1965


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PART I. A NOVEL SYNTHESIS OF DIHYDRO-
JASMONE. PART II. POLYMETHYLENEKETENE
DIMERS AND TRIMERS.

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PART I.  A NOVEL SYNTHESIS OF DIHYDROJASMONE

PART II.  POLYMETHYLENEKETENE DIMERS AND TRIMERS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Frank E. Collins, Jr.
B. S., Northeast Louisiana State College, 1961
M. S., Louisiana State University, 1963
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ABSTRACT
Part I. A Novel Synthesis of Dihydrojasmine. — 3-Methylcyclopent-2-en-2-ol-1-one, a readily available substance of natural occurrence, was utilized in the synthesis of the well-known dihydrojasmine (2-α-amyl-3-methylcyclopent-2-en-1-one). This was the first practical synthesis of dihydrojasmine which did not involve a condensation reaction, thus the possibility of obtaining an isomeric mixture of products was eliminated.

Acetylation of 3-ethylcyclopent-2-en-2-ol-1-one with acetic anhydride gave 2-acetoxyl-3-methylcyclopent-2-en-1-one, which was converted by the action of propylene oxide to 2-acetoxyl-3-methylcyclopent-2-en-1-one propylene ketal. Saponification of this ketal gave 3-methyl-1,2-cyclopentanedione-1,1-propylene ketal, which served as a precursor to dihydrojasmine. Upon treatment of this compound with α-amylmagnesium chloride, followed by hydrolysis with ammonium chloride solution, 2-α-amyl-3-methylcyclopentan-2-ol-1-one propylene ketal was obtained. Dehydration and deketilation of the latter compound with sulfuric acid solution yielded dihydrojasmine.

Part II. Polymethyleneketene Dimers and Trimers. — An excellent method for the preparation of ketoketene dimers involves the dehydrohalogenation of an acyl chloride with triethylamine. The reaction of cyclopropanecarbonyl chloride with triethylamine gave no dimer but instead a solid product, presumably the acyl ammonium chloride, which reacted with aniline to form cyclopropanecarbonilide. Cyclobutane-carboxynilide and triethylamine yielded at temperatures below 25° a similar addition compound which gave cyclobutane-carboxyanilide when treated with aniline. When the latter reaction was carried out at a higher temperature, dispiro[3.1.3.1]decane-5,10-dione was obtained.

Dispiro[3.1.3.1]decane-5,10-dione, trimethyleneketene dimer, underwent cleavage and decarboxylation in alkali to give dicyclobutyl ketone. The ketone was obtained without acidification of the alkaline solution, which is
generally necessary for the decarboxylation of a β-keto acid in the form of its sodium salt. A mechanism was proposed for its formation. Trimethylene-ketene dimer reacted with ethanol in the presence of a catalytic amount of base to give ethyl 1-(cyclobutanecarbonyl)cyclobutane carboxylate, and was reduced to the corresponding glycol, dispiro[3.1.3.3]decane-5,10-diol with lithium aluminum hydride.

It is known that dimethylketene dimer, tetramethyl-1,3-cyclobutanedione, when treated with a catalytic amount of sodium methoxide, yields the cyclic trimer, hexamethyl-1,3,5-cyclohexanetetronic. In the present investigation, this base-catalyzed process was utilized in the synthesis of trimethylene-ketene trimer, trispiro[3.1.3.3]pentadecane-5,10,15-trione, from trimethylene-ketene dimer.

In this study it was found that the alkaline hydrolysis of dimethylketene trimer with barium hydroxide gave 2,4,4,6-tetramethylheptan-3,5-dione. Trimethylene-ketene trimer, upon treatment with the same reagent gave 1,1-(dicyclobutanecarbonyl)cyclobutane and dicyclobutyl ketone. Ethanolysis of trimethylene-ketene trimer gave ethyl 1-[cyclobutanecarbonyl]cyclobutane-carboxylate. Reduction of the trimer was accomplished with lithium aluminum hydride to give trispiro[3.1.3.3]pentadecane-5,10,15-triol.

Tetramethylene-ketene dimer, dispiro[4.1.4.3]dodecane-6,12-dione, a known compound, was the only product isolated in an attempted synthesis of tetramethylene-ketene monomer by dehydrohalogenation of cyclopentancarbonyl chloride with triethylamine. The dimer underwent cleavage and decarboxylation when treated with alkali to give dicyclopentyl ketone.

Only one polymethylene ketene, pentamethylene-ketene, has been reported in the literature. It was found that hexamethylene-ketene could be synthesized by
dehydrohalogenation of cycloheptanecarbonyl chloride with triethylamine. This monomer reacted with aniline to give cycloheptanecarboxanilide, and gave with cyclopentadiene a cycloaddition product, hexamethylenebicyclo[3.2.0]hept-3-en-1-one. Hexamethyleneketene dimerized upon standing to give dispiro-5,1.6.11 hexadecane-8,16-dione which underwent reduction with lithium aluminum hydride to give the corresponding glycol, dispiro[5.1.6.11]hexadecane-8,16-diol.
A NOVEL SYNTHESIS OF DIHYDROJASMONE

Dihydrojasmone (VI) was first synthesized by Staudinger and Ruzicka\textsuperscript{1} by a Dieckmann ring closure of the necessary dicarboxylic ester, and has since been prepared by several general methods. Small amounts of dihydrojasmone were obtained by the catalytic hydrogenation of the well-known natural product, jasmone\textsuperscript{2,3} and by the reduction of 4-chlorotetrahydropyrethrene\textsuperscript{4-6} a derivative of pyrethrolone obtained from pyrethrin. Various methods have been described\textsuperscript{7-14} utilizing \( \gamma \)-hexyl-\( \gamma \)-methylbutyrolactone, and also the closely related paraconic acid, which upon dehydration yield dihydrojasmone. Decarboxylation\textsuperscript{11,13} of the paraconic acid has been accomplished prior to, or simultaneous with, the dehydration step. VI has also been obtained by the cyclization of 2,5-undecenedione\textsuperscript{15-17} or its carbethoxy derivative.\textsuperscript{18}

In this investigation it is shown that dihydrojasmone may be synthesized from 3-methylcyclopent-2-en-2-ol-1-one (I), a readily available substance of natural occurrence which was first isolated by the dry distillation of beech wood\textsuperscript{19} and later was found in the acetic oil fraction of pyroligneous acid,\textsuperscript{20} in tall oil,\textsuperscript{21} and in a number of soluble wood tars.\textsuperscript{22,23} It was also obtained by the alkaline hydrolysis of spruce wood,\textsuperscript{24} and recently has been identified as an important component in the coffee bean.\textsuperscript{25} Reported syntheses of this compound include dehydrogenation of divinyl glycol\textsuperscript{26} over copper at 280\textdegree; hydrolysis of the 5,5-dichloro derivative of 2-methylcyclopentanone,\textsuperscript{27} and methylation of the condensation product of ethyl oxylate and ethyl glutarate, followed by decarboxylation.\textsuperscript{28}

There has been some controversy with regard to the correct structure of this compound. From such evidence\textsuperscript{19,29,30} as a positive ferric chloride test, a positive iodoform test, the reduction of both Fehling's and Tollen's
reagents; the formation of a monoacetate, a dioxime and a phenyllosazone, and the fact that the compound was found to be 100% enolic, it was determined that the structure was an enol of 3-methyl-1,2-cyclopentanedione. Of the two possible enolic tautomers, 3-methylcyclopent-2-en-2-ol-1-one (I) was designated as the correct structure because the substance condensed with two moles of benzaldehyde to give a dibenzylidene derivative, which demanded the presence of four active methylene hydrogen atoms. Structure (Ia) contains an asymmetrical carbon atom which permits the possibility of optical activity, but no activity was observed.

Almost thirty years later, evidence which seemed compelling was presented to show that the enol structure of the diketone was not 3-methylcyclopent-2-en-2-ol-1-one (I) as earlier reported, but the enolic structure (Ia). Chlorination of the compound in aqueous solution gave a dichloride which upon standing eliminated hydrogen chloride to yield a monochloro derivative. Oxidation of the latter with alkaline permanganate gave β-acetylacrylic acid, which seemed to require Ia as the correct structure.

The question of structure was resolved recently by n.m.r. spectral studies of this substance which demanded the structure 3-methylcyclopent-2-en-2-ol-1-one (I). The n.m.r. spectrum exhibited signals at 7.97, 7.57, and 3.25, which were attributed to the methyl, methylene, and enol protons, respectively. The areas associated with these peaks were in the ratio 3:4:1 which is consistent with the enolic structure (I). Upon ozonolysis, levulinic was obtained.

Similarities in the structure of 3-methylcyclopent-2-en-2-ol-1-one (I) and dihydrojasmon (VI) prompted this investigation to determine the feasibility of converting I into VI. Of the general methods of syntheses reported, those involving condensations are subject to the possibility of obtaining a mixture of isomeric condensation products. 3-Methylcyclopent-2-en-2-ol-1-one
has the advantage that the methyl group is attached to a five-membered ring thereby eliminating possible formation of such isomeric products.

\[
\begin{align*}
\text{CH}_3\text{C} & \text{H} \text{g} - \text{T} = \text{r} - \text{OH} \quad \text{CH}_3\text{C} \\
\text{C} & \text{H}_3 \quad \text{C} \text{H}_3 \quad \text{C} \text{H}_3
\end{align*}
\]

The success of the synthesis depended primarily upon the acquisition of the ketone ketal (IV). Attempts to obtain IV directly from 3-methylcyclopent-2-en-2-ol-1-one (I) proved unsuccessful. An investigation of the literature revealed that cyclic ketals had been obtained in low yield, however, by the action of ethylene oxide on ketones in the presence of catalytic amounts of stannic chloride. Higher yields of cyclic ketals were reported by addition of a mixture of epichlorohydrin and ketone, dissolved in carbon tetrachloride to a dilute solution of stannic chloride in the same solvent at 20° to 30°. Accordingly, 3-methylcyclopent-2-en-2-ol-1-one (I) was acetylated with acetic anhydride to give 2-acetoxy-3-methylcyclopent-2-en-1-one (II), thus removing the enolic hydrogen and leaving the carbonyl group intact for
ketel formation. Of the various oxides investigated, propylene oxide proved
most suitable. Thus II reacted with propylene oxide in the presence of stan­
nic chloride to give 2-acetoxy-3-methylcyclopent-2-en-1-one propylene ketal
(III) in 53% yield. Saponification of III with 10% sodium hydroxide solution
gave the unstable vinyl alcohol which reverted to methyl-1,2-cyclopentane-
dione-l,l-propylene ketal (IV) in 80% yield.

3-Methyl-1,2-cyclopentanedione-1,l-propylene ketal (IV) is a novel and
important compound, since it might very well serve as a precursor to the acquisi­
tion of many interesting natural and synthetic products, and it exhibits an
interesting case of stereoisomerism. The projection formula of IV might indi­
cate the possibility of two structural isomers, depending upon the mode of ad­
dition of propylene oxide. This is not the case, however, since the two rings
are in perpendicular planes and IV has only the possibility of existing as four
sets of optical enantiomorphs. Thus, reversing the mode of addition of pro­
pylene oxide leads only to diastereoisomers. Vapor phase chromatographic an­
alysis, however, revealed only a single peak, indicating a very pure compound.

Upon treatment of IV with n-amylmagnesium chloride, followed by hydrolysis
with ammonium chloride solution, 2-n-amyl-3-methylcyclopentan-2-en-l-one pro­
pylene ketal (V) was obtained, and its physical properties determined. De­
hydration and deketalization of V to yield dihydrojasmonc (84%) was accomplished
by stirring and refluxing V with 25% sulfuric acid solution, followed by
steam distillation.

The infrared spectrum of dihydrojasmonc was characterized by absorption
bands at 5.85 μ and 6.05 μ, which were attributed to a conjugated carbonyl
and a C=C double bond, respectively. It also exhibited EtOH 236 μ (ε12,000).
The purity of dihydrojasmonc (97%), obtained directly from very pure IV or V,
seems to be limited only by the purity of the n-amyl chloride used.
There seems to be no doubt regarding the position of the C=C double bond since
the acid dehydration of V to form dihydrojasmonone no doubt requires carbonium
ion formation, and ejection of a tertiary rather than a secondary hydrogen
ion.

There are two steps in the reaction sequence that may be bypassed.
II may be converted to IV directly, thus avoiding the isolation of III. In
doing this, however, it was found that the yield was slightly impaired and the
operations involved in the isolation of IV were cumbersome due to contaminating
products accompanying the formation of the ketal. Conversely, the iso-
lation of V proved entirely unnecessary and higher yields were obtained by
converting IV into VI directly, saving both time and effort.

The overall yield of dihydrojasmonone (VI) from 3-methylcyclopent-2-en-2-
ol-1-one (I), based on the recommended sequence of reactions, I → II → III → IV →
VI, was 26%. Obviously, the method may be extended to yield other 2-alkyl-
3-methylcyclopent-2-en-1-ones.
3-Methylcyclopent-2-en-2-ol-1-one (I). — This substance was obtained as a hydrate, m.p. 77-81°. Purification was accomplished by refluxing the crude material dissolved in benzene in a flask fitted with a Dean-Stark trap until the water was removed. The benzene solution was concentrated by distillation until only a small quantity of solvent remained, and the residue was recrystallized from isopropyl alcohol to give a white solid, m.p. 105.5-106.5°; lit. 29 m.p. 105-106°, m.p. 106-107° (sublimed). Ultraviolet spectrum: \( \lambda_{\text{max}}^{\text{EtOH}} = 258 \text{ nm} \) (e 710); infrared spectrum: \( \lambda_{\text{max}}^{\text{CCl}} = 2.83, 2.97, 3.42, 5.80, 5.97, 6.95, 7.08, 7.14, 7.34, 7.77, 8.14, 8.33, 9.00, \) and 9.77 μ. 

**Anal. Calcd.** for C₁₀H₁₄O: C, 64.27; H, 7.19. **Found:** C, 64.25; H, 7.31.

2-Acetoxy-3-methylcyclopent-2-en-1-one (II). — A mixture of 336 g. (3 moles) of 3-methylcyclopent-2-en-2-ol-1-one (I) and 918 g. (9 moles) of acetic anhydride was refluxed for 1 hr. The acetic acid and excess acetic anhydride were removed by distillation and the residue was fractionated to yield 435 g. (94%) of a liquid, b.p. 105-106° (3 mm.). Upon standing the product crystallized slowly to yield a hard, white solid, m.p. 61.5-62.5°, which gave a negative ferric chloride test. Recrystallization from either benzene, methanol, or water gave crystals, m.p. 62-62.5°; lit. 19 m.p. 65° (water), b.p. 129-130° (12 mm.). Infrared spectrum: \( \lambda_{\text{max}}^{\text{CCl}} = 3.41, 5.60, 5.77, 6.93, 7.09, 7.22, 7.30, 7.52, 8.38, 9.19, 9.61, \) and 11.43 μ. 

**Anal. Calcd.** for C₁₄H₂₂O₃: C, 62.32; H, 6.54. **Found:** C, 62.22; 62.20; H, 6.55; 6.60.

2-Acetoxy-3-methylcyclopent-2-en-1-one Propylene Ketal (III). — To 34 g. (0.13 mole) of stannic chloride dissolved in 150 ml. of carbon tetrachloride was added dropwise with stirring at 20° a mixture of 200 g. (1.3 moles) of 2-acetoxy-3-methylcyclopent-2-en-1-one (II), 93 g. (1.6 moles) of propylene

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oxide, and 475 ml. of carbon tetrachloride. The mixture was hydrolyzed by
addition of 520 ml. of 10% sodium hydroxide solution. The organic layer was
separated and washed with 150 ml. of water, and then dried over anhydrous
potassium carbonate. The solvent was removed and the residue was distilled to
give 5.2 g. of forerun, b.p. 66-102° (3 mm.), 146 g. (53%) of the product, b.p.
102-107° (3 mm.), and 38 g. of a tarry residue. Refractionation through a 10-
inch, vacuum-jacketed, packed column gave 136 g. of III, b.p. 104-106.5°(3 mm.),
H crystalline methanol, 

The product was shown to be 83% pure
by vapor phase chromatographic analysis. Acid hydrolysis of III gave I, m.p.
105-106°, m.m.p. 105-106°.

Anal. Calcd. for C\textsubscript{11}H\textsubscript{16}O\textsubscript{4}: C, 62.25; H, 7.60; mol. wt., 212.2. Found: C, 61.93; H, 7.81; mol. wt. (benzene), 197, 201.

3-Methyl-1,2-cyclopentanedione-1,1-propylene ketal (IV). — To 450 ml. of
10% sodium hydroxide solution at 25° was added 134 g. (0.63 mole) of 2-acetoxy-
3-methylcyclopent-2-en-1-one propylene ketal (III) and the resulting suspension
was stirred for 0.5 hr. The reaction mixture was extracted with three 75 ml.
portions of ether and the combined ethereal extracts were washed with 50 ml.
of water, and then dried over anhydrous potassium carbonate. The ether was
removed by evaporation, and the clear residual oil was distilled through a 10-
inch, vacuum-jacketed, packed column to give 86 g. (80%) of IV, b.p. 65.5-
66° (3 mm.), H\textsubscript{2}O crystalline methanol, 

Vapor phase chromatographic analysis gave a single peak.

Anal. Calcd. for C\textsubscript{9}H\textsubscript{14}O\textsubscript{3}: C, 63.51; H, 8.29. Found: C, 63.15; H, 8.35.
2-n-Amyl-3-methylcyclopentan-2-ol-1-one Propylene Ketal (V). — To an ethereal solution of n-amylmagnesium chloride, prepared from 76 g. (0.72 mole) of n-amyl chloride and 15.6 g. (0.64 atom) of magnesium, was added over a period of 15 min. 68 g. (0.4 mole) of 3-methyl-1,2-cyclopentanecdione-1,1-propylene ketal (IV). The mixture was stirred and refluxed for 15 min., and then poured into a mixture of 250 ml. of a saturated ammonium chloride solution containing 250 g. of crushed ice. The ethereal solution was separated and washed successively with 50 ml. of water, 50 ml. of 1% sodium hydroxide solution, and again with 50 ml. of water, and then dried over anhydrous potassium carbonate. The ethereal solution was concentrated and the residue was fractionated through a 10-inch, vacuum-jacketed, packed column to yield 12 g. of forerun, b.p. 75-110° (2 mm.), and 70 g. (72%) of V, b.p. 110-111° (2 mm.), n[^25]D 1.4590, d[^25] 0.9951, MP 66.52 (calcd. 67.27), infrared spectrum: \( \lambda_{\text{max}} \) 2.80, 3.45, 6.83, 7.27, 7.60-7.70, 8.62, 9.15, 9.65, 10.27, 10.55, 10.72, and 11.42.  

**Anal.** Calcd. for C_{14}H_{26}O_{3}: C, 69.38; H, 10.81. Found: C, 69.65; H, 10.50.

Dihydrojasmonol (VI). — To 38 g. (0.157 mole) of 2-n-amyl-3-methylcyclopentan-2-ol-1-one propylene ketal (V) was added 100 ml. of 25% sulfuric acid solution and the resulting suspension was stirred and refluxed for 2 hr., and then the reaction mixture was steam distilled. The organic layer was separated and the water layer was saturated with sodium chloride before extraction with 200 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate; the ether was removed, and the residue was distilled to give 22 g. (84%) of dihydrojasmonol, b.p. 87-88° (2 mm.), n[^25]D 1.4771, d[^25] 0.9157, MP 51.31 (calcd. 37 50.34); lit.  b.p. 101-102° (5 mm.), n[^15]D 1.48107, d[^15] 0.9252; lit.  b.p. 117° (9 mm.), n[^18]D 1.4810, d[^18] 0.9165. Ultraviolet spectrum: \( \lambda_{\text{max}} \) 236 nm (c 12,000); infrared spectrum: \( \lambda_{\text{max}} \) 3.43, 5.85, 6.05, 6.93.
7.09, 7.25, 7.40, 7.48, 7.72, 7.90, 8.50, 9.33, 9.84, 10.05, 10.62, 10.80,
12.20, and 13.75 μ. The product was shown to be 97% pure by vapor phase chro-
matographic analysis.

**Anal.** Calcd. for C₁₁H₁₈O₂: C, 79.46; H, 10.91. Found: C, 79.61; H,
11.38.

3-Methyl-1,2-cyclopentanedione-1,1-propylene ketal (IV). — 2-Acetoxy-
3-methylcyclopent-2-en-1-one (II) may be converted into IV directly, thus
making unnecessary the isolation of III. To a stirred solution of 19.5 g.
(0.075 mole) of stannic chloride dissolved in 150 ml. of carbon tetrachloride
was added dropwise over a period of 1.5 hr. at 20° three-fourths of a mixture
consisting of 154 g. (1 mole) of II, 72.5 g. (1.25 moles) of propylene oxide,
and 450 ml. of carbon tetrachloride. An additional 6.5 g. (0.025 mole) of
stannic chloride was introduced, and the remaining portion of the above mix-
ture was added dropwise under the same conditions. The reaction mixture
was hydrolyzed by addition of 240 ml. of 10% sodium hydroxide solution. The or-
ganic layer was separated and washed with two 100-ml. portions of water, and
then dried over anhydrous potassium carbonate. The carbon tetrachloride was
removed by distillation under reduced pressure; the residue was stirred at 25°
with 800 ml. of 10% sodium hydroxide solution for 0.5 hr., and the resulting
suspension was extracted with five 100-ml. portions of ether. The combined
etheral extracts were washed with 100 ml. of water, and then dried over anhy-
drous potassium carbonate. The ether was removed, and the residue was frac-
tionated through a 10-inch, vacuum-jacketed, packed column to yield 56 g. (33%)
of IV, b.p. 66° (3 mm.), R²D 1.4481, and a tarry residue. The infrared spec-
trum of this product was identical with that of IV obtained by the hydrolysis
of III.
Dihydrojasmon (VI). — 3-Methyl-1,2-cyclopentanedione-1,1-propylene ketal (IV) may be converted into VI directly, thus avoiding the isolation of V, and with profit in yield. To an ethereal solution of n-amylmagnesium chloride, prepared from 69 g. (0.65 mole) of n-amyl chloride and 13.6 (0.56 atom) of magnesium, was added over a period of 15 min. 61 g. (0.36 mole) of IV. The mixture was stirred and refluxed for 15 min., and then poured into a mixture of 150 ml. of concentrated hydrochloric acid and crushed ice. The ethereal solution was separated, and washed successively with 75 ml. of water, 75 ml. of 1% sodium hydroxide solution, and again with 75 ml. of water, and then dried over magnesium sulfate. The ether was removed by evaporation; the residue was refluxed and stirred for 2 hr. with 120 g. of 25% sulfuric acid solution, and then steam distilled. The organic layer was separated, and the water layer was saturated with sodium chloride prior to extraction with 200 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate. The ether was removed, and the residual oil was distilled to give 1 g. of forrun, b.p. 83-85° (2 mm.), 39 g. (65%) of VI, b.p. 85-89° (2 mm.), and 2.4 g. of residue. Refractionation of the odorous material through a 10-inch, vacuum-jacketed, packed column gave 35.5 g. of VI, b.p. 86.5-88° (2 mm.), n°D1 1.4771. The infrared spectrum of this liquid was identical with that of VI obtained by dehydration of V.
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(35) Melting points are corrected and boiling points are uncorrected. Microanalyses were determined by Mr. R. L. Seab of this laboratory. Spectra were recorded on a Perkin Elmer Model 21 infrared spectrophotometer, and a Cary Model 14 ultraviolet spectrophotometer. Gas phase chromatographic analyses were performed on a Barber-Colman Model 20 gas chromatograph using a 100 ft. GE 96 capillary column.

(36) Supplied as Ketonarome by Givaudan-Delwama, Inc., New York, N. Y.

(37) Uncorrected for exaltation.
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A Novel Synthesis of Dihydrojasmine

J. L. E. Erickson and Frank E. Collins, Jr.
3-Methylcyclopent-2-en-2-ol-1-one (I), a readily available substance of natural occurrence, may be utilized in the preparation of dihydrojasmon. The synthesis is described, and confirms structure I assigned to this enol.

Dihydrojasmon (VI) was first synthesized by Steudinger and Ruzicka by a Dieckmann ring closure of the necessary dicarboxylic ester, and more recently has been prepared by several general methods. Dihydrojasmon was obtained by the catalytic hydrogenation of the well-known natural product, jasmine, and by the reduction of 2-chlorotetrahydropyrrole, a derivative of pyrethrolone obtained from pyrethin. Various methods have been described utilizing γ-hexyl-γ-methylbutyrolactone and also the closely related peraconic acid, which upon dehydration yielded dihydrojasmon. Decarboxylation of the peraconic acid has been accomplished prior to, or simultaneously with, the dehydration step. VI has also been obtained by the cyclization of 2,5-undecanenedione or its carbethoxy derivative.

In this investigation it is shown that dihydrojasmon may be synthesized from 3-methylcyclopent-2-en-2-ol-1-one (I), a readily available substance of natural occurrence which was first isolated by the dry distillation of beech wood and later was found in the exotic oil fraction of pyrroglycerine oil, and in a number of valuable wood tars. It was also obtained by the alkaline hydrolysis of spruce wood, and recently has been identified as an important component of the coffee bean. Reported syntheses of this compound include dehydration of divinyl glycol over copper at 280°, hydrolysis of the 5,5-

dichloro derivative of 2-methylcyclopentanone, and methylation of the condensation product of ethyl oxalate and ethyl glutarate, followed by decarboxylation.

There has been some controversy with regard to the correct structure of this compound. Early evidence supported the enolic structure (I). Almost 30 years later, evidence which seemed compelling was presented to show that the enol structure of the diketone was not 3-methylcyclopent-2-en-2-ol-1-one (I) as earlier reported, but the enolic structure (II). The question of structure was resolved recently by n.m.r. spectral studies of this substance which demanded the structure, 3-methylcyclopent-2-en-2-ol-1-one (I). If the enol structure of this compound is accepted, then it does not contain a double bond, which has been described as a product of ethyl chloroacetate on ketones in the presence of catalytic amounts of stannic chloride. Higher yields of cyclic ketals were reported by addition of a mixture of epichlorohydrin and ketone, dissolved in carbon tetrachloride, to a dilute solution of stannic chloride in the same solvent at 20 to 30°. Accordingly, 2-methylcyclopent-2-en-2-ol-1-one (I) was treated with a mixture of a cinnamic acid to give 2-cinnamyl-3-methylcyclopent-2-en-1-one (II), thus removing the enolic hydrogen and leaving the carboxyl group intact for further cyclization. Of the various oxides investigated, propylene oxide
proven most suitable. Thus, II reacted with propylene oxide in the presence of stannic chloride to give 2-acetoxy-3-methylcyclopent-2-en-1-one propylene ketal (III) in 53% yield. Saponification of III with 10% sodium hydroxide solution gave the unstable vinyl alcohol which reverted to 3-methyl-1,2-cyclopentanediol 1,1-propylene ketal (IV) in 80% yield.

3-Methyl-1,2-cyclopentanediol 1,1-propylene ketal (IV) is a novel and important compound, since it might very well serve as a precursor to the acquisition of many interesting natural and synthetic products, and it exhibits an interesting case of stereoisomerism. The projection formula of IV might indicate the possibility of two structural isomers, depending upon the mode of addition of propylene oxide. This is not the case, however, since the two rings are in perpendicular planes and IV has only the possibility of existing as four sets of optical enantiomers. Thus, reversing the mode of addition of propylene oxide leads only to diastereoisomers.

Upon treatment of IV with n-amylmagnesium chloride, followed by hydrolysis with ammonium chloride solution, 2-n-amyl-3-methylcyclopentan-2-01-1-one propylene ketal (V) was obtained, and its physical properties were determined. Dehydration and deketalization of V to yield dihydrojasmonate (84%) was accomplished by stirring and refluxing V with 25% sulfuric acid solution, followed by steam distillation.

The infrared spectrum of dihydrojasmonate was characterized by absorption bands at 5.85 and 5.05 µ, which were attributed to a conjugated carbonyl and a tertiary rather than a secondary hydrogen ion. The method may be extended to yield other 2-alkyl-3-methylcyclopent-2-en-1-ones.

**Experimental**

3-Methylcyclopent-2-en-2-ol-1-oac (I).—This substance was obtained as a hydride, m.p. 77-81°. Purification was accomplished by refluxing the crude material dissolved in benzene in a flask fitted with a Dean-Stark trap until the water was removed. The benzene solution was concentrated by distillation until only a small quantity of solvent remained, and the residue was recrystallized from isopropyl alcohol to give a white solid: m.p. 105.5-106.5° [lit. m.p. 105-107° (sublimed)]; u 236 µ (ε 12,000). The purity of dihydrojasmonate (97%), obtained directly from very pure IV or V, seems to be limited only by the purity of the n-amyl chloride used. There seems to be no doubt regarding the position of the C=C double bond since the acid dehydration of V to form dihydrojasmonate no doubt requires carbonium ion formation and ejection of a tertiary rather than a secondary hydrogen ion. This synthesis confirms structure I assigned to this enol.

There are two steps in the reaction sequence that may be bypassed. II may be converted to IV directly, thus avoiding the isolation of III. In doing this, however, it was found that the yield was impaired slightly and the operations involved in the isolation of IV were cumbersome owing to contaminating products accompanying the formation of the ketal. Also, the isolation of V proved entirely unnecessary and higher yields were obtained by converting IV to VI directly.

The over-all yield of dihydrojasmonate (VI) from 3-methylcyclopent-2-en-2-ol-1-one (I), based on the recommended sequence of reactions, I —> II —> III —> IV —> VI, was 20%. Obviously, the method may be extended to yield other 2-alkyl-3-methylcyclopent-2-en-1-ones.

**Acknowledgments**

(35) Melting points are corrected and boiling points are uncorrected. Microanalyses were determined by Mr. H. L. Sch, of this Laboratory. Spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer and a Cary Model 14 ultraviolet spectrophotometer. Gas-liquid chromatographic analyses were performed on a Harbor-Cahn Model 20 gas chromatograph using a 15% Apiezon L 50 capillary column.

(39) Supplied as “Kotonarmo” by Givaudan-Delbecq, Inc., New York, N. Y.

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column to yield 12 g. of forerun, b.p. 75-110° (2 mm.), and 70 g. (72%) of V: b.p. 110-111° (2 mm.); n^D 1.4590, d^4 0.9951; MR 66.52 (calcd. 67.27); and λ_max 2.80, 3.90, 6.83, 7.27, 7.60-7.70, 8.62, 9.15, 9.45, 10.27, 10.55, 10.72, and 11.42 μ.

Anal. Caled. for C_{14}H_{16}O: C, 69.38; H, 10.81. Found: C, 69.65; H, 10.50.

Dihydrojasmine (VI).—To 38 g. (0.157 mole) of 2-n-amyl-3-methylcyclopentan-2-ol-1-one propylene ketal (V) was added 100 ml. of 25% sulfuric acid solution, the resulting suspension was stirred and refluxed for 2 hr., and then the reaction mixture was steam distilled. The organic layer was separated and the water layer was saturated with sodium chloride before extraction with 200 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate, the ether was removed, and the residue was distilled to give 22 g. (84%) of dihydrojasmine: b.p. 87-88° (2 mm.); n^D 1.4771; d^4 0.9165; (37) Uncorrected for exaltation.

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INTRODUCTION

This is an investigation which involves the preparation of polymethyl-eneketene monomers, dimers, and trimers, and a study of their reactions. Only a few members of these types of compounds have been reported, so a further study and extension of this work was undertaken. No ketene monomers having rings smaller than six carbon atoms have been described, and the only ketene dimers previously synthesized are those with four, five, and six-membered rings. Two ketene trimers with five and six carbon atoms in the ring have recently been prepared in this laboratory.

Interest in this work developed from a knowledge of the reactions of dimethylketene dimer, a compound which is now readily available, and which was used initially in this work to prepare dimethylketene trimer. The reactions of this trimer then were applied to a number of similar compounds under investigation. All ketoketene dimers reported in the literature are 1,3-cyclobutanediones, with two exceptions, the α-lactone dimers of dimethylketene and diphenylketene. These lactones are not pertinent to this study.

DIMETHYLKETENE DIMER AND TRIMER

The dimer of dimethylketene, tetracarbomethyl-1,3-cyclobutanedione (I), was first prepared by Wedekind and Weisswange\(^1\) by the dehydrohalogenation of isobutyryl chloride with triethylamine. The chemistry of this interesting cyclic β-diketone has been extensively investigated by a number of investigators.

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*} \]

I

19
Dimethylketene dimer (I) underwent cleavage and decarboxylation in the presence of alkali to give diisobutyl ketone.²

The alcoholysis of the dimer (I) was accomplished in the presence of a catalytic amount of base to give esters of 2,2,4-trimethyl-3-oxovaleric acid.³

Catalytic hydrogenation of the dione (I) to give the corresponding glycol (II) was performed by Miller⁴ over Raney nickel and by Hasek, Elam, Martin, and Nations⁵ over a ruthenium catalyst.

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{CH}_3 \\
&\text{H}_3\text{C} \quad \text{OH} \\
&\text{H}_3\text{C} \quad \text{OH} 
\end{align*}
\]

Erickson and Kitchens⁶ have recently reported that dimethylketene dimer (I) underwent a base-catalyzed conversion to hexamethyl-1,3,5-cyclohexanetetraone (III), a trimer of dimethylketene.

\[
\begin{align*}
&\text{H}_3\text{C} \quad \text{OH} \\
&\text{H}_3\text{C} \quad \text{CH}_3 \\
&\text{H}_3\text{C} \quad \text{CH}_3 \\
&\text{H}_3\text{C} \quad \text{CH}_3
\end{align*}
\]

In this investigation a method was sought whereby III might be cleaved and decarboxylated to give the β-diketone, 2,4,6-tetramethyl-3,5-heptanedione (IV), a compound which has not been reported in the literature. It was found that the use of barium hydroxide gave a satisfactory yield of IV, in spite of the fact that competition of the β-diketone (IV) with the trimer

\[
(\text{CH}_3)_2\text{CH}-\text{C}-\text{C}(\text{CH}_3)_2-\text{C}-\text{CH}(\text{CH}_3)_2
\]
(III) for the base, results in cleavage of IV. Thus, the cleavage of IV was largely avoided since barium hydroxide was converted to insoluble barium carbonate as decarboxylation occurred.

The reduction of dimethylketene trimer (III) has been investigated by Ayers and Hauser,⁷ who obtained a high yield of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol (V) by catalytic reduction of III with copper chromite catalyst, and by Erickson and Kitchens,⁶ who found potassium borohydride to be a satisfactory reducing agent. V underwent dehydration and rearrangement when treated with concentrated sulfuric acid to yield a hydrocarbon, hexamethylbenzene (VI).⁷

![Diagram of dimethylketene dimer and trimer]

**DIMETHYLENEKETENE DIMER AND TRIMER**

In an attempt synthesis of dimethyleketene (VIII), Walborsky⁸ obtained from the reaction between cyclopropanecarbonyl chloride and triethylamine a solid product which acylated aniline to give cyclopropanecarbonilide. This solid was designated as an acyl quaternary ammonium salt (VII). The failure to obtain VIII was attributed to I-strain.

\[
\begin{align*}
\text{CH}_3\text{C}=\text{C}^\text{\text{-Cl}} + (\text{C}_2\text{H}_5)_3\text{N} & \rightarrow \text{CH}_3\text{C}^+\text{\text{(C}_2\text{H}_5)_3\text{Cl}^-} \\
\text{VII} & \rightarrow \text{C}=\text{O} \text{ VIII}
\end{align*}
\]

The present study revealed that a highly reactive solid was obtained from the reaction of cyclopropanecarbonyl chloride with triethylamine
reacted with aniline to give cyclopropanecarboxamidine, as reported by Walborsky. A change in reaction medium so as to obtain a higher reaction temperature did not yield any of the desired product.

The acyl quaternary ammonium salt (VII) suggested by Walborsky prompted an investigation of the literature to learn more about the reaction of an acyl halide with a tertiary amine. It was surprising to find that a very limited amount of work has been reported concerning this reaction.

The initial product from the reaction of a tertiary amine with an acyl halide was first formulated by Minunni, who worked with benzoyl chloride and pyridine, and postulated the following formula, \( \text{C}_8\text{H}_5\text{CONCl} \cdot \text{C}_2\text{H}_5\text{N} \). An identical product was isolated by Adkins and Thompson, who also extended the work by using a number of other acyl chlorides. These authors also used triethylamine in reactions of this type with such acyl halides as acetyl chloride and furanoyl chloride. A benzoylepyridinium ion, \( \text{C}_6\text{H}_5\text{CONC}_5\text{H}_4\text{Cl} \), was later postulated by von Doering, and Baumgarten obtained a high yield of cinnamoylpyridinium chloride, which he reported as a powerful acylating agent.

In view of such evidence, it appears that an acyl ammonium salt is the initial product resulting from the reaction of an acyl halide with a tertiary amine.

**Trimethyleneketene Dimer and Trimer**

The dimer of trimethyleneketene, dispiro[3.1.3.1]decane-5,10-dione (IX), has been mentioned, but not described in the chemical literature. In this study IX was prepared in 70% yield from the reaction of cyclobutanecarboxyl chloride and triethylamine at 50°. When the reaction was carried out below 25°, a precipitate was formed, presumably the acyl ammonium chloride salt. The high melting precipitate reacted with aniline to give cyclobutanecarbox-
anilide, and it dissolved in cold aqueous alkali to give a homogeneous solution, indicating no neutral organic material, such as dimer, was present in the material. The solid, suspended in refluxing benzene for 24 hours, gave trimethyleneketene dimer (IX) and triethylammonium chloride.

Assuming that an acyl ammonium salt was obtained from both cyclopropanecarbonyl chloride and cyclobutanecarbonyl chloride while only the latter gave a ketene dimer, a monomer as precursor to dimer seems to be indicated.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{Cl} + (\text{C}_2\text{H}_5)_3\text{N} & \rightarrow \text{C}_6\text{H}_5^+ (\text{C}_2\text{H}_5)_3\text{Cl}^- \\
\text{C}_6\text{H}_5\text{O} & \rightarrow \text{IX}
\end{align*}
\]

A plausible alternate route to the dimer, which would involve acylation of the acyl chloride by the acylium salt followed by an intramolecular acylation to give ketene dimer and triethylammonium chloride, would demand no additional I-strain in the cyclopropane ring and permit the formation of dimethyleneketene dimer. The failure to obtain dimethyleneketene dimer, and the fact that some heating was necessary for the formation of trimethyleneketene dimer (IX), while higher members of the cyclic acyl chlorides dehydrohalogenated readily at room temperature, suggested that I-strain was probably an important factor, so that the latter route to ketene dimer is not favored.

Trimethyleneketene dimer (IX), upon hydrolysis with 20% sodium hydroxide solution followed by steam distillation, gave a 67% yield of dicyclobutyl ketone (X). It is of interest to note that the ketone was obtained without acidification of the alkaline solution. Generally, it is necessary to acidify
the sodium salt of a β-keto acid before decarboxylation occurs.

The decarboxylation of β-keto acids has been thoroughly studied. Pedersen suggested that the reaction proceeded through a dipolar-ion tautomeric whose concentration is proportional to that of the undissociated acid.

\[
\begin{align*}
\text{CH}_3\text{-}C\text{-}C\text{(CH}_3\text{)}_2\text{-CO}_2\text{H} & \rightleftharpoons \text{CH}_3\text{-}C\text{-}C\text{(CH}_3\text{)}_2\text{CO}_2^- \\
\text{CO}_2 + \text{CH}_3\text{-}C\text{-}C\text{(CH}_3\text{)}_2 & \rightarrow \text{CH}_3\text{-}C\text{-}C\text{(CH}_3\text{)}_2
\end{align*}
\]

In the presence of strong base, it was obvious that this mechanism could not take place. Dicyclobutyl ketone (X), however, was obtained in the presence of strong base, and may be accounted for by a mechanism analogous to the one reported by Steinberger and Westheimer for the decarboxylation of dimethyl oxaloacetic acid. They found that both the monoanion and dianion took part in the reaction but found no term in the kinetic equation proportional to the concentration of the acid itself.
Trimethyleneketene dimer (IX) underwent алкоголysis when treated with ethanol containing a catalytic amount of sodium ethoxide to give ethyl 1-(cyclobutanecarbonyl)cyclobutanecarboxylate (XII) in 86% yield.

\[
\text{XI}
\]

Upon reduction of trimethyleneketene dimer (IX) with lithium aluminum hydride, an excellent yield of the glycol, dispiro[2.1.3.1]decane-5,10-diol (XII) was obtained.

\[
\text{XII}
\]

It was found in this study that dispiro 2,1,3,1 decane-5,10-dione (IX) was converted by a process similar to that of Erickson and Kitchens to trimethyleneketene trimer, trispiro[2.1.3.1.3.1]pentadecane-5,10,15-trione (XIII). This trispiro-cycloalkanetrione represents a new and unusual type of chemical structure which has not been previously reported.

\[
\text{XIII}
\]

Identification of XIII was made on the basis of elemental analyses and molecular weight determinations, which strongly suggested a trimer of trimethyleneketene. The compound was characterized by C=O absorption at 5.88 μ, a value identical to the one obtained from the infrared spectrum of dimethyl-
ketene trimer (III), prepared either by the base-catalyzed reaction of tetramethyl-1,3-cyclobutanedione (I) or by the total methylation of phloroglucinol.18

Trimethyleneketene trimer (XIII) underwent cleavage and decarboxylation when treated with barium hydroxide solution to give both 1,1-(dicyclobutane-carbonyl)cyclobutane (XIV) and dicyclobutyl ketone (X). The obtention of the \[ \text{XIV} \]

\( \beta \)-diketone (XIV) may be accounted for by the same mechanism written for the alkaline cleavage and decarboxylation of trimethyleneketene dimer (IX).

The base-catalyzed alcoholysis was found to apply to trimethyleneketene trimer (XIII) as well as trimethyleneketene dimer (IX). Thus, trispiro \( \{3,1.3.1.3.1\} \) pentadecane-5,10,15-trione (XIII) gave, with ethanol in the presence of a catalytic amount of sodium ethoxide, an excellent yield of ethyl 1-[1-(cyclobutane-carbonyl)cyclobutane-carbonyl]cyclobutane-carboxylate (XV).

\[ \text{XV} \]

The reduction of the trimer XIII was accomplished with lithium aluminum hydride to yield trispiro\( \{3,1.3.1.3.1\} \) pentadecane-5,10,15-triol (XVI). Complete reduction was evidenced in the infrared spectrum by strong absorption at 2,84-3,05 \( \mu \), and the absence of any O-O absorption around 5,70-5,93 \( \mu \).

Trispiro\( \{3,1.3.1.3.1\} \) pentadecane-5,10,15-triol (XVI) reacted violently with concentrated sulfuric acid at 0\(^\circ\) to give an intensely colored solution,
but no hydrocarbon corresponding to hexamethylbenzene (VI) was obtained. The action of 50% sulfuric acid solution on the triol (XVI), as well as the action of concentrated phosphoric acid on XVI gave a resinous material which was not the anticipated hydrocarbon.

TETRAMETHYLENEKETENE DIMER AND TRIMER

Several attempts were made to prepare the unreported tetramethyleneke­
tene monomer by dehydrohalogenation of cyclopentanecarbonyl chloride with triethylamine, but only the dimer, dispiro [4.1.4.1] dedecane-6,12-dione (XVII), was obtained. The monomer apparently dimerizes rapidly in the presence of base, thus making its isolation difficult.

\[
\text{XVII}
\]

Tetramethyleneketene dimer (XVII) was prepared\textsuperscript{19,20} and shown in this investigation to undergo cleavage and decarboxylation in the presence of aqueous alkali to give dicyclopentyl ketone (XVIII).

\[
\text{XVIII}
\]

Walborsky\textsuperscript{20} reported that tetramethyleneketene dimer (XVII) was reduced by lithium aluminum hydride to give dispiro [4.1.4.1] dedecane-6,12-diol (XIX).

\[
\text{XIX}
\]
Tetraremethylene ketene trimer (XX) was synthesized by Owen\textsuperscript{21} of this laboratory and subjected to alcoholysis and reduction. He found that the reduction product, trispiro[4.1.4.1]octadecane-6,12,18-triol (XXI) underwent dehydration and rearrangement to give dodecahydrotriphenylene (XXII).

\[ \text{XXI} \]

\[ \text{XXII} \]

PENTAMETHYLENEKETENE DIMER AND TRIMER

Hill\textsuperscript{22} prepared both pentamethyleneketene (XXIII) and its dimer, dispiro[5.1.5.1]tetradecane-7,14-dione (XXIV) by dehydrohalogenation of cyclohexanecarbonyl chloride with triethylamine.

The alkaline hydrolysis of pentamethyleneketene dimer (XXIV) has been investigated and found to give dicyclohexyl ketone (XXV).\textsuperscript{19}

\[ \text{XXIII} \]

\[ \text{XXIV} \]

\[ \text{XXV} \]

Catalytic hydrogenation of the dimer (XXIV) with Raney nickel gave the hydroxy ketone, dispiro[5.1.5.1]tetradecane-7-ol-14-one (XXVI),\textsuperscript{22} while reduction with lithium aluminum hydride yielded the glycol, dispiro[5.1.5.1]tetradecane-7,14-dione (XXVII).\textsuperscript{20}

Pentamethyleneketene trimer (XXVIII)\textsuperscript{21} has been synthesized in this laboratory and subjected to ethanolysis and reduction with lithium aluminum hydride.
HEXAMETHYLENEKETENE MONOMER AND DIMER

The only monomer reported in the polymethyleneketene series, pentamethyleneketene, (XXIII), was prepared in 32% yield by dehydrohalogenation of cyclo-hexanecarbonyl chloride with triethylamine.22

In this investigation hexamethyleneketene (XXIX) has been synthesized. Cycloheptanecarbonyl chloride, a previously undescribed compound, was prepared from the corresponding acid, which was obtained by carbonation of cycloheptylmagnesium chloride. Dehydrohalogenation of cycloheptanecarbonyl chloride with triethylamine gave hexamethyleneketene (XXIX), a yellow liquid which had an extremely pungent odor.

It is known that ketenes, which contain twinned double linkages, react with aniline to form anilides. XXIX was identified by its reaction with aniline to form cycloheptanecarbonylanilide (XXX), which was shown to be identical with the product prepared independently from cycloheptanecarbonyl chloride and aniline.

Another characteristic reaction of ketenes, which was first reported by Staudinger,23 involves cycloaddition of cyclopentadiene. Thus, hexamethyleneketene (XXIX), upon standing three days in a petroleum ethereal solution of cyclopentadiene gave 2-hexamethylenecyclo[3,2.0]hept-3-ene-1-one (XXXI) in

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40% yield. The structure was assigned by analogy to the cycloaddition prod-
duct obtained from (a) cyclopentadiene and diphenylketene$^{24}$ and (b) cyclo-
pentadiene and dimethylketene$^{25}$. The infrared spectrum of XXXI exhibited
a strong band at $5.62 \mu$, a characteristic of the C=O absorption of cyclobutane-
one.

\[
\begin{align*}
\text{XXIX} & \quad + \quad \text{C}_6\text{H}_5\text{NH}_2 \\
\rightarrow & \\
\text{XXX} & \\
\end{align*}
\]

A freshly distilled sample of hexamethyleneketene (XXIX) dimerized almost
entirely upon standing overnight to give a new cyclobutane-1,3-dione, dispiro
$[6.1.6.1]$ hexadecane-8,16-dione (XXXII). The dimer (XXXII) was identified by
elemental analyses and molecular weight determinations. The infrared spectrum
of XXXII had a C=O absorption at 5.73 $\mu$, which is typical of 1,3-cyclobutan-
diones. When dehydrohalogenation of cycloheptancarbonyl chloride took place
in refluxing benzene for 36 hr., the product isolated was nearly all dimer.

Finally, hexamethyleneketene dimer (XXXII) was reduced with lithium
aluminum hydride to give a 95% yield of dispiro $[6.1.6.1]$ hexadecane-8,16-diol
(XXXIII).
EXPERIMENTAL

The Reaction of Cyclopropanecarbonyl Chloride with Triethylamine. —

This reaction gave no dimethyleneketene monomer or dimer, but instead the acyl triethylammonium salt, a product previously obtained by Walborsky. 8

Cyclopropanecarbonyl chloride, prepared in 90% yield by the action of thionyl chloride on cyclopropanecarboxylic acid, was fractionated through a 10-inch, packed column and the fraction, b.p. 119° (lit. 27 b.p. 119-119.5°) was collected. To 45.5 g. (0.435 mole) of this acyl chloride in 150 ml. of ether was added dropwise 65.5 g. (0.65 mole) of sodium-dried triethylamine, b.p. 89.5°. During the addition an exothermic reaction occurred and a large precipitate formed. After stirring 24 hr., the solid was separated by inverted filtration, and then it was washed with three 100-ml. portions of ether. The combined ethereal extracts were washed with 200 ml. of cold 10% hydrochloric acid solution and 100 ml. of water, and then they were dried over anhydrous magnesium sulfate. The ether was removed by evaporation leaving a dark residue which upon distillation gave 5 g. of cyclopropanecarboxylic acid, the only product identified from the ether extract. No dimethyleneketene dimer was isolated.

A total of 51 g. of the acyl quaternary ammonium salt was obtained which was extremely hygroscopic and reactive. When 2 g. of the solid was added to 5 ml. of aniline, a violent reaction occurred. The aniline solution was taken up in 25 ml. of benzene and washed successively with 10% hydrochloric acid, 10% sodium carbonate solution, and water. Upon addition of an equal volume of petroleum ether to the benzene solution, which had been dried by azeotropic removal of the water, there was obtained 1.1 g. (72%) of cyclopropanecarboxanilide, m.p. 111-112° (lit. 28 m.p. 111-112°).
The Reaction of Cyclobutanecarbonyl Chloride with Triethylamine.

Cyclobutanecarbonyl chloride, prepared in 89% yield by the action of thionyl chloride on cyclobutanecarboxylic acid, was fractionated and the fraction, b.p. 137° (lit. 29 b.p. 137-139°) was collected. To 8.8 g. (0.074 mole) of this acyl chloride in 25 ml. of ether at -15° was added 9 g. (0.09 mole) of cold triethylamine; a light precipitate formed immediately. The suspension was allowed to stand 48 hr. during which time the temperature rose to room temperature. The precipitate was separated by filtration and washed with three 100-ml.-portions of ether. Care was taken to prevent air from being drawn through the solid. A total of 13.8 g. of the white precipitate was obtained, m.p. 225-230° (decomp.). The solid dissolved readily in dilute aqueous alkali indicating the absence of trimethyleneketene dimer.

Cyclobutanecarboxanilide, m.p. 113-113.5°, m.m.p. 113-113.5° (lit. 30 m.p. 112.5-113°) was obtained in 81% yield upon treatment of 3 g. of the salt with aniline.

Dispiro [3.1.3.1] decane-5,10-dione (IX), m.p. 86-87° was isolated along with triethylammonium chloride after the salt had been suspended in refluxing benzene for 24 hr.

Dispiro [3.1.3.1] decane-5,10-dione (IX). — To 103 g. (0.87 mole) of cyclobutanecarbonyl chloride, b.p. 137° in 800 ml. of a benzene-ether mixture, under an atmosphere of dry nitrogen, was added 145 g. (1.4 moles) of triethylamine and the resulting suspension was stirred and refluxed at 50° for 25 hr. The triethylammonium chloride (116 g., 97%) was removed by filtration and the filtrate was washed with 400 ml. of cold 10% hydrochloric acid solution to remove the excess amine. The filtrate was then washed with 200 ml. of water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature and the residual solid was recrystallized from a
benzene-pentane mixture to yield 50 g. (70%) of IX, m.p. 84-86°. A second re-
crystallization raised the melting point to 86-87°; \( \lambda_{\text{max}} \) \( \text{CCl}_4 \) 3.41, 5.77, 7.02,
7.92, 8.34, and 10.93 \( \mu \).

The Alkaline Hydrolysis of Dispiro [3.1.3.1] decane-5,10-dione (IX). — To
50 ml. of a 20% sodium hydroxide solution was added 5 g. (0.031 mole) of di-
spiro [3.1.3.1] decane-5,10-dione (IX), and the resulting suspension was re-
fluxed 0.5 hr. then steam distilled. The distillate was extracted with 10 ml.
of benzene. The organic layer was separated and dried by azeotropic removal
of the water. After removal of the benzene by distillation, the odorous resi-
due was distilled to give 2.8 g. (67%) of dicyclobutyl ketone (X), b.p. 201-
202°, \( n^\text{D}^25 \) 1.4682 (lit.\(^3\) b.p. 201°, \( n^\text{D}^25 \) 1.4678).

Ethyl 1-(cyclobutanecarbonyl)cyclobutanecarboxylate (XI). — To a solu-
tion of 12 ml. of absolute ethanol containing 0.03 g. of sodium ethoxide was
added in small portions 5 g. (0.031 mole) of dispiro [3.1.3.1] decane-5,10-
dione (IX), which dissolved immediately with evolution of heat. The solution
was acidified with 0.2 ml. of glacial acetic acid, and the solvent was re-
moved under reduced pressure. The colorless residue was distilled to yield
5.5 g. (86%) of XI, b.p. 99.5° (2 mm.), \( n^\text{D}^25 \) 1.4646, \( d_4^\text{25} \) 1.0419, MFD 55.73
(calcd. 55.84); \( \lambda_{\text{max}} \) \( \text{CCl}_4 \) 3.38, 3.47, 5.75, 5.85, 6.92, 7.32, 7.40, 7.87, 8.03,
8.22, 8.53, 8.95, 9.85, and 10.32 \( \mu \).

Anal. Calcd. for C\(_{12}\)H\(_{18}\)O\(_3\): C, 68.54; H, 8.63. Found: 68.26, 68.28;
H, 8.75, 8.71.

Dispiro [3.1.3.1] decane-5,10-diol (XII). — A solution of 0.5 g. (0.00424
mole) of dispiro [3.1.3.1] decane-5,10-dione (IX) in 25 ml. of ether was slowly
added to a slurry of 0.241 g. (0.00636 mole) of lithium aluminum hydride in
25 ml. of ether, and the suspension was stirred for 1 hr. Excess lithium
aluminum hydride was destroyed with ethyl acetate, followed by addition of
25 ml. of cold 10% sulfuric acid solution. The ether layer was separated and washed with 5% sodium carbonate, then it was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure leaving 0.51 g. of a residue. Recrystallization of the material from benzene gave 0.46 g. (89%) of XII, m.p. 99.5-101°; \( \lambda_{\text{max}} \) 2.95, 3.40, 6.98, 7.13, 7.75, 8.06, 8.93, 9.13, 9.50, and 9.78 µ. Recrystallization of the material from benzene gave 0.46 g. (89%) of XII, m.p. 99.5-101°; \( \lambda_{\text{max}} \) 2.95, 3.40, 6.98, 7.13, 7.75, 8.06, 8.93, 9.13, 9.50, and 9.78 µ.

**Anal.** Calcd. for C\textsubscript{10}H\textsubscript{16}O\textsubscript{2}: C, 71.39; H, 9.59. Found: C, 70.89, 70.91; H, 9.61, 9.61.

**Trispiro [3.1.3.1.3]pentadecane-5,10,15-trione (XIII).** — To 16.4 g. (0.1 mole) of dispiro [3.1.3.1] decane-5,10-dione (IX) dissolved in 20 ml. of toluene was added 0.12 g. of sodium methoxide and the suspension was stirred and heated rapidly to reflux, at which time a vigorous reaction occurred that lasted 5 min. Heating was continued for 1 hr. during which time three 0.06 g. portions of catalyst were added. The reaction mixture was cooled to room temperature, then the toluene solution was carefully decanted from the catalyst into a distillation flask. The toluene was removed under reduced pressure and the residue was distilled to yield 11.1 g. (68%) of XIII, b.p. 139-140° (2 mm.); \( \lambda_{\text{max}} \) 3.38, 5.88, 6.97, 7.70, 8.03, 8.58, 8.74, 9.74, 10.27, and 10.65 µ.

**Anal.** Calcd. for C\textsubscript{15}H\textsubscript{13}O\textsubscript{3}: C, 73.14; H, 7.37; mol. wt. 246.3. Found: C, 73.21, 73.17; H, 7.55, 7.54; mol. wt. (benzene) 238.

**The Alkaline Hydrolysis of Dimethylketene Trimer (III).** — To 15.8 g. (0.075 mole) of III, m.p. 81-82° suspended in 50 ml. of water at 80° was added dropwise with vigorous stirring 7.4 g. (0.0375 mole) of barium hydroxide dissolved in 426 ml. of water. The suspension was stirred 15 min. then cooled to room temperature. The barium hydroxide (7 g.) was separated by filtration and the filtrate was extracted with 50 ml. of benzene. Drying was accomplished by azeotropic removal of the water at atmospheric pressure and the
residue was distilled to yield 7.7 g. (56%) of 2,4,4,6-tetramethylheptane-3,5-dione (IV), b.p. 95-100° (10 mm.), which was collected in three fractions. The principal fraction, b.p. 95-97° (10 mm.) was redistilled at atmospheric pressure, b.p. 212-214°, n25D 1.4356. Infrared spectrum: \( \lambda_{\text{max}} \) 3.36, 3.45, 5.82, 6.78, 7.22, 7.30, 7.92, 8.12, 8.14, 8.52, 9.27, 9.47, 9.67, 9.84, 10.03, and 11.41 μ. The product was shown to be 95% pure by vapor phase chromatographic analysis.

**Anal.** Calcd. for C11H20O2: C, 71.70; H, 10.94. Found: C, 70.84, 70.72; H, 10.79, 10.89.

The Alkaline Hydrolysis of Trispiro[3.1.3.1.3.1]pentedecane-5,10,15-trione (XIII). — To 7.4 g. (0.03 mole) of trispiro[3.1.3.1.3.1]pentedecane-5,10,15-trione (XIII) at 80° was added dropwise with vigorous stirring 3 g. (0.0165 mole) of barium hydroxide dissolved in 187 ml. of water. The stirring and heating were continued until the reaction mixture was neutral to litmus paper. The precipitate (2.5 g.) that formed was separated by filtration and the filtrate was extracted with 50 ml. of benzene. Drying was accomplished by azeotropic removal of the water. The last traces of benzene were removed at 3 mm. pressure leaving 5.3 g. of a clear residual oil which was fractionated to yield 1 g. of dicyclobutyl ketone (X), b.p. 56-58° (3 mm.), n25D 1.4713, semicarbazone 129.5-130° (lit. 31 b.p. 201°, n21D 1.4678, semicarbazone 129-130°), 2.5 g. (38%) of 1,1-(dicyclobutanecarbonyl)cyclobutane (XIV), b.p. 129-135° (3 mm.), n25D 1.4994, and 1.6 g. of material, b.p. 135-139° (3 mm.). Redistillation of the second fraction to obtain an analytical sample gave 1.6 g., b.p. 130-134° (3 mm.), n25D 1.4986, NMR 61.10 (calcd. 61.71); \( \lambda_{\text{max}} \) 3.37, 3.47, 5.88, 6.92, 7.39, 7.68, 8.03, 8.19, 8.60, 9.02, 10.27, 10.33, 10.70, and 11.10 μ.

**Anal.** Calcd. for C14H20O2: C, 76.32; H, 9.15. Found: C, 75.88, 75.82; H, 9.15, 9.07.

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Ethyl 1-(cyclobutanecarbonyl)cyclobutanecarbonyl)cyclobutanecarboxylate (XV). — To a solution of 12 ml. of absolute ethanol containing 0.03 g. of sodium ethoxide was added 3 g. (0.0122 mole) of trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (XIII). The trione dissolved slowly with slight evolution of heat. After 0.5 hr., the solution was acidified with 0.2 ml. of glacial acetic acid, and the excess alcohol was removed under reduced pressure to yield a residue which upon distillation gave 3.1 g. (85%) of a clear viscous liquid, b. p. 148-149° (2 mm.); \( \eta^\text{max} \) 3.38, 3.46, 5.72, 5.92, 6.93, 7.33, 7.40, 7.77, 8.04, 8.23, 8.36, 8.65, 9.07, 9.77, and 10.38 \( \mu \).

Anal. Calcd. for C_{17}H_{24}O_3: C, 69.83; H, 8.27. Found: C, 70.00, 69.94; H, 8.29, 8.23.

The Reduction of Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (XIII). — A solution of 1.3 g. (0.00528 mole) of XIII in 75 ml. of ether was added dropwise to a stirred slurry of 0.5 g. (0.0132 mole) of lithium aluminum hydride, and the resulting suspension was stirred 1.5 hr. The excess lithium aluminum hydride was destroyed with ethyl acetate, followed by addition of 25 ml. of cold 10% sulfuric acid solution. The ethereal solution was separated, washed with 5% sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The ether was removed by evaporation and the residue recrystallized from benzene to give 0.7 g. (54%) of trispiro[3.1.3.1.3.1]pentadecane-5,10,15-triol (XVI), m.p. 185.5-187°, m.p. 191-192.5 (from methanol); \( \eta^\text{max} \) 2.86, 3.02, 3.24, 3.40, 7.00, 7.60, 7.75, 8.06, 8.84, 9.10, 9.63, and 10.27 \( \mu \).

Anal. Calcd. for C_{15}H_{24}O_3: C, 71.36; H, 9.59. Found: C, 71.01, 70.67; H, 9.69, 9.61.
Dehydration of Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-triol (XVI). — To 10 ml. of sulfuric acid at 0° was added in small portions 0.2 g. of XVI. Upon each addition a vigorous reaction occurred and the solution became intensely colored. The mixture was allowed to stand 30 hr. then it was extracted with 50 ml. of pentane, which upon evaporation, gave no residue. The acid solution was poured into 50 g. of ice then it was steam distilled, however, no volatile material was present. A resinous material remained in the pot.

Experiments were conducted with 50% sulfuric acid solution, and also with concentrated phosphoric acid, but no material obtained could be identified.

Attempted Synthesis of Tetramethyleneketene. — To 44.4 g. (0.44 mole) of triethylamine in 100 ml. of ether was added dropwise 53 g. (0.4 mole) of cyclopentanecarbonyl chloride, b.p. 161° (lit.29 b.p. 160°) dissolved in 100 ml. of ether. The suspension was allowed to stand at room temperature for 16 hr. The precipitate was separated by inverted filtration. The ether was removed by distillation at reduced pressure and the residue was heated to 100° at 10 mm. pressure but no volatile material was obtained. The residue from the distillation was combined with the precipitate then washed with ether and filtered to give 60 g. (110%) of triethylammonium chloride. Upon evaporation of the ether, 13 g. (34%) of tetramethyleneketene dimer (XVII), m.p. 73-75° was obtained. Recrystallization of the dimer from pentane raised the melting point to 76-77° (lit.19 m.p. 74-75°; lit.20 m.p. 70-70.5°).

The Alkaline Hydrolysis of Tetramethyleneketene Dimer (XVII). — To 50 ml. of 20% sodium hydroxide solution was added 5 g. (0.026 mole) of XVII, and the resulting suspension was refluxed 0.5 hr., then steam distilled. The distillate was extracted with 10 ml. of benzene. After removal of the benzene by distillation, the residue was distilled to give 3.1 g. (72%) of dicyclopentyl ketone (XVIII), b.p. 244-246°, n^25D 1.4768 (lit.32 b.p. 113-116° (14 mm.),
Vapor phase chromatographic analysis indicated a very pure compound.

**Hexamethyleneketene (XXIX).** — An ethereal solution of cycloheptylmagnesium chloride, prepared from 100 g. of cycloheptyl chloride and 18.5 g. of magnesium, was carbonated to give 90.5 g. (85%) of cycloheptanecarboxylic acid, b.p. 136-137° (9 mm.), \( n^0 1.4704 \) (lit. \( n^0 1.4710 \); lit. \( n^0 1.4730 \)). Treatment of this acid with 120 g. of thionyl chloride gave 97.7 g. (96%) of cycloheptanecarbonyl chloride, b.p. 85-86° (9 mm.).

To 16 g. (0.1 mole) of cycloheptanecarbonyl chloride, b.p. 85-86° (9 mm.) in 200 ml. of dry ether was added rapidly 15.2 g. (0.15 mole) of triethylamine and the resulting suspension was stirred and refluxed for 8 hr. The precipitated triethylammonium chloride was separated by inverted filtration under an atmosphere of dry nitrogen, and the ethereal solution was concentrated to 25 ml. by distillation through a packed column, during which time an additional amount of the hydrochloride formed making a total of 13 g. (95%). The liquid residue was carefully transferred to a distillation flask where it was rapidly distilled at 10 mm. pressure to yield 5.4 g. (45%) of the yellow hexamethyleneketene monomer (XXIX), which was redistilled, b.p. 59° (20 mm.).

**The Reaction of Hexamethyleneketene (XXIX) with Aniline.** — To 1 ml. of aniline in 30 ml. of ether was added slowly 0.4 g. (0.0032 mole) of hexamethyleneketene (XXIX). A vigorous reaction occurred and the yellow color disappeared immediately. The ether was removed by evaporation and the solid residue was recrystallized from a benzene-pentane mixture to give 0.5 g. (67%) of cycloheptanecarboxanilide (XXX), m.p. 139.5-140.5°.

An authentic sample of the previously unreported cycloheptanecarboxanilide was prepared by treating pure cycloheptanecarbonyl chloride with an ethereal...
solution of aniline, evaporating the ether, and recrystallizing the anilide from a benzene-pentane mixture. The cycloheptanecarboxanilide thus obtained melted at 139.5-140°. A mixed melting point of this anilide and that formed from the reaction of XXIX with aniline showed no depression.

**Anal.** Calcd. for C_{16}H_{19}NO: C, 77.38; H, 8.81. Found: C, 77.26, 77.35; H, 8.90, 8.85.

**Reaction of Hexamethyleneketene (XXIX) with Cyclopentadiene.** — To 0.9 g. (0.0072 mole) of hexamethyleneketene (XXIX) in 20 ml. of petroleum ether, b.p. 40° was added 1.7 g. (0.026 mole) of freshly distilled cyclopentadiene, b.p. 41°. The solution was mixed thoroughly and allowed to stand 3 days, by which time the yellow color had dissipated. The solvent was removed by distillation at atmospheric pressure and the oily residue was fractionated to give 0.2 g. of dicyclopentadiene, b.p. 43.5° (4 mm.), 0.6 g. (40%) of 2-hexamethylenebicyclo[2.2.0]hept-3-en-1-one (XXXI), b.p. 127-129° (4 mm.), and 0.2 g. of residue. The infrared spectrum of the second fraction was characterized by a strong band at 5.62 μ which is typical of the carbonyl absorption of cyclobutanones.

**Anal.** Calcd. for C_{13}H_{18}O: C, 82.06; H, 9.52. Found: C, 80.81, 80.79; H, 9.54, 9.55.

**Dimerization of Hexamethyleneketene (XXIX).** — **Procedure A.** By Dehydrohalogenation of Cycloheptanecarbonyl Chloride. To 56 g. (0.35 mole) of cycloheptanecarbonyl chloride, b.p. 85-86° (9 mm.) in 500 ml. of dry benzene was added slowly 54 g. (0.53 mole) of triethylamine and the resulting suspension was stirred and refluxed 36 hr., and then allowed to stand overnight at room temperature. The triethylammonium chloride was separated by filtration and the benzene along with the remaining triethylamine were removed under reduced pressure leaving a yellow residue, most of which was crystalline. The crystalline material was separated by filtration, and washed with 25 ml. of ether.
It was recrystallized from methanol to give 18.5 g. of dispiro[6.1.6.1]hexadecane-8,16-dione (XXXII), m.p. 143.5-145°. The filtrate was combined with the ether washing, and was distilled to yield 1.3 g. (3%) of hexamethyleneketene (XXIX), b.p. 60° (20 mm.) and 15.4 g. of a solid residue. Recrystallization of the residue from methanol gave 6.7 g. of XXXII, m.p. 143-145°, making a total of 25.2 g. (88%) of dimer (XXXII). Recrystallization of the dimer, obtained from both steps, from methanol gave 25 g. of white crystals, m.p. 144.2-145°; \( \lambda_{\text{max}} ^{\text{CCl}_4} 3.39, 3.43, 5.73, 6.83, 6.89, 7.38, 8.04, 8.65, 9.05, \) and 10.83 μ.

**Anal.** Calcd. for C₁₆H₂₄O₂: C, 77.37; H, 9.74, mol. wt., 248.35. Found: C, 77.18, 77.13; H, 9.89, 9.82; mol. wt. (benzene) 222.

**Procedure B.** From Hexamethyleneketene. A 2 g. sample of freshly distilled hexamethyleneketene, upon standing overnight, almost completely solidified. A portion of the solid was taken up in pentane and recrystallized to yield a white solid, m.p. 139-142°, m.p. 144-145° (from methanol). When mixed with authentic dispiro[6.1.6.1]hexadecane-8,16-dione (XXXII), the melting point was not depressed. The yellow color, present in the 2 g. sample, did not completely disappear for two weeks.

**The Reduction of Dispiro 6.1.6.1 hexadecane-8,16-dione (XXXII).** — To 0.38 g. (0.009 mole) of lithium aluminum hydride suspended in 100 ml. of ether was added dropwise with stirring 1.45 g. (0.00585 mole) of dispiro[6.1.6.1]hexadecane-8,16-dione (XXXII) and the resulting suspension was stirred for 2 hr. The excess lithium aluminum hydride was destroyed with ethyl acetate and hydrolysis was accomplished by addition of 40 ml. of 10% sulfuric acid solution. The ether layer was separated and washed successively with water, 10% sodium bicarbonate solution, and again with water; it was dried over magnesium sulfate. Upon removal of the ether by evaporation, a white solid
was obtained which was recrystallized from benzene to yield 1.4 g. (95%) of
dispiro[6.1.6.1]hexadecane-8,16-diol (XXXIII), m.p. 148-150.5°; $\lambda_{\text{max}}^{\text{CCl}_4} 2.74, 

Anal. Calcd. for C_{16}H_{28}O_2: C, 76.14; H, 11.18. Found: 76.23
76.01; H, 11.29, 11.14.
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SUMMARY

3-Methylcyclopent-2-en-2-ol-1-one, a readily available substance of natural occurrence, was utilized as a starting material for the synthesis of the well known dihydrojasmonone. The obtention of dihydrojasmonone confirmed the enol structure assigned to 3-methylcyclopentano-1,2-dione.

Hexamethyl-1,3,5-cyclohexanetrione gave upon hydrolysis with barium hydroxide 2,4,4,6-tetramethylheptane-1,3-dione, thus introducing a new method of preparation of highly substituted \( \beta \)-diketones.

The acyl quaternary ammonium salts formed from the reaction of (a) cyclopropanecarbonyl chloride and triethylamine and (b) cyclobutanecarbonyl chloride and triethylamine were isolated and treated with aniline to give the corresponding anilides. The latter salt yielded trimethylene ketene dimer when heated in benzene.

Trimethylene ketene dimer was cleaved and decarboxylated to give dicyclobutyl ketone, cleaved with ethanol to give a \( \beta \)-keto ester, and reduced by lithium aluminum hydride to yield the corresponding glycol.

Trimethylene ketene trimer was obtained from trimethylene ketene dimer by a base-catalyzed process, then subjected to hydrolysis, ethanolysis and reduction.

An attempted synthesis of tetramethylene ketene gave only tetramethylene ketene dimer which underwent cleavage and decarboxylation in alkali to give dicyclopentyl ketone.

Hexamethylene ketene was prepared. The polymethylene ketene monomer yielded an anilide with aniline and gave a cycloaddition product with cyclopentadiene. Upon standing, hexamethylene ketene dimerized to give a new 1,3-cyclobutanedione, which was reduced to the corresponding glycol with lithium aluminum hydride.
VITA
Frank E. Collins, Jr., the son of Mr. and Mrs. Frank E. Collins of Jonesville, Louisiana, was born in Silsbee, Texas on September 19, 1939. He received both his primary and secondary education in the public schools of Jonesville, Louisiana.

He entered Northeast Louisiana State College in June, 1957. While at Northeast, he received the Lewis C. Slater Chemistry Award for being the most outstanding senior in chemistry and was named to Who's Who in American Colleges and Universities. He completed requirements for the B.S. degree in January, 1961.

On the following day, he entered the Graduate School of Louisiana State University where he received a Graduate Teaching Assistantship and worked under the direction of Professor J. L. E. Erickson until he received the degree of Master of Science in Chemistry in January, 1963. Continuing his work under Professor Erickson at Louisiana State University, he was the recipient of a University Research Assistantship, a Monsanto Fellowship for the summer session of 1964, and the Cities Service Honor Fellowship. He was also selected for membership in the Alpha Mu Chapter of the Phi Lambda Upsilon honorary chemical society and became a member of the American Chemical Society. He is now a candidate for the degree of Doctor of Philosophy in Chemistry.
EXAMINATION AND THESIS REPORT

Candidate: Frank E. Collins, Jr.
Major Field: Chemistry
Part II. Polymethyleneketene Dimers and Trimers.
Approved:

J. L. E. Ericsson
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Virginia E. Williams
Paul E. Karrig
Robert V. Nauman

Date of Examination:
July 22, 1965

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