a range of five to six degrees at 170°C plus or minus seven degrees. A small amount of this material was recrystallized six times to a constant melting point of 193-196°C. This is believed to be a constant composition mixture of the two alcohols. Newman and Yu (17) report a melting point of 173-176°C for bicyclo-(3,2,1)-2-octanol. Other melting points reported in the literature for this same alcohol are 183-184°C (14) and 184-185°C (18).

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(18) K. Alder and E. Windermuth, Ber., 71, 1939 (1938).

In view of the melting point information, it appears evident that the experimentation in this laboratory did not produce a very pure yield of 2-hydroxybicyclo(3,2,1)octane. This means the reaction did not proceed in exclusively one manner. The conclusion drawn is that the reaction went by both of the paths proposed earlier in the discussion. The melting point of 196°C is above those reported for the (3,2,1) alcohol and below that of the (2,2,2) alcohol.

Some of the alcohol mixture was treated with thionyl chloride to yield, after vacuum distillation, a slushy waxy product believed to be mostly 2-chlorobicyclo(3,2,1)octane and some of the (2,2,2) isomer. This material, after one recrystallization, melted at 94-96°C. Newman and Yu (17) report a melting point of 66.6-67.6^{o}C for their 2-chlorobicyclo(3,2,1)octane which they believed was contaminated with oxy compounds.

This chloride was dehydrohalogenated by adding it, dissolved in aniline, to a solution of hot potassium anilide. The olefin, after recovery from the distillate of aniline, was distilled through a column to yield a product with a melting point of 70-72°C. One sublimation of a bit of the olefin gave a material melting at 69-70°C which seems to indicate the bicyclo(3,2,1)-2-octene is more volatile (bicyclo(2,2,2)-2-octene melts at 113-114°C).

Hydrogenation of the olefin yielded a saturated hydrocarbon which melted at 147.5-148.5^{o}C which is rather high

as compared to the hydrocarbon obtained from the first reaction series.

The infrared spectra of the olefin mixture and the saturated hydrocarbon mixture definitely indicate the presence of mixtures of the (3,2,1) and (2,2,2) octane series.

Some 2-acetoxybicyclo(2,2,2)-5-octene was hydrogenated to produce 2-acetoxybicyclo(2,2,2)octane. The saponification of this saturated ester yielded 2-hydroxybicyclo-(2,2,2)octane, which after one recrystallization, had a melting point of 215-216°C. A melting point of 216-217°C for this alcohol has been reported (5) (19). This alcohol was oxidized to bicyclo(2,2,2)-2-octanone in a media of acetic acid and chromium trioxide.

The mixed alcohols synthesized from the hydration of bicyclo(2,2,2)-2-octene were oxidized in an aqueous solution of potassium dichromate and sulfuric acid. The ketones were extracted from the oxidation media and isolated from the solvent. Some of the ketone mixture isolated from the solvent, after one recrystallization, gave a melting point of 125-134°C, indicating a mixture.

The infrared spectra of the mixed ketones definitely indicate the presence of mixtures. This means the alcohols must have been a mixture also.

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(19) G. Komppa, Ber., 68B, 1267 (1935).

The 2,4-dinitrophenylhydrazone derivative of the mixed ketones was made according to standard methods. This dried derivative melted at 135-137°C. A small amount of this material was recrystallized five times to a constant melting point range of 145-146°C. This material is believed to be a constant composition mixture and not a pure compound. A mixture of one part pure bicyclo(2,2,2)-2-octanone derivative mixed with nine parts of the mixture (which melted at 145-146°C) gave a melting point of 148-150°C. This increase in the melting point of the mixture indicates it is not a pure compound as might have been suspected. A mixture of nine parts pure bicyclo(2,2,2)-2-octanone, (which melted at 163.5-165°C) and one part of the mixture (which melted at 145-146°C) gave a melting point of 160-162°C. This decrease in the melting point of the pure (2,2,2) ketone derivative indicates the mixture is not the (2,2,2) ketone derivative in anywhere near a pure state.

The possibility of separating the mixed ketones by chromatography was entertained. The 2,4-dinitrophenylhydrazone derivatives offer a material which can be seen on a column. Reports in recent literature (20) indicate alumina

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(20) E. Lederer and M. Lederer, Chromatography: A Review of Principles and Applications, Elsevier Publishing Co., New York, 1953; H. G. Cassidy, Techniques of Organic Chemistry, Vol. V., Adsorbtion and Chromatography, Interscience Publishers Inc., New York, 1951; J. F. Carson, J. Am. Chem. Soc., 73, 4652 (1951); H. Adkins and G. Kresek, ibid., 71, 3051 (1949); H. R. Strain, ibid., 57, 758 (1935); R. G. Rice, G. J. Keller and J. G. Kirchner, Anal. Chem., 23, 194 (1951).

is a good packing for the columns used in separating the derivatives. Previous to a concerted effort to separate the derivatives they were first run through a column of alumina to remove any unreacted materials. The melting point of the mixed derivatives was 130-137°C after it had been run through the column with benzene.

A small amount of this mixed derivative was then chromatographed on an alumina packed column using a mixture of n-hexane and benzene as the developer. It was found from previous attempts that a mixture of hexane and benzene was the best developer. This solution moved the band slowly which was desired because the structural differences in the two derivatives is not very pronounced for good chromatographic separation. The slower the development the better the separation because the column will operate in a countercurrent flow which depends upon nearly equilibrium conditions. The band increased in size but did not separate into two distinct bands. As the band was run off the column it was collected in four fractions representing roughly the four quarters of the band. The melting points of the residues from these fractions definitely indicated a separation took place. There was roughly a thirty degree difference between the melting points of the first quarter and the last one. This partial separation, for the purpose of this investigation, was as good as a complete separation because it proved there were two compounds present.

A similar chromatographic experiment was run on the mixed ketones. A mixture of cyclohexane and benzene was used for the developing in this case. Here too, it was necessary to proceed very slowly in order to get a separation and not just a flushing of the ketones down the column. The ketones were detected with a spot test as they came out of the column. The 2,4-dinitrophenylhydrazone derivative was made from several of the fractions taken. The melting point of these derivatives indicated a partial separation of the ketones took place.

Some of the starting 2,4-dinitrophenylhydrazone mixture of the ketones was cleaved into the starting ketone mixture and 2,4-dinitrophenylhydrazine. This was done by refluxing the derivatives in a media of acetone, water and sulfuric acid in catalytic amounts. Removal of the acetone and steam distillation of the residue yielded the bicyclic ketones. Some of this ketone mixture was used for infrared spectra. This mixture would be free of any bicyclic alcohols and thus give a more concise infrared spectra of the ketones. The rest of the ketone mixture was reconverted into the 2,4-dinitrophenylhydrazones and the melting point checked to see if any significant changes took place in the cleavage. None did.

EXPERIMENTAL

Preparation of Cyclohexene Dibromide.--Most of the cyclohexene used in our experiments was obtained from Eastman or Dow. At times it was made according to the procedure described in Organic Synthesis (21). This method was simply the dehydration of cyclohexanol with sulfuric acid.

The standard method of preparing cyclohexene dibromide was essentially the same as that reported in Organic Synthesis (2) except in this case no solvent was used.

Cyclohexene (5.0 moles) and 15 ml of glacial acetic acid was placed in a two-liter, three necked flask equipped with stirrer, dropping funnel, condenser and a thermometer immersed in the liquid. Bromine was added slowly so that the temperature did not rise above 0°C during the reaction period. The addition was continued until there remained a slight red tinge to the solution. Vacuum distillation of this 700 ml of liquid produced 40 ml of forerun and left 44 ml of black residue. The heavy clear liquid boiling at 101-102°C at 15 mm pressure was the desired product. This was the method used to produce all of the dibromide in this laboratory.

Preparation of Pure Cyclohexene Dibromide.--Three moles of cyclohexene was placed in an one-liter flask with similar

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(21) H. Gilman and A. H. Blatt, Organic Synthesis, Collective Volume I, John Wiley and Sons, Inc., New York, 1943, p. 183.

attachments as described. The flask was chilled with dry ice and acetone mixture to prevent the liquid from warming above $0^{o}C$ during the bromine addition. After about three quarters of the bromine had been added, a white solid would form which slowed the stirring considerably. The rest of the bromine was added more slowly until there remained a slight red tinge to the solution. This material was then vacuum distilled under a nitrogen atmosphere. Only the material boiling between 101-101.5 ^{o}C at 15 mm pressure was kept.

The density of this clear heavy liquid was 1.7583 g/ml at $26.5^{o}C$. Its refractive index was 1.5423 at $26.5^{o}C$. The molar refraction, as calculated from this data, was 43.21. A summation of atomic refractions gave 43.24 (22). The material melts at -5° to $-4^{o}C$. Exposure of the liquid to the air causes fuming and discoloration of the liquid ranging from pink to black depending upon the amount of exposure.

Preparation of 1,3-cyclohexadiene Using Triethanolamine.--Cyclohexene dibromide (0.985 moles) was added dropwise to a two-liter, three necked flask containing commercial triethanolamine (4.0 moles) and equipped with a ten inch Vigreaux column, dropping funnel and a thermometer immersed in the liquid. The temperature was maintained as near as possible to

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(22) F. Daniels, Outlines of Physical Chemistry, John Wiley and Sons, Inc., New York, 1948, p. 71.

210°C while the dibromide was added at the same rate the products distilled. Most of the product distilled at 68-69°C yielding 75 grams of wet light yellow organic liquid. This material was dried with calcium chloride and slowly distilled through a small column packed with glass helicies. The liquid boiling between 79.5-80°C was only 37 per cent diene as determined by infrared and refractive index analysis; the rest being benzene and cyclohexene.

Preparation of 1,3-Cyclohexadiene Using Ethylene Glycol and Sodium Hydroxide.--Procedure I.--Cyclohexene dibromide (0.395 moles) was added dropwise to a solution of ethylene glycol (1.78 moles) and sodium hydroxide (1.0 moles) in an one-liter, three necked flask equipped with Claisen head, dropping funnel, stirrer and thermometer. The flask temperature was kept as close to 160°C as possible. The dibromide was added at the same rate as the distilling vapors whose temperature was maintained between 70° and 85°C. The distillation ceased when the dibromide was all added. The product was in two phases, organic and aqueous. The yield was 14.5 grams of light yellow undried liquid.

The mixture in the reaction flask, after the reaction was done, contained salts and unreacted starting materials. A thin layer of brown liquid floated on the surface which had a sweet smell. No investigation was made on this brown liquid.

Procedure II.--The same experiment was again run except in this case a thirty inch Vigreaux column was inserted between the reaction flask and the take-off condenser. The yield was 8.5 grams of undried material.

Procedure III.--Cyclohexene dibromide (1.15 moles) was dropwise added to a solution of ethylene glycol (3.6 moles) and sodium hydroxide (2.5 moles) in a two-liter, three necked flask equipped with a thirty inch Vigreaux column, dropping funnel, stirrer and thermometer. The liquid in the flask was kept as close to 210°C as possible during the addition. The addition was made at the same rate as the distillation while keeping the temperature of the distilling vapors between 70° and 85°C. This took about 1½ hours with a cessation of distillation immediately after the addition was complete. The yield of organic product varies between 50 and 60 grams of wet product using these experimental conditions. The brown liquid was noted floating in the reaction vessel after the reaction was complete. It was present in all of these runs.

Procedure IV.--The same experiment was again run except in this case the system was flushed with nitrogen before and during the reaction. This modification did not alter the yield or inhibit the formation of the brown liquid ubiquitously present at the end of the reaction.

Procedure V.--Cyclohexene dibromide (1.15 moles) was added dropwise at the rate of three drops per two seconds to a solution of ethylene glycol (7.2 moles) and sodium hydroxide (5.0 moles) contained in the same set-up as described in Procedure III. The pot temperature was kept close to 210°C during the three hour addition time of the dibromide. The yield was 87.6 grams of nearly colorless organic liquid.

In all of these cases, from Procedure I to V, the product is the crude diene undried. Fractional distillation of this crude diene gives the material used for the Diels-Alder reactions.

Fractional Distillation of Crude 1,3-Cyclohexadiene.--A fractionating column 750 mm long and 16 mm in diameter, heated with nichrome wire and insulated within a glass tube was used for all of the diene distillations.

The crude diene, after drying over calcium chloride, was slowly distilled with reflux ratios of ten and fifteen to one. The distillation proceeded smoothly producing a few drops of water at the start which was discarded. The clear liquid which boiled at 79-80°C was the product assumed to be the diene. Refractive index and infrared data indicated the material was between 80 and 90 per cent diene; the rest being benzene and cyclohexene as indicated by infrared spectra.

Kistiakowsky and co-workers (23) have reported the refractive index of pure 1,3-cyclohexadiene which was used for our interpolation.

Preparation of 2-chlorobicyclo(3,2,1)-3-octene.--The ester, 2-acetoxybicyclo(2,2,2)-5-octene was first prepared (4) (24) and then saponified according to the technique of Wildman and Saunders (5) to produce 2-hydroxybicyclo(2,2,2)-5-octene[1]. This alcohol was treated with thionyl chloride in about ten per cent excess whilst the flask was immersed in cold water. The mixture was then refluxed for an hour and the excess thionyl chloride distilled off leaving a brown residue which was vacuum distilled using a water aspirator to reduce the pressure. The clear liquid chloride boiled at 187-190°C at atmospheric pressure. Brown reports a boiling point of 106°C at 54 mm for this material (25). This distillation can be satisfactorially accomplished with mild vacuum or it can be done at atmospheric pressure.

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(23) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, J. Am. Chem. Soc., 58, 146 (1936).

(24) K. Alder and H. F. Rickert, Ann., 543, 1 (1940).

[1]Wildman and Saunders (5) have reported this alcohol. They prepared it by the saponification of 2-acetoxybicyclo-(2,2,2)-5-octene and by lithium aluminum hydride reduction of 2-ketobicyclo(2,2,2)-5-octene. They proved the alcohols were identical by comparing the infrared spectra and the p-nitrobenzoate derivatives. Alder and Rickert (24) saponified the 2-acetoxybicyclo(2,2,2)-5-octene to the alcohol previous to the work of Wildman and Saunders.

(25) J. A. Brown, Ph. D. Thesis, Georgia Institute of Technology, 1954.

Preparation of Bicyclo(3,2,1)-2-octene.--Small pieces of sodium (5.5 grams all together) were slowly added to a solution of isopropanol (115 ml) and 2-chlorobicyclo(3,2,1)-3-octene (7.1 grams) in a 200 ml flask equipped with a reflux condenser. After the mixture had reacted for half of an hour it was refluxed for five hours. Seventy five ml of isopropanol was distilled from the reaction flask and 150 ml of cold water added to the distillate producing white waxy crystals along with small drops of an oil. Pentane was used for extracting the water solution, dried over calcium chloride and slowly distilled through a small column leaving about two ml of an oily residue.

The salt residue from the reaction was treated with 150 ml of water to produce three or four ml of a sweet smelling oil. This oil, presumably the isopropyl ethers of the bicyclo compounds, was extracted with pentane, dried over calcium chloride and the pentane distilled away leaving a residue of about three ml of oil.

The same process was run for a second time using 5.5 grams of 2-chlorobicyclo(3,2,1)-3-octene, 5.0 grams of sodium and 100 ml of isopropanol.

The combined olefin residues were distilled through a 5 mm bore column 450 mm long equipped with a spiral wire packing. The first few drops of material obtained (at 132°C) remained in the liquid state in the receiver but the subsequent distillate was a combination of liquid and solid which on

occasion clogged the exit stopcock. The olefin distilled at 133-135°C and slowly solidified in the receiver to a waxy slush. This material decolorizes bromine solutions immediately. The yield was estimated at 2 to 3 grams.

The combined ether residues were distilled in a similar fashion to produce about 4 ml of sweet smelling oil which boiled over a range of 190-196°C. This material rapidly decolorizes bromine solutions. Neither the ether nor the olefin produced a precipitate upon refluxing with alcoholic silver nitrate.

Hydrogenation of Bicyclo(3,2,1)-2-octene.--This hydrogenation was carried out according to the methods of Seka and Tramposch (8). A pinch of Adam's platinum catalyst was used in a test tube containing 0.56 grams of bicyclo(3,2,1)-2-octene dissolved in 10 ml of absolute ethanol. This mixture was hydrogenated at 50 p. s. i. for 15 hours. The platinum was filtered off and the solution diluted to a volume of 100 ml with water and the mixture extracted with pentane. The dried pentane solution was distilled through a small column leaving a white residue which gave a melting point of 125-133°C without being recrystallized. This material did not decolorizes bromine solutions.

Preparation of 2-hydroxybicyclo(3,2,1)octane According to the Method of Newman and Yu (17).--All of the bicyclo(2,2,2)octane used in this investigation was obtained from Dr. Hine.

Bicyclo(2,2,2)-2-octene (0.925 moles) was placed in a one-liter flask with a mixture of 1.02 moles of sulfuric acid and 11.1 moles of water. The mixture was stirred at room temperature for two to three days depending on how long it took to dissolve the olefin completely. The reddish brown liquid was subjected to steam distillation using at least three times its volume of water as a diluent. An air condenser was used to prevent solidification of the alcohol during distillation. The white crystalline alcohol, along with a small amount of clear oil, was then separated from the chilled receiving flask by extraction with either n-hexane or n-heptane and the extract dried over calcium chloride. About half of the solvent was distilled from the alcoholic solution and the solution remaining chilled in an ice bath to produce precipitation of the alcohol which was filtered through a Buchner funnel. This same distillation and chilling procedure was repeated several times until there remained about 20 to 30 ml of solution which was discarded. The solid alcohol was allowed to dry in the open until it was fluffy and dry of solvent.

The yield is between 60 to 70 per cent, based on the hydrocarbon used. It melts over a range of 5° to $7^{o}C$ at $170 \pm 7^{o}C$. Recrystallizations will give higher melting materials but will not yield a material which is pure. All melting points were taken in sealed tubes.

Preparation of 2-Chlorobicyclo(3,2,1)octane.--Thionyl chloride (0.60 moles) was slowly added to 0.555 moles of 2-hydroxy-bicyclo (3,2,1)octane. The mixture was then warmed over the steam bath for an hour thence the excess thionyl chloride was distilled off and the residue vacuum distilled by carefully heating the material at its surface with a micro burner. From time to time an electric heating lamp was needed to melt the solid in the condenser during the distillation. The yield was 0.47 moles of the chloride which distilled at 107-180°C at pressures between 60 and 65 mm. At room temperature it was a white waxy material.

Preparation of Bicyclo(3,2,1)-2-octene.--In a 500 ml, three necked flask equipped with thermometer, stirrer, dropping funnel and Claisen head was dissolved 0.95 moles of potassium in 2.15 moles of freshly distilled aniline. The system was slowly swept with nitrogen at all times, especially during the dissolving of the potassium and during the addition of the 0.47 moles of 2-chlorobicyclo(3,2,1)octane dissolved in 0.75 moles of aniline. The aniline in the flask was barely kept at reflux while the chloride solution slowly dripped into the flask. The exothermicity of the reaction permitted slow distillation of the olefin as it was produced. Towards the end of the addition heat was applied to complete the distillation until the distilling vapors reached a temperature of 180°C. At the beginning of the reaction steam was run through the condenser to prevent clogging by the olefin. Later, the aniline which co-distilled with the olefin gave sufficient heat

to keep the distilling products in the liquid state.

A cold solution consisting of 100 ml of water and 100 ml of concentrated hydrochloric acid was added to the aniline distillate while the flask was immersed in ice water. The white solid olefin was extracted from the pink solution with 200 ml of pentane. The dried pentane was removed through a small column leaving a residue which melted at 65-67°C in a sealed tube. The yield was 0.373 moles of olefin.

Purification of Bicyclo(3,2,1)-2-octene.--The crude olefin was distilled using no vacuum. An infrared lamp was needed from time to time to melt the waxy olefin as it clogged the exit tube during the distillation. The yield was 27.5 grams from 33.5 grams of starting crude material. Only the olefin boiling at 129-135°C was kept which gave a melting point of 70-72°C. Sublimation of a bit of the olefin gave crystals melting at 69-70°C indicating the (3,2,1) olefin sublimed faster than the (2,2,2) olefin.

Hydrogenation of Bicyclo(3,2,1)-2-octene.--A few milliliters in excess of the minimum amount of 95 per cent ethanol was used to dissolve 2.48 g. of bicyclo(3,2,1)-2-octene in a low pressure hydrogenation bottle. A pinch of Adam's platinum catalyst was added and the mixture hydrogenated at pressures around 50 p. s. i. until the gauge indicated no further pressure drop. The solid hydrocarbon was filtered off, dissolved in n-hexane, dried over calcium chloride and crystallized out

of the solvent by chilling. One sublimation of this material gave a product melting at 147.5-148.5^{o}C.

Preparation of 2-acetoxybicyclo(2,2,2)octane.--In a hydrogenation jar was placed 0.517 moles of 2-acetoxybicyclo(2,2,2)-5-octene with 140 ml of ethanol and one half gram of platinum catalyst. The mixture was hydrogenated at pressures around 50 p. s. i. to finally yield a two phase liquid solution which was filtered to remove the platinum.

Saponification of 2-acetoxybicyclo(2,2,2)octane.--The latter mentioned alcoholic solution of ester was placed in a flask with a solution of 30 g. of sodium hydroxide dissolved in 200 ml of water. After six hours of refluxing, the alcoholic water was distilled off through a tall Vigreaux column until small traces of solid were detected in the condenser. Steam distillation of the residue in the pot proved to be unsatisfactory due to too much bumping. Subsequently, n-hexane was used to extract the solid alcohol. The extract was dried over calcium chloride and nearly all of the pale yellow color removed from the solution with charcoal. The hexane was taken down to about half its volume and the solution chilled to produce 14.7 g. of white crystalline material. Recrystallization from nitromethane gave a product which melted at 215-216°C, the yield being 11.8 grams.

Preparation of Pure Bicyclo(2,2,2)-2-octanone.--This oxidation was performed according to the method of Fieser and Szmuszkovitz (26). In a half-liter flask was placed 0.0397 moles of 2-hydroxybicyclo(2,2,2)octane and 155 ml of glacial acetic acid. While the mixture was being stirred, 0.15 moles of fresh chromium trioxide was added in small portions over a period of a half hour being careful to not allow the temperature to rise above that of the room during the addition and during the following hour of stirring. After 150 ml of water had been added, the mixture was extracted with three portions of ether totalling 200 ml after the solution had been treated with sodium hydroxide pellets to neutralize the acetic acid. The ether was washed with 100 ml of water which removed the yellow tint probably caused by chromic salts or chromic esters. The dried ether extract, after having been distilled through a small column, left a 4.1 g. residue of ketone (0.0331 moles) which melted at 177-178°C, after four recrystallizations. The melting points of bicyclo(2,2,2)-2-octanone reported in the literature are 176°C (19), 178-179°C (27) and 178°C (28).

The 2,4-dinitrophenylhydrazone was prepared according to standard methods described in text books (29). The

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(26) L. Fieser and J. Szmuszkovitz, J. Am. Chem. Soc., 70, 3352 (1948).

(27) O. Diels and K. Alder, Ann., 478, 137 (1930).

(28) K. Alder and G. Stein, Ber., 67, 613 (1934).

(29) R. L. Schriner and R. C. Fuson, Identification of Organic Compounds, John Wiley and Sons, Inc., New York, 1948, p. 171.

derivative was recrystallized to a constant melting point range of 163.5-165°C.

The semicarbazone was recrystallized to a constant melting point of 197-198°C. Diels and Alder report a melting point of 204-205°C with decomposition for this same derivative (27).

Preparation of Mixed Bicyclo(2,2,2)-2-octanone and Bicyclo-(3,2,1)-2-octanone by the Method of Alder and Windermuth (13).-- The alcohol, as prepared according to the methods of Newman and Yu, was believed to be a mixture of 2-hydroxybicyclo(2,2,2)-octane and 2-hydroxybicyclo(3,2,1)octane. If so, the oxidation of this material would produce two ketones.

In a half-liter flask containing a solution of 0.085 moles of potassium dichromate, 0.188 moles of sulfuric acid and 200 ml of water was added 0.0675 moles of the mixed alcohols dissolved in 100 ml of methylene chloride. After the mixture had been stirred for nine hours with the temperature between 20° and 30°C the organic layer was separated and a bit of fresh methylene chloride used to extract the last vestiges of ketone from the acidic water. The combined extracts left a residue of about 10 to 20 ml of solution after the methylene chloride had been distilled away. Steam distillation of this residue produced white crystalline ketone which was taken up in methylene chloride, dried and the solvent distilled through a small column leaving a residual white

waxy material weighing 7 grams (0.565 moles). A bit of this material, upon one recrystallization, gave a melting point of 125-134°C, indicating a mixture. The melting point of bicyclo(3,2,1)-2-octanone reported in the literature in 129°C (17) (13).

2,4-dinitrophenylhydrazone Derivative of the Mixed Ketones.--About 9 grams of the mixed ketones was dissolved in 150 ml of ethanol and a solution of 12 grams of 2,4-dinitrophenylhydrazine dissolved in 150 ml of alcohol containing 16 drops of sulfuric acid was added. The mixture was refluxed for one hour and then chilled on ice to produce fine red crystals which, when dry, gave a melting point of 135-137°C. The yield was 16 grams.

Some of this material, after recrystallizing five times to a constant melting point, gave a material melting at 145-146°C which was believed to be a constant composition mixture of the two derivatives.

Crude Chromatography of the Mixed Derivatives.--Alumina[1] of "grade F-20" was used for all the chromatography in this laboratory.

A minimum amount of benzene was used to dissolve 11.5 grams of the derivatives and this solution run through the

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[1]Activated alumina, Grade F-20, Aluminum Ore Company, East St. Louis, Ill.,

column packed with alumina using benzene as the developer. A broad band moved rapidly down the column leaving a small band of brown material at the top. Evaporation of the benzene from the red solution gleaned from the column left 10.5 grams of material which melted at 130-137°C. This was the material used for further chromatography.

Cleavage of the 2,4-dinitrophenylhydrazone Mixture.--About a half gram of the red derivative in 10 ml of acetone was refluxed with one ml of water to which two drops of sulfuric acid had been added. After eight hours of reflux the acetone was carefully distilled through a small Vigreaux column until the volume in the flask was about two ml. The residue was steam distilled producing fine white crystals in the condenser which were taken up in ethanol and the 2,4-dinitrophenylhydrazone derivative remade from the ketones. The new derivative gave a melting point of 131-134°C which was in good agreement with that of the starting material. This cleavage technique offers a method of obtaining the ketones uncontaminated with the corresponding alcohols.

Chromatography of the 2,4-dinitrophenylhydrazone Mixture of Bicyclo(2,2,2)-2-octanone and Bicyclo(3,2,1)-2-octanone.--A column 13 mm in diameter and 380 mm high equipped with a dropping funnel (attached to the column with a standard glass ground joint) was packed with a slurry of alumina and n-hexene which, when allowed to settle, presented a well packed column

of alumina 300 mm high.

A minimum amount of benzene was used to dissolve 0.210 grams of the "purified" derivative which was then carefully placed on the top of the column according to standard techniques. A solution of 10 per cent benzene, by volume, in n-hexane was used for the developing of the derivatives. This solution moved the front of the band 2 to 3 mm for every 100 ml of the developer run through. The take-off rate was one drop every second. The band kept getting wider but at no time did it indicate a definite splitting into two bands. The band was about 70 mm long when it was in the middle of the column and did not appreciably widen any more as it moved down. Four fractions of the band were taken representing roughly the four quarters of the whole. Evaporation of the solvent from the four containers yielded red crystals which were each recrystallized once from ethanol and gave the following melting points in the order in which they came off the column; first, 156-160°C: second, 136-139°C: third, 139-142°C: fourth, 126-130°C.

Chromatography of Mixed Bicyclo(2,2,2)-2-octanone and Bicyclo-(3,2,1)-2-octanone.--The same column, packed in the same manner, as previously described was here used only this time the 300 mm high alumina packing was made with a slurry of a 15 per cent solution of benzene in cyclohexane because this solution was used as the developer. The minimum amount of developer solution was used to dissolve 0.250 grams of the mixed

ketone and this solution carefully introduced to the top of the column. The addition rate of the developer was the same as in the previously mentioned run.

The first signs of the ketones were detected at the bottom of the column after nearly 20 hours of chromatographing. The ketones were detected in a spot plate by removing a few drops of liquid from a fraction and adding a drop of 2,4-dinitrophenylhydrazine solution. To this was added a drop of alcoholic sodium hydroxide which caused an immediate darkening of the solution even if there was only a trace of ketone present. This test proved very successful and very sensitive. Twelve samples of 15 ml each were first taken, then, five samples of 30 ml each, lastly, two samples of 75 ml each were taken.

The 2,4-dinitrophenylhydrazone derivative of several of the samples were made and the melting point of the crystalline derivative observed. The following table gives the melting points of the derivative made from four of the fractions taken.

Table 1

Derivative melting points of some of the ketone samples from the column.

Sample Number	Melting Point Range
1.	129-132°C.
5.	134-136°C.
13.	138-140°C.
18.	138.5-141°C.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions.-- There were two reaction paths proposed in the introduction. Both of them involved the rearrangement of a bicyclo(2,2,2)octane compound to a bicyclo(3,2,1)octane compound. It was desired to find out if the rearrangements were a good way to produce the (3,2,1) series. The mechanisms and theory relating to the process have been presented in the discussion.

The melting point data relating to the olefins bicyclo(2,2,2)-2-octene and bicyclo(3,2,1)-2-octene indicate these compounds were obtained mixed when the two reaction paths were performed in the laboratory. The saturated hydrocarbons bicyclo(2,2,2)octane and bicyclo(3,2,1)octane were found as mixtures also.

The work in chromatography indicated there was not pure bicyclo(3,2,1)-2-octanone or bicyclo(2,2,2)-2-octanone in the sample obtained from the oxidation of the alcohols synthesized by the method first used by Newman and Yu but the two ketones were there as a mixture. Admittedly, a clear seperation of the ketones was not achieved but such was not necessary to prove that the material was a mixture.

The infrared spectra clearly indicates the presence of mixtures in the samples of olefins and hydrocarbons synthesized by both methods. The spectra of the ketones (figure 6) clear-

ly indicate the presence of isomers.

From this information it is concluded that the step in which rearrangement takes place does not produce one and only one species. It is further concluded that this method has definitely illustrated the possibility of obtaining bicyclo-(3,2,1)octane derivatives through rearrangements with the essential qualifying statement that mixtures will be formed in the product.

In a negative sense, it is concluded that recrystallization of (3,2,1) and (2,2,2) mixtures will not yield pure (3,2,1) compounds even if the process is repeated many times. Distillation did not offer seperation either. However, chromatography does offer a method of seperation but it would be tedious. In this case, chromatography was used to indicate the presence of mixtures. If a complete seperation had been effected it would have given the same corroberative proof as a partial seperation.

Recommendations for Future Work.-- It would be interesting to know if some or all of a given sample of 2-hydroxybicyclo(2,2,2)-octane would rearrange to the (3,2,1) isomer. It would be important to use the same sulfuric acid-water mixture as was used for the hydration of bicyclo(2,2,2)-2-octene. Through experiments of this type, information relating to equilibrium between the (3,2,1) and (2,2,2) series might be found.

More work should be done on the chlorination of 2-hydroxy-

bicyclo(2,2,2)-5-octene using thionyl chloride alone or possibly with pyridine. The intermediate carbonium ion formed in the rearrangement is of the allylic type which is known to be quite stable. This should offer a great driving force towards the formation of the (3,2,1) series. The pyridine could be used in conjugation with the thionyl chloride to indicate whether the yields of the (3,2,1) derivatives could be changed significantly thereby.

A P P E N D I X

Appendix I

Discussion of Infrared Spectra

The spectra of several mixtures are presented. No attempt to extract quantitative information from these spectra is here intended or was intended when the spectra were made. In general, one can observe the difference in the various spectra when comparing that of a pure compound to that of the same compound mixed with an isomer of it.

There are two methods of preparation for the olefins and hydrocarbons as proposed in the introduction. Both the olefin and hydrocarbon produced were mixtures and their spectra are listed according to the paths they followed in the scheme of synthesis. Figure 2 was a spectra made by Zalkow who obtained the sample from this investigator. He unfortunately recrystallized the material to a melting point of 158°-160°C believing this would enrich the mixture in the (3,2,1) constituent. All the rest of the graphs were made by this investigator.

Zalkow presents infrared spectra of bicyclo(2,2,2)-2-octene, bicyclo(2,2,2)octane, bicyclo(3,2,1)-2-octene and bicyclo(3,2,1)octane in his thesis (7). Consequently, these spectra will not be illustrated in this work. His spectra were used for comparitive purposes as mentioned in the first

paragraph of this discussion.

The following bands were found in both samples of the mixed bicyclo(2,2,2)-2-octene and bicyclo(3,2,1)-2-octene but were not found in the spectra of pure bicyclo(2,2,2)-2-octene.

Table 2

bicyclo(3,2,1)-2-octene bands

14.70[1]	8.90
9.72	7.73
9.50	7.64
13.02	8.07
11.42	

In view of the fact that these bands are not attributable to bicyclo(2,2,2)-2-octene it is concluded the bicyclo(3,2,1)-2-octene constituent is responsible for their presence. It is of further interest to note that all of these bands are in excellent agreement with those found in the compound Zalkow reports as being the (3,2,1) olefin. Some of the bands listed will be more prominent in one of the spectra as compared to the other. In general, the bands are listed according to their decreasing intensity, the stronger ones coming first. This will be the case for the following tables also.

The bands listed in Table 3 were found in the two spectra of mixed bicyclo(3,2,1)octane and bicyclo(2,2,2)-octane that pertain only to the bicyclo(3,2,1)octane consti-

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[1]All the bands in the tables are expressed in microns.

tuent. These bands are in excellent agreement with those found in the spectra Zalkow believed represented pure bicyclo-(3,2,1)octane. In view of the fact that figure 3 is known to contain more bicyclo(3,2,1)octane it was used as a guide to find the (3,2,1) bands. All of these bands are to be found in figure 4 but not as intense.

Table 3

bicyclo(3,2,1)octane bands

7.96	8.45
9.10	10.24
7.63	8.32
8.60	9.60
12.65	14.13
9.96	

Here too, it definitely appears that the saturated hydrocarbons synthesized were mixtures of bicyclo(3,2,1)-octane and bicyclo(2,2,2)octane.

Figure 5 is the spectra of pure bicyclo(2,2,2)-2-octanone. Figure 6 is the spectra of the mixed ketones as obtained from the mixed alcohols. The alcohols came from the treatment of bicyclo(2,2,2)-2-octene with sulfuric acid and water. Figure 7 is a spectra of the mixed ketones obtained from the cleavage of the 2,4-dinitrophenylhydrazone mixture of the two ketones. The derivative used for this cleavage was that material run through the column for a preliminary purification previous to the work in slow chromatography. This red material was known to be the derivatives of the ketones and was not contaminated with any other materials. By the cleavage of this, one can obtain ketones that are not

contaminated by the alcohols they came from. Figure 7 is submitted so that it becomes clear that figure 6 is a true representation of the ketonic mixture and is not contaminated too greatly. Normally, one would expect the product of oxidation to be contaminated with traces of the alcohol and thus somewhat distort the spectra of the ketones. Table 4 lists the bands found present in the mixture of ketones (figure 6) which are not found in figure 7.

Table 4

bicyclo(3,2,1)-2-octanone bands

9.13	8.53	9.95
10.76	8.77	10.10
9.58	8.34	10.30
7.77	12.35	14.65
11.00	11.45	14.10
7.07	12.65	

From this data and the knowledge of how these ketones were made, one can conclude that figure 6 represents a mixture of bicyclo(3,2,1)-2-octanone and bicyclo(2,2,2)-2-octanone.

No attempt to render an interpretation of the quantities of bicyclo(2,2,2)octane derivatives contaminating bicyclo(3,2,1)octane isomers was intended when this investigation of spectra was made. This would be a difficult task and such an interpretation would not be valid based on the data here submitted.

It should be stated, however, that in all of the cases

of mixtures whose spectra are presented the indications are strongly in favor of there being more than just traces of the (2,2,2) series contaminating the (3,2,1) series.

Appendix II

Infrared Spectra

The figures in this section are photographs of the actual spectra. A Perkin-Elmer model 21 recording spectrophotometer equipped with sodium chloride optics and prism was exclusively used. All the spectra were run using slit program of "927" which gave slit widths ranging from 12 microns at a wavelength of two microns to 280 microns at a wavelength of 14 microns, and a scanning speed of approximately one micron every three minutes.

Figures 2, 4, 5, 6, and 7 show per cent transmission (ordinate) versus wavelength (abcissa). Figures 1 and 3 show per cent transmission (ordinate) versus wavelength (abcissa).

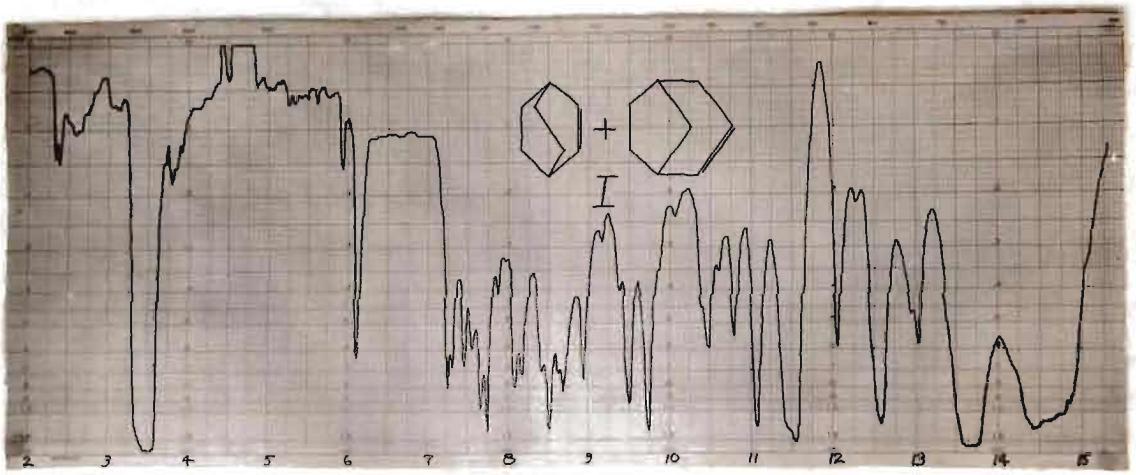

Figure 1
Bicyclo(2,2,2)-2-octene and Bicyclo(3,2,1)-2-octene
as Synthesized by Method I.
Phase- liquid
Cell Thickness[1]- 0.510 vs. 0.506
Concentration- 0.1645 g./0.5 ml.
vs. CS_2

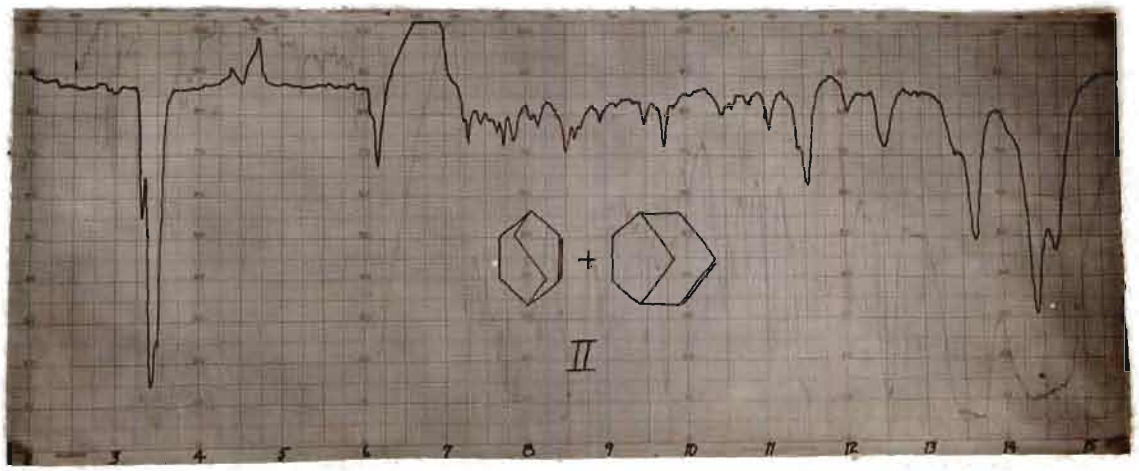

Figure 2
Bicyclo(2,2,2)-2-octene and Bicyclo(3,2,1)-2-octene
as Synthesized by method II. (m.p. 65-67°C.)
Phase- liquid
Cell Thickness- 0.11 vs. 0.09
Concentration- 0.0627 g./0.5 ml.
vs. CS_2

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[1]The first number represents the thickness (millimeters) of the cell containing the solution, and the second number represents the thickness of the cell containing the solvent.

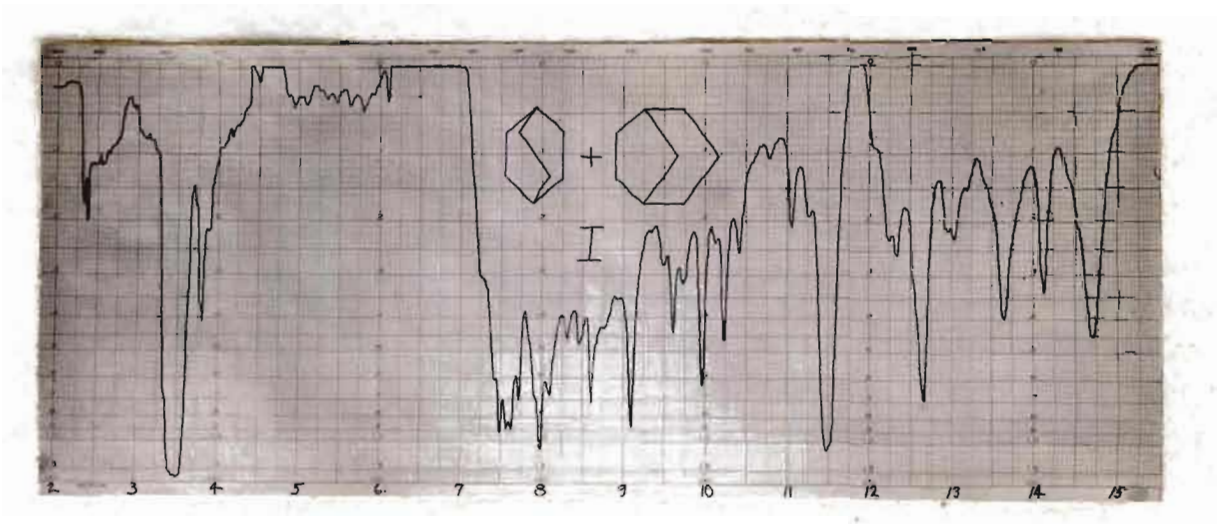

Figure 3
Bicyclo(2,2,2)octane and Bicyclo(3,2,1)octane
as Synthesized by Method I (m.p. 125-133°C.)
Phase- liquid
Cell Thickness- 0.510 vs. 0.506
Concentration- 0.1572 g./ 0.5 ml.
vs. CS_2

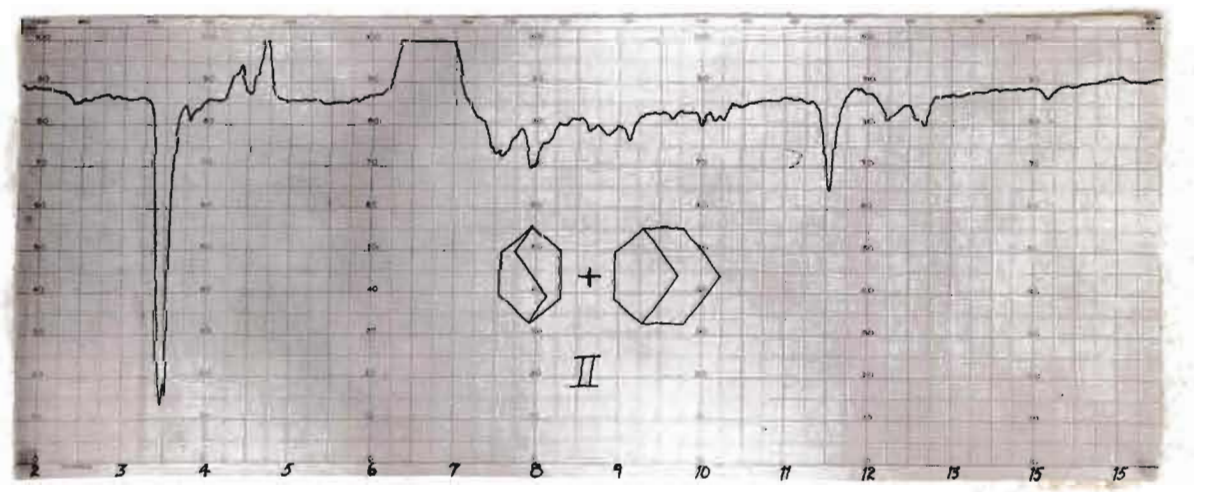

Figure 4
Bicyclo(2,2,2)octane and Bicyclo(3,2,1)octane
as Synthesized by Method II (m.p. 158-160°C.)
Phase- liquid
Cell Thickness- 0.11 vs. 0.09
Concentration- not recorded
vs. CS_2

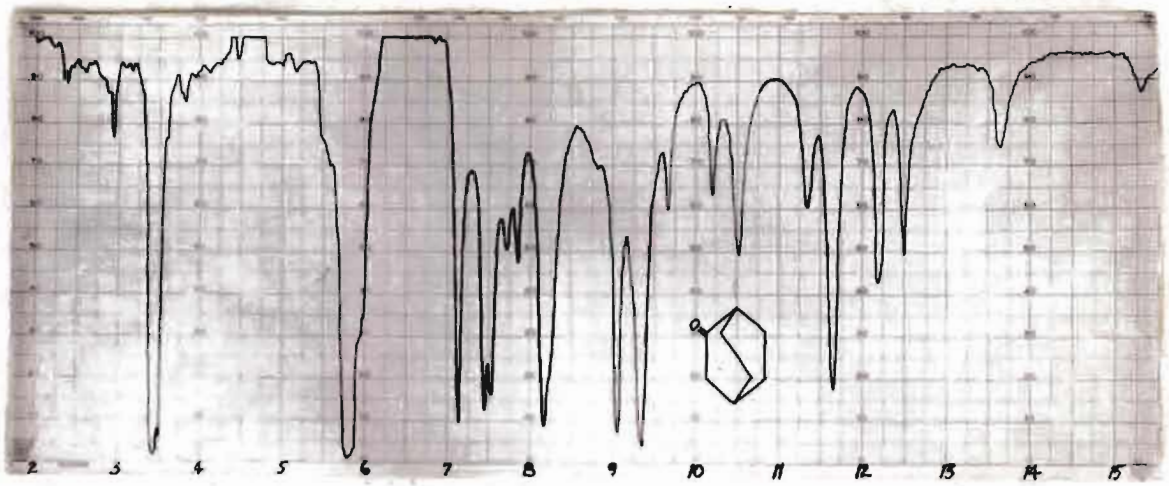

Figure 5
Pure Bicyclo(2,2,2)-2-octanone (m.p. 177-178°C.)
Phase- liquid
Cell Thickness- 0.110 vs. 0.09
Concentration- 0.1778 g./ 0.5 ml.
vs. CS_2

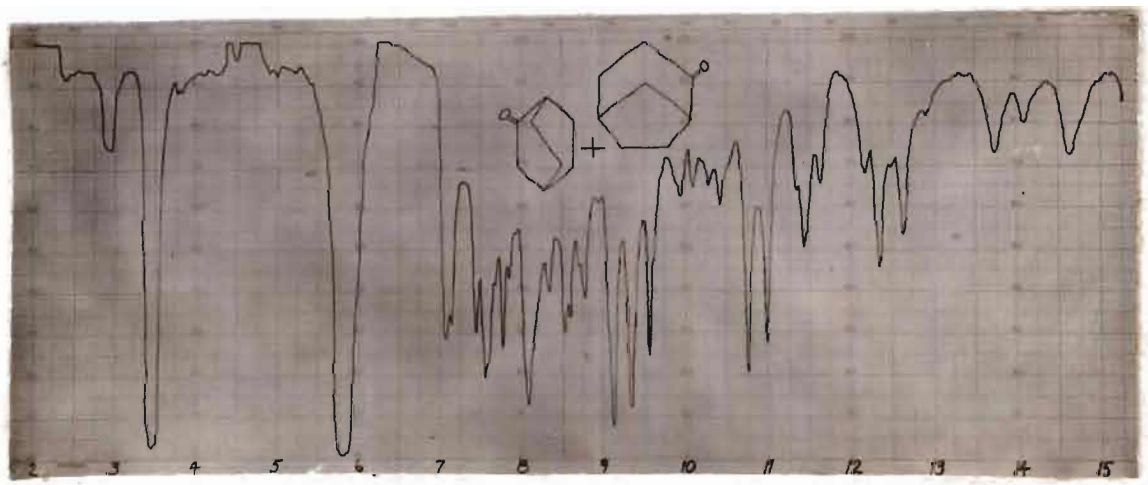

Figure 6
Bicyclo(2,2,2)-2-octanone and Bicyclo(3,2,1)-2-octanone
from the oxidation of the mixed alcohols (m.p. 125-134°C.)
Phase- liquid
Cell Thickness- 0.11 vs. 0.09
Concentration- 0.1953 g./ 0.5 ml.
vs. CS_2

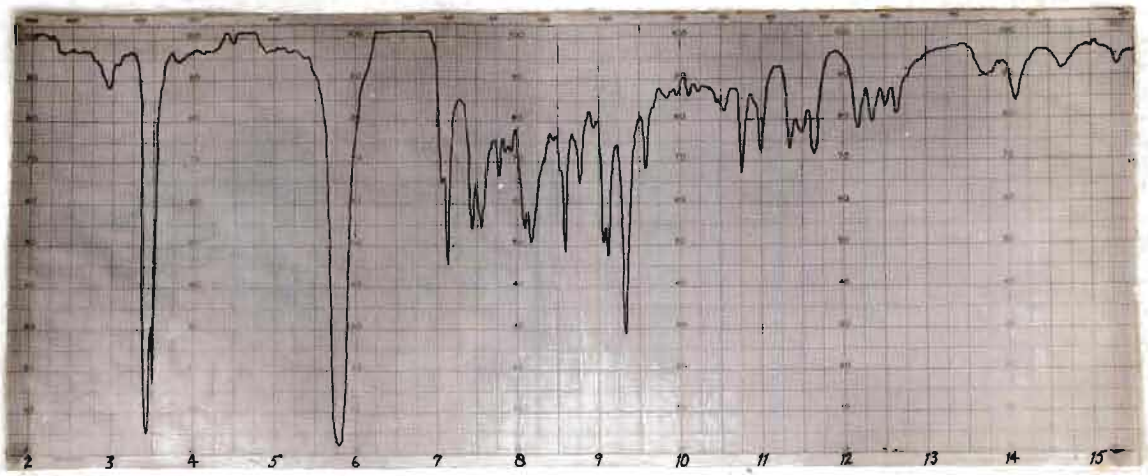

Figure 7
Bicyclo(2,2,2)-2-octanone and Bicyclo(3,2,1)-2-octanone
from the cleavage of the 2,4-dinitrophenylhydrazones
m. p. 131-134 °C.
Phase- liquid
Cell Thickness- 0.110 vs. 0.09
Concentration- 0.0777 g./ 0.5 ml
vs. CS_2

B I B L I O G R A P H Y

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