

An Investigation of the
Synthesis for Tricyclo [1.4.4] Tetradecane

A Thesis

presented to the Department of Chemistry of
Washington and Lee University as the comple-
tion of work for the Bachelor of Science with
Special Attainments in Chemistry degree.

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V I T A

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TABLE OF CONTENTS

INTRODUCTION	1
HISTORICAL	3
DISCUSSION	10
Reduction of Na phthalene	11
Oxidation of Octalin	12
Preparation of 1-Acetoxybutadiene-1,3	13
The Diels-Alder Reaction	13
EXPERIMENTAL	15
$\Delta^{9,10}$ -Octalin	15
$\Delta^{9,10}$ -Octalindiol-1,5-diacetate	16
$\Delta^{9,10}$ -Octalindione-1,5	18
1-Acetoxy-butadiene-1,3	18
1-Acetoxytricyclo(4.4.4.) Tetradecen-2-Dione-5,9	19
SUMMARY	20
BIBLIOGRAPHY	21

INTRODUCTION

The principle object of this work was an extensive search of the literature for possible synthetic routes to the compound tricyclo- $\underline{[4.4.4]}$ tetradecane ($C_{14}H_{24}$). The synthesis of the compound was first suggested by O. B. Ramsey¹ as part of a larger project on synthesis of exotic pure hydrocarbons. Tricyclo $\underline{[4.4.4]}$ tetradecane is of interest for several reasons. It has a unique symmetry which is appealing and challenging; its synthesis would involve interesting steric and conformational problems along several routes; and the petroleum industry in general is interested in procuring pure hydrocarbons for closer studies of the effects of cyclization and branching and other structural properties on the fuel and general chemical properties of compounds of that class.

Tricyclo $\underline{[4.4.4]}$ tetradecane consists of three cyclohexane rings all of which share a common bond and two common carbon atoms. Models indicate that the most stable conformation would be a triple-chain conformation. This structure is itself very closely packed, compact, and thus could be expected to be a solid at room temperature.²

Several possible synthetic routes occur immediately. The first general class of these involves ring-closure from a 9,10-substituted decalin, involving the more severe conformational problems, as models of 9,10-decalindiacetic acid would seem to indicate. Such a ring could be closed by Acetoin condensation. Other possible substituents would seem to be bromoethyl groups, anticipating a Wurtz-Fittig closure. The second synthetic route in order of occur-

rence is through a Diels-Alder reaction with an octalin derivative and a butadiene derivative. The problems involved here are in activating the octalin double-bond and in obtaining a non-gaseous (at room temp.) butadiene to work with. Almost all suggested methods are derivatives of one of these two general classes.

HISTORICAL

An extensive search of the literature revealed that the synthesis of neither the desired compound nor any closely related fused polycyclic hydrocarbon had been previously attempted except for tricyclo $\underline{[0,1,4,4]}$ undecane. The latter was prepared by the ring-closure method from $\Delta^{1,9}$ -10-hydroxymethyloctalin.³ More closely related and more pertinent are tricyclic compounds of the 6-6-5 or 6-6-6 type, but in all of these which have been synthesized, one ring is heterocyclic. The most important are imides and anhydrides of $\Delta^{2,6}$ -hexalin-9,10-dicarboxylic acid and decalin-9,10-dicarboxylic acid. These were first synthesized by Alder and Backendorf by the Diels-Alder addition of butadiene to cyclohexene-1,2-dicarboxylic anhydride. This was reported to yield exclusively the cis-decalin or cis-hexalin derivative. This is an essential characteristic for the ring-closure method being investigated. Interestingly in the same work it was also found that when $\Delta^{1,4}$ -dihydrophthalic acid was used, it was found that the butadiene preferably attacks the double-bond between the two carboxylic acid groups. This group did not report yields.⁴ Repeating Alder's work later, Brigl obtained yields of 58% of the $\Delta^{2,3}$ -octalin-9,10-dicarboxylic anhydride.⁵ Using various derivatives of butadiene but the same acids, as dienophiles, later workers obtained yields in about the same range, 57 to 60%.⁶ The cyclohexene-1,2-dicarboxylic acid required can be readily synthesized by the Diels-Alder addition of butadiene to maleic anhydride and subsequent isomerization of the Δ^4 -product with P_2O_5 .⁷

Theoretically such products as these could after a conventional chain-lengthening process, be subjected to an acetoin condensation to yield cyclic ketones very closely related to the product sought. A more desirable alternative would be a decalin derivative with acetic acid groups at the 9 and 10 positions. Chuang and Ma have arrived at a rather involved synthesis yielding a mixture of cyclohexane-1,2-diacetic acids. The ester of cyclohexanoneacetic acid is subjected to an ethyl bromoacetate condensation, decarboxylation, a Reformatsky reaction and a dehydration.⁸ No attempt to isomerize the mixture to a single product or to separate the mixture is reported. As no attempt at chain-lengthening of these di-acids has been attempted, this is the extent to which this particular pathway has been explored.

The second major synthetic route is the Diels-Alder addition of a butadiene derivative to an activated $\Delta^{9,10}$ -octalin derivative. There are two previously attempted routes to an activated $\Delta^{9,10}$ -octalin derivative. The first of these involves the synthesis of the octalin itself, followed by the oxidation of it. The synthesis for $\Delta^{9,10}$ -octalin are numerous. The largest class of these methods involves the pressure hydrogenation of naphthalene or a naphthalene derivative. The most important of these has proven to be the dehydration of β -decalol as proposed by Linstead⁹ and modified by Cope and Dauben. In this modified procedure β -naphthol is hydrogenated to β -decalol, which is subsequently dehydrated with boric acid to yield 80-95% of a mixture of isomeric octalins, about 70% of which is $\Delta^{9,10}$ -octalin. The same source reports that reduction of tetralin with lithium in ethylene diamine yields a mixture

in 70% yield, 80-90% of which is $\Delta^{9,10}$ -octalin.¹⁰ Closely related to the latter is the reduction of naphthalene with lithium in ethylamine. Yields here were 71% for the isomeric mixture with a 50 to 1 ratio of $\Delta^{9,10}$ -to $\Delta^{1,9}$ -octalin by dehydrating 9,10-dehydroxydecalin, and reducing the resulting hexalin with sodium in liquid ammonia.¹² The starting material itself has a rather involved synthesis, and yields were not reported. Quite a bit of work has been done on the purification of the octalin mixture. It was originally thought that the phosphorous pentoxide used by Linstead isomerized the $\Delta^{1,9}$ product to $\Delta^{9,10}$ -octalin.⁹ However it has since been proposed that the phosphorous pentoxide merely equilibrates the mixture¹⁰ while the work of Hussey indicates that the acid catalyst merely preferentially polymerizes the $\Delta^{1,9}$ -octalin leaving a purer $\Delta^{9,10}$ -octalin.¹³ The phosphorous pentoxide procedure consistently gives mixtures of 80-90% $\Delta^{9,10}$ -octalin¹⁰, though Benkeser, beginning with a much purer mixture of 50:1 increases the purity to 95:1 by this method.¹¹ The method yielding purest samples appears to be the isolation of the pure nitroschloride derivative of the $\Delta^{9,10}$ -isomer, and subsequent regeneration of the octalin in pure form.^{10,12} Benkeser estimates that based on the original β -naphthol, a yield of purified $\Delta^{9,10}$ -octalin might be 50% at best through the Linstead-Cope method. It is suggested that by using equal amounts of ethylamine and dimethylamine in the lithium reduction, an 80% $\Delta^{9,10}$ -octalin mixture can be obtained. It is further suggested that a superior purification method would involve the use of bis-3-methyl-2-butylborane which adds to the less hindered $\Delta^{1,9}$ -octalin, the adduct being oxidized to an alcohol with

H₂O₂, and the desired octalin distilled off.¹⁴ Once the octalin has been obtained the double-bond must be activated for the Diels-Alder reaction. The most convenient available activated derivative is the $\Delta^{9,10}$ -octalin-1,5-dione, prepared by Campbell and Harris. Here the $\Delta^{9,10}$ -octalin was oxidized with selenium dioxide to yield $\Delta^{9,10}$ -octalindiol-1,5-diacetate. This was hydrolyzed, and the product further oxidized to $\Delta^{9,10}$ -octalindione-1,5, by the Oppenauer method. The yield for the overall process is difficult to estimate from the data given, but probably would run very nearly ten per cent.

An alternative procedure would be in synthesizing the octalindione from other than naphthalene derivatives, for example, by a ring-closure method. This has been reported the compound $\Delta^{9,10}$ -octalone-1. Here the monoacid chloride of dimethyl succinate substitutes for a vinyl hydrogen on cyclohexene under AlCl₃ catalysis. The keto-group is reduced by the Wolff-Kischner method and the methyl ester group is hydrolyzed. The acid is made into the acylchloride and the ring is closed. Overall yields are about 13% for the octalone.¹⁶ This might indicate another route for the octalin-dione if (1) it could be oxidized to the dione by the methods used on the octalin, or (2) the synthesis could be attempted omitting the reduction of the carbonyl group. It has, however, not been attempted. In addition it has been reported that double-bonds activated at only a single methyl carbon are known to undergo Diels-Alder reaction,¹⁷ so that the $\Delta^{9,10}$ -octalone might well be capable of forming adducts with butadiene derivatives. Another possibility might be the adaptation of this synthesis to a cyclohexen-3-one. There are several other possible routes to the 4-(1-cyclohexenyl) butyric acid from which the ring-closure is finally effected. These are involved

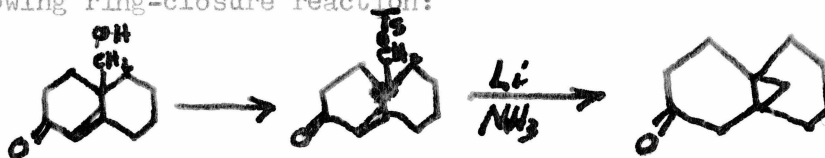
starting products, however, which render their usefulness doubtful. Hill and Conley obtained it by reacting Spiro [5,5]-undecanone-1-oxime in polyphosphoric acid, in a Beckmann rearrangement.¹⁸

After the activated octalin has been synthesized it is necessary to synthesize a butadiene derivative which will be a liquid at room temperature, in order that the reaction may be run without the use of gas equipment. This derivative must be of such nature that the added functional group can be easily removed. The derivative selected for literature investigation was 1-acetoxybutadiene-1,3. The reports of this synthesis are all quite recent. The most convenient seems to be the method of Barclay and Bailey, which is a modification of the standard Hull and Hagemeyer method of 1949.¹⁹ In this procedure isopropenyl acetate is decomposed with heat to yield ketene, and the acetone is driven off. The ketene then acetylates crotonaldehyde which is added to the system. The reported yield was 52%.²⁰ The original Hagemeyer method gave superior yields (90%) but essentially just involved superior equipment, and a much simpler clean up method based on flash distillation from the original pot;¹⁹ it is essentially the same method as that reported in an Eastman Kodak patent, yielding 96%.²¹

The next method involves the more direct acetylation of crotonaldehyde by acetic anhydride. It was reported in 1960 by Georgeriff and Dupré, with yields of about 60%.²² The same method was reported by Blanc in 1961 to give only a 35% yield, but with 65% of the crotonaldehyde recovered unchanged and thus reusable.²³ There is no readily discernible reason for the difference in reported yields.

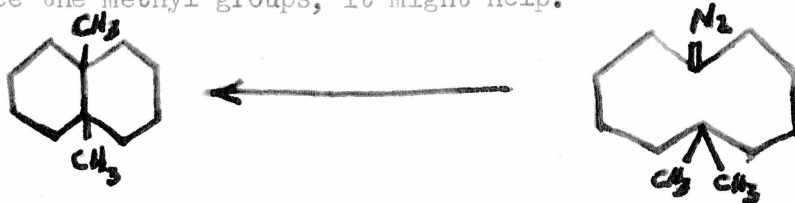
Additional investigation was then conducted on the nature of the Diels-Alder reaction and of that reaction in particular as applied to the particular reagents to be employed in this project. One excellent survey of the general reaction has been noted.¹⁷ An additional review has been made of this reaction in terms of cyclo-none dienophiles, including experimental conditions.²⁴ Another study was found indicating that highly-branched dienophiles (into which class $\Delta^{9,10}$ -octalin-diones surely fit) are much less reactive, and require considerably higher reaction temperatures for good yields.²⁵ Blanc used 1-acetoxybutadiene to get yields of 60-70% with maleic anhydride.²³ Russian chemists reported the Diels-Alder reactions with 1-acetoxybutadiene to be highly stereospecific.²⁶

There are several approaches to this synthesis which do not fit into the general categories which have been more extensively investigated in this work. Most of these were first discovered in the literature by O. B. Ramsey.¹ Little can be done here but to list the starting points. Stork and Tsujie in 1961 reported the following ring-closure reaction:



This one-sided ring-closure scheme might be applied by lengthening the chain.²⁷ In another reaction proposed by Friedman and Schechter, 1,1-dimethyl-6-diazocyclodecane undergoes a transannulation to yield 9,10-dimethyldecalin, 18% of which is in the cis-conformation required for ring-closure.²⁸ This product, however, might be hard to carry along the reaction route. If carboxyl groups could

replace the methyl groups, it might help.



Another one-sided ring-closure might be effected from the decalin-9-acetic acid synthesized by Burgstahler and Nordin. This was accomplished by a Claisen rearrangement of $\Delta^{9,10}$ -octalyl-1-vinyl ether to yield a $\Delta^{1,9}$ -octalin-10-acetaldehyde which was oxidized to the acid.²⁹ This single chain might be lengthened and closed to the double-bond.

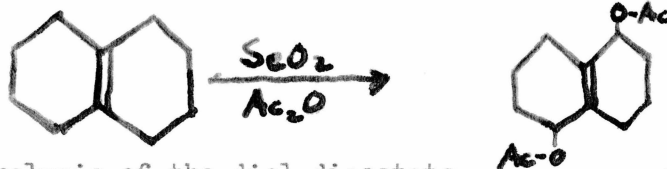
DISCUSSION

It was decided that the most feasible synthetic route to attempt was that of a Diels-Alder reaction to close the third ring. The diene/ophile, octalin would be activated by keto-groups at the 1 and 5 positions. The diene selected was 1-acetoxybutadiene. All the steps preceding the Diels-Alder reaction itself have previously been reported as outlined above. The whole synthetic route as finally visualized is outlined below:

1. Reduction of naphthalene to $\Delta^{9,10}$ -octalin.



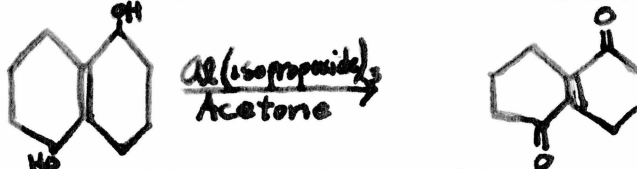
2. Oxidation of the octalin to a diol-diacetate with SeO_2 .



3. Hydrolysis of the diol-diacetate.



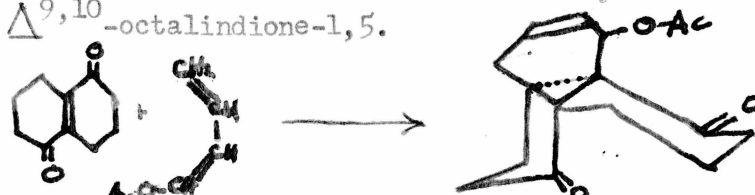
4. Oppenauer oxidation of the diol to the dione.



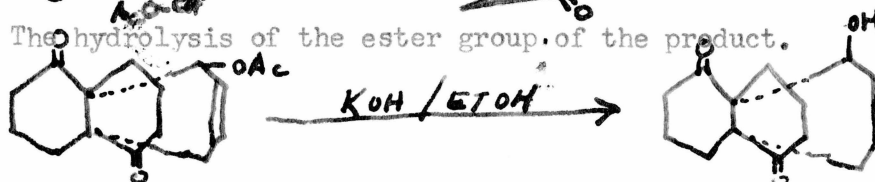
5. Condensation of ketene and crotonaldehyde to yield the 1-acetoxybutadiene.



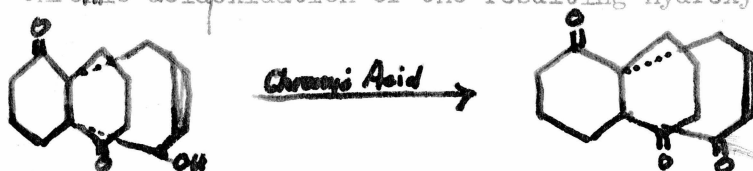
6. A Diels-Alder reaction between acetoxybutadiene and $\Delta^{9,10}$ -octalindione-1,5.



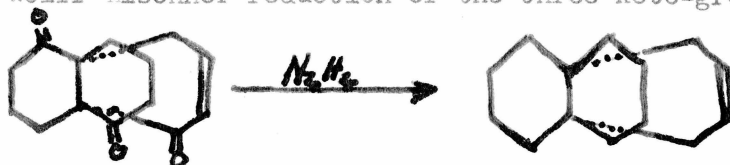
7. The hydrolysis of the ester group of the product.



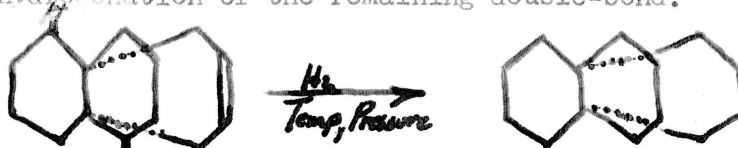
8. Chromic acidoxidation of the resulting hydroxy group.



9. Wolff-Kischner reduction of the three keto-groups.



10. Hydrogenation of the remaining double-bond.



Reduction of Naphthalene - Considerable work had already been done on the reduction of organic compounds by the lithium/amine method.

These workers noted a selectivity of reduction of naphthalene resulting in a 50:1 molar ratio of $\Delta^{9,10}$ -to $\Delta^{1,9}$ -octalin as product.

The reaction is apparently a series of 1,4-reductions and consequent rearrangements which can take place at lower temperatures than can the 1,2-reduction which would be necessary for complete reduction.¹¹

The fact that virtually all (95%) of the lithium was reacted in our work indicates that the yields are probably good, although uncertainty as to the amount of naphthalene in the solution finally makes the actual yield uncertain. The usefulness of the P₂O₅ isomerization reaction cannot be judged here, since the whole produce of the reduction, presumably a mixture of octalins and decalins, was subjected directly to the isomerization. However the pure product boiled at precisely the point reported in the literature for a mixture of 95:1 ratio of $\Delta^{9,10}$ -to $\Delta^{1,9}$ -octalins.¹¹

The reaction in general presented no difficulties other than the inconvenience of handling ethylamine and the deleterious effect of the solvent on the Teflon stirrer blade.

Oxidation of the Octalin - The oxidation of the α -methylene groups of the octalin had not been reported since the work of Campbell and Harris in 1941,¹⁵ so their procedures were adapted in full. An error was made in the molar calculations so that the ratio of selenium dioxide to octalin was not 1:1 but rather 1:2. The result was a large excess of unreacted octalin, some of the desired product, and .07 moles or 41% yield of the $\Delta^{9,10}$ -octalol-1-acetate. This was then further oxidized, this time again at a 1:2 ratio of selenium dioxide, along with an amount estimated as sufficient to oxidize the excess octalin. This was run as a single reaction. The result, when combined with the desired product from the first oxidation gave an extremely disappointing yield. The yields reported by Campbell and Harris were 12.5% from the correctly-run oxidation of the octalin, and 16% (based on the monoacetate) from the secondary oxidation of the monoacetate.¹⁵ Yields in either case were severely reduced by decomposition due to excessive pot temperatures required by a long distillation path and the boiling points of the compounds. The transition to short-path equipment at an earlier stage and use of the high-vacuum system in all distillation should increase the yields markedly. The boiling point of the fraction finally selected was 122-140°C/1.2 mm. as compared to a literature value of 145-148°C/2 mm.,¹⁵ which is fair agreement. Because of the small amounts available at this point it was decided not to isolate further intermediates.

Hydrolysis of the Acetate - The procedure followed here was exactly that of Campbell and Harris for hydrolysis of the comparable monoacetate with adjustments for the doubled equivalents of the diacetate. The produce solidified in the reaction vessel after the solvent was

removed, as should have been expected.

Oxidation of the diol to the dione - Again the procedures of Campbell and Harris for the oxidation of the octalol were modified for oxidation of a diol. One additional modification was the substitution of aluminum isopropoxide for aluminum tert-butoxide because of the greater convenience in the preparation of the former.¹⁵ General reviews of the Oppenauer reaction seemed to indicate no clear opinion as to the comparable efficacy of the two reagents.³⁰ Again, the product was not isolated but remained in the reaction vessel.

Preparation of 1-Acetoxybutadiene-1,3 - In this case the method of Bailey and Barclay was adopted without significant deviation. The boiling point of the product was precisely as reported in the literature. Although reported to polymerize on standing,²² the product maintained under nitrogen at 0°C. showed no sign of deterioration after 7 days. The yield was 50% as compared to a literature value of 55%,¹⁹ the additional loss being attributed to the necessity of repeating a filtration. The reaction is a simple displacement of acetone by crotonaldehyde as the substrate for a ketene acetylation, the ketene being generated in situ by heating the isopropenyl acetate.

The Diels-Alder Reaction - This reaction is the most crucial step in the synthesis, having not previously been reported. The 0.30 grams of dione used in this case were of doubtful quality. An excess, six-fold, of the diene was used to displace the equilibrium in favor of the adduct. The solvent as recommended was benzene and the reaction was planned to run for 24 hours. A freak blockage in the water line

caused condensation to be discontinued overnight. The residue was considerably decomposed by the dry heat which resulted. At this point experimental work was discontinued until the entire sequence could again be attempted. Presumably this reaction should go without much hindrance from the dienophile, although there may be some difficulty with the C-1 substitution of an electron-withdrawing group on the diene.³¹

The Wolff-Kischner Reduction Chromic Acid Oxidation, and Hydrogenation
have not been attempted yet.

EXPERIMENTAL

Ethylamine: Ethylamine was obtained as a 70% aqueous solution from Matheson, Coleman, and Bell. 500 ml. was distilled through a circulatory ice-water condenser at 30-45°C. Receiver also was packed in ice. Material was stored in refrigerator for 48 hours over NaOH pellets. (Note: Material dissolves rubber. Use glass stoppers.) The residual water was discarded. The 500 ml. distillate was then re-distilled through an ice-water condenser at 23°C into a 1-liter 3-neck flask with 2 closed necks.

^{9,10}
Δ - Octalin: The above receiver was fitted with a mechanical stirrer, nitrogen inlet, and a Dewar (cold-finger) condenser cooled with dry-ice and acetone. 25.0g. naphthalene were added. At this point the condenser broke, and the naphthalene and ethylamine mixture was stored in refrigerator for 3 days. During this time the stopper was pushed out and a large plug of naphthalene had sublimed in the neck and around in the refrigerator. A new charge of 25.6g. was added to the ethylamine and the reaction set up as before. Flask was flushed with N₂, and 20 g. of Li was added over 2.5 hours. Li was obtained in bars, hammered into thin sheets, cut into small pieces, and dropped in while the N₂ inlet was removed. The solution first became bright red around the Li fragments. Gradually the solution acquired a cloudy grape color. Reflux was stopped after 5 hours from first addition of lithium and then refluxed 3 additional hours after 4 days refrigerator storage. Nitrogen atmosphere was maintained through both reflux periods and stirring was maintained only during first five hours, because of serious deterioration of

the Teflon blade. During first 5 hours of reaction, flask was ice-water cooled to control the reaction. In second part, heat was applied to maintain reflux. 1.1g. of unreacted Li was recovered as a lump, with forceps.

During next storage period, white crystals formed, along with a grainy gray sludge.

15g. NH_4Cl was added until solution was light yellow and largely solid. The ethylamine was distilled off, 250 ml. recovered at 26°C .

The flask was then fitted with a dropping funnel and the Dewar condenser. 500 ml. H_2O was added slowly. The resulting mixture was extracted with about 1 liter of ether. Ether layer was dried over MgSO_4 and the ether removed by distillation. A residue of about 50 ml. was transferred to a 250 ml. flask, round bottom, and 16g. P_2O_5 was added. Mixture refluxed at 140° for 2 hours, was cooled, ice added and solution extracted with ether, resulting solution having a bright-yellow color. The ether was stripped off and the residue transferred to a 100 ml. flask. This was distilled and the fraction boiling $192-195^\circ\text{C}/739$ mm was retained, weighing 22.8 grams.

$\Delta^{9,10}$ - Octalindiol-1,5-diacetate: The produce above was added to a mixture of 12g. SeO_2 , 200 g. acetic anhydride, and 29 ml. H_2O , and left for 18 hours to reflux at 30°C with stirring. [These calculations of quantities were in error. All amounts should have been doubled]. Heat was removed and filtered. Yield was a dark brown clear liquid and a red Se sludge. The acetic anhydride was removed at $34-5^\circ\text{C}/18-20$ mm. $\Delta^{9,10}$ - Octalin in ~~XS~~^{excess} came over at $49^\circ/22$ mm. 13.6 grams of a yellow clear liquid was collected at $110-140^\circ\text{C}/22$ mm,

presumably the monoacetate. The remainder of the pot was retained. The latter three fractions, including the acetic anhydride were mixed, with 14.0g SeO_2 and 30 ml. H_2O , and the mixture stirred at $25-30^\circ$ for 24 hours. This solution was filtered and the acetic anhydride removed as before. Operations were then shifted to a high-vacuum system with dry-ice traps and acid-traps. The second filtrate was distilled, producing fractions at $45^\circ\text{C}/1.5$ mm and $79^\circ\text{C}/3$ mm. Because of uncertainty with respect to these pressures due to blocked trap they were combined with the pot retained from the first oxidation and transferred to micro equipment. The following fractions were obtained. I $52^\circ-61^\circ/1.3$ mm, 1.64g; II $85^\circ-112^\circ/1.1$ mm, 0.46 g.; III $120^\circ-135^\circ/1.2$ mm, 1.37g., and IV, $135^\circ-140^\circ/1.2$ mm, 0.35 g. The latter two were combined as the presumed diol-diacetate.

$\Delta^{9,10}$ - Octalindiol - 1,5: 35 g. Na metal were dissolved in 160 ml. of absolute ethanol. The diol-diacetate prepared above (1.72g.) was dissolved in 20 ml. ethanol. The two solutions were mixed, giving a dark green color, becoming almost black, in a 250 ml. erlenmeyer flask. Reflux was maintained for 2 hours. Result was a brown mixture. The ethanol was removed at reduced pressure, water added, and an ether extraction was made. The ether layer was dried over MgSO_4 and the ether stripped off. 3 ml. benzene were added and stripped off to insure dryness. The residue weighed 0.75 grams and was not further isolated.

Aluminum isopropoxide: 27 g. Al foil was cleaned and placed in a 1-l. RB flask containing 300 ml. isopropyl alcohol (prepared by distillation after 3 hours reflux of 500 ml. over 250g. unslaked lime,

and 2.5g. NaOH) and 0.5g. HgCl₂. It is refluxed with a drying tube affixed to condenser. 2 ml. CCl₄ are added when boiling commences. Reaction must be controlled with ice-water bath. Reflux is then maintained until the Al dissolves. The hot solution was poured into a 500 ml. claisen flask with a 250 ml. suction flask and heated over oil at 90° under reduced pressure. When nearly all the alcohol was collected, and temperature exceeded 90°C., full vacuum was applied, bath heated to 170°, condenser removed, and 500 ml. dist. flask employed as a receiver. B.P. 130-140°/7 mm, 140-150°/12 mm is literature value. 164g. were obtained at 145-155°/35 mm, for an 80.3% yield. Storage is in wax-sealed jar in refrigerator.

$\Delta^{9,10}$ - Octalindione - 1,5: To the 0.75g. residue of diol in the 200 ml ~~RB~~ flask were added 23.2 ml. acetone and 31.8 ml. benzene. A hot solution of 3.52 grams aluminum isopropoxide in 15.9 ml. benzene is added. The mixture was refluxed for 8.5 hours. 3 M sulfuric acid, 150 ml, was added and the solutions separated. The aqueous layer was extracted with benzene. The benzene layer and extracts were washed with distilled water. The extracts were dried, and the benzene was removed under vacuum. A residue of 0.35 grams of a brown oil remained. This was not further isolated.

1-Acetoxybutadiene-1,3: 135.2 grams (1.35 moles isopropenyl acetate, 2.0 g. p-toluenesulfuric acid, and 0.5g CuAc₂ were mixed in a 1-l. 3 neck flask fitted with a 30"-helix packed vacuum-insulated column, stirrer, dropping funnel, and pot thermometer. While refluxing, 70.0 grams (1 mole) of freshly-distilled crotonaldehyde (B.P.101-103°C) are added dropwise over 5-3/4 hours. Acetone is removed through the

column at 58° until 90% of the theoretical 50g acetone was recovered (64 ml.). Then 3.5g of triethanolamine and 200 ml. H₂O were added to the pot. Distilled the two-phase solution at 52-58 mm. The aqueous layer was extracted with ether, and the extracts combined with the organic layer. This was washed twice with 10% K₂CO₃, 1.0g. N-phenyl-β-naphthylamine was added. The mixture was dried over Mg SO₄. Fractional distillation yielded 54.5 gs (50%) at 52-58°/36 mm of a clear liquid. Stored in refrigerator under nitrogen.

1-Acetoxytricyclo (4.4.4.) Tetradecen-2-Dione-5,9. - 2.0g 1-Acetoxybutadiene, 50 ml. benzene, and one microspatula full of trichloroacetic acid are added to the dione residue and refluxed for 24 hours gently.

SUMMARY

The synthesis of tricyclo [4.4.4.7] tetradecane has been proposed. Possible synthetic routes have been suggested, and these have been investigated in the literature. A method involving a Diels-Alder addition to an activated $\Delta^{9,10}$ -octalin derivative was selected for experimentation. The initial reactions in the selected scheme have been tried.

In further work the scheme should be investigated further with larger starting quantities. Then if this method proves unsuccessful, the alternatives should be selected. The attempt to synthesize a cyclohexene-diacetic acid for Diels-Alder reaction might be most fruitful. The one-sided ring closure from the $\Delta^{1,9}$ -octalin-9-acetic acid might be pursued along the lines of the Lindsey ring-closure synthesis for $\Delta^{9,10}$ -octalin. Almost infinite variation on these themes is possible.

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