SYNTHESES IN THE BICYCLO[3.3.0]OCTANE SERIES

BY

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Submitted for the degree of Doctor of Philosophy to the

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Abstract

1. The Linstead synthesis of cis- and trans-bicyclo[3.3.0]octane has been repeated. Numerous modifications have been introduced into the synthesis in order to increase the yields of several crucial steps.

2. The Tiffeneau-Demanjow ring expansion reaction has been applied to bicyclo[3.2.0]-2-hepten-6-one and has been shown to yield a mixture of 85% bicyclo[3.3.0]-2-octen-6-one and 15% bicyclo[3.3.0]-2-octen-7-one.

3. The mixture of bicyclo[3.3.0]-2-octen-6-one and bicyclo[3.3.0]-2-octen-7-one has been converted to a mixture of bicyclo[3.3.0]octadienes. Attempts at catalytic dehydrogenation of this mixture of bicyclo[3.3.0]octadienes to pentalene have been unsuccessful.

4. Attempts at the conversion of the mixture of bicyclo[3.3.0]-octadienes to pentalene by chemical methods have been carried out. Most of the results obtained indicate that the introduction of more than two double bonds into the bicyclo[3.3.0]octane ring system renders the resulting olefin too unstable to be isolated.

5. The reaction of the p-toluenesulfonates of bicyclo[3.3.0]-2-octen-6-ol and bicyclo[3.3.0]-2-octen-7-ol with organic tertiary amines has been shown to yield a mixture of bicyclo[3.3.0]octadienes and an acyclic "octatetraene."

ACKNOWLEDGEMENT

To Mother and Dad

TABLE OF CONTENTS

Part II

THE RING EXPANSION OF BICYCLO[3.2.0]-2-HEPTEN-6-
ONE TO A MIXTURE OF BICYCLO[3.3.0]-2-OCTEN-6-ONE AND
BICYCLO[3.3.0]-2-OCTEN-7-ONE

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

PART I

THE PREPARATION OF CIS- AND TRANS-BICYCLO[3.3.0]OCTANE

INTRODUCTION

The bicyclo[3.3.0]octane ring system is of interest to chemists for numerous reasons. Among the foremost of these are the relative stabilities of the cis- and trans-isomers in the series.

In any case where two ring systems are fused in the 1,2-position, cis-trans isomerism is theoretically possible. The most thorough study of cis-trans isomerism in the bicyclo[3.3.0]octane series was carried out by Linstead, Meade, Cook, and Barrett.[1] These workers were the first to synthesize by unequivocal methods cis-bicyclo[3.3.0]octane, I, and trans-bicyclo[3.3.0]octane, II.
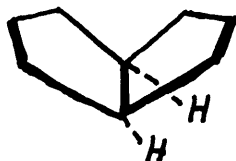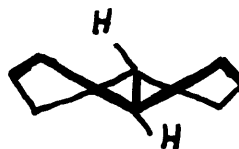
I   II

Models show the cis-isomer to consist of two, essentially planar, strainless, cyclopentane rings, while in the trans-isomer both rings must be multiplanar and considerable distortion must exist from the regular tetrahedral valency angles between the adjacent carbon atoms of the ring. On the basis of the Sachse-Mohr theory of ring strain the

trans-isomer would be predicted to be the more unstable and energy rich. This has been confirmed by comparison of the heats of combustion[1d] of the two isomers, I and II, and by comparison of the relative ease of formation of the two isomeric ring systems under identical reaction conditions.[1b]

DISCUSSION

In order to have suitable reference compounds for
the present study of the bicyclo[3.3.0]octane series the
Linstead synthesis of I and II has been repeated. Numerous
modifications have been introduced in order to improve the
yields of certain critical steps. The modified synthesis
is outlined in Fig. I.

The starting point in the synthesis is α-carbethoxy-
cyclopentanone, III. Alkylation of III with ethyl bromo-
acetate yields α-carbethoxy-α-carbethoxymethylcyclopentanone,
IV. Hydrolysis and decarboxylation of IV is effected with
20% hydrochloric acid, and yields 2-ketocyclopentane-
acetic acid, V. Direct esterification of V with ethanolic
hydrogen chloride produces ethyl 2-ketocyclopentaneacetate,
VI. To this point in the synthesis the procedures described
by Linstead and co-workers were followed and found to pro-
ceed as reported. As some minor modifications were intro-
duced, the procedures used in this work are given in the
experimental section.

The next step in the synthesis involves the con-
densation of VI with ethyl cyanoacetate. It is apparent
that the English workers[1d] failed to recognize the equilib-
rium nature of the reaction. Using piperdine as solvent
and a reaction time of fifteen days, the best yields reported

were 40% of the condensation product, VII. Five years later,
Cope, Hofmann, Wyckoff, and Hardenbergh,[2] in a thorough study
of this type of condensation reaction, found that the yields
could be considerably increased and the reaction time con-
siderably shortened by distilling out the water as formed,
thus forcing the equilibrium to the right. Using the best
conditions reported by Cope and co-workers[2] for unreactive
ketones and aldehydes, the yield of VII has been increased
to 68% and the reaction time shortened to fifteen hours.

The next step involves the reduction of the con-
densation product, VII, to the saturated, dihydro deriva-
tive, VIII. The English workers[1d] were unable to carry out
the reduction catalytically. Attempts at catalytic reduc-
tion of the double bond in the presence of Adam's platinum
catalyst, Raney nickel, or palladium-on-barium sulfate,
proved unsuccessful. The reaction was carried out by chem-
ical reduction with aluminum amalgam followed by catalytic
hydrogenation. It has been found in the present work that
the reduction can be very smoothly carried out in the pres-
ence of freshly prepared palladium-on-carbon catalyst.

Hydrolysis and decarboxylation of VIII with boiling,
concentrated hydrochloric acid leads to the formation of a
mixture of cis- and trans-cyclopentane-1,2-diacetic acids,
IX-A and IX-B respectively. The ratio of the two isomers
obtained is dependent on the ratio obtained in the reduction

of the condensation product. The English workers[1d] reported
the cis/trans ratio to be roughly 3:1 using chemical reduc-
tion. It was this unfavorable product ratio which prevented
these same workers from entering the trans-bicyclo[3.3.0]-
octane series for quite some period of time. It has been
found that the cis/trans ratio obtained by catalytic reduc-
tion is roughly 1:1.

As mentioned above, a mixture of cis- and trans-
cyclopentane-1,2-diacetic acids is obtained by hydrolysis
and decarboxylation of VIII. The English workers[1d] found
it inconvenient to separate the isomers by fractional crys-
tallization of the acids or of salts of the acids. However,
in an elegant piece of work, the same authors found that the
cis-isomer, IX-A, could be "fractionally ketonized" with
barium oxide at 280-300°, and that the trans-isomer, IX-B,
could be recovered from the reaction residue. They were
able to obtain absolute proof of the assigned configura-
tions by resolution of IX-B by means of the neutral brucine
salt.[1f] By fractional crystallization of the initial mix-
ture of cis- and trans-acids they were also able to isolate
the pure cis-isomeride, IX-A, which proved incapable of
resolution, as required by theory. In the present work the
separation by fractional ketonization has been substantiated.

From the fractional ketonization indicated above
cis-β-bicyclo[3.3.0]octanone, X, is obtained.

trans-Cyclopentane-1,2-diacetic acid is ketonized with
barium oxide at 340-350° to yield trans-β-bicyclo[3.3.0]-
octanone, XI. The English workers[1d] proved the structure
of XI by oxidation to trans-cyclopentane-1-carboxy-2-
acetic acid.

It is of interest that only three saturated
ketones in the bicyclo[3.3.0]octane series are apparently
capable of existence as stable compounds. These are X, XI,
and cis-α-bicyclo[3.3.0]octanone. Linstead and Cook[1b]
found that both cis- and trans-cyclopentane-1-carboxy-2-
propionic acids ketonized in the presence of barium oxide
to yield cis-α-bicyclo[3.3.0]octanone. As the trans-isomer
required more drastic conditions it is believed that trans-
α-bicyclo[3.3.0]octanone is first formed, but due to the
presence of the labile tertiary hydrogen is immediately
converted to the more stable cis-isomer. A sample of cis-
α-bicyclo[3.3.0]octanone has been obtained.[5] Fig. II shows
the infrared curves of the three ketones, X, XI, and cis-α-
bicyclo[3.3.0]octanone.

To effect the conversion of X and XI to the respec-
tive cis- and trans-bicyclo[3.3.0]octanes, Linstead and
Barrett[1d] employed the Kishner reduction of the semicarba-
zone of the ketone in the presence of sodium ethoxide. It
has been found that the same reduction may be carried out
more conveniently by a modified Wolff-Kishner reduction.[4]

In assigning the cis- and trans-configurations to
I and II it is assumed that, during the reduction of the
keto group of X and XI, no other change has occurred in the
structure of the molecule (i.e. no change in the configura-
tion of the two fused rings, and no more fundamental re-
arrangement of the carbon skelton). The infrared curves of
I and II are given in Fig. III together with the infrared
curve of an authentic sample of cis-bicyclo[3.3.0]octane.[3]
Both I and II are saturated to the usual reagents and the
infrared curves are different from that[6] of the most prob-
able rearrangement product, bicyclo[4.2.0]octane.

Figure I

SCHEMATIC REPRESENTATION OF THE SYNTHESES

OF CIS- AND TRANS-BICYCLO[3.3.0]OCTANE

EtOOC(CH₂)₄COOEt $\xrightarrow[\textbf{75\%}]{\textbf{Na}}$ [cyclopentanone-COOEt] $\xrightarrow[\textbf{Br-CH₂COOEt}]{\textbf{Na}}$ **IV** [cyclopentanone COOEt CH₂-COOEt] $\xrightarrow[\substack{\textbf{2. HCl, C₂H₅OH}\\\textbf{82.5\%}\\\textbf{OVERALL}}]{\textbf{1. HCl, H₂O}}$ **VI** [cyclopentanone CH₂-COOEt]

$\downarrow$ 68% $\quad\substack{CH_2\diagdown^{CN}_{COOEt}\\ CH_3COOH\\ CH_3-\overset{O}{C}-O^{\ominus} NH_4^{\oplus}}$

VII [cyclopentane =C$\diagdown^{CN}_{COOEt}$ CH₂-COOEt]

$\xleftarrow[\substack{\textbf{2. HCl, H₂O}\\\textbf{53.3\%}\\\textbf{OVERALL}}]{\textbf{1. H₂, Pd on C}}$ [cyclopentane CH₂-COOH CH₂-COOH] **IX-A** **IX-B** CIS AND TRANS

$\xleftarrow[\textbf{62\%}]{\substack{\textbf{BaO}\\\textbf{280-300°}}}$

X [bicyclooctanone with H] $\xrightarrow{}$ O

$\xleftarrow[\textbf{75\%}]{\substack{\textbf{H₂N-NH₂·H₂O}\\\textbf{KOH}}}$ **I** [bicyclooctane H H]

[cyclopentane CH₂-COOH CH₂-COOH]

$\downarrow$ 50% $\quad\substack{\textbf{BaO}\\\textbf{350°}}$

XI [bicyclooctanone H···H =O] $\xrightarrow[\textbf{65\%}]{\substack{\textbf{H₂N-NH₂·H₂O}\\\textbf{KOH}}}$ **II** [bicyclooctane H···H]

FIG. 1

EXPERIMENTAL

α-Carbethoxycyclopentanone (III).---The synthesis
was carried out according to the method of Organic Syntheses.[7]
In a typical run, 420 g. of diethyl adipate, b.p. 118-120°
(5mm.), n^{25}_D 1.4252, was converted to 244 g (75.3%) of III,
b.p. 77-79° (2.7 mm.), n^{25}_D 1.4505.

α-Carbethoxy-α-carbethoxymethylcyclopentanone (IV).---
In a 5-l. three-necked flask equipped with stirrer, dropping
funnel, reflux condenser, and protected from atmospheric
moisture was placed 19.5 g. (0.85 g. atom) of sodium in 2 l.
of anhydrous toluene. The solution was heated to reflux and
stirred vigorously until all the sodium was converted to
sodium sand. To this suspension was added dropwise 123.5 g.
(0.79 mole) of III over forty minutes. The mixture was then
heated to reflux and stirred for two hours and then 132 g.
(0.79 mole) of ethyl bromoacetate was added dropwise over
one hour. The solution was heated under reflux for an
additional five hours. The reflux condenser was replaced
by a still head and 1 l. of toluene distilled from the
solution. After cooling, 300 ml. of ether was added and
the organic layer washed successively with 1 l. of 8%
sulfuric acid, two 400-ml. portions of water, 400 ml. of
5% sodium bicarbonate, and 300 ml. of water. The organic

layer was dried over magnesium sulfate and concentrated
under reduced pressure. Distillation yielded 149 g. (78%)
of IV, b.p. 114-117° (0.7 mm.), n^{25}_D 1.4525.

Anal. Calcd. for $C_9H_{18}O_5$: C, 59.45; H, 7.44.
Found: C, 59.51; H, 7.66.

Ethyl 2-Ketocyclopentaneacetate (VI).---In a 500-ml.
round-bottomed flask was placed 149 g. (0.615 mole) of IV
and 300 ml. of 20% hydrochloric acid. The reactants were
heated under reflux for twenty hours. The solution was
concentrated under reduced pressure to 90 g. (the theoreti-
cal yield of 2-ketocyclopentaneacetic acid was 87.5 g.) and
the crude acid directly esterified by addition of 450 ml.
of absolute ethyl alcohol containing 125 g. of anhydrous
hydrogen chloride. The reactants were thoroughly mixed and
allowed to stand at room temperature for twenty hours. The
solution was concentrated under reduced pressure. Distilla-
tion yielded 86.5 g. (82.5% overall) of VI, b.p. 120-125°
(11.5 mm.), n^{25}_D 1.4503.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.55; H, 8.23.
Found: C, 63.50; H, 8.30.

Ethyl 2-Carbethoxymethylcyclopentylidine Cyanonacetate
(VII).---In a 100-ml. round-bottomed flask was placed 17.3 g.
(0.102 mole) of VI, 4.8 g. (0.08 mole) of acetic acid, 1.93 g.
(0.025 mole) of ammonium acetate, 11.3 g. (0.10 mole) of
ethyl cyanoacetate, and 30 ml. of benzene. The flask was

fitted with a water separator, which in turn was equipped
with a reflux condenser. The flask was heated with a bath
at 130-140° for fourteen hours. Water was removed at ap-
propriate intervals. After cooling, 50 ml. of benzene and
30 ml. of ether were added and the mixture extracted with
three 40-ml. portions of water. The combined washings were
extracted with a small portion of benzene, the benzene layers
combined, and dried over magnesium sulfate. The solution was
concentrated under reduced pressure. Distillation through a
10 cm. Vigreux still head yielded 18 g. (68%) of VII, b.p.
172-174° (2.8 mm.), n^{25}_D 1.4831.

Anal. Calcd. for $C_{14}H_{19}O_4N$: C, 63.40; H, 7.71;
N, 5.28. Found: C, 63.39; H, 7.35; N, 5.39.

Preparation of a Mixture of cis- and trans-Cyclo-
pentane-1,2-diacetic Acids (IX-A, and IX-B).---In a 1-1.
reduction flask was placed 104 g. (0.39 mole) of VII, 300 ml.
of 95% ethanol, and 2.5 g. of freshly prepared palladium-on-
charcoal catalyst[8] (7.5% palladium). The reduction was
carried out under a pressure of 1-2 atmospheres. Over five
hours the theoretical amount of hydrogen (0.39 mole) was
taken up. The catalyst was removed by filtration and the
ethanol by distillation under reduced pressure until the
residue amounted to 110 g. The crude product was transferred
to a 1-1. round-bottomed flask, 450 ml. of concentrated
hydrochloric acid added, and the mixture heated under reflux

for fifteen hours. The boiling solution was filtered by gravity to remove a small amount of polymer and steam distilled until 1 l. of distillate was obtained. During the steam distillation the volume in the reaction flask was kept at approximately 500 ml. On cooling, a mixture of cyclopentane-1,2-diacetic acids crystallized from solution. A total of 58 g. of crude product was obtained. The crude product was dissolved in 500 ml. of boiling water and the solution treated with 2 g. of decolorizing carbon. The carbon was removed by filtration and the solution allowed to cool slowly to room temperature. On crystallization, 35.5 g. of IX, m.p. 149.5°, was obtained. Concentration of the solution to 100 ml. and further crystallization yielded an additional 3 g. of IX, m.p. 138°. The total yield was 38.5 g. (53.3% overall, 73% in each step). Using the melting point curve of Linstead and Barrett[1d] the composition of the first crop was 45% trans and 55% cis, and the composition of the second crop was 70% trans and 30% cis.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.59. Found: C, 58.10; H, 7.59.

The above procedure combines the reduction of VII to VIII with the hydrolysis and decarboxylation of VIII to IX and was found to be the best procedure for the synthesis of large amounts of IX. In some instances VIII was isolated. In a typical synthesis, 24.2 g. of VII was converted to 17.4 g. (71%) of VIII, b.p. 150-153° (1.5 mm.), n_D^{25} 1.4599.

From the steam distillate, obtained in the above procedure after the hydrolysis of VIII, it was possible to obtain small quantities of a semicarbazone, m.p. 193-194° (dec.). The semicarbazone proved to be identical with the semicarbazone of cis-β-bicyclo[3.3.0]octanone. This confirms the observation of Linstead and Meade[1a] that cis-β-bicyclo[3.3.0]octanone is formed during the hydrolysis of VIII.

cis-β-Bicyclo[3.3.0]octanone (X), and Isolation of trans-Cyclopentane-1,2-diacetic Acid (IX-B).----In a 100-ml. round-bottomed flask was placed 34 g. (0.183 mole) of IX-A and IX-B, m.p. 149.5°, and 2 g. of barium oxide. The flask was fitted with a 10 cm. Vigreux column and the flask heated with a Wood's metal bath from 280-300° over one hour, during which time organic material distilled freely, and from 300-305° for two hours to insure complete cyclization of the cis-isomer. The distillate was taken up in 50 ml. of ether and the ether layer washed with 25 ml. of 5% sodium bicarbonate solution and 25 ml. of water. The ether layer was dried over magnesium sulfate and the ether removed under reduced pressure. Distillation through a micro column[9] yielded 7.65 g. (61% based on percentage composition of starting material) of X, b.p. 88° (17 mm.), n^{25}_D 1.4772.

The infrared spectrum is given in Fig. II.

<u>Anal.</u> Calcd. for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 77.66; H, 9.79.

The semicarbazone was prepared by the method of Fuson and Shriner.[10] The product after crystallization from ethanol-water had m.p. 194-195° (dec.), (lit.,[1a] m.p. 197-198° (dec.).

<u>Anal.</u> Calcd. for $C_9H_{15}ON_3$: C, 59.70; H, 8.28; N, 23.20. Found: C, 59.66; H, 8.45; N, 23.42.

The 2,4-dinitrophenylhydrazone was prepared by the method of Fuson and Shriner.[10] The product after recrystallization from ethanol had m.p. 115-116°.

<u>Anal.</u> Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.30; H, 5.26; N, 18.42. Found: C, 55.61; H, 5.29; N, 18.39.

Isolation of <u>trans</u>-Cyclopentane-1,2-diacetic Acid (IX-B).---The tarry reaction residue from the cyclization was extracted with one 50-ml. portion and one 25-ml. portion of boiling 5% hydrochloric acid. It was necessary to treat the combined solutions three times with decolorizing carbon to remove all polymeric and tarry material. After cooling, the crude product was separated by filtration and purified by sublimation. The mother liquor was then concentrated to 25 ml. and the second crop of IX-B purified in a similar manner. A total of 10 g. (65% based on the percentage composition of the starting material) of pure IX-B, m.p. 133° (lit.,[1d] m.p. 133°). was obtained.

<u>Anal</u>. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.53. Found; C, 57.86; H, 7.66.

<u>trans</u>-β-Bicyclo[3.3.0]octanone (XI).---In a 50-ml. round-bottomed flask equipped with a still head was placed 10 g. (0.054 mole) of IX-B, and 1.5 g. of barium oxide. The flask was heated with a Wood's metal bath. At 340° a vigorous reaction took place and organic material distilled freely while the temperature was raised slowly to 360° over two and one-half hours. The organic distillate was taken up in 30 ml. of ether and the ether layer washed with 25 ml. of 5% sodium bicarbonate solution and 25 ml. of water. The ether layer was dried over magnesium sulfate and the ether removed under reduced pressure. Distillation through a micro column[9] yielded 3.23 g. (48%) of XI, b.p. 87-88° (22 mm.), n^{25}_D 1.47.55.

The infrared curve is given in Fig. II.

<u>Anal</u>. Calcd. for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 77.21; H, 9.73.

The semicarbazone was prepared by the method of Fuson and Shriner.[10] The product after crystallization from ethanol-water had m.p. 243-244° (dec.), (lit.,[1d] m.p. 248-249° (dec.)).

<u>Anal</u>. Calcd. for $C_9H_{15}ON_3$: C, 59.70; H, 8.28; N, 23.20. Found: C, 59.66; H, 8.24; N, 23.02.

The 2,4-dinitrophenylhydrazone was prepared by the method of Fuson and Shriner.[10] The product after crystallization from ethanol had m.p. 156.5-157.5°.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.30; H, 5.26; N, 18.42. Found: C, 55.22; H, 5.32; N, 18.66.

The residue from the cyclization was extracted with two 25-ml. portions of 5% hydrochloric acid. The combined portions were treated with decolorizing carbon and concentrated to 10 ml. After cooling the crude product was separated by filtration and on sublimation 1.1 g. of IX-B was recovered, m.p. 133°.

cis-Bicyclo[3.3.0]octane (I).---In a 50-ml. flask, fitted with a 10 cm. Vigreux column, was placed 1.8 g. (0.0145 mole) of X, 1.8 g. of hydrazine hydrate, and 12 ml. of butyl carbitol. To this was added a solution of 2.5 g. of potassium hydroxide in 12 ml. of butyl carbitol. The reactants were heated with a bath from 100-200° over ninety minutes. The distillate was taken up in 25 ml. of ether, and the ether layer washed with two 25-ml. portions of 5% hydrochloric acid and two 15-ml. portions of water. The ether layer was dried over magnesium sulfate and the ether removed by distillation at atmospheric pressure. Distillation through a micro column[9] yielded 1.2 g. (75%) of I, b.p. 135-136°, n_D^{25} 1.4580. cis-Bicyclo[3.3.0]octane prepared in

this way contained small amounts of ether. The ether was removed by the silica-gel method of Cope and Hochstein.[6] After five passages over silica gel, the refractive index was constant at n^{25}_D 1.4598 (lit.,[69] n^{25}_D 1.4595).

The infrared curve is given in Fig. III.

Anal. Calcd. for C_8H_{14}: C, 87.30; H, 12.70. Found: C, 87.04; H, 12.64.

trans-Bicyclo[3.3.0]octane (II).---The synthesis was carried out in an analogous manner to that described above for _cis_-bicyclo[3.3.0]octane. In this way, 2 g. (0.016 mole) of XI was converted to 1.14 g. (65%) of II, b.p. 136-136.5°, n^{25}_D 1.4568. Product prepared in this manner was contaminated with small amounts of ether which was removed by the silica-gel method indicated above. After five passes over silica-gel the refractive index remained constant at n^{25}_D 1.4592.

The infrared curve is given in Fig. III.

Anal. Calcd. for C_8H_{14}: C, 87.30; H, 12.70. Found: C, 87.31; H, 12.73.

Figure II

Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2-5.0μ   and 6.2-7.4μ   where carbon tetrachloride was used as solvent.

Curve 1.   cis-α-Bicyclo[3.3.0]octanone.

Curve 2.   cis-β-Bicyclo[3.3.0]octanone.

Curve 3.   trans-β-Bicyclo[3.3.0]octanone.

Figure III

Infrared spectra: Baird spectrograph with NaCl
prism. Pure samples of compounds in 0.025 mm. cell.

Curve 1. cis-Bicyclo[3.3.0]octane. Authentic
sample prepared by Cope and Schmitz.[4]

Curve 2. cis-Bicyclo[3.3.0]octane. Sample pre-
pared by Wolff-Kishner reduction of X.

Curve 3. trans-Bicyclo[3.3.0]octane. Sample pre-
pared by Wolff-Kishner reduction of XI.
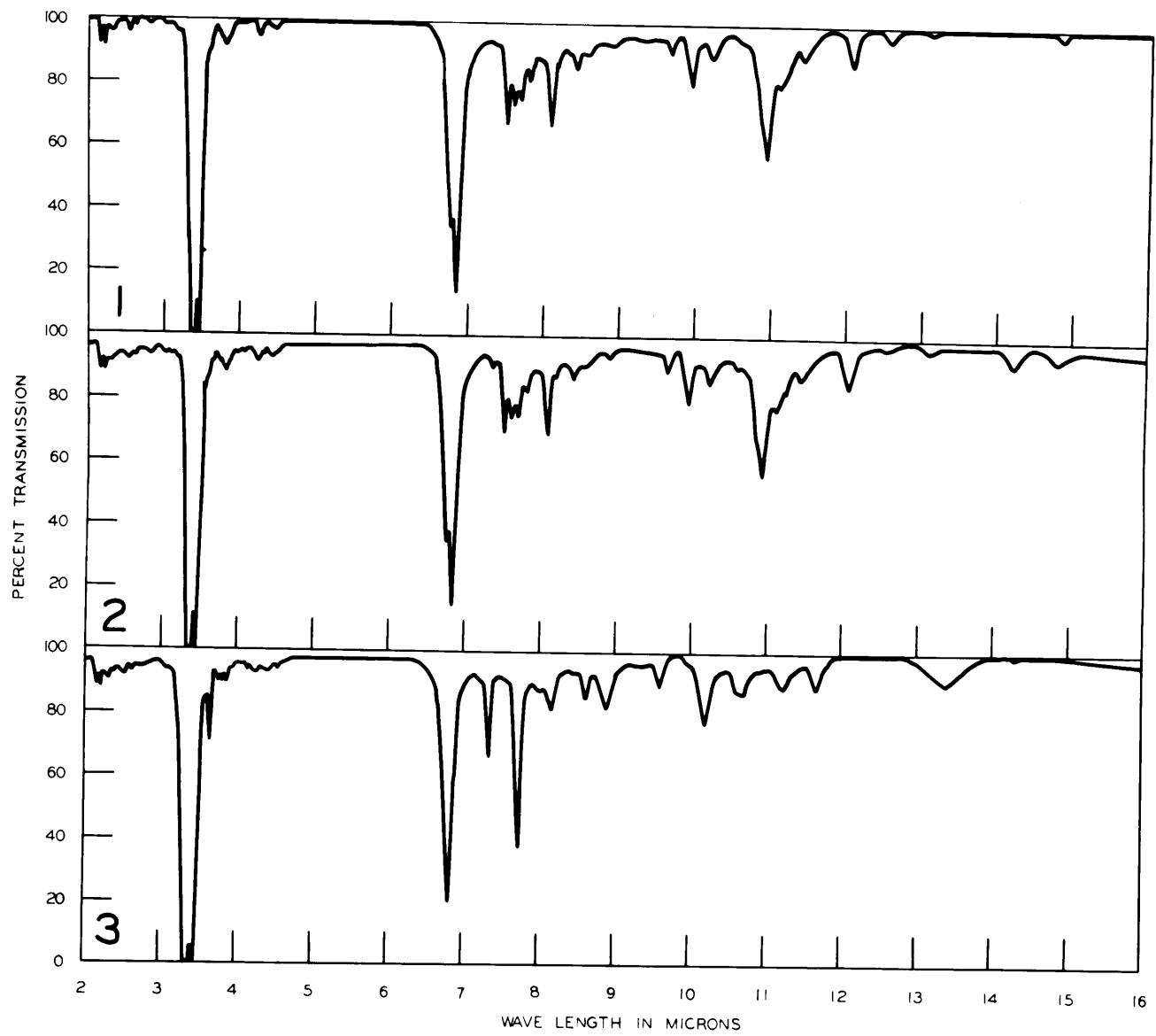
PART II

THE RING EXPANSION OF BICYCLO[3.2.0]-2-HEPTEN-6-ONE TO A MIXTURE OF BICYCLO[3.3.0]-2-OCTEN-6-ONE AND BICYCLO[3.3.0]-2-OCTEN-7-ONE

THEORETICAL

Much of the present interest in the chemistry of the bicyclo[3.3.0]octane ring system has its origin in theoretical discussions concerning the stability or instability, and the possible existence or nonexistence of of pentalene (bicyclo[3.3.0]octatetraene), XXV, for which two equivalent resonance structures similar to the Kekule forms of benzene may be written.

XXV

Possibly the first authors to recognize the interest in this compound were Armit and Robinson[11] who mentioned that the compound might be aromatic in character. In 1934 Ruzicka, de Almeida, and Brack[12] suggested that a compound prepared by them, bicyclo[3.3.0]octan-2,6-dione, would be a good starting material for an attempted synthesis of pentalene. However they made no prediction as to what they believed its properties might be.

In 1936 Barrett and Linstead[1f] reported the first attempted synthesis of pentalene, by catalytic dehydrogenation of cis-bicyclo[3.3.0]octane.

For the past fifteen years much of the literature

on pentalene has been mathematical in nature. In 1940,
Coulson and Rushbrooke[13] examined pentalene by the molecular
orbital method. Coulson and Rushbrooke, on the basis of
their calculations feel that the mobile electrons (π-elec-
trons) in pentalene might tend to accumulate on carbon
atoms 1,3,5, and 7 at the expense of carbon nuclei 2, 4, 6,
and 8. In cases such as this, Coulson and Rushbrooke re-
port that, "Any predictions we might make from this (the
molecular orbital) theory would have less theoretical basis
than for molecules such as benzene and naphthalene."

Craig and Maccoll[14,15] have recently made a thorough
quantum-mechanical study of pentalene by both the valence-
bond method and the molecular-orbital method. On the basis
of their calculations they feel that considerable resonance
energy should be associated with the molecule. However,
these same authors found that calculation of the bond orders
of pentalene by the method of Penney[16] showed the bond join-
ing the 1 and 5 carbon atoms, the central bond, should have
a small negative order. This would indicate some repulsion
between the π-electrons across the bond.

The more general molecular orbital theory of cyclic
systems as developed by Huckel,[17] however, ascribes special
stability to those fully unsaturated, cyclic, planar, poly-
olefins which contain (2 + 4n) π-electrons (n = 0, 1, 2$\cdots\cdots$).
A π-electron by definition is an electron in a "p" orbital

which is used solely in the formation of multiple bonds
through interaction with other π-electrons. Indeed it
must be admitted that this rule holds in most cases as
cyclobutadiene (n = 1/2), pentalene (n = 1 1/2), and
heptalene (n = 2 1/2) have not been synthesized, while
ethylene (n = 0), benzene (n = 1), naphthalene (n = 2),
and anthracene (n = 3) are all well known compounds, and,
with the exception of ethylene, can all be considered to
be resonance-stabilized.

Huckel's rule appears equally applicable to cyclic
resonating ions of either the carbanion or carbonium ion
type. For example, cyclopentadiene very readily forms a
carbanion, which possesses six π-electrons, by reaction
with Grignard reagents but all attempts to form the cor-
responding carbonium ion, which possesses four π-electrons,
have been unsuccessful. As a further example of the applica-
tion of this rule to ionic species Boekelheide and Larrabee[25]
have recently reported the synthesis of perinaphthene. They
found that all attempts to form the perinaphthenyl carbonium
ion led to extensive decomposition of the reactants. The
perinaphthenyl carbonium ion is seen to be an extremely sym-
metrical species. One may draw seven completely equivalent

Perinaphthene
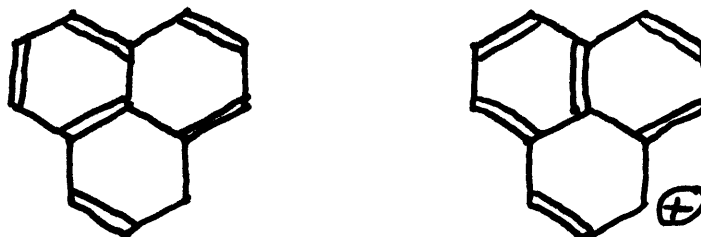
resonance forms for the perinaphthenyl carbonium ion, which,
it would seem should result in considerable stabilization.
However the ion has twelve π-electrons which does not satisfy
the (2 + 4n) rule for cyclic resonating systems.

Doering and Detert,[18] and Dauben and Ringold[19] have
recently explained the properties of cycloheptatrenylium
oxide, indicated below, by the fact that the molecular orbital
theory predicts special stability for six electrons in a
cyclic resonating system.

behaves as
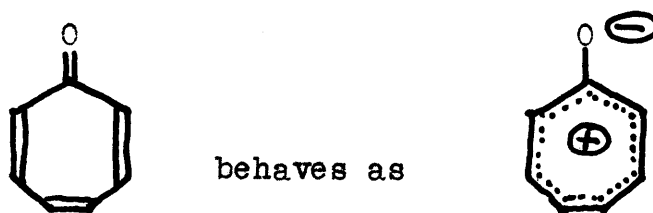
Baker,[20] in the Tilden Lecture in 1945, summarized
the chemical evidence available at that time and came to the
conclusion that pentalene would not be an aromatic type. His
reasons were that pentalene was a fulvene derivative, the
molecule would contain a moderate cyclic strain, and that
each ring in pentalene does not contain the "aromatic sextet"
of electrons present in all known aromatic types. There
seems to be, however, a logical answer for each of these
objections. With regard to the strain involved, both cyclo-
propene[21] and cyclobutene[22] have been synthesized and certainly
considerably more strain occurs in these compounds than in
pentalene. The objection that pentalene does not possess an

"aromatic sextet" of electrons in each ring can be answered by the calculations of Craig and Maccoll,[14, 15] which indicate that pentalene is considerably resonance stabilized. Finally, Patrick[23] has noted that pentalene should no more be considered a fulvene derivative than benzene should be considered a cyclohexatriene derivative.

Recently M. J. S. Dewar[24] has stated that he believes pentalene is probably not capable of stable existence and that Craig and Maccoll's[14, 15] calculations are not likely to be valid.

Brown,[61,62] has recently reported theoretical studies of some non-benzenoid hydrocarbons. Brown's calculations lead him to believe that pentalene should be a reasonably stable hydrocarbon, that it would be colored, and that the resonance energy would be 37 kcal. Brown, on the basis of his calculations, even predicted the point of attack by electrophilic, nucleophilic, and free radical species. Brown, in a summation of his work, reported that "It is likely pentalene is sufficiently stable to be isolated when a suitable synthesis has been devised."

From the above discussion it is obvious that considerable disagreement exists concerning the possible existence and properties of pentalene. It is also obvious that a decision can only be reached by attempted synthesis by all logical synthetic approaches. The object of this thesis has been to investigate one of these approaches.

GENERAL BICYCLO[3.3.0]OCTANE SYNTHESES

It is of interest that the first compounds prepared containing the bicyclo[3.3.0]octane ring system are perhaps the most complicated compounds yet prepared containing this ring structure. Reimer,[26] in 1881, reported that 2,3-diphenylsuccinic acid was converted to "dibenzyldicarbonid" on treatment with sulfuric acid. Roser[27] investigated the reaction further and reported that the reaction product was 3,4,7,8-dibenzbicyclo[3.3.0]-3,7-octadien-2,6-dione. Brand[28] found that reaction of this latter compound with two moles of phenyl magnesium bromide, followed by dehydration led to the formation of 2,6-diphenyl-3,4,7,8-dibenzpentalene.
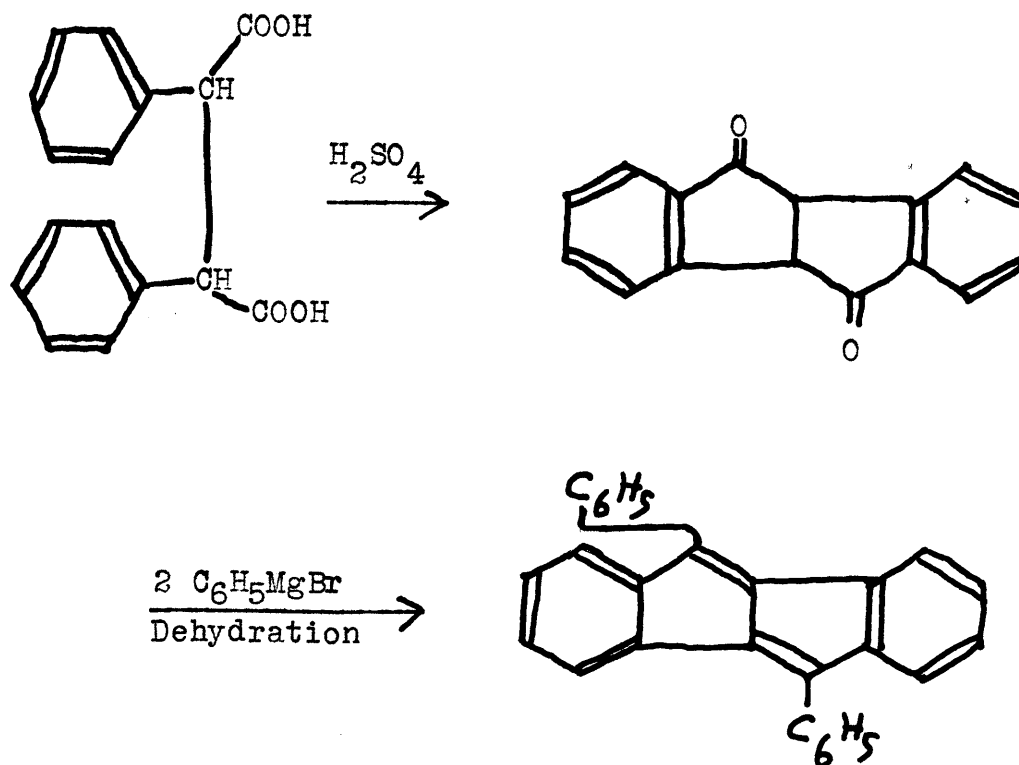
Brand then continued to make a thorough study of this ring system and made numerous other derivatives of dibenzpentalene. An account of much of his work and descriptions of many compounds of this structure are found in Elsevier.[29] Some of the more interesting compounds of this structure prepared by Brand and Mueller[30] were dihydrodibenzpentalene, 2,6-dichlorodibenzpentalene, and 2,6-dibenzalpentalene. The structures of these compounds are as follows:
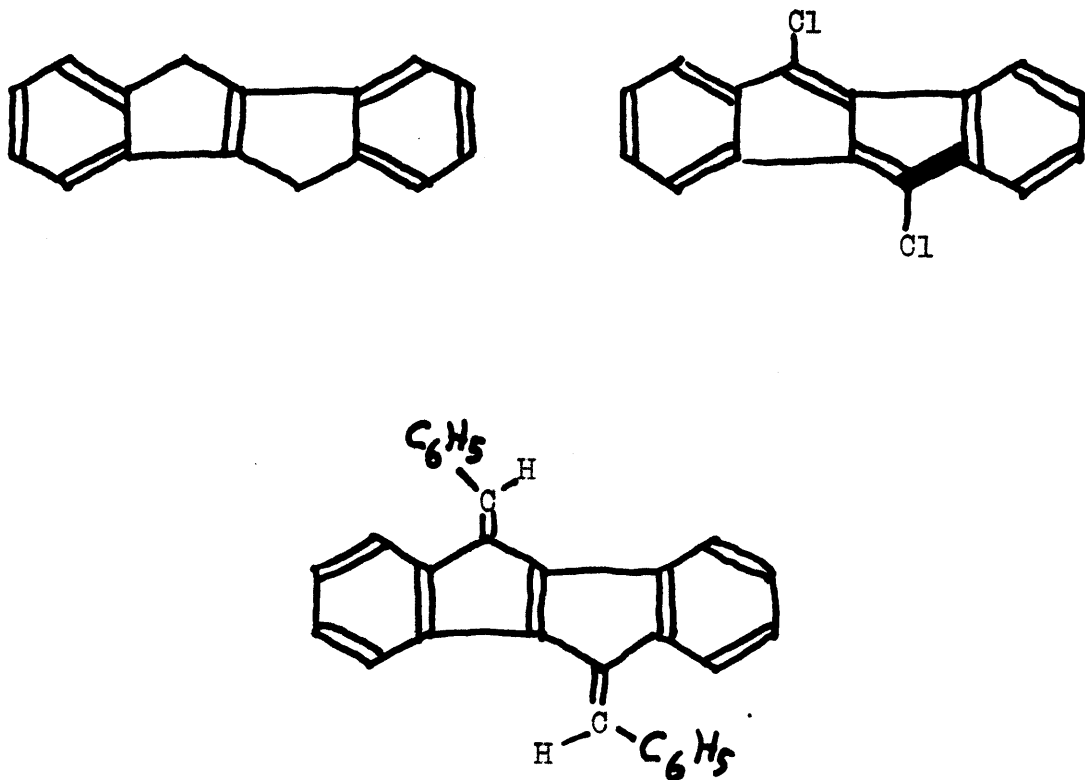
Wawzonek[31] has repeated and confirmed much of Brand's work. Even more recently Cope and Fenton[32] have repeated

Brand's synthesis of 2,6-dichlorodibenzpentalene. Consequently there is no doubt but what these compounds do possess a true pentalene ring system. This does not, however, detract from the interest in pentalene itself as it has not yet been decided whether resonance interaction exists in the two central rings or if the double bonds are fixed.
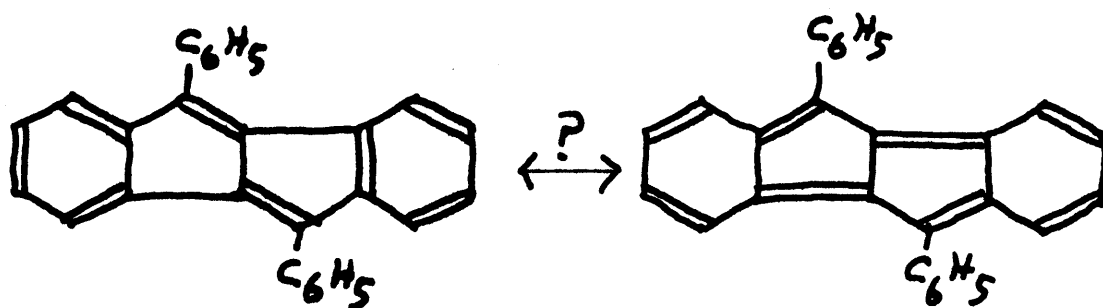
Furthermore, the stabilizing effect of fused benzene rings on unstable ring systems is well exhibited in Lothrop's[33] synthesis of dibenzcyclobutadiene, diphenylene. This latter compound is the only cyclobutadiene derivative known. For some time after its synthesis the structure of this compound was in doubt as an alternative structure, 2,3-benzpentalene, was proposed and seemed to explain some of the observed reactions. Lothrop prepared this interesting compound by the reaction of 2,2'-diiododiphenyl with cuprous oxide.
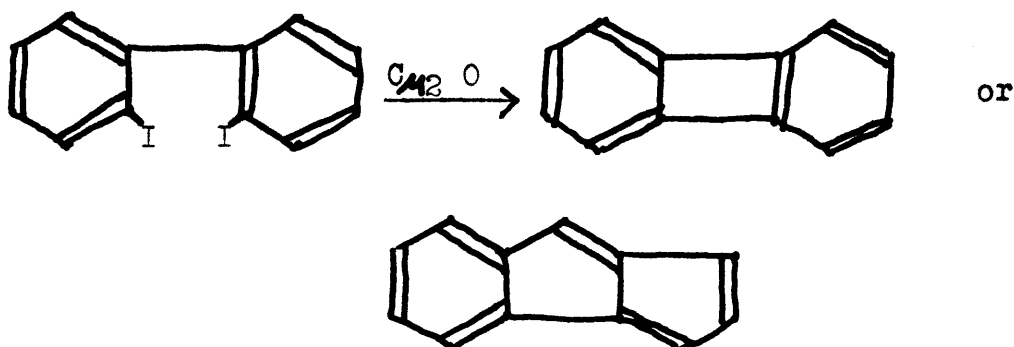
The product appeared to be reasonably stable, and aromatic in character. Lothrop's proof of structure included oxidation to phthalic anhydride and reduction in low yield to a sample of impure biphenyl. Baker,[34] however, found that under different conditions for reduction the compound took up three moles of hydrogen forming an unidentified product. Uptake of three moles of hydrogen seemed to favor the 2,3-benzpentalene structure and Coulson[35] soon after argued that the latter structure should be considerably more stable.

However, conclusive evidence in favor of the cyclobutadiene structure originally proposed by Lothrop was soon forthcoming in an electron diffraction analysis by Waser and Schomaker[36] and an X-ray crystallographic analysis by Waser and Lee.[37] Finally, Baker[20] found that reduction of the reaction product in ethanol in the presence of Raney nickel led to the formation of biphenyl in 85% yield.

The ultraviolet spectrum of dibenzcyclobutadiene was investigated by Carr, Pickett, and Voris[38] who showed that it was similar to the spectrum of naphthalene and fluorene and cited this as evidence in favor of the dibenzcyclobutadiene structure. Ilse[39] has recently re-interpreted the spectrum as supporting the alternative 2,3-benzpentalene structure. The reduction in 85% yield to biphenyl seems, however, to settle the question beyond reasonable doubt in favor of the dibenzcyclobutadiene

structure.

While dibenzcyclobutadiene did not turn out to be 2,3-benzpentalene the synthesis of this latter compound is of considerable interest as it would be one step closer to the solution of the pentalene problem. Recently syntheses of compounds of this general structure have been reported by Baker and Jones;[40] Baker, Coates, and Glockling;[63] Clemo, Groves, Munday, and Swan;[64] Groves and Swan[65] and Dahn.[41]

Baker and Jones[40] have reported the synthesis of 2,3-benzbicyclo[3.3.0]-2-octene by the following series of reactions.
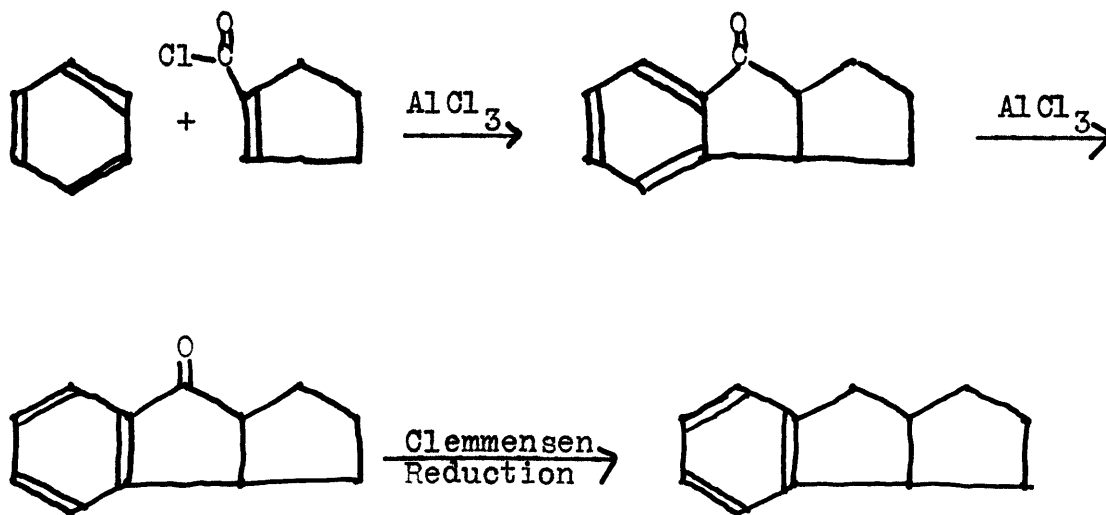
All attempts to catalytically dehydrogenate 2,3-benzbicyclo[3.3.0]-2-octene by either chemical or catalytic methods were unsuccessful. The list of dehydrogenating

conditions and reagents in their unsuccessful attempts in-
clude practically all such conditions and reagents reported
in the chemical literature.

Baker, Coates, and Glockling[63] have reported that
3-keto-2-phenylcyclopentane-1-carboxylic acid is cyclized
in the presence of fluorosulfonic acid to 2,3-benzbicyclo-
[3.3.0]-2-octen-4,8-dione. This route to benzpentalene
appears quite promising and the English workers report they
are continuing their study of this interesting compound.
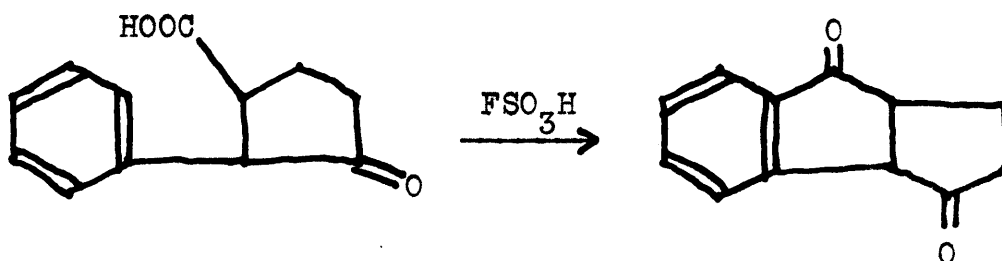
Clemo, Groves, Munday, and Swan[64] have reported the
synthesis of 2,3-benzbicyclo[3.3.0]-1(5),2-octadien-6-one.
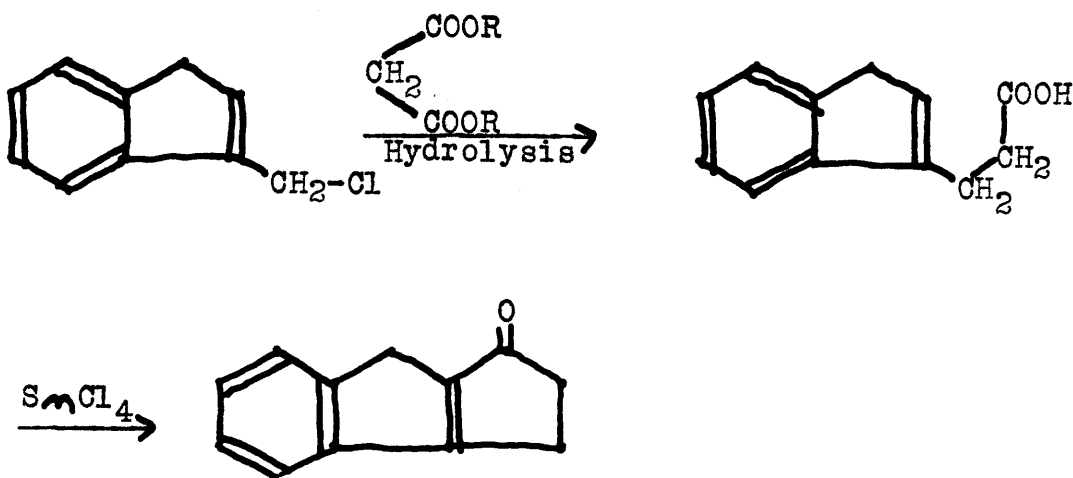
Work with the cyclized ketone did not prove encouraging. Attempts at dehydrogenation of the ketone were unsuccessful as were attempts to convert the ketone by chemical methods to 2,3-benzpentalene.

Groves and Swan[65] have reported the synthesis of 2,3-benzbicyclo[3.3.0]-2-octen-7-one by a synthesis resembling the Linstead[1a] synthesis of cis-β-bicyclo[3.3.0]octanone. Groves and Swan converted the former ketone to 2,3-benzbicyclo[3.3.0]-2,6-octadiene by standard procedures. This latter olefin could not be dehydrogenated and attempts to introduce allylic bromines with N-bromosuccinimide followed by dehydrohalogenation led only to the formation of black, polymeric material.
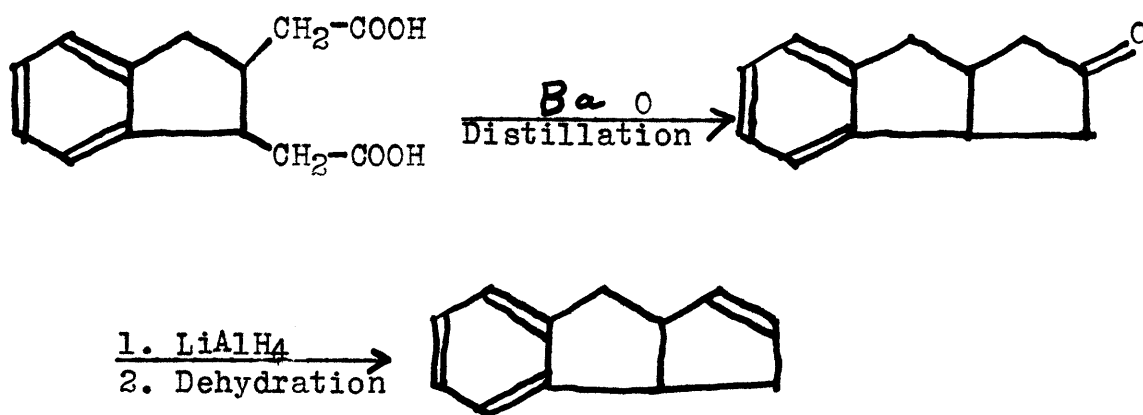
Dahn[41] has also reported syntheses in this series. His starting material was indanone which was converted by the Stobbe condensation and cyclization of the resulting product to 2,3-benz-8-carbethoxybicyclo[3.3.0]-1(5),2-octadien-6-one.
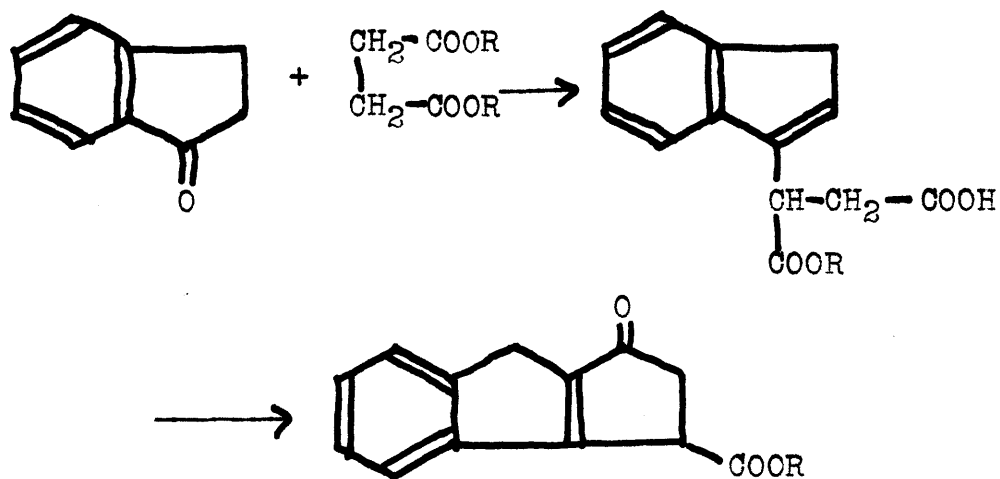
Dahn's plan of attack then involved reaction of the keto ester with excess methyl magnesium bromide followed by dehydration. This would lead to the formation of a fulvene derivative which would be isomeric with 2-methyl-4-isopropyl-6,7-benzpentalene. The dehydration step was unsuccessful and Dahn was only able to isolate polymeric material. While the final step was unsuccessful the approach to the problem is novel and most interesting.
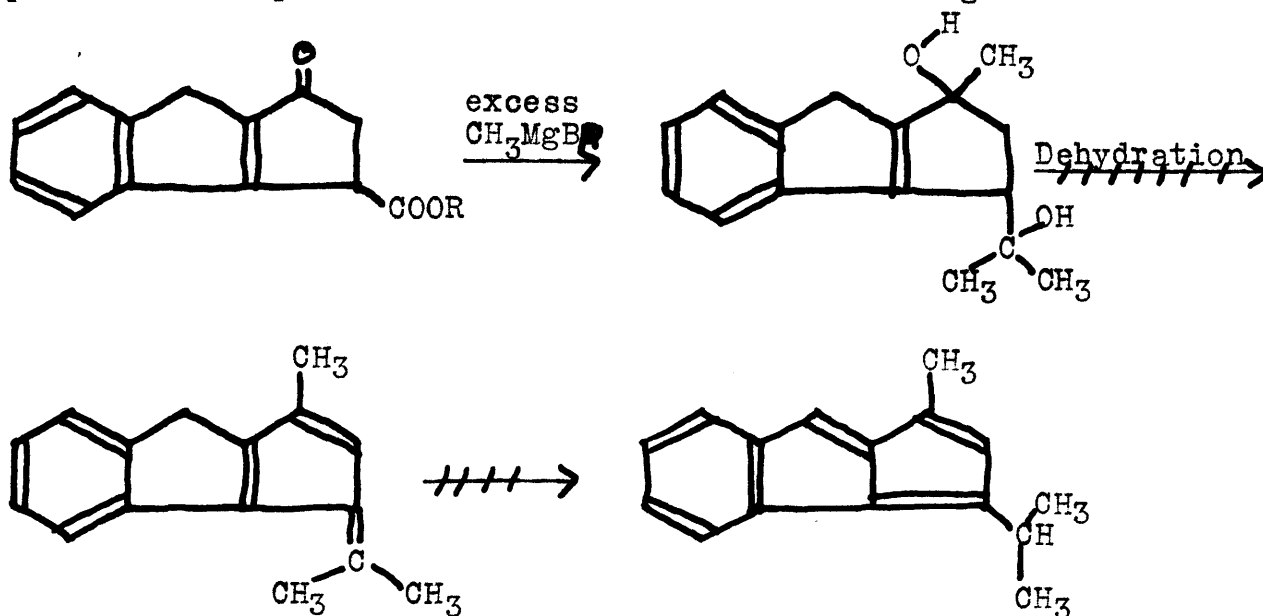
All the above work on benzpentalene has been reported in 1951. From the evidence now at hand it seems safe to conclude that benzpentalene can not be prepared by dehydrogenation and that preparation by chemical methods does not appear promising.

Georgi,[42] and independently Stobbe,[43] were probably the first to prepare a compound having the simple bicyclo[3.3.0]octane ring system. Their synthesis involved 1,4 addition of cyclopentanone to benzalacetophenone, in the presence of piperdine, and subsequent pinacol reduction with sodium amalgam in alcohol.

$$C_6H_5\text{-}\overset{\overset{\text{O}}{\|}}{C}\text{-CH=CH-}C_6H_5 \quad + \quad \square \quad \xrightarrow{\text{piperdine}} \quad C_6H_5\text{-}\overset{\overset{\text{O}}{\|}}{C}\text{-}CH_2\text{-}\underset{C_6H_5}{CH}$$

$$\xrightarrow[\text{alcohol}]{Na Hg}$$
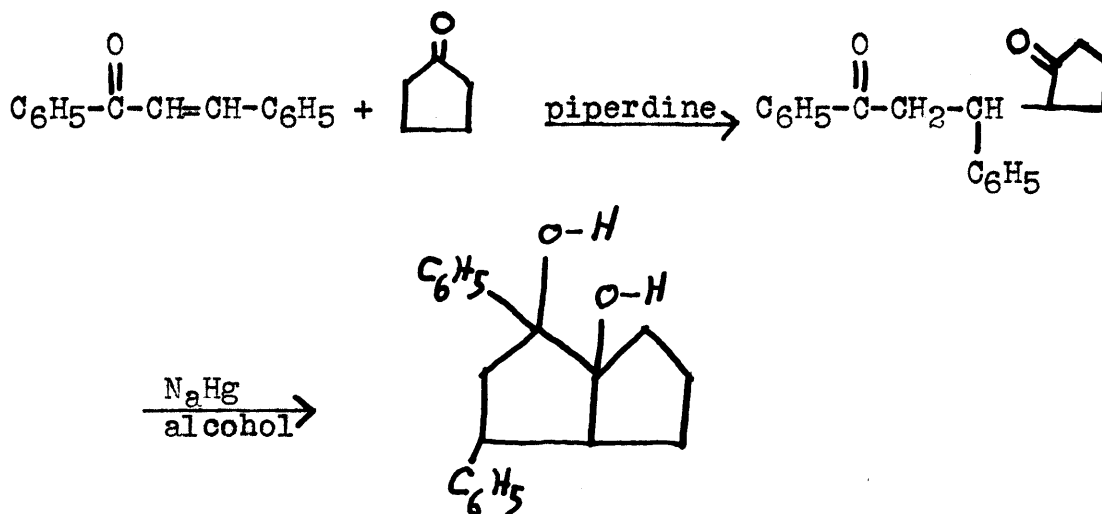
In 1922 Schroeter[44] suggested that the condensation of chloral with dimethyl malonate, under conditions not reported in the experimental section, led to the formation of a highly complex bicyclo[3.3.0]octane derivative. By a series of decarboxylations and reductions the product was reduced to a hydrocarbon. The properties reported by

Shroeter for this hydrocarbon are in close agreement with the accepted properties of cis-bicyclo[3.3.0]octane.

$$CCl_3-\overset{H}{\underset{O}{C}} \quad + \quad CH_3-O-\overset{O}{C}-CH_2-\overset{O}{C}-O-CH_3 \quad \xrightarrow[?]{?}$$
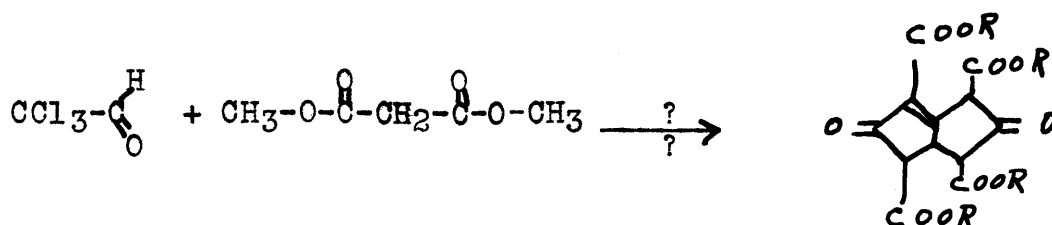
It must be admitted that the above condensation is a rather unusual reaction. Schroeter further mentions that the product had been converted by Vossen[45] to bicyclo[3.3.0]-octan-3,7-dione. As this latter compound would be of great interest as a precursor in an attempted synthesis of pentalene the condensation should probably be further investigated.

Another reported synthesis of bicyclo[3.3.0]octane derivatives involves the rearrangement of decalin in the presence of aluminum halides. This rearrangement has been studied by Zelinsky and Turowa-Pollack,[46] and by Jones and Linstead.[47] These workers feel the rearrangement leads to the formation of either 2,6-dimethylbicyclo[3.3.0]octane or 2,8-dimethyl-bicyclo[3.3.0]octane.
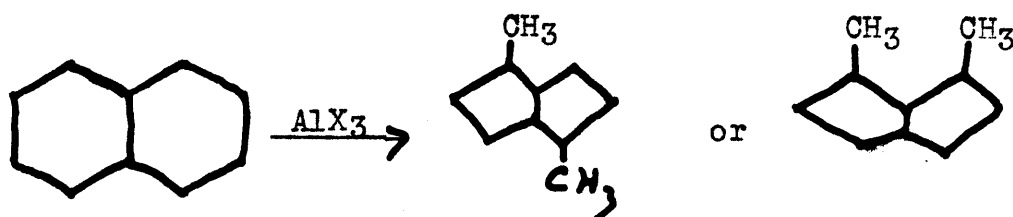
The structure proof of the products was interesting but not adequate. In line with this work it should be

mentioned that Barrett and Linstead[1f] found that cis-bicyclo-
[3.3.0]octane is rearranged in the presence of aluminum hal-
ides to bicyclo[3.2.1]octane.
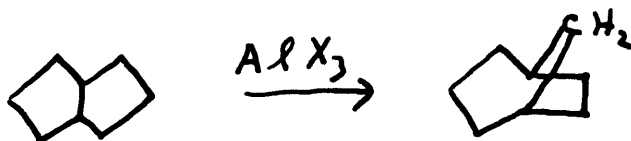
It is difficult to believe that the steric effect
of two methyl groups would prevent either of the two pro-
posed rearrangement products of decalin, 2,6- or 2,8-di-
methylbicyclo[3.3.0]octane, from undergoing the more com-
plex rearrangement exhibited by cis-bicyclo[3.3.0]octane
under identical conditions.

In 1934 Ruzicka, de Almeida, and Brack[12] reported
the synthesis of diethyl bicyclo[3.3.0]octan-2,6-dion-3,7-
dicarboxylate. The synthesis involved a double Dieckmann
condensation. Degradation of the diester led to the forma-
tion of bicyclo[3.3.0]octan-2,6-dione.
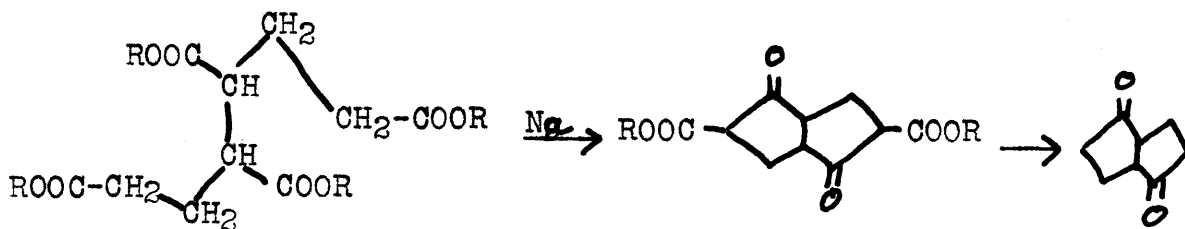
The Swiss workers reported that they believed
bicyclo[3.3.0]octan-2,6-dione would be a good starting
material for an attempted synthesis of pentalene but

apparently have not investigated the possibility further.

In 1934-36 Linstead, Cook, Meade, and Barrett[1] reported in a series of papers the synthesis of cis- and trans-bicyclo[3.3.0]octane, cis- and trans-β-bicyclo[3.3.0]-octanone, and cis-α-bicyclo[3.3.0]octanone. Some of this work has been reported in Part I of this Thesis. The English workers also investigated many of the fundamental properties of the ring system. Their work is by far the most thorough and reliable study of this particular ring system yet reported. Most of the work being carried out in the field today relies on ultimate comparison of the compounds prepared with those of the English workers. The approach of the English workers involved barium oxide ring closures of cis- and trans-cyclopentane-1,2-diacetic acids and cis- and trans-cyclopentane-1-carboxy-2-propionic acids.

Bardhan and Banerjee;[48] Mitter and Banerji;[49] and Banjeree[50] have reported the synthesis of several bicyclo-[3.3.0]octane derivatives with alkyl, carbethoxy, and keto groups on various positions in the ring. All of these syntheses start with substituted cyclopentane compounds and form the bicyclo[3.3.0] octane ring by a Dieckmann condensation.

In 1943 Wawzonek[51] reported the synthesis of 2,6-diphenyl bicyclo[3.3.0]-2,6-octadiene and 2,6-diphenylbicyclo-[3.3.0]-1,5-octadiene. His starting material was

bicyclo[3.3.0]octan-2,6-dione, prepared by the method of
Ruzicka, de Almeida, and Brack.[12]

$$2 \ C_6H_5MgX \longrightarrow$$

Dehydration

$$CH_3 \langle \rangle SO_3H \longrightarrow$$
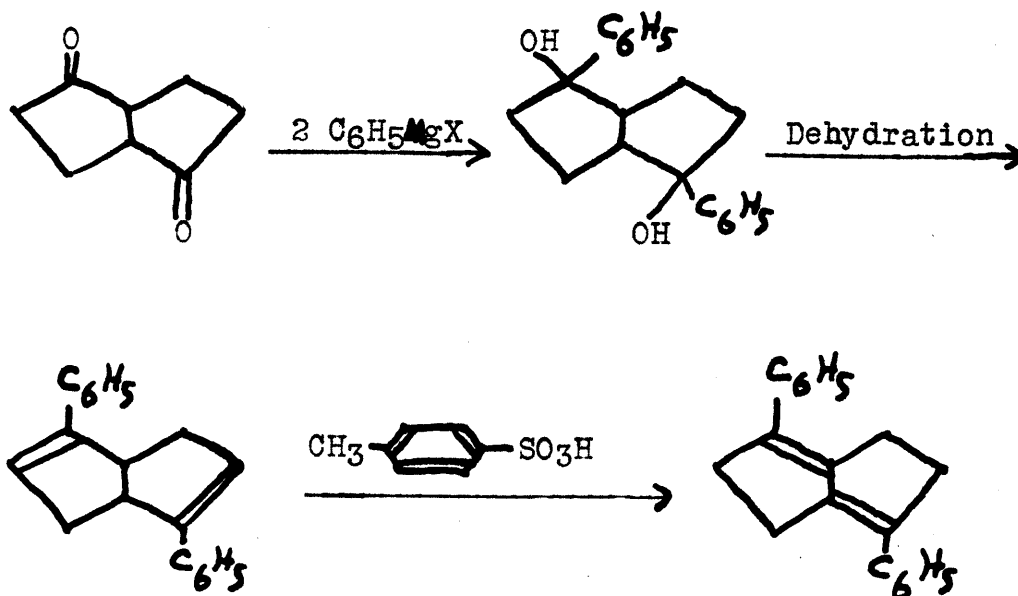
As neither of the diphenylbicyclo[3.3.0]octadienes
would form well-defined addition products with bromine,
Wawzonek concluded that 2,6-diphenyl-pentalene does not
exist as a stable aromatic compound.

Another method of entry into the bicyclo[3.3.0]-
octane ring system involves dicyclopentadiene as starting
material. The approach was originally studied by Bruson
and Reiner[66] but it remained for Bennett[67] to develop an
acceptable synthesis of cis-bicyclo[3.3.0]octane-2,4-di-
carboxylic acid by this route.
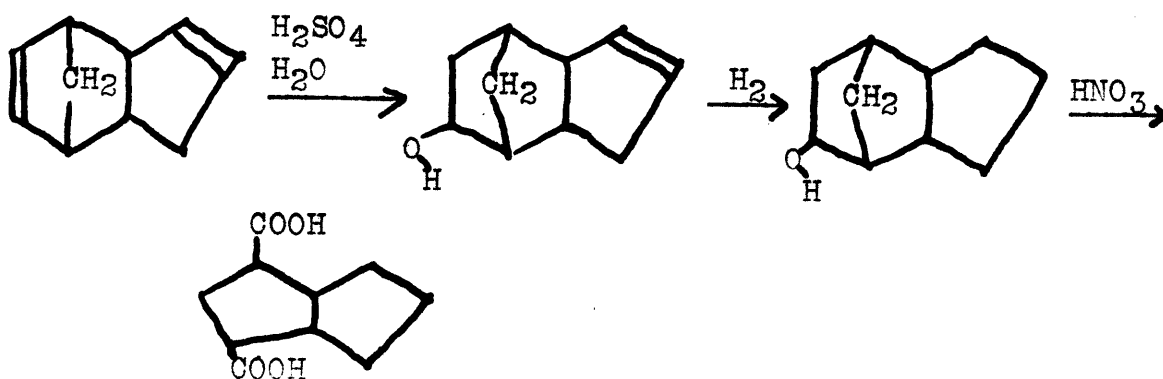
Recently Cope and Schmitz[69] have reported that sulfuric acid hydrolysis of the eight-membered cyclic dimer of chloroprene led to the formation of bicyclo[3.3.0]-1(5)-octen-2-one. This interesting reaction is believed to involve initial hydrolysis of the dimer to cyclooctan-1,4-dione, which, under the reaction conditions is converted to the bicyclic ketone.
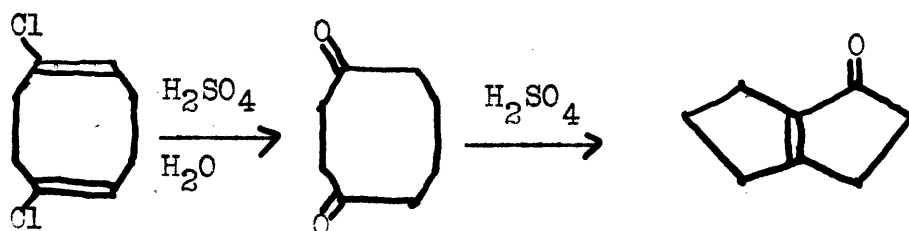
The above survey of bicyclo[3.3.0]octane syntheses is not intended to be a complete survey of all known compounds of this ring system but it is intended to describe most of the synthetic routes into this series which have been used by other investigators. A compilation of many of the known compounds of this ring system is found in Elsevier.[68]

DISCUSSION

In 1940 Brooks and Wilbert[52] reported the synthesis of bicyclo[3.2.0]-2-hepten-6-one, XII, from the reaction of cyclopentadiene and ketene. The ketone XII was of interest in this work as it provided the starting material for a new method of entry into the bicyclo[3.3.0]octane ring system.

The reaction of ketoketenes and conjugated dienes to give substituted cyclobutanones had been investigated earlier by Staudinger and Suter,[53] and Staudinger and Rheimer,[54] but the work of Brooks and Wilbert represents the first reported example of the reaction of ketene and a conjugated diene to give a substituted cyclobutanone.

Brooks and Wilbert reported a partial structure proof of XII which involved catalytic reduction of the double bond to give the dihydro derivative, XIII, and permanganate oxidation of XIII to glutaric acid. The most probable alternative structure for the initial reaction product is dehydronorcamphor, XII-B. It is easily seen after the reduction of the double bond of both XII and XII-B that glutaric acid could only arise from the dihydro form of XII on oxidation.
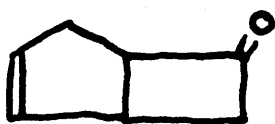
XII   XII-A   XII-B   XIII

The reaction of ketene with conjugated dienes has recently been reinvestigated by Blomquist and Kwiatek.[55] In further work with XIII they found that on careful oxidation of this compound with dilute nitric acid cis-cyclopentane-1,2-dicarboxylic acid could be isolated. This provides absolute proof of 1,2-addition of ketene to cyclopentadiene rather than possible 1,4-addition.

It is seen that XII consists of a five-membered ring, containing an isolated double bond, fused in the 1,2-position to a four-membered ring containing a carbonyl group. The four-membered ring has been expanded to a five-membered ring by the Tiffeneau-Demanjow[60] reaction thereby giving rise to a bicyclo[3.3.0]octane derivative with a double bond in one ring and a carbonyl group in the other.

In this work the preparation of XII has been carried out on a much larger scale than that previously reported. Brooks and Wilbert isolated the desired reaction product, XII, by direct distillation of the reaction mixture. It was found that XII prepared in this manner is contaminated with considerable amounts of dicyclopentadiene. In order to obtain a pure product it was found convenient to convert the ketone to the semicarbazone, and regenerate the ketone by steam distillation of an aqueous solution of the semicarbazone and oxalic acid.

Further work on the structure of XII has been car-
ried out. Dehydronorcamphor, XII-B, the most probable al-
ternative reaction product of ketene and cyclopentadiene,
had been previously prepared in the M.I.T. Laboratories[56]
and direct comparison of the physical properties of suit-
able derivatives of the two ketones indicated beyond doubt
that the two are different compounds. The infrared spec-
trum of XII has been obtained and is given in Figure V.
The carbonyl band occurs at 5.6μ which is quite specific
for a carbonyl group in a four-membered ring.[57] Two fur-
ther points concerning the structure of XII are the ster-
eochemistry of the two fused rings and the position of
the double bond. There seems to be little doubt that the
ring fusion is cis since considerable strain would be in-
volved if the juncture were trans. Even if the initial
addition of ketene to cyclopentadiene were trans, the
presence of the carbonyl group next to the bridge and a
labile tertiary hydrogen on the bridge would in all prob-
ability result in isomerization to the more stable cis
form.

The position of the double bond in XII is depend-
ent on whether the carbonyl group of ketene becomes at-
tached to carbon atom 1 or 2 of 1,3-cyclopentadiene during
the addition reaction. If the carbonyl group becomes at-
tached to carbon atom 1, XII is the product, if the point

of attachment is carbon atom 2, XII-A is the product. The question has been settled for the dimethylketene-cyclopentadiene adduct,[59] and for the diphenylketene-cyclopentadiene adduct.[58] In both cases the carbonyl group adds to carbon atom 1. Some evidence has been obtained which indicates that in XII the addition is in the same direction and the carbonyl group of ketene becomes attached to carbon atom 1 of 1,3-cyclopentadiene. Inspection of XII shows that it is an γ-δ unsaturated ketone, while XII-A is a β-γ unsaturated ketone. A control experiment has been run with a 2,4-dinitrophenylhydrazone of a β-γ unsaturated aldehyde under the conditions of which the derivative was converted to the more stable α-β form.[81] Under the same conditions the 2,4-dinitrophenylhydrazone of XII was unaffected.
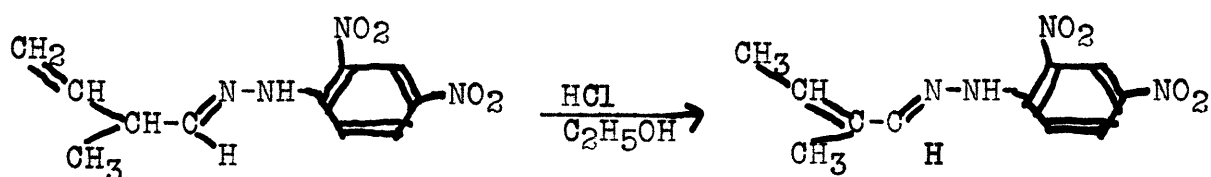
On the basis of the direction of addition found with both diphenylketene and dimethylketene with cyclopentadiene, and the evidence cited above, the double bond is assigned to the γ-δ position. Blomquist and Kwiatek[55] have reported that they are investigating this point further.

On the basis of the evidence presented above, it is felt that the structure of the reaction product of ketene and cyclopentadiene is best represented as XII, below.
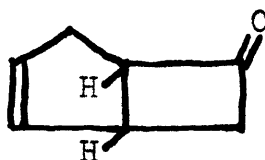
XII

The first step in the ring expansion of XII involves the formation of the cyanohydrin, XIII. It was found that the cyanohydrin could be best formed by reaction of XII with anhydrous hydrogen cyanide at 0° in the presence of a catalytic amount of piperdine. The cyanohydrin was never isolated as such but was acetylated with a mixture of acetic anhydride and acetyl chloride to give the cyanohydrin acetate, XIV. The cyanohydrin acetate XIV is believed to be a mixture of two stereoisomers (i.e. the cyano group may be either cis or trans with respect to the hydrogens at the ring juncture). Reduction of XIV to the amino alcohol, XV, was carried out using lithium aluminum hydride as reducing agent. As with XIV the amino alcohol XV is believed to be a mixture of the two possible stereoisomers.

XII   + HCN $\xrightarrow{\text{piperdine}}$ XIII $\xrightarrow[\text{AcCl}]{\text{Ac}_2\text{O}}$

O-Ac   O-H

[structure XIV with CN]   LiAlH₄→   [structure XV with CH₂-NH₂]

XIV   XV
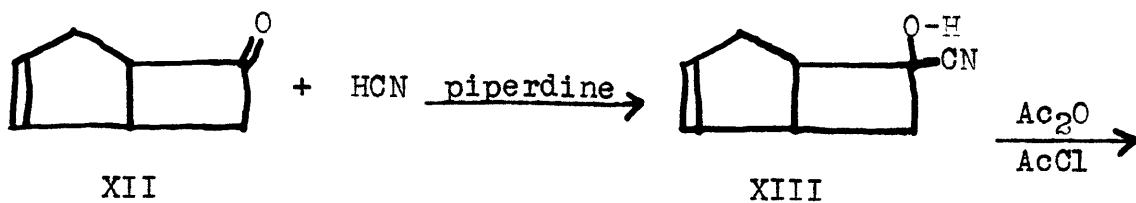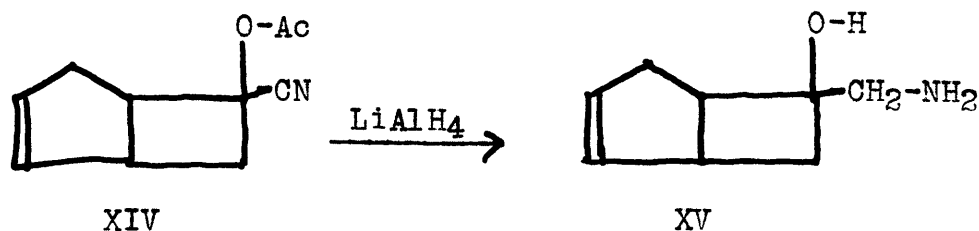
Deamination of XV with nitrous acid resulted in
ring expansion and formation of bicyclo[3.3.0]-2-octen-7-
one, XVII, and bicyclo[3.3.0]-2-octen-6-one, XVI. The ring
expansion is pictured as involving, (1) diazotization of
the amino group, (2) loss of nitrogen to form a carbonium
ion, and (3) rearrangement and loss of a proton to form one
of the two ring-expanded ketones. The rearrangement step
is depicted below.

(a)

– H⁺

XVI

(b)

O-H ⊕
CH₂
(a)

(b)
-H⁺

XVII
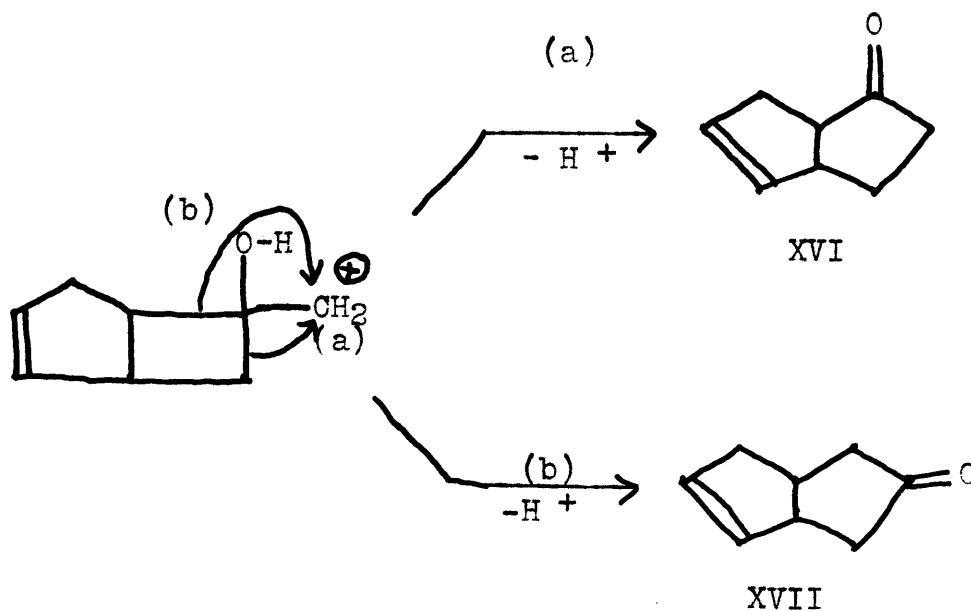
Rearrangement proceeding by path (a) involves migra-
tion of a primary alkyl group with its bonding pair of

electrons, while, rearrangement by path (b) involves migration of a secondary alkyl group with its bonding pair of electrons. It was of considerable interest to determine which alkyl group migrated. Reduction of the double bond of XVI and XVII lead to the formation of a mixture of α- and β-bicyclo[3.3.0]octanone. The infrared curve of this latter mixture indicated a composition of 85% of the α-isomer and 15% of the β-isomer and was identical to the infrared curve, within experimental error, of an authentic mixture of this composition. Thus in the case studied, the primary alkyl group displayed the greater migratory aptitude (rearrangement by path (a)).

Tchoubar,[70] however, has shown that the nitrous acid deamination of 1-hydroxy-1-aminomethyl-2-methylcyclopentane gives chiefly 3-methylcyclohexanone.
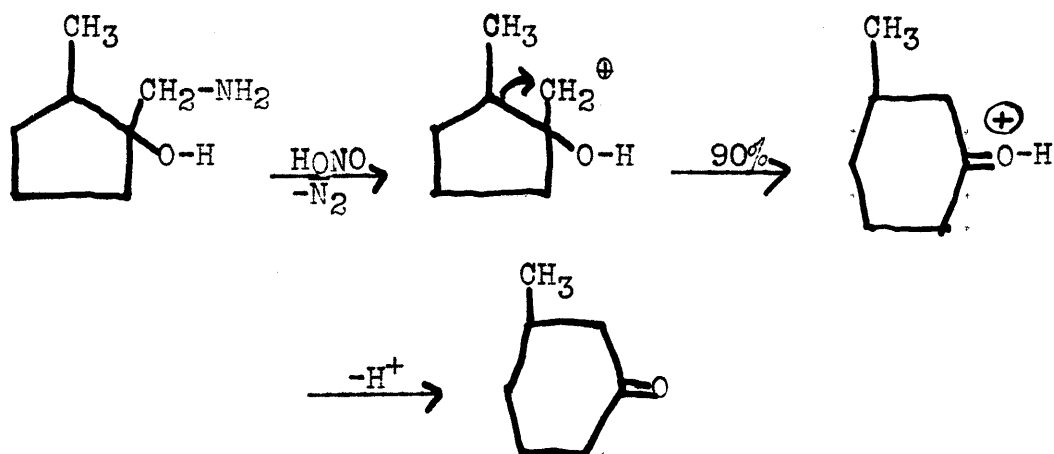
In this latter case, then, the secondary alkyl group with its bonding pair of electrons migrated

preferentially to the primary group. Consequently it is
impossible to generalize and say that either a primary or
a secondary alkyl group will migrate predominantly in re-
arrangements of this type. It is possible, however, that
accurate predictions on the predominant course of rear-
rangements of this type could be made if the stereochem-
istry of the amino alcohol intermediates were known.

The structure proof of XVI and XVII was completed
by Wolff-Kishner reduction of the mixture of α- and β-bi-
cyclo[3.3.0]octanone indicated above. The product isolated
from the reaction was pure cis-bicyclo[3.3.0]octane, I.
The isolation of pure cis-bicyclo[3.3.0]octane from this
reaction indicates that the stereochemistry of the two
fused rings (cis-juncture) is retained during the ring
expansion.

Figure IV

SCHEMATIC REPRESENTATION OF THE RING EXPANSION OF BICYCLO-
[3.2.0]-2-HEPTEN-6-ONE AND SUBSEQUENT WORK IN THE BICYCLO-
[3.3.0]OCTANE SERIES
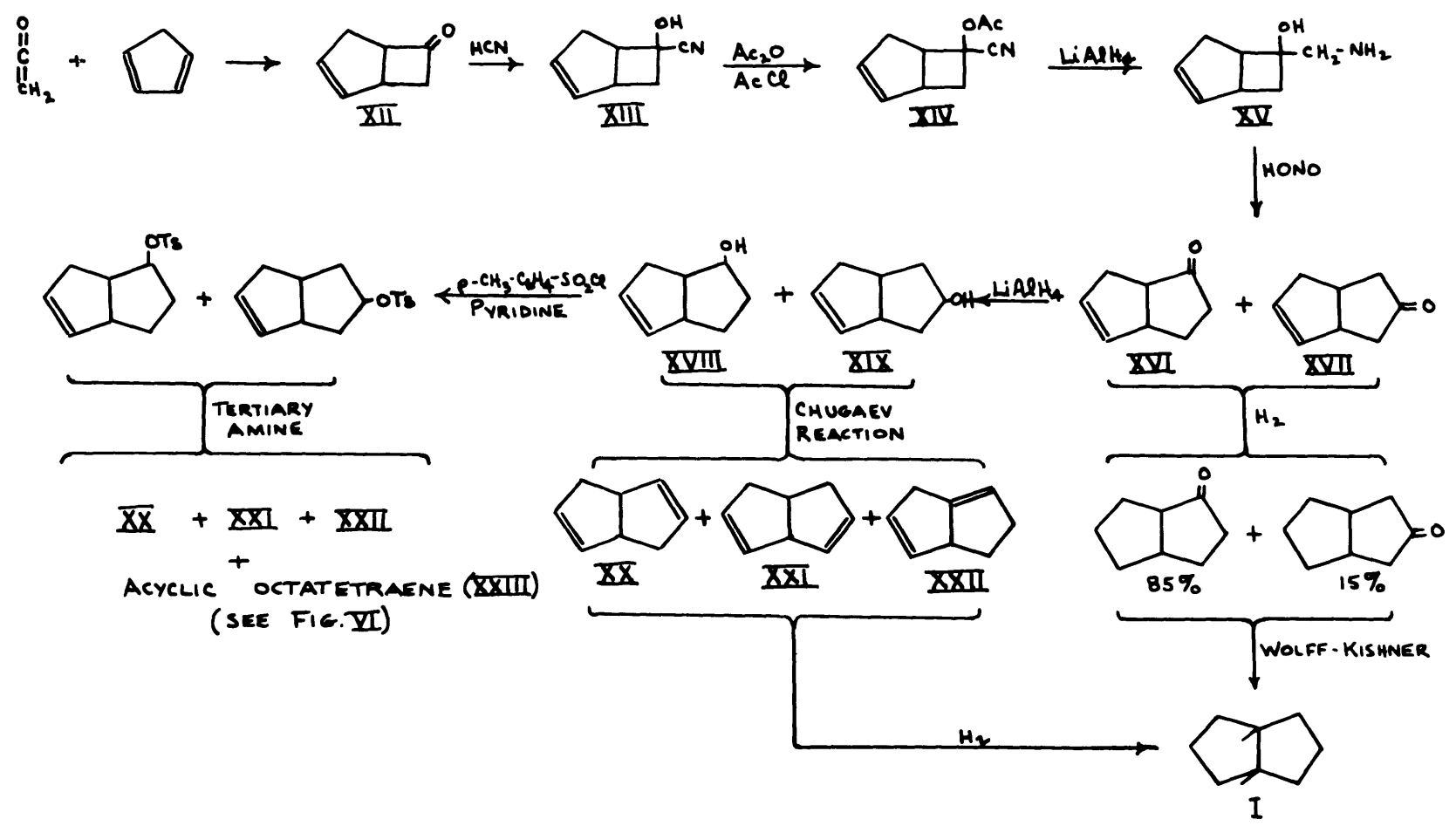
FIG. 4

EXPERIMENTAL

Ketene.---Ketene was prepared by pyrolysis of reagent acetone in a ketene generator similar to that described by Williams and Hurd.[71] The generator was calibrated by passing ketene through two sodium hydroxide solutions, of known normality, in series and back titrating the excess base with standard acid. In the preparation of XII the ketene was collected by passing the ketene through two Dry-Ice traps in series partially filled with sodium-dry toluene.

Cyclopentadiene.---Cyclopentadiene was prepared by cracking redistilled dicyclopentadiene, b.p. 84° (40 mm.). The dicyclopentadiene was placed in a round-bottomed flask, which was attached to a 60 x 1.5 cm. glass-helix packed column, and heated to the point where cyclopentadiene distilled freely. The cyclopentadiene was collected in an ice-cooled receiver. All material was used immediately after preparation and had b.p. 40-42°.

Bicyclo[3.2.0]-2-hepten-6-one Semicarbazone.---In a steel hydrogenation bomb, which had been previously cooled to -78°, was placed a mixture of 0.9 mole of ketene in 80 ml. of dry toluene and 160 g. (2.5 mole) of cyclopentadiene.

The bomb was immediately sealed and heated to 100° for one and one-half hours. A second run was made using the same quantities and the liquid products from the two runs combined. The liquid products were placed in a 1-l. round-bottomed flask and distilled through a 20 cm. Vigreux still head taking two fractions. The lower boiling fraction had b.p. < 60° (45 mm.) and consisted of acetone, toluene, and ketene dimer. The higher boiling fraction had b.p. 60° (45 mm.) to 60° (10 mm.) and consisted of small amounts of ketene dimer, XII, and dicyclopentadiene. About 280 ml. of higher boiling material was obtained. The higher boiling fraction was transferred to a 1-l. Erlenmeyer flask and 500 ml. of 95% ethanol, 80 g. (0.71 mole) of semicarbazide hydrochloride, and 120 g. of sodium acetate trihydrate added. The solution was heated to reflux on a steam bath for fifteen minutes and cooled. The solid products were collected by filtration on a Buechner funnel. The residue was heated for fifteen minutes with 400 ml. of boiling water (to remove inorganic salts). On cooling the solid product was collected on a Buechner funnel and air dried as thoroughly as possible. The residue was crystallized from 300 ml. of ethanol. The product was collected on a Buechner funnel and dried under vacuum in a desiccator. A total of 88.5 g. (0.535 mole) of semicarbazone was obtained, m.p. 221-222° (dec.) (lit.,[52] m.p. 221-222° (dec.)).

The yield was 11% based on cyclopentadiene.

Anal. Calcd. for $C_8H_{11}ON_3$: C, 58.20; H, 6.67; N, 25.45. Found: C, 58.00; H, 6.95; N, 25.56.

Bicyclo[3.2.0]-2-hepten-6-one (XII).---In a 500-ml. round-bottomed flask was placed 20 g. (0.12 mole) of bicyclo[3.2.0]-2-hepten-6-one semicarbazone, 15 g. (0.12 mole) of oxalic acid dihydrate, and 200 ml. of water. The solution was steam distilled until 200 ml. of distillate was obtained. The distillate was extracted with two 50-ml. portions of ether and then continuously with ether for six hours. The ether layers were combined, dried over magnesium sulfate, and the ether removed under reduced pressure. Distillation through a 10 cm. Vigreux still head yielded 11.5 g. (88%) of XII, b.p. 83-84° (51 mm.), n^{25}_D 1.4801, (lit.,[55] b.p. 62-63.5° (20mm.), n^{20}_D 1.4819).

The infrared curve is given in Figure V.

Anal. Calcd. for C_7H_8O: C, 77.80; H, 7.42. Found: C, 77.75; H, 7.55.

The 2,4-dinitrophenylhydrazone was prepared by the method of Fuson and Shriner.[10] After crystallization from ethanol the product had m.p. 114-115°.

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.15; H, 4.17; N, 19.45. Found: C, 54.35; H, 4.35; H, 19.30.

Hydrogen Cyanide.---Hydrogen cyanide was prepared
by the method of Organic Syntheses,[72] and was dried over
calcium chloride before use. In a typical run 74 g. (1.5
mole) of sodium cyanide was converted to 30 ml. (21 g., 50%)
of hydrogen cyanide.

6-Acetoxy-6-cyanobicyclo[3.2.0]-2-heptene (XIV).---
In a 500-ml. round-bottomed flask, immersed in an ice bath,
was placed 84.5 g. (0.78 mole) of XII and 32 ml. (0.83 mole)
of anhydrous hydrogen cyanide. The reactants were thoroughly
mixed and 0.25 ml. of piperdine added. The flask was tightly
stoppered and the reactants thoroughly mixed. There was con-
siderable heat of reaction. The flask was placed in an ice
bath for twenty-four hours. The piperdine was neutralized
by addition of 0.25 ml. of concentrated sulfuric acid and
0.1 g. of sulfonic acid ion exchange resin. The cyanohydrin
was acetylated by addition of 50 ml. of anhydrous ether,
150 ml. of acetic anhydride and 5 ml. of acetyl chloride.
The reactants were thoroughly mixed and kept at 0° for
twenty-four hours. The flask was then allowed to stand at
room temperature for seven days. The excess hydrogen cya-
nide and ether were removed by distillation at atmospheric
pressure, the acetic acid and acetic anhydride by distilla-
tion through a 20 cm. Vigreux column under reduced pressure.
Distillation of the residue yielded 95 g. (67% overall) of

XIV, b.p. 106-110° (3 mm.), n^{25}_D 1.4785.

The infrared curve is given in Fig. V.

<u>Anal</u>. Calcd. for $C_{10}H_{11}O_2N$: C, 67.80; H, 6.22; N, 7.91. Found: C, 67.80; H, 6.44; N, 7.77.

<u>6-Aminomethyl-6-hydroxybicyclo[3.2.0]-2-heptene (XV)</u>, <u>Bicyclo[3.3.0]-2-octen-6-one (XVI), and Bicyclo[3.3.0]-2- octen-7-one (XVII)</u>.---In a 2-l. three-necked flask equipped with stirrer, addition funnel, reflux condenser, and protected from atmospheric moisture was placed 16 g. (0.42 mole) of lithium aluminum hydride in 400 ml. of sodium-dry ether. To the stirred solution, 42.5 g. of XIV (0.24 mole) in 75 ml. of anhydrous ether was added dropwise over forty minutes. The reaction was then heated to reflux for forty-five minutes. The reaction flask was immersed in an ice bath, 25 ml. of water cautiously added to destroy the excess reagent, and 800 ml. of 20% sodium potassium tartrate solution added. The solution was vigorously stirred for fifteen minutes and transferred to a separatory funnel. The ether layer was removed and the aqueous layer extracted with 300 ml. of ether and continuously with ether for three days. The ether layers were combined and dried over calcium oxide. The ether was removed under reduced pressure until the crude product had been concentrated to 40 g. One tenth of the crude product was then removed for purification and the remainder directly

converted to XVI and XVII as follows: The larger portion
of crude amino alcohol, 36 g., was transferred to a 1-l.
round-bottomed flask equipped with stirrer, reflux con-
denser, and addition funnel. The flask was placed in an
ice bath and over ten minutes a solution of 15 g. (0.23
mole) of acetic acid in 225 ml. of water was added. The
solution was stirred until homogeneous. A solution of 16
g. (0.23 mole) of sodium nitrite in 50 ml. of water was
then added over five minutes, the mixture stirred at 0°
for forty minutes, heated on the steam bath for forty min-
utes, and allowed to stand at room temperature for twenty
hours. The solution was steam distilled until 450 ml. of
distillate was obtained. The distillate was extracted
with three 80-ml. portions of ether and continuously ex-
tracted with ether for twenty hours. The ether layers
were combined, dried over magnesium sulfate, and concentrated
under reduced pressure. Distillation yielded 14.5 g. (55%
overall, 74% per step) of XVI and XVII, b.p. 80-82.5° (17 mm.),
n^{25}_D 1.4902.

The 2,4-dinitrophenylhydrazone was prepared by the
method of Fuson and Shriner.[10] The product after crystalli-
zation from ethanol had m.p. 145°.

Anal. Calcd. for $C_{14}H_{14}O_4N_4$: C, 55.60; H, 4.65;
N, 18.65. Found: C, 55.92; H, 5.05; N, 18.33.

The semicarbazone was prepared by the method of

Fuson and Shriner[10]. The product after crystallization from
ethanol-water had m.p. 166-167°.

$\underline{\text{Anal}}$. Calcd. for $C_9H_{13}ON_3$: C, 60.30; H, 7.25; N,
23.50. Found: C, 60.30; H, 7.51; N, 23.20.

The mixture of XVI and XVII prepared in this manner
showed a weak hydroxyl band in the infrared curve. This is
believed to be due to the presence of bicyclo[3.2.0]-2-
hepten-6-ol, which would be formed during the reduction of
the cyanohydrin acetate, XIV, by preliminary reduction of
the acetoxy group and reversal of the cyanohydrin synthesis
prior to the reduction of the nitrile group. The ketone
was easily purified by conversion to the semicarbazone, and
regeneration of the ketone by steam distillation of a solu-
tion of semicarbazone in the presence of oxalic acid. De-
tails for a procedure of this type have been given in the
preparation of XII. In this way 80% of the ketone could be
recovered pure. The pure ketone had b.p. 81-83° (17 mm.)
n^{25}_D 1.4880. The infrared curve is given in Fig. V.

$\underline{\text{Anal}}$. Calcd. for $C_8H_{10}O$: C, 78.70; H, 8.20. Found:
C, 78.39; H, 8.30.

It is believed that the percentage of reversal of
the cyanohydrin synthesis is dependent on the activity of
the lithium aluminum hydride used. In preparations where
a freshly opened can of lithium aluminum hydride was used
the mixture of ketones, XVI and XVII, was obtained

essentially pure on the first distillation and infrared showed no hydroxyl band.

Distillation through a micro column[9] of the portion of amino alcohol set aside for purification yielded 2.26 g. (68%) of XV, b.p. 80-83° (0.9 mm.). Nitrogen analysis indicated the product contained approximately 90% amino alcohol. The other component, as mentioned above, is believed to be bicyclo[3.2.0]-2-hepten-6-ol. The amino alcohol was purified by dissolving the mixture in 70 ml. of 5% sulfuric acid and continuously extracting the solution with ether for twenty-four hours. The aqueous layer was then made basic by addition of 5 g. of sodium hydroxide and the basic solution continuously extracted with ether for twenty-four hours. The ether layer was dried over calcium oxide and the product concentrated under reduced pressure. Distillation through a micro column[9] yielded 0.9 g. of XV, b.p. 83-84° (1.5 mm.).

Anal. Calcd. for $C_8H_{13}ON$: C, 69.10; H, 9.34; N, 10.07. Found: C, 69.41; H, 9.50; N, 9.62.

The picrate of V could not be prepared in the usual manner. It was finally prepared by heating equivalent amounts of the amino alcohol and picric acid in benzene and allowing the benzene to evaporate. The picrate was recrystallized by dissolving in benzene-ethanol and then adding hexane. The picrate crystallized in this manner had

m.p. 137-138°.

Anal. Calcd. for $C_{14}H_{16}O_8N_4$: C, 45.65; H, 4.35; N, 15.20. Found: C, 45.76; H, 4.30; N, 15.17.

Hydrogenation of XVI and XVII to α-Bicyclo[3.3.0]-octanone and cis-β-Bicyclo[3.3.0]octanone, and Hydrogenation and Wolff-Kishner Reduction of XVI and XVII to cis-Bicyclo-[3.3.0]octane.---A solution of 3 g. of XVI and XVII in 25 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of 0.6 g. of prereduced Adam's platinum oxide. Reduction to the point that the solution no longer decolorized permanganate required 1.3 molar equivalents of hydrogen. Previous work had indicated that reduction of the double bond competed with reduction of the carbonyl group. The catalyst was removed by filtration and the solution concentrated by distillation to 8 ml. The ketone was converted to the semicarbazone by the method of Fuson and Shriner[10] and purified by crystallization. The ketone was regenerated by steam distillation of a solution of the semicarbazone and oxalic acid. A typical procedure for this reaction has been given in Part I for the preparation of bicyclo[3.2.0]-2-hepten-6-one. Distillation yielded 1 g. of the reduced mixture of ketones, b.p. 84-86° (18 mm.), n^{25}_D 1.4758. The infrared curve is given in Fig. V together with the infrared curve of an authentic mixture

of 85% α-bicyclo[3.3.0]octanone and 15% β-bicyclo[3.3.0]-octanone. Catalytic hydrogenation of 1.5 g. of XVI and XVII followed by Wolff-Kishner reduction (for a typical procedure see preparation of cis-bicyclo[3.3.0]octane, Part I) of the crude mixture of ketones yielded 0.5 g. of cis-bicyclo[3.3.0]octane. After purification by the silica-gel method[6] the refractive index was constant at n^{25}_{D} 1.4590. The infrared curve was identical, within experimental error, to that of authentic cis-bicyclo-[3.3.0]octane.

Anal Calcd. for C_8H_{14}: C, 87.27; H, 12.73. Found C, 87.28; H, 12.61.

Figure V

Infrared Spectra: Baird spectrograph with NaCl
prism, solutions of 50 mg. of compounds in 0.50 ml. of
carbon disulfide except in the regions 4.2-5.0$\mu$and 6.2-7.4μ
where carbon tetrachloride was used as solvent.

Curve 1. Bicyclo[3.2.0]-2-hepten-6-one (XII).

Curve 2. 6-Acetoxy-6-cyanobicyclo[3.2.0]-2-heptene (XIV).

Curve 3. Synthetic Mixture of Bicyclo[3.3.0]-2-octen-6-
one (XVI) and Bicyclo[3.3.0]-2-octen-7-one (XVII).

Curve 4. Authentic Mixture of 85% α-Bicyclo[3.3.0]-
octanone and 15% cis-β-Bicyclo[3.3.0]octanone.

Curve 5. Catalytic Reduction Product of XVI and XVII.
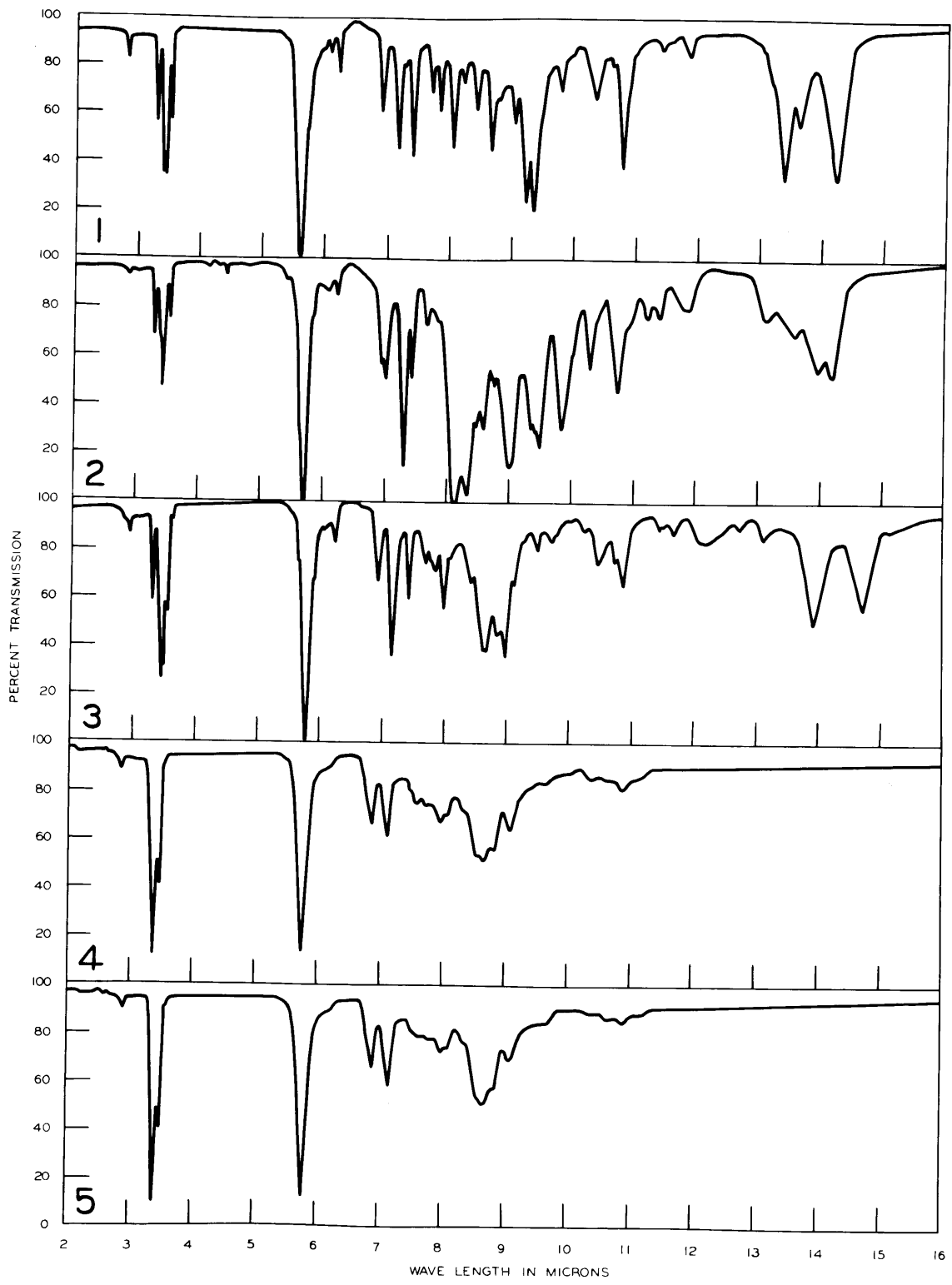
PART III

THE PREPARATION AND REACTIONS OF A
MIXTURE OF BICYCLO[3.3.0]OCTADIENES

HISTORICAL

The introduction of double bonds into the unsubstituted bicyclo[3.3.0]octane ring system has not been widely studied. Cope and Schmitz[69] have reported the preparation of a mixture of bicyclo[3.3.0]octenes by Wolff-Kishner reduction of bicyclo[3.3.0]-1(5)-octen-2-one. Cope and Keller[73] have recently converted this latter ketone to bicyclo[3.3.0]-1(5),2-octadiene by the following reactions.
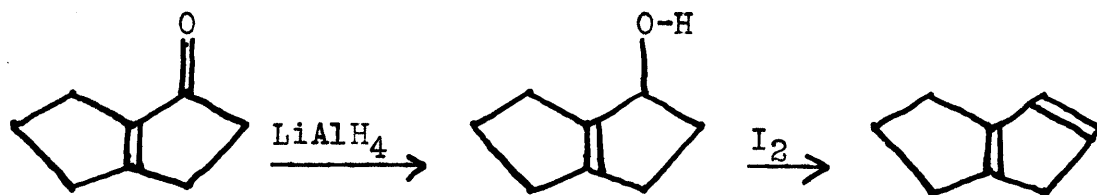
The bicyclo[3.3.0]octadiene prepared in this manner proved to be relatively unstable and extremely acid sensitive. Cope and Keller also attempted the preparation of a bicyclo[3.3.0]octatriene but were unable to isolate any product.
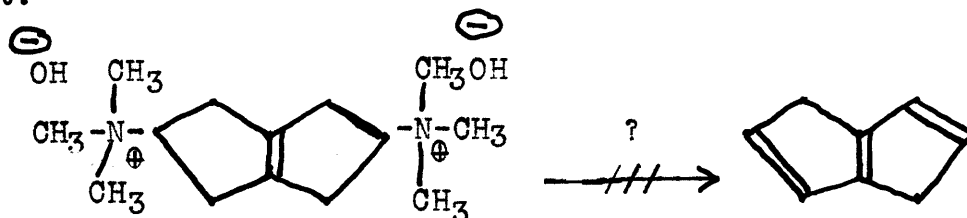
The above syntheses represent practically all reported attempts at the introduction of double bonds into the

unsubstituted bicyclo[3.3.0]octane ring system. In Part II
of this thesis the preparation of olefins with either ben-
zene rings fused to the ring system or phenyl groups at-
tached to the ring system was discussed.

It is of interest to consider the number of isomers
possible for the various olefins in this series. There ap-
pear to be four bicyclo[3.3.0]octenes, A, B, C, and D, the-
oretically capable of existence.

A   B   C   D
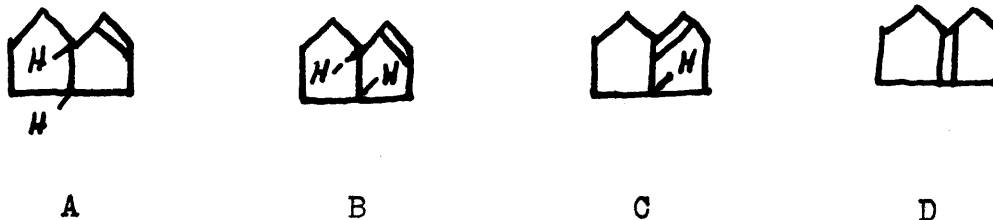
Olefin A belongs to the cis-bicyclo[3.3.0]octane
family, olefin B to the trans-bicyclo[3.3.0]octane family,
while in olefins C and D, the double bond, attached to
either one or both of the bridge carbon atoms, has de-
stroyed the stereochemical specificity of the two fused
rings.

With the introduction of the second double bond
the number of isomers increases to ten, bicyclo[3.3.0]-
octadienes E to N.

E   F   G   H   I

J   K   L   M   N
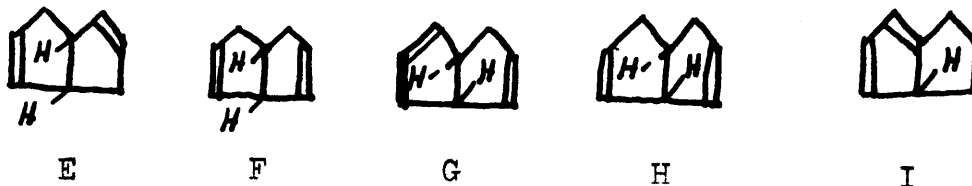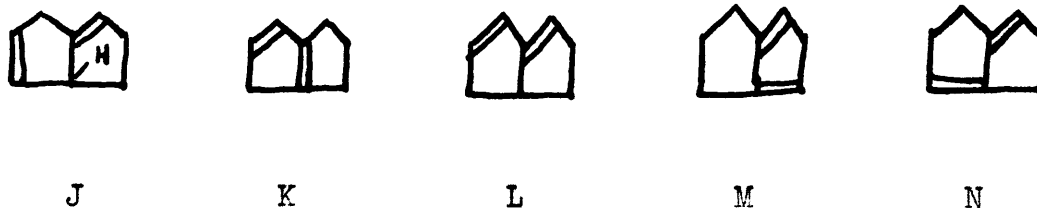
Olefins E and F belong to the cis-bicyclo[3.3.0]-octane family, and, on theoretical grounds, would be predicted to be capable of stable existence as the double bonds are not in conjugation. Olefins G and H belong to the trans-bicyclo[3.3.0]octane family and it is quite probable that they would be converted to the more stable cis-family in the presence of strong bases. Olefins I through N belong to neither family due to the attachment of a double bond to at least one of the bridge carbon atoms. Olefins I, K, and M are substituted cyclopentadiene derivatives, while olefins L and N are butadiene derivatives. It is quite probable that all the olefins of this latter group, I, K, L, M, and N, would show a marked tendency to polymerize. Olefin J has isolated double bonds and for this reason would be predicted to be reasonably stable.

With the introduction of the third double bond the number of isomers decreases to six, none of which belong to either the cis- or trans-bicyclo[3.3.0]octane family.

O   P   Q

R   S   T

It is quite probable that all of the trienes would be considerably more unstable than the dienes or monoolefins in the series. It is of interest that all the above olefins are isomeric with cycloöctatetraene.

With the introduction of the fourth double bond the possibility of isomerism disappears and on paper it is possible to write only one structure, that of pentalene, XXV.

XXV

The arguments for and against the stability of this compound have been discussed in Part II.

DISCUSSION

The mixture of bicyclo[3.3.0]-2-octen-6-one, XVI, and bicyclo[3.3.0]-2-octen-7-one, XVII, synthesized by the ring expansion of bicyclo[3.2.0]-2-hepten-6-one, has been used as the starting material in the synthesis of a mixture of bicyclo[3.3.0]octadienes.

All preparative methods studied for this conversion involved initial reduction of XVI and XVII with lithium aluminum hydride to bicyclo[3.3.0]-2-octen-6-ol, XVIII, and bicyclo[3.3.0]-2-octen-7-ol, XIX. It is believed that both XVIII and XIX are mixtures of the two possible stereoisomers (i.e. the hydroxyl group may be either cis or trans with respect to the tertiary hydrogens on the bridge). Trevoy and Brown[74] have found that reductions of this type are not stereospecific. These workers found that reduction of camphor under very mild conditions, -80°, led to the formation of both borneol and isoborneol. Plattner, Heusser, and Feurer,[75] and Fieser, Fieser, and Chakravarti[76] have found that in the lithium aluminum hydride reduction of several keto steroids both epimers are formed.

XVI + XVII $\xrightarrow{\text{LiAlH}_4}$

XVIII   XIX
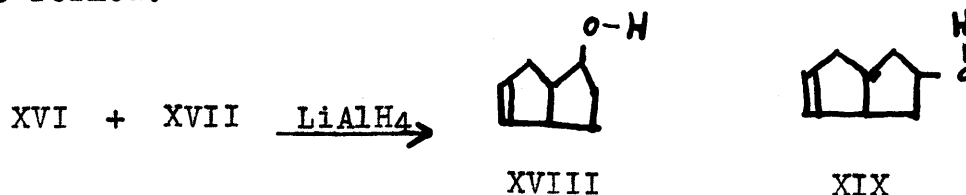
The products obtained on dehydration of XVIII and
XIX proved to be dependent on the reaction employed. The
best synthetic procedure for the preparation of a mixture
of bicyclo[3.3.0]octadienes proved to be the Chugaev re-
action.
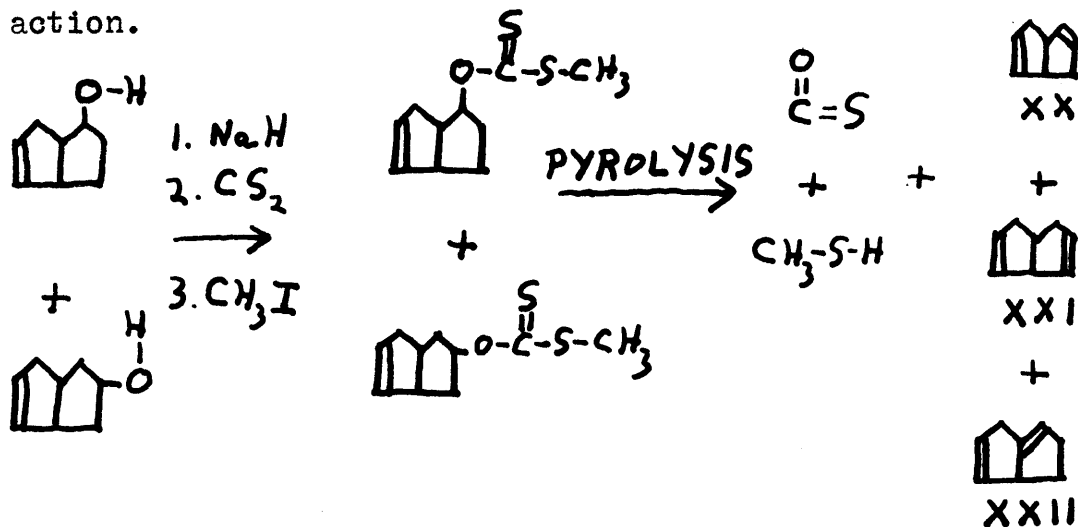
The product from the Chugaev reaction is believed
to be best represented as a mixture of three dienes, bi-
cyclo[3.3.0]-2,6-octadiene, XX, bicyclo[3.3.0]-2,7-octadiene,
XXI, and bicyclo[3.3.0]-1,6-octadiene, XXII. The mixture of
dienes took up two moles of hydrogen on catalytic hydrogena-
tion and the reduction product proved to be pure cis-bicyclo-
[3.3.0]octane. The ultraviolet spectrum showed no maximum
in the region 220-350 mμ. This would seem to indicate that
the double bonds were not conjugated. The mixture of dienes
was colorless, and stable enough to be stored for several
months at 0° without decomposition.

A second method of dehydration studied was the

reaction of the p-toluenesulfonates of XVIII and XIX with various organic tertiary amines. The reaction took an unexpected course and for quite some period of time gave misleading results. The product from this reaction had a distinct yellow color, not unlike that of cycloöctatetraene, and catalytic hydrogenation of several samples required varying amounts, but always more than two moles of hydrogen. The infrared curve indicated the presence of the expected mixture of dienes and some other product. The same colored mixture was obtained when either diethylaniline, 2,6-dimethylpyridine, or 2,4,6-trimethylpyridine was used as the tertiary amine but the percentage of the yellow component varied from preparation to preparation under apparently identical reaction conditions.

In one preparation using 2,4,6-trimethylpyridine as the tertiary amine, a sample was obtained which on catalytic hydrogenation required 3.35 moles of hydrogen. The infrared curve indicated a small percentage of the mixture of bicyclo-[3.3.0]octadienes, XX, XXI, and XXII. This fact, coupled with the hydrogenation data, requires that the other component be a tetraene. The analysis of this fraction agreed well with the formula C_8H_{10} and precluded the possibility that the additional unsaturation observed was due to dehydrogenation of the bicyclo[3.3.0]octane ring. The requirements of the unknown component proved to be a molecular

formula of C_8H_{10} and the presence of four double bonds. These requirements are satisfied only by an acyclic octatetraene. Excluding cis-trans isomerism and compounds with allene-type bonding, there appear to be four possible tetraenes, XXIII-A, XXIII-B, XXIII-C, and XXIII-D.

$$CH_2 = CH(- CH = CH)_2 - CH = CH_2$$

XXIII-A

$$CH_2 = C - CH = CH - CH = CH_2$$
$$\overset{\displaystyle \underset{H}{\diagup}\overset{C}{\diagdown}_{CH_2}}{}$$

XXIII-B

$$CH_2 = CH - C = CH - CH = CH_2$$
$$\overset{\displaystyle \underset{H}{\diagup}\overset{C}{\diagdown}_{CH_2}}{}$$

XXIII-C

$$CH_2 = CH - C - C - CH = CH_2$$
$$\underset{CH_2 \quad CH_2}{}$$
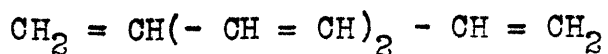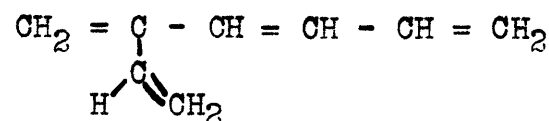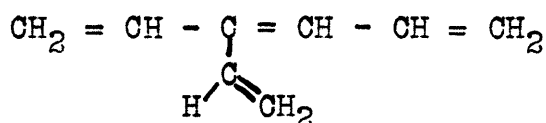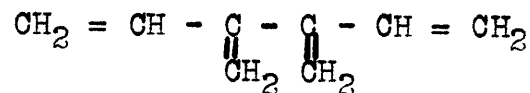
XXIII-D

Of these, XXIII-A may exist as three geometrical isomers and XXIII-B as two geometrical isomers. Tetraene XXIII-B may be excluded however as there is no reasonable way it can be formed by a double cleavage of the two fused five-membered rings of the bicyclo[3.3.0]octane ring system. Possible mechanistic interpretations of the formation of the other three tetraenes are given in Fig. VI.

The only acyclic tetraene reported in the chemical literature is XXIII-A, octatetraene, the preparation of which has been reported by Woods and Schwartzman.[77] Their

Figure VI

POSSIBLE MECHANISTIC INTERPRETATIONS OF THE FORM-
ATION OF THREE ACYCLIC TETRAENES FROM THE REACTION OF THE
p-TOLUENESULFONATE OF XVIII WITH TERTIARY AMINES.
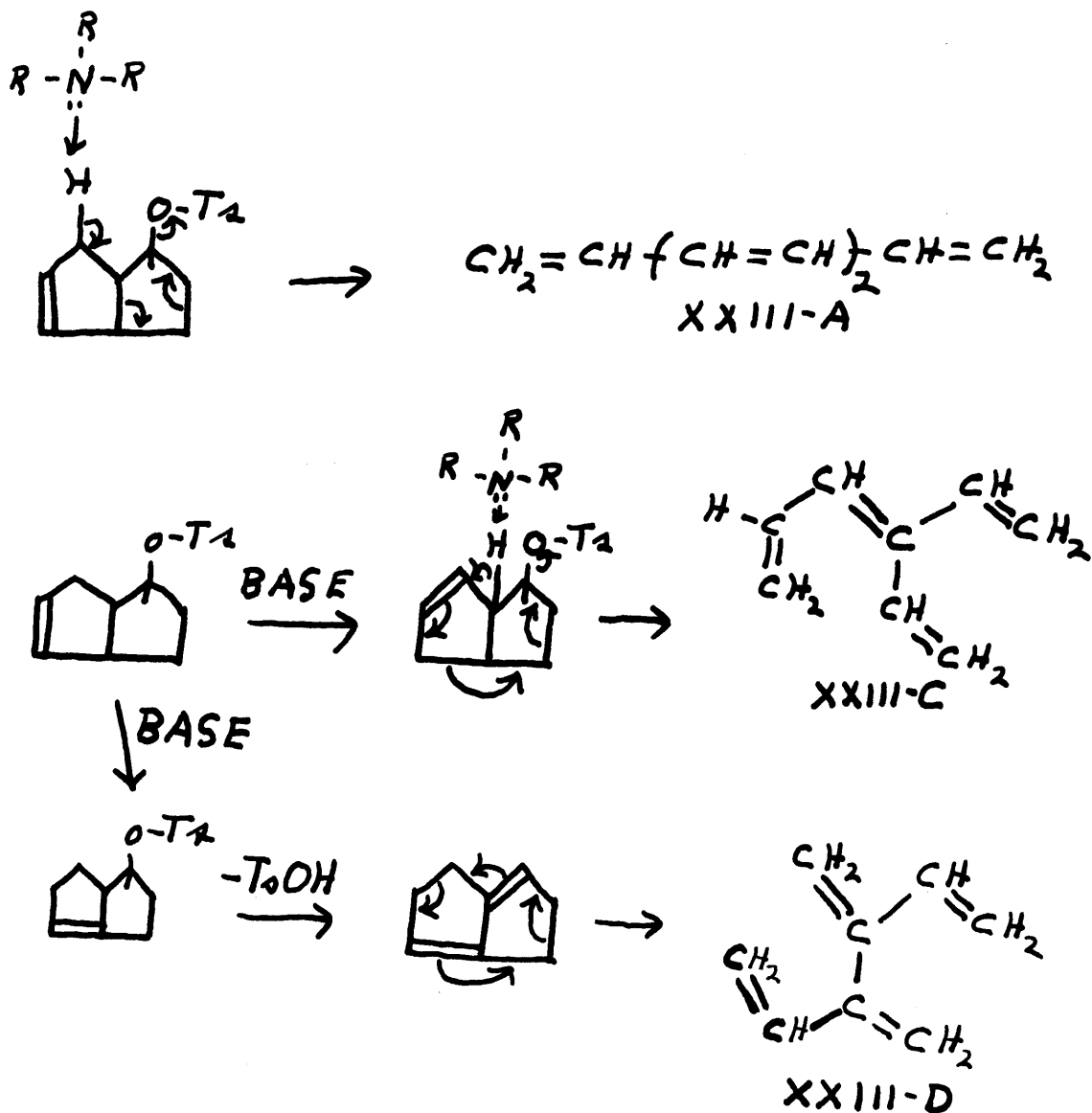
product was a white, highly explosive solid. Woods and Schwartzman give no indication as to which of the three geometrical isomers their product may be.

The ultraviolet spectrum of the mixture of tetraene and bicyclo[3.3.0]octadienes was then obtained. The spectrum of a solution of the freshly prepared mixture exhibited a maximum at 260 mμ, log ϵ_{Max} 3.66. On standing for six weeks at 0° the maximum shifted to 248 mμ, log ϵ_{Max} 3.87. The ultraviolet spectra are given in Fig. VII. In some cases the ultraviolet spectrum of the freshly prepared solution exhibited this latter maximum, 248 mμ, log ϵ_{Max} 3.87.

There appear to be at least two explanations as to why the spectrum should change on standing. The first is that a change in the geometrical configuration has occurred (i.e. change in the cis-trans configuration of a double bond). The second possibility is that an actual change in the nature of the bonding within the molecule has occurred.
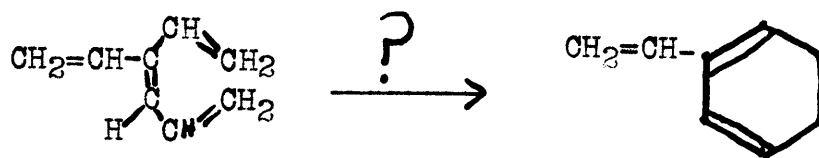
An example of this latter phenomenon has recently been reported by Cope and Hochstein.[6]
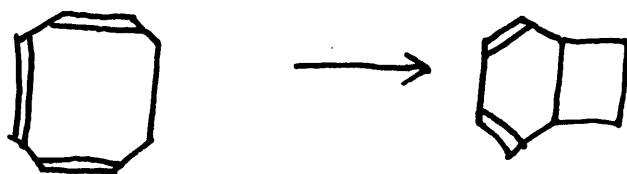
Separation of the tetraene from the mixture of bicyclo[3.3.0]octadienes proved difficult. Attempted fractionation in an efficient center-tube column was unsuccessful. Attempts at the formation of the picric acid or 1,3,5-trinitrobenzene addition complex of the tetraene were also unsuccessful. Chromatographic methods of separation were then investigated but no suitable adsorbent could be found.

The only successful method of separation involved formation of the maleic anhydride adduct of the tetraene. It was first found that addition of maleic anhydride to a benzene solution of the tetraene-diene mixture resulted in the slow disappearance of the characteristic yellow color of the tetraene and on gentle refluxing the solution became clear and colorless. After removal of the benzene and bicyclo[3.3.0]octadienes by distillation under reduced pressure it was possible to isolate by sublimation a colorless solid which analyzed correctly for the mono-maleic anhydride adduct of the tetraene. The adduct on catalytic hydrogenation took up three moles of hydrogen as required by theory.

The above procedure represented a separation of the tetraene but it proved inconvenient to separate the bicyclo-[3.3.0]octadienes from the solvent, benzene. It was found finally that separation could be achieved by adding maleic

anhydride directly to the mixture of tetraene and bicyclo-
[3.3.0]octadienes and allowing the mixture to stand at room
temperature for several days. In contrast to the clean
reaction in benzene the reaction without solvent led to
extensive decomposition. It was possible, however, to
distill the colorless mixture of bicyclo[3.3.0]octadienes
directly from the reaction mixture under reduced pressure.
The adduct of the tetraene was then separated and purified
by sublimation. Some evidence was obtained which indicated
that two isomeric mono-maleic anhydride adducts are obtained.
All efforts to obtain the di-maleic anhydride of the tetraene
have proven unsuccessful. It was further observed that the
tetraene slowly decomposed on standing, leaving the colorless
mixture of bicyclo[3.3.0]octadienes.

Attempts were made to catalytically dehydrogenate the
mixture of bicyclo[3.3.0]octadienes to pentalene. Standard
dehydrogenation procedures[79,80] were used involving passage
of the vaporized compound over platinized-asbestos and plat-
inized-charcoal catalysts. In no case did it appear that
dehydrogenation was taking place. The conditions used were
found sufficient to dehydrogenate cyclohexene to benzene.
These findings are in accord with the observation of Barrett
and Linstead[1f] that cis-bicyclo[3.3.0]octane is resistant to
catalytic dehydrogenation and the observations of numerous
investigators[40, 64, 65] that the 2,3-benzbicyclo[3.3.0]-2-
octene series is incapable of either chemical or catalytic

dehydrogenation to benzpentalene.

Scouting reactions were then run to investigate possible synthesis by chemical methods of either a bicyclo[3.3.0]octatriene or of pentalene from the mixture of bicyclo[3.3.0]octadienes. Most of the syntheses attempted involved reaction of the mixture of bicyclo[3.3.0]-octadienes with either one or two moles of N-bromosuccinimide. This initial reaction was apparently successful as in every case it was possible to isolate the theoretical quantity of succinimide. Both the monobromide and dibromide decomposed, however, on attempted distillation. Reaction of either the monobromide or dibromide with quinoline at 0° resulted in extensive decomposition and no products could be isolated. Reaction of the crude dibromide with magnesium, in an attempt to bring about intramolecular removal of bromine to form a triene, was unsuccessful.

The most promising approach appears to be reaction of the mixture of bicyclo[3.3.0]octadienes with mercuric acetate. Conditions were worked out in which a small yield of a monoacetoxy compound could be obtained. The acetoxy compound could be distilled and in general appeared to be considerably more stable than the corresponding bromo derivative.

$+ \text{Hg(OAc)}_2 \longrightarrow$ reaction scheme (see figure)

$+ \text{H}_2 + \text{HO}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

$O=\overset{}{C}-CH_3$
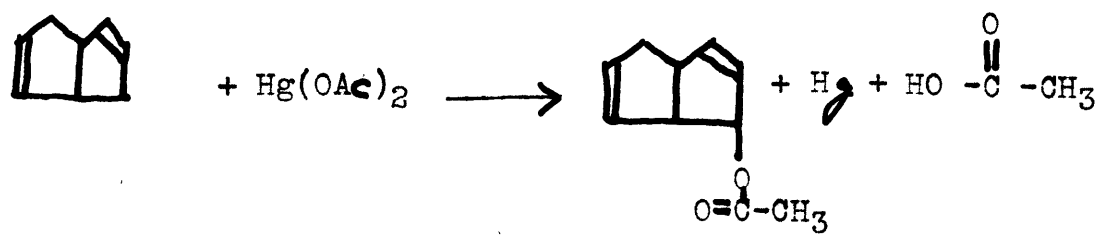
EXPERIMENTAL

Bicyclo[3.3.0]-2-octen-6-ol (XVIII) and Bicyclo-
[3.3.0]-2-octen-7-ol (XIX).---In a 500-ml. three-necked
flask equipped with stirrer, addition funnel, reflux con-
denser, and in an atmosphere of dry nitrogen was placed
3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml.
of dry ether. To the stirred solution was added dropwise
21.6 g. (0.177 mole) of XVI and XVII in 50 ml. of dry
ether over twenty-five minutes. The solution was heated
to reflux for forty minutes. The flask was immersed in
an ice bath and the excess reagent and reaction complexes
destroyed by the careful addition of 20 ml. of water fol-
lowed by 150 ml. of 12% sulfuric acid solution. The ether
layer was separated and the aqueous layer extracted with
two 50-ml. portions of ether and then continuously with
ether for two days. The ether layers were combined, dried
over magnesium sulfate, and concentrated under reduced
pressure. Distillation yielded 18.4 g. (84%) of XVII and
XIX, b.p. 91-94° (17 mm.), n^{25}_D 1.5025.

Anal. Calcd. for $C_8H_{12}O$: C, 77.42; H, 9.69. Found:
C, 76.93; H, 9.77.

Solid derivatives of XVIII and XIX proved difficult
to crystallize and had wide melting point ranges which might
be expected from the mixture present. The acetate of XVIII

and XIX was prepared as follows: To a solution of 1 g.
(0.008 mole) of XVIII and XIX in 4 ml. of pyridine was
added 1 g. of acetyl chloride with stirring over five
minutes. The reaction mixture was allowed to stand at
0° for five hours and at room temperature for one hour.
The reaction mixture was poured into 25 ml. of water
and the mixed acetates extracted with 25 ml. of ether.
The ether layer was washed with 25 ml. of 1N hydrochloric
acid, 25 ml. of 5% sodium bicarbonate, and 25 ml. of
water. The ether layer was dried over magnesium sulfate
and concentrated under reduced pressure. Distillation
yielded 0.95 g. of the mixed acetates, b.p. 91-94° (16 mm.),
n^{25}_D 1.4675.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.43.
Found: C, 72.04; H, 8.69.

The formate of XVIII and XIX was prepared by heat-
ing a solution of 4 g. (0.032 mole) of XVIII and XIX and
25 ml. of 98-100% formic acid on a steam bath for one hour.
After cooling the mixture was poured into 100 ml. of water
and the formate extracted with three 50-ml. portions of
ether. The ether layer was washed with 100 ml. of 10%
sodium bicarbonate solution, dried over magnesium sulfate,
and concentrated under reduced pressure. Distillation
yielded 3.4 g. (75%) of XVIII and XIX formate, b.p. 98-
100° (28 mm.), n^{25}_D 1.4838.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.07; H, 7.88. Found: C, 71.17; H, 8.07.

Chugaev Reaction of Bicyclo[3.3.0]-2-octen-6-ol (XVIII) and Bicyclo[3.3.0]-2-octen-7-ol (XIX).---In a 200-ml. three-necked flask equipped with stirrer, addition funnel, reflux condenser, and in an atmosphere of dry nitrogen was placed 1 g. (0.042 mole) of sodium hydride in 50 ml. of dry ether. To the stirred suspension 2.7 g. (0.022 mole) of XVIII and XIX in 30 ml. of dry ether was added over ten minutes. The suspension was heated under reflux and stirred for twenty hours. A solution of 5 ml. of carbon disulfide in 20 ml. of dry ether was then added over five minutes and the stirring and heating under reflux continued for six hours. Methyl iodide (5 ml.) dissolved in 20 ml. of ether was added over five minutes, and the stirring and heating under reflux continued for twenty hours. The reaction flask was immersed in an ice bath and the excess sodium hydride destroyed by the careful addition of 25 ml. of water. The reaction mixture was transferred to a separatory funnel and all inorganic salts extracted from the ether layer with 25 ml. of water. The aqueous washings were extracted with 25 ml. of ether, the ether layers combined, dried over magnesium sulfate, and concentrated under reduced pressure. The crude xanthate was transferred to a

50-ml. round-bottomed flask and pyrolyzed by heating the flask with a Wood's metal bath from 180-220° over forty minutes. Gas evolution was steady during this period and organic material distilled over regularly. The pyrolysate was taken up in 25 ml. of ether and sulfur-containing compounds removed by thorough extraction of the ether layer with 50 ml. of 20% sodium hydroxide solution. The ether layer was dried over calcium chloride and concentrated by distillation at atmospheric pressure. Distillation of the residue through a micro column[9] yielded 1.23 g. (53%) of the mixture of bicyclo[3.3.0]octadienes, XX, XXI, and XXII, b.p. 129-131°, n^{25}_D 1.4852. With purification of the olefin by the silica-gel method[6] the refractive index became constant at n^{25}_D 1.4865.

The infrared curve is given in Fig. VIII.

<u>Anal</u>. Calcd. for C_8H_{10}: C, 90.57; H, 9.43. Found: C, 90.28; H, 9.62.

In general, good analyses of the olefin were difficult to obtain due to the high volatility of the product.

Microhydrogenation of two samples of the olefin in glacial acetic acid, in the presence of pre-reduced Adam's platinum catalyst, required 102 and 103% of two molar equivalents of hydrogen. The reduction product was obtained by reduction of a 1.2 g. sample of the mixture of dienes in glacial acetic acid followed by neutralization

of the acetic acid with 10% sodium hydroxide solution and
extraction of the reduction product with ether. After
working up the ether layer in the usual manner distilla-
tion through a micro column[9] yielded 0.6 g. (50%) of cis-
bicyclo[3.3.0]octane, b.p. 135-137°, n^{25}_D 1.4584. After
five passages over silica gel the refractive index was
constant at n^{25}_D 1.4593. The infrared curve is given in
Fig. VIII and is identical within experimental error to
that of authentic cis-bicyclo[3.3.0]octane, I.

Reaction of the Mixture of Bicyclo[3.3.0]octadienes
with Mercuric Acetate.---In a 15 ml. centrifuge tube was
placed 0.6 g. (0.0056 mole) of the mixture of bicyclo[3.3.0]-
octadienes and 1.8 g. (0.0056 mole) of mercuric acetate. The
air was displaced by dry nitrogen and the tube fitted with a
cold-finger condenser. The tube was heated with an oil bath
from 150-160° for ten hours. Considerable decomposition oc-
curred. After cooling 3 ml. of ether was added and the
liquid products thoroughly extracted. The solid products
were centrifuged into the bottom of the tube and the liquid
layer removed. Distillation through a micro column[9] yield-
ed 0.06 g. (8%) of a product with b.p. 94° (17 mm.), n^{25}_D
1.4910. The product is believed to be chiefly bicyclo-
[3.3.0]-2,6-octadien-4-ol acetate or an isomer thereof.

Anal. Calcd. for $C_{10}H_{12}O$: C, 73.20; H, 7.32.
Found: C, 72.29; H, 7.36.

Reaction of the p-Toluenesulfonates of Bicyclo-
[3.3.0]-2-octen-6-ol (XVIII) and Bicyclo[3.3.0]-2-octen-7-ol
(XIX) with 2,4,6-Trimethylpyridine.---In a 100-ml. round-
bottomed flask was placed 2.5 g. (0.02 mole) of XVIII and
XIX, 3.84 g. (0.02 mole) of p-toluenesulfonyl chloride (m.p.
69°), and 3.5 ml. of dry pyridine. The reactants were thor-
oughly mixed, allowed to stand at 0° for three hours, and at
room temperature for twelve hours. The reaction mixture was
taken up in 60 ml. of ether and the ether layer washed with
three 25-ml. portions of 1N hydrochloric acid, two 25-ml.
portions of 5% sodium bicarbonate, and 25 ml. of water. The
ether layer was dried over potassium carbonate and concen-
trated under reduced pressure (final pressure 0.5 mm.). All
attempts at crystallization of the p-toluenesulfonates failed.
A mixture of the crude p-toluenesulfonates and 25 ml. of
2,4,6-trimethylpyridine (b.p. 172°), in a 200-ml. round-bot-
tomed flask equipped with a reflux condenser and protected
from atmospheric moisture, was heated with an oil bath from
150-160° for two and one-half hours. After cooling the re-
action mixture was taken up in 100 ml. of ether and the
solution transferred to a separatory funnel. The 2,4,6-
trimethylpyridine was thoroughly extracted with 150 ml. of
iced 10% sulfuric acid. The ether layer was washed with
two 25-ml. portions of water and dried over magnesium sul-
fate. After concentration by distillation at atmospheric

pressure the residue was distilled taking fractions through a micro column[9] as follows: Fraction I, 0.37 g., b.p. 70-74° (158 mm.), n^{25}_D 1.5078; Fraction II, 0.38 g., b.p. 74-75° (160 mm.), n^{25}_D 1.5010; Fraction III, 0.27 g., b.p. 74-75° (160 mm) n^{25}_D 1.4950.

The infrared curve of Fraction I is given in Fig. VIII. The analysis of Fraction I was as follows:

Anal. Calcd. for C_8H_{10}: C, 90.57; H, 9.43. Found: C, 90.33; H, 9.18.

Microhydrogenation of a portion of Fraction I required 3.35 molar equivalents of hydrogen.

The ultraviolet spectrum of Fraction I was determined for a solution in purified cyclohexane with a Beckman model DU quartz ultraviolet spectrophotometer. The spectrum is given in Fig. VII . Curve A represents the spectrum of the freshly prepared solution and Curve B the spectrum of the solution after standing for six weeks at 0°.

The refractive index of Fraction II indicated a composition of approximately 40% tetraene, 60% bicyclo[3.3.0]-octadienes. Fraction II was added to a solution of 0.35 g. of maleic anhydride in 5 ml. of benzene. The solution initially had the characteristic yellow color of the tetraene. After standing for two hours the solution was nearly colorless. The solution was heated to reflux for four hours and all liquid products distilled under vacuum into a Dry-Ice

trap. Sublimation of the solid residue at 70° (1 mm.)
yielded 0.2 g. of maleic anhydride. Sublimation at 150°
(1 mm.) yielded two products, a solid (0.035 g.), m.p.
96-98°, and a liquid which solidified on standing for two
weeks, m.p. 64-76°. The solid product, m. p. 96-98°
analyzed correctly for a monomaleic anhydride adduct of a
C_8H_{10}-tetraene.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.60; H, 5.88.
Found: C, 70.34; H, 5.70.

Microhydrogenation of a sample of the solid prod-
uct, m.p. 96-98°, required 105% of three molar equivalents
of hydrogen.

Reaction of the p-Toluenesulfonates of XVIII and
XIX with 2,6-Dimethylpyridine and Separation of the Tetraene
and Bicyclo[3.3.0]octadienes.---The p-toluenesulfonates of
2.5 g. of XVIII and XIX were prepared and worked up exactly
as described above in the reaction of the p-toluenesulfonates
with 2,4,6-trimethylpyridine. After concentration under vac-
uum a solution of the crude p-toluenesulfonates and 25 ml. of
2,6-dimethylpyridine, in a 200-ml. round-bottomed flask
equipped with a reflux condenser, was heated with an oil
bath from 150-155° for three and one-half hours. The re-
action mixture was taken up in 100 ml. of ether and the
2,6-dimethylpyridine extracted with 200 ml. of iced 12%

sulfuric acid. The ether layer was washed with two 35-ml. portions of water, dried over magnesium sulfate, and concentrated by distillation at atmospheric pressure. Distillation of the residue through a micro column[9] taking fractions proceeded as follows: Fraction I, 0.42 g., b.p. 76-78° (166 mm.), n^{25}_D 1.4970; Fraction II, 0.32 g., b.p. 79-80° (165 mm.) n^{25}_D 1.4930; Fraction III, 0.22 g., b.p. 80-82° (163 mm.), n^{25}_D 1.4868. The three fractions were combined and 0.27 g. of maleic anhydride added. The mixture was allowed to stand at room temperature for four days. Considerable decomposition occurred. Distillation of all liquid products into a Dry-Ice trap under reduced pressure yielded 0.525 g. of the colorless mixture of bicyclo[3.3.0]-octadienes. Sublimation of the solid residue at 70° (1 mm.) yielded a small amount of maleic anhydride. Sublimation at 150° (1 mm.) yielded 0.15 g. of the crude maleic anhydride adduct of the tetraene. After two more sublimations 0.105 g. of the white, crystalline adduct was obtained, m.p. 96-99° (softens 88-90°). Microhydrogenation of a portion of the adduct in methanol in the presence of pre-reduced Adam's platinum oxide required three molar equivalents of hydrogen.

Reaction of the p-Toluenesulfonates of XVIII and XIX with Diethylaniline.---The p-toluenesulfonates of

5.05 g. of XVIII and XIX were prepared and worked up in a similar manner to that described above. After concentration, the crude $\underline{p}$-toluenesulfonates were heated with 120 ml. of diethylaniline for three hours at 160-170°. The reaction mixture was taken up in 150 ml. of ether and the diethylaniline extracted with 450 ml. of iced 12% sulfuric acid. The ether layer was washed with two 100-ml. portions of water and dried over magnesium sulfate. After concentration by distillation at atmospheric pressure the residue was distilled through a 10 cm. Vigreux still head taking fractions as follows: Fraction I, 0.365 g., b.p. 74-76° (152 mm.), n^{25}_D 1.4935; Fraction II, 1.65 g., b.p. 76-78° (152 mm.), n^{25}_D 1.4892; Fraction III, 0.63 g., b.p. 78-80° (152 mm.), n^{25}_D 1.4870.

Figure VII

Ultraviolet Spectra

Curve 1. Freshly prepared solution of bicyclo[3.3.0]octa-diene-"octatetraene" mixture (n^{25}_D 1.5078) in cyclohexane.
Curve 2. Spectrum of same solution after standing at 0°
for six weeks.
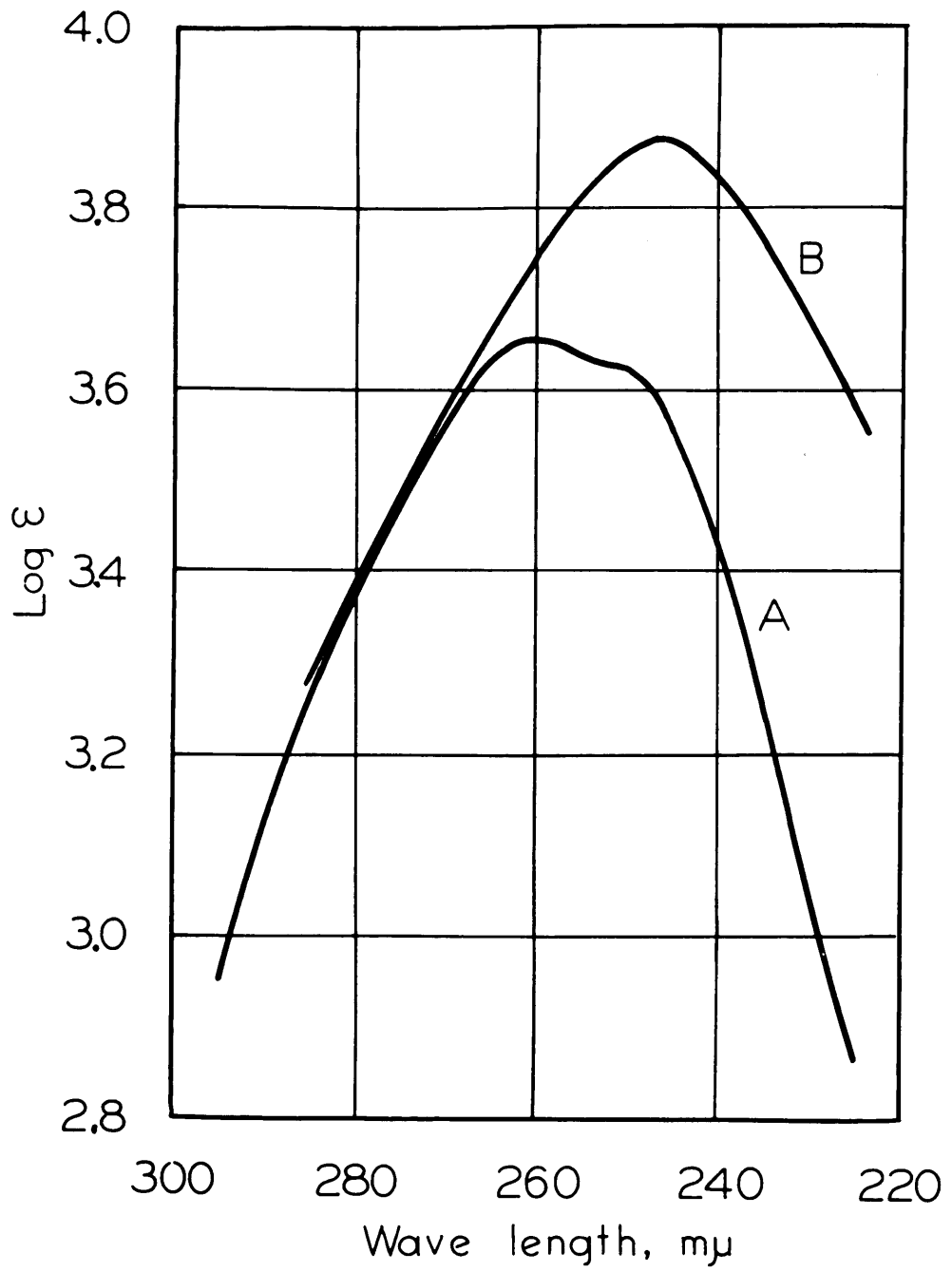
Figure VIII

Infrared spectra: Baird spectrograph with NaCl
prism, solutions of 50 mg. of compounds in 0.50 ml. of
carbon disulfide except in the regions 4.2-5.0μ and
6.2-7.4μ where carbon tetrachloride was used as solvent.

Curve 1. Mixture of bicyclo[3.3.0]octadienes pre-
pared by Chugaev reaction of XVIII and XIX.

Curve 2. Reduction product of the mixture of bi-
cyclo[3.3.0]octadienes.

Curve 3. Bicyclo[3.3.0]octadiene-"Octatetraene"
mixture (n^{25}_D 1.5079). prepared by reaction of the p-tol-
uenesulfonates of XVIII and XIX with 2,4,6-trimethylpyri-
dine.

PERCENT TRANSMISSION

WAVE LENGTH IN MICRONS
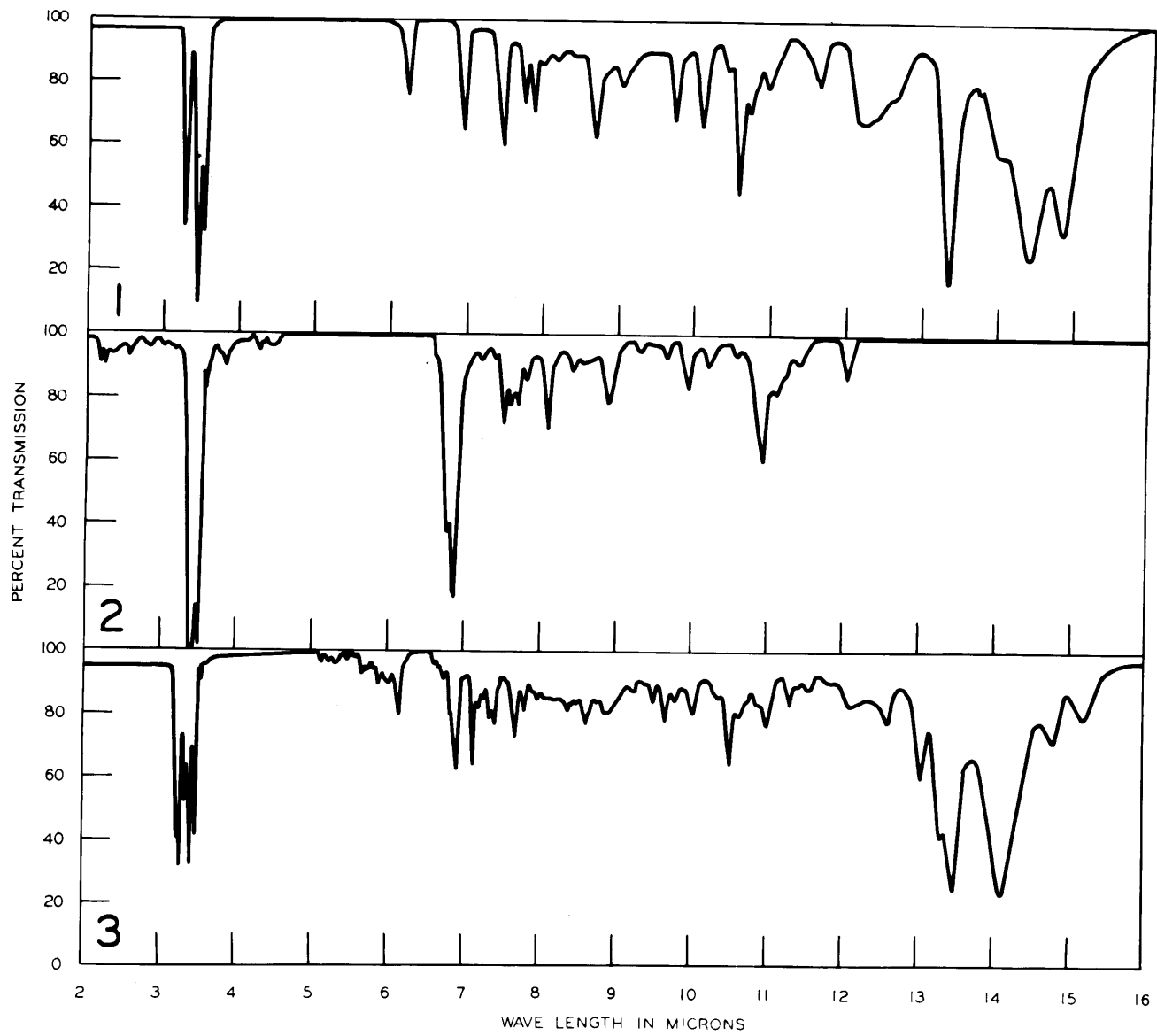
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BIOGRAPHICAL NOTE

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