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THE SYNTHESSES OF NEOPENTYLEBENZENE AND
CIS- AND TRANS-1,2-DINEOPENTYLETHYLENES

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Narinder Gill, B. Sc. (Hons.), M. Sc. (Hons.)

* * * * * * *

The Ohio State University
1965

Approved by

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Adviser
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ACKNOWLEDGMENTS

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PUBLICATIONS


FIELD OF STUDY

Major Field: Organic Chemistry
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PART I

SYNTHESIS OF NEOPENTYLBENZENE
INTRODUCTION AND OBJECTIVE OF THE PRESENT WORK

Molecular complexes of benzene

Molecular complexes of aromatic compounds are well known. In these complexes the aromatic moiety shares its \( \pi \) electrons with suitable electron acceptors and the process is believed to involve a loose coordinate linkage between the entire \( \pi \) system of the donor and the vacant orbital of the electron deficient acceptor. This type of interaction between a benzene molecule and an electron acceptor, A, can be depicted\(^1\) as follows.

\[ \begin{array}{c}
\text{Benzene}^+ \\
A^- 
\end{array} \]


Alkyl derivatives of benzene and naphthalene and several other aromatic hydrocarbons are known to function as Lewis bases in forming molecular complexes. Silver-ion, iodine, iodine monochloride, aluminum bromide, s-tri-nitrobenzene, 2,4,7-trinitrofluorenone and tetracyanoethylene may be mentioned among others as examples of electron deficient species which function as electron acceptors in these complexes.\(^2,3,4\)


\(^4\)G. Briegleb, "Elektronen-Donator-Acceptor Komplexe" (Heidelberg: Springer-Verlag, 1961).
The precise geometrical configurations of these complexes are unknown. The question as to whether complex formation involves symmetrical orientation of the electron acceptor with respect to all six nuclear carbons or not is yet to be answered. To obtain more information about the geometrical requirement for molecular complex formation, the following hydrocarbons were desired.

These compounds were chosen for the following reason. Examination of molecular models showed that in II and III the bulky part of the neopentyl substituents (the t-butyl groups) can lie on the same side of the benzene ring without interfering with each other. In this structure one side of the benzene ring is protected from attack by an acceptor, while the other is unhindered. The entire $\pi$ system of one side is available to complex with reagents. However, in I the t-butyl groups of the neopentyl radicals would have to lie on opposite sides of the plane of the benzene ring. Consequently in this conformation both sides of the benzene ring are partially screened and only a portion of the $\pi$ system on either side is available for coordination with the complexing reagent.

It followed from these models that if a $\pi$ complexing reagent needs to be fairly symmetrically oriented with regard to the six carbon
atoms of the benzene ring, then a complex would be expected with II and III only and not with I. On the other hand if a less symmetrical orientation would suffice for the acceptor, then complexing should be possible with I, II, and III. Hence a study of complex formation by various electron acceptors with these three dinesopentylbenzenes should afford some indication of the ability of the electron acceptors to complex with only a part of the aromatic \( \pi \) system.

Since I, II, and III were unknown at the start of this work, a route to the synthesis of neopentyl methylated benzenes was needed. One route to the substituted neopentylbenzenes would be the replacement of the halogen of the appropriate benzyl halides by t-butyl groups. This route was attractive in view of the easy accessibility of the benzyl halides through halomethylation of the corresponding tetramethyl benzenes. A survey of the literature revealed that the Grignard reagent from benzyl chloride reacts with t-butyl bromide to afford neopentyl benzene.\(^5\) This

\(^{5}\) A. Bygden, *Ber.* **45**, 3479 (1912).

method has been frequently used for the synthesis of neopentylbenzene, and a yield of 57% has been reported.\(^6\) Extension of this step, however, for the synthesis of substituted neopentylbenzenes was thought not promising for the following reason. The Grignard reagent in these cases constitutes a benzyl anion flanked by two ortho substituents. Nucleophilic substitution by such a species would mean a very crowded transition state with severe interaction between the ortho substituents of the

Grignard reagent and the methyl groups of the tertiary halide. Such a reaction was deemed unlikely to succeed.

Two new routes for the conversion of a halomethyl group into a neopentyl group were investigated in this laboratory. This thesis is concerned with one of them, which involved the reaction sequence described in Chart A. The synthesis of neopentylbenzene was undertaken to become familiar with the reagents and techniques of this proposed route. The syntheses of substituted neopentylbenzenes were to be attempted later after ascertaining the feasibility of this route.

The model compound, neopentylbenzene, was successfully synthesized in 29% overall yield from benzyl chloride. No attempt was made to extend the present route for the syntheses of substituted neopentylbenzenes, since benzyl halides having two alkyl ortho substituents were found to afford Grignard reagents only in traces even when a high dilution technique was employed.

---

7 Dr. G. Axelrad of this laboratory observed that only a coupled product was formed even when a high dilution technique was employed to prepare the Grignard reagent of 1,2,4,5-tetramethyl benzyl chloride.

8 D. C. Rowland, K. Greenlee, Cecil E. Boord, unpublished work.

---

While the present work was in progress the syntheses of hydrocarbons I, II and III were accomplished by an alternate route and hence the present work was restricted to the synthesis of neopentylbenzene.

---

CHART A

\[ \text{(1) Mg, Et}_2\text{O} \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \overset{\text{(1) Mg, Et}_2\text{O}}{\rightarrow} \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}\text{(COOEt)}_2 \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}_{\text{COOH}} \overset{\text{VI}}{\rightarrow} \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}_{\text{COOH}} \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}_{\text{COOH}} \overset{\text{Pd-BaSO}_4, \text{H}_2}{\rightarrow} \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}_{\text{CHO}} \]

\[ \Delta \text{Pd-C} \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{C}\text{(CH}_3\text{)}_2\text{CH}_{\text{CHO}} \overset{\Delta \text{Pd-C}}{\rightarrow} \text{CH}_3\text{C} \text{CH}_3 \]

\[ \text{CH}_2\text{CH}_3 \]

\[ \text{IX} \]
DISCUSSION OF RESULTS

The Grignard reagent prepared from benzyl chloride was added to the ethyl isopropylidenemalonate in presence of cuprous chloride to obtain diethyl (α,α-dimethylphenethyl)-malonate, IV, in 54% yield. No increase in the yield of IV was observed by inverse addition. Considerable amount of dark brown viscous material was formed as a by-product in both cases. Formation of by-products has also been observed in the reaction between methyl magnesium iodide and ethyl isopropylidenemalonate, where the condensation proceeded only to the extent of 37%.10 The NMR spectrum of IV was in agreement with its structure.

NMR Spectrum of IV:

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant $J$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.083</td>
<td>Singlet</td>
<td>6</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>1.20</td>
<td>Triplet</td>
<td>6</td>
<td>$J_{be} = 7$ cps</td>
<td>b</td>
</tr>
<tr>
<td>2.83</td>
<td>Singlet</td>
<td>2</td>
<td>--</td>
<td>c</td>
</tr>
<tr>
<td>3.20</td>
<td>Singlet</td>
<td>1</td>
<td>--</td>
<td>d</td>
</tr>
<tr>
<td>4.11</td>
<td>Quartet</td>
<td>4</td>
<td>$J_{be} = 7$ cps</td>
<td>e</td>
</tr>
<tr>
<td>7.16</td>
<td>Singlet</td>
<td>5</td>
<td>--</td>
<td>f</td>
</tr>
</tbody>
</table>

Alkaline saponification of IV afforded (α,α-dimethyl phenethyl) malonic acid, V, in 90% yield. In one instance, when the product of alkaline saponification of IV was neutralized by adding hydrochloric acid to the alkali solution a mono potassium salt was obtained. On heating, this salt decarboxylated to yield the potassium salt of the monoacid, VI, which on dissolving in water and addition of acid afforded the monoacid, VI.

The structure of the diacid, V, was confirmed by its NMR spectrum.

**NMR Spectrum of V: (d^6-DMSO)**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.083</td>
<td>Singlet</td>
<td>6</td>
<td>- C - CH₃</td>
</tr>
<tr>
<td>2.83</td>
<td>Singlet</td>
<td>2</td>
<td>C₆H₅ - CH₂ -</td>
</tr>
<tr>
<td>3.15</td>
<td>Singlet</td>
<td>1</td>
<td>- C - H</td>
</tr>
<tr>
<td>7.24</td>
<td>Singlet</td>
<td>5</td>
<td>Aromatic Protons</td>
</tr>
<tr>
<td>10.20</td>
<td>Broad Doublet</td>
<td>2</td>
<td>O</td>
</tr>
</tbody>
</table>

In acetone the carboxylic proton resonates as a sharp singlet. However, in dimethylsulfoxide-D₆ the carboxylic proton resonance appeared as a broad doublet centered at $\delta = 10.20$ ppm. These observations can be rationalized as follows. In dimethylsulfoxide-D₆ the rate of proton exchange is significantly reduced to permit observation of coupling between carboxylic and methine protons, whereas in acetone rapid proton exchange causes spin decoupling of carboxylic and methine protons and hence only a sharp singlet was observed.
The diacid, V, on heating above its melting point (bath temp. 175°-177°) underwent decarboxylation smoothly and afforded 4-phenyl-3,3-dimethyl butyric acid, VI, in almost quantitative yield. The structure of VI was in agreement with its NMR spectrum.

NMR Spectrum of VI:

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$(ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.037</td>
<td>Singlet</td>
<td>6</td>
<td>$-C-CH_3$</td>
</tr>
<tr>
<td>2.20$^{12}$</td>
<td>Singlet</td>
<td>2</td>
<td>$CH_2-O-C-O$</td>
</tr>
<tr>
<td>2.66$^{12}$</td>
<td>Singlet</td>
<td>2</td>
<td>$CH_2-C_6H_5$</td>
</tr>
<tr>
<td>7.16</td>
<td>Singlet</td>
<td>5</td>
<td>Aromatic Protons</td>
</tr>
<tr>
<td>12.03</td>
<td>Singlet</td>
<td>1</td>
<td>$O-H$</td>
</tr>
</tbody>
</table>

$^{12}$By using Shoolery's shielding constants, the calculated $\delta$ values of the methylene protons adjacent to the carboxylic group and methylene protons adjacent to the phenyl group were 2.25 and 2.55 ppm, respectively.


Decarboxylation of the acid, VI, to neopentylbenzene could not be effected thermally even when catalyst was used. The desired decarboxylation was, however, achieved by converting the carboxyl group to an aldehydic function via the acid chloride, VII, and decarbonylating$^{14}$

thermally the resulting aldehyde, VIII. This two-step sequence offers a useful route for decarboxylation of acids that cannot be thermally decarboxylated.

The acid chloride, 4-phenyl-3,3-dimethyl butyroyl chloride, VII, was prepared in 91% yield by reacting VI with thionyl chloride.

**NMR Spectrum of VII:**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.933</td>
<td>Singlet</td>
<td>6</td>
<td>- C - CH₃</td>
</tr>
<tr>
<td>2.33</td>
<td>Singlet</td>
<td>2</td>
<td>- CH₂ - C - Cl</td>
</tr>
<tr>
<td>2.68</td>
<td>Singlet</td>
<td>2</td>
<td>- CH₂ - C₆H₅</td>
</tr>
<tr>
<td>7.28</td>
<td>Multiplet</td>
<td>5</td>
<td>Aromatic Protons</td>
</tr>
<tr>
<td>7.94</td>
<td>Multiplet</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reduction of the acid chloride, VII, to 4-phenyl-3,3-dimethyl butyraldehyde, VIII, was effected with hydrogen and 5% palladium on barium sulfate. This reduction, as indicated by the evolution of hydrogen chloride, occurred at 90 to 95°. The yields were generally in the range of 70 to 77%. The maximum yield (77%) of VIII was obtained only when the catalyst was freed from traces of moisture by drying at 76° under vacuum for eight hours before use. A small amount of the acid, VI, was always present in the reaction product. The origin of the acid is uncertain. It could have been formed either by oxidation of the aldehyde, VIII, or by hydrolysis of the acid chloride, VII, by traces of moisture present in the system (in hydrogen, nitrogen or the catalyst used). Attempts were made to determine whether decarboxylation of VIII occurred during the
course of the reaction. Samples of the effluent gas were withdrawn at different intervals of time and analyzed by gas chromatography. No trace of carbon monoxide was detected in any run, indicating that no decarbonylation of the aldehyde occurred during the course of the reaction. The aldehyde, VIII, was characterized through its 2,4-DNPH derivative. The NMR spectrum indicated the presence of only one of the two possible geometrical isomers in the derivative. The "syn" structure, X was assigned to this compound on steric grounds.
**NMR Spectrum of X:**

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant $J$ (cps)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>Singlet</td>
<td>6</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>2.24</td>
<td>Doublet</td>
<td>2</td>
<td>$J_{bf} = 6.2$</td>
<td>b</td>
</tr>
<tr>
<td>2.60</td>
<td>Singlet</td>
<td>2</td>
<td>--</td>
<td>c</td>
</tr>
<tr>
<td>7.26</td>
<td>Singlet</td>
<td>5</td>
<td>--</td>
<td>d</td>
</tr>
<tr>
<td>7.85</td>
<td>Doublet</td>
<td>1</td>
<td>$J_{eg} = 9.7$</td>
<td>e</td>
</tr>
<tr>
<td>8.20</td>
<td>Triplet</td>
<td>1</td>
<td>$J_{bf} = 6.2$</td>
<td>f</td>
</tr>
<tr>
<td>8.34</td>
<td>Quartet</td>
<td>1</td>
<td>$J_{eg} = 9.7 \quad J_{gh} = 2.5$</td>
<td>g</td>
</tr>
<tr>
<td>8.86</td>
<td>Doublet</td>
<td>1</td>
<td>$J_{gh} = 2.5$</td>
<td>h</td>
</tr>
<tr>
<td>11.45</td>
<td>Singlet</td>
<td>1</td>
<td>--</td>
<td>i</td>
</tr>
</tbody>
</table>
Decarbonylation of VIII at 220° with 10% palladium on charcoal afforded neopentylbenzene, IX, in 90% yield. Addition of a small amount of soft-glass powder facilitated decarbonylation, when the gas evolution became sluggish toward the end of the reaction. The boiling point 186.0-187.5° and the characteristic I.R. absorption at 8.05, 12.95 and 13.90 μ agree well with the values reported in the literature.15 The


NMR spectrum of IX agreed well with its structure.

NMR Spectrum of IX:

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.891</td>
<td>Singlet</td>
<td>9</td>
<td>- C - CH₃</td>
</tr>
<tr>
<td>2.43</td>
<td>Singlet</td>
<td>2</td>
<td>- CH₂ - C₆H₅</td>
</tr>
<tr>
<td>7.11</td>
<td>Multiplet (closely spaced)</td>
<td>5</td>
<td>Aromatic Protons</td>
</tr>
</tbody>
</table>

The overall yield of neopentylbenzene, IX, from benzyl chloride by this new route was 29%. 

Attempted synthesis of IX

1. Decarboxylation of the acid, VI, to neopentylbenzene, IX, could not be effected even by prolonged heating at 230° with copper powder and quinoline. Also copper chromite and quinoline proved equally ineffective for this decarboxylation.

2. The acid, VI, was reduced by lithium aluminum hydride to obtain 4-phenyl-3,3-dimethyl butanol-1, XI, in 67% yield.
Attempt to convert the alcohol, XI, into IX by heating with 10% palladium on charcoal\textsuperscript{14} afforded only 12% of the hydrocarbon, IX. About 40% of the starting material was recovered unchanged.

\textsuperscript{14} K. S. Newman and H. V. Zahm, J. Am. Chem. Soc. 65, 1097 (1943).
PART II

SYNTHESIS OF CIS- AND TRANS-1,2-DINEOPENTYLETHYLENE
INTRODUCTION

The strain energy in o-di-t-butylbenzene has been the subject of considerable interest during the past several years. Brown and his co-workers\textsuperscript{16,17} estimated a value of 25 kcal/mole for the strain-energy of this molecule and ever since attempts have been made to verify this prediction. The obvious method, of course, was to synthesize this compound and determine the steric strain from its heat of combustion. Hence the synthesis of o-di-t-butylbenzene has aroused considerable interest.\textsuperscript{18,19} This objective has now been achieved by several groups of workers.\textsuperscript{20,21,22,23}

\begin{thebibliography}{99}
\bibitem{20} E. M. Arnett and M. E. Strem, Chemistry and Industry (London), 2008 (1961).
\end{thebibliography}

But even before this hydrocarbon was available, from the heats of combustion of the isomers 1,2,4- and 1,3,5-tri-tert-butylbenzenes the
strain introduced by o-di-tert-butyl groups was estimated to be $16.8 \pm 1.7$ kcal/mole,\textsuperscript{24} a value much lower than the predicted value of 25 kcal/mole.

\textsuperscript{24}U. Krueker, C. Hoogzand and W. Hüb, Ber. 94, 2817 (1961).

In cis-di-t-butylethylene, which represents an acyclic analog of o-di-tert-butylbenzene, the strain energy is about 10 kcal/mole.\textsuperscript{25,26}


This energy difference of 10 kcal/mole between XII and XIII is the largest yet found for cis-trans isomeric acyclic olefins, with the cis the higher in energy. This value of 10 kcal/mole may be regarded as the minimum strain energy present in o-di-tert-butylbenzene due to the interaction of o-di-tert-butyl groups.

In cis di-tert-butylethylene, XII, the interaction of the tert-butyl groups could be lowered by twisting the molecule slightly so that the t-butyl groups lie on either side of the olefinic bond. However, in o-di-t-butylbenzene the interaction of the t-butyl groups is not likely
to be significantly reduced by forcing them to lie on either side of the benzene ring, since such a process leads to distortion of the benzene ring. Hence the steric strain resulting from the interaction of the tert-butyl groups would be relatively larger in o-di-t-butylbenzene than in cis-di-t-butylethylene, XII. The observed value of 16.8 kcal/mole as the strain energy due to the interaction of o-di-tert-butyl groups and 10 kcal/mole as the strain energy for cis-di-t-butylethylene, XII, are in keeping with the expectation.

The strain in o-di-tert-butylbenzene, XIV, has been compared with the strain in 4,5-dimethylphenanthrene, XV. This comparison followed from

\[ 27 \text{M. A. Frisch, C. Barker, J. L. Margrave and M. S. Newman, J. Am. Chem. Soc. 85, 2356 (1963).} \]

the observation that in steric effect, a fused aromatic ring containing a methyl group ortho to the point of fusion approximates that of an ortho-tert-butyl group.\[ 28 \text{M. S. Newman and W. H. Powell, J. Org. Chem. 26, 812 (1961).} \]

butylbenzene, XIV, should be comparable to that of 4,5-dimethylphenanthrene, XV. From heat of combustion data, the strain in
4,5-dimethylphenanthrene has been found to be $12.6 \pm 1.5$ kcal/mole, lower than $16.8 \pm 1.7$ kcal/mole, the determined strain energy in 1,2,4-tri-tert-butylbenzene due to the interaction of o-di-tert-butyl groups.

**Objective of the present work**

The objective of the present work was to synthesize dineopentylacetylene and the olefins, cis- and trans-1,2-dineopentylethylene. Dineopentylacetylene was needed to prepare ortho-dineopentyltetramethylbenzene, I, possibly by cyclization of dimethylacetylene with the mono-adduct of dineopentylacetylene and dicobalt octacarbonyl as in the case of o-di-tert-butylbenzene. This hydrocarbon, I, was desired for the study of molecular complex formation with various electron acceptors.

The olefins, cis- and trans-1,2-dineopentylethylene were prepared for the following reasons. In the first place to determine the magnitude of the steric interaction between the neopentyl groups in cis-1,2-dineopentylethylene, XVI. This value would be the difference in heats of combustion or heats of hydrogenation between XVI and XVII. The strain energy in cis-1,2-dineopentylethylene, XVI, should be lower than...
10 kcal/mole,\textsuperscript{25} the strain energy in cis-di-t-butylethylene, XII, for the following reason. In cis-di-t-butylethylene, XII, the bulky tert-butyl groups are attached directly to the olefinic carbons and there is severe interaction among them. Free rotation of the tert-butyl groups about the olefinic carbon-tert-butyl carbon bond is virtually impossible and the molecule is highly strained. However, in cis-dineopentylethylene, XVI, a methylene group intervenes between the olefinic carbon and tert-butyl carbon, reducing considerably the interaction between the bulky tert-butyl parts of the neopentyl chains. Rotation about the olefinic carbon-methylene carbon bond can confer upon the molecule a conformation in which there is less interaction between the tert-butyl groups and the molecule has less strain.

The second objective behind these syntheses was to measure the relative rates of addition across the double bond of these ethylenes, XVI and XVII, from reactions that undergo addition to the double bond. It has been reported\textsuperscript{29} that 1,1-dineopentylethylene is very resistant to addition reactions. Hence a comparison of the rate data with those obtained with 1,1-dineopentylethylene could indicate whether the neopentyl chains are more effective in shielding the olefinic bond when attached to the same olefinic carbon or when attached to different olefinic carbon atoms. Likewise, comparison with the rate data obtained with cis- and trans-di-tert-butylethylenes, XII, XIII, could indicate whether the neopentyl groups are more effective than the tert-butyl groups in hindering the addition of the reagents across the double bond.


\textsuperscript{29} P. D. Bartlett, G. L. Fraser and R. B. Woodward, J. Am. Chem. Soc. 61, 495 (1939).
It is predicted that dineopentylethylenes would add reagents more slowly than di-tert-butylethylenes. The prediction follows from the application of the "rule of six"\textsuperscript{30,31} to these systems. According to this empirical rule, besides branching at the $\alpha$-carbons, the number of atoms in the sixth position greatly influence the rate of addition to the unsaturated function. The greater the number of atoms in the sixth position, the greater will be the steric effect. Since dineopentylethylenes have eighteen hydrogen atoms in the sixth position and di-tert-butylethylenes have none, one should anticipate the former to undergo addition reactions at rates much lower than the latter.

The objective of the present work, namely, the synthesis of cis and trans dineopentylethylenes, XVI and XVII, has been achieved. However, highly pure trans isomer, XVII, is not available at present in sufficient quantity. The last step in the synthesis involves separation of XVI, XVII and their saturated analog XVIII by preparative gas chromatography and so far a liquid phase capable of separating XVIII from XVII on a sample size larger than 25 $\mu$L. has not been found.
The cis isomer, XVI, can be easily separated from other two components up to a maximum sample size of 100 µl. However, on this scale separation of XVIII and XVII could not be effected.

Work is in progress\textsuperscript{32} to find a better preparative column affording satisfactory separation on a larger scale. When sufficient quantities of XVI\textsuperscript{33} and XVII are available, their energy difference and rate data will be determined.

\textsuperscript{32}The keen interest and advice of Dr. Earl Taft of Wilkens Instrument and Research Inc., Walnut Creek, California, is greatly appreciated.

\textsuperscript{33}Sufficient quantity of cis isomer, XVI, for determining heat of hydrogenation is available.
DISCUSSION OF RESULTS

THE SYNTHESIS OF CIS- AND TRANS-1,2-DINEOPENTYLETHYLENES, XVI AND XVII

The synthetic route, that was successfully followed to obtain these olefins, is outlined in Chart B. The commercially available

We thank Antara Chemicals, General Aniline and Film Corp. for a generous supply of 1,4-dichloro-2-butyne.

1,4-dichloro-2-butyne was condensed with sodio diethyl methylmalonate in ethanol to obtain tetraethyl-4-octyne-2,2,7,7-tetracarboxylate, XIX, in yields averaging about 70%. That tautomerism of the acetylene to an allene did not occur was confirmed by its NMR spectrum. When sodium hydride in N-methylpyrrolidone was used as the base for this condensation, the yield of XIX was only 40%. Only tars were obtained when potassium t-butoxide in dimethylsulfoxide was used as the base for this reaction.

Sodium hydride suspension in mineral oil (Metal Hydride, Inc.)
The tetraester, XIX, was smoothly reduced by lithium aluminum hydride in ether to 2,2,7,7-tetrakis (hydroxymethyl)-4-octyne, XX, in yields ranging between 72 to 86%. Triple bond was not reduced, as the structure of XX was in agreement with its NMR spectrum.
NMR Spectrum of XX: (Dimethylsulfoxide-D₆)

<table>
<thead>
<tr>
<th>Chemical Shift δ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant J (cps)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>Singlet</td>
<td>6</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>2.07</td>
<td>Singlet</td>
<td>4</td>
<td>--</td>
<td>b</td>
</tr>
<tr>
<td>3.30</td>
<td>Doublet</td>
<td>8</td>
<td>J₉₋₈ = +5 cps</td>
<td>o</td>
</tr>
<tr>
<td>4.37</td>
<td>Triplet</td>
<td>4</td>
<td>J₉₋₈ = +5 cps</td>
<td>d</td>
</tr>
</tbody>
</table>

When dimethylsulfoxide-D₆ was used as a solvent, the hydroxyl proton splitting was observed as a clearly resolved triplet (J = +5 cps). centered at δ = 4.37 ppm, since in this solvent the rate of proton exchange is sufficiently reduced to permit observation of the coupling between hydroxylic and methylenic protons.


The structure of XX was further confirmed by determining the spectrum in deuterium oxide. The hydroxyl proton resonance was absent since the hydroxylic hydrogens are replaced by deuterium.

2,2,7,7-Tetrakis(hydroxymethyl)-4-octyne tetramethanesulfonate, XXI, was prepared by treating the tetraalcohol, XX, with methanesulfonyl chloride and collidine. The yields were in the range of 90 to 95%. The NMR spectrum of the tetramesylate, XXI, was in agreement with the required structure.

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>Singlet</td>
<td>6</td>
<td>$\text{- CH}_3 -$</td>
</tr>
<tr>
<td>2.35</td>
<td>Singlet</td>
<td>4</td>
<td>$\text{C} = \text{C} - \text{CH}_2$</td>
</tr>
<tr>
<td>3.05</td>
<td>Singlet</td>
<td>12</td>
<td>$\text{O} - \text{S} - \text{CH}_3$</td>
</tr>
<tr>
<td>4.15</td>
<td>Singlet</td>
<td>8</td>
<td>$\text{CH}_2 - \text{O} -$</td>
</tr>
</tbody>
</table>

2,2,7,7-Tetrakis(iodomethyl)-4-octyne, XXII, was prepared in about 90% yield by heating the tetramesylate, XXI, with sodium iodide in ethylene glycol monoethyl ether. The structure of the tetraiodide, XXII, was confirmed by its NMR spectrum.
### Chemical Shift Multiplicity Number of Protons Assignment

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.19</td>
<td>Singlet</td>
<td>6</td>
<td>- C - CH₃</td>
</tr>
<tr>
<td>2.39</td>
<td>Singlet</td>
<td>4</td>
<td>C ≡ C - CH₂</td>
</tr>
<tr>
<td>3.36</td>
<td>Singlet</td>
<td>8</td>
<td>- CH₂ - I</td>
</tr>
</tbody>
</table>

By treating the tetraiodide, XXII, with sodium sulfide nonahydrate in ethylene glycol monoethyl ether, 3,3'-(2-butynylene)bis(3-methyl-thietane), XXIII, was obtained in 85% yield.

![Diagram](image-url)

**XXIII**

---

38 H. J. Bernstein, J. A. Pople and W. G. Schneider, Can. J. Chem., 35, 65 (1957). As suggested by these authors, the nonequivalent methylene protons separated by small chemical shift are designated with the letters A and B, and no attempt is made to assign stereochemistry to Hₐ and Hₐ protons in the above figure.
### NMR Spectrum of XXIII:

<table>
<thead>
<tr>
<th>Chemical Shift ( \delta ) (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant ( J ) (ops)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35</td>
<td>Singlet</td>
<td>6</td>
<td>--</td>
<td>(- \text{CCH}_3)</td>
</tr>
<tr>
<td>2.41</td>
<td>Singlet</td>
<td>4</td>
<td>--</td>
<td>(\text{C} = \text{C} - \text{CH}_2)</td>
</tr>
<tr>
<td>(\delta_B = 2.83)</td>
<td>AB type</td>
<td>8</td>
<td>-9 ops</td>
<td>(H_A) and (H_B) Protons</td>
</tr>
<tr>
<td>(\delta_A = 3.05)</td>
<td>Quartet</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By using equations (1), (2) or (3) and (4), mentioned in the Appendix, page 82, the following parameters of AB quartet of bithiastene, XXIII, were calculated.

\[ J_{AB} = -9 \text{ ops} \]

\[ \delta_A - \delta_B = 13.23 \text{ ops}; \quad \delta_B = 2.83 \text{ ppm}; \quad \delta_A = 3.05 \text{ ppm} \]

\[ \frac{I_2}{I_1} = \frac{I_3}{I_4} = 3.57 \]
This calculated relative intensity of the inner and outer pairs of lines was in agreement with the observed intensity ratio of 3.4:1.

Calculation showed that $\delta_A$ and $\delta_B$ lie nearer to the strong inner lines than to the outer lines. An error of only 1.4 cps would be introduced if $\delta_A$ and $\delta_B$ were to be calculated from the midpoints of the doublets, when $J_{AB}/\delta_A - \delta_B = 0.67$ and $J_{AB} = 9$ cps even though the intensity ratio of the doublet components were 3.57:1.

Attempt to convert the tetramesylate, XXI, directly to bisthietane, XXIII, by using sodium sulfide nonahydrate (crystallized from ethanol), in ethylene glycol and ethylene glycol monoethyl ether led to a product boiling over a range of 136-141°C (0.8 mm.). V.P.C. analysis showed that this material was a mixture of two components in relative ratio of 1:4. The major component was identified as the bisthietane, XXIII, by comparison of the v.p.c. retention times, with an authentic sample of XXIII. From NMR data of the mixture, the major component was assigned the structure, XXIII, and the minor component was inferred to be either $3,3'-(2$-butynylene)bis(3-methyloxetane), XXIV, or a mixture of XXIV and $3$-methyl-$3[4-(3$-methyl-3-thietanyl)-2$-butynyl] oxetane, XXV. The latter possibility seems less likely on the basis of v.p.c. analysis.
The yield of the mixture by this procedure was estimated to be only about 28%. The mixture was originally assumed to be homogenous, XXIII, and analyzed for elements. The carbon content was found to be 1% higher and the sulfur content 1% lower than the theory. These deviations are obviously due to the presence of some of the corresponding cyclic oxide, XXIV, in XXIII. When tetramesylate, XXI, was treated with commercial sodium sulfide nonahydrate* (Baker analyzed) in ethanol, only XXI was recovered in almost quantitative yield. However, when the commercial sample of sodium sulfide nonahydrate used was purified by two recrystallizations from ethanol and dried over phosphorous pentoxide, a liquid, b.p. 130-140° (0.7 mm.) was obtained in 70% yield. V.P.C. analysis of this liquid showed it to contain equal amounts of two components. Comparison of v.p.c. retention times showed these two components to be identical with the two components obtained above in the relative ratios of 1:4 (in the order of increasing retention time).

*Without crystallization from ethanol.
The formation of XXIV is not surprising and has analogy\textsuperscript{39} in the formation of cyclic oxide, XXVI, besides the cyclic sulfide, XXVII, by the reaction of the dimesylate, XXVIII with sodium sulfide in ethanolic solution.

\[ \text{NOgS'SHgO} \]
\[ \text{2X3ZHC} \]
\[ \text{CH2-O-SO2CH3} \]
\[ \text{CH2OSO2CH3} \]

The formation of XXIII and XXIV from tetramesylate, XXI, could be visualized by the following mechanistic path.

\[ \text{R} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{H3C} \]
\[ \text{CH2 O-S-CH3} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{SNa} \]

Path 'A'

\[ \text{R} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{H3C} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{CH3SO3Na} \]

XXI

Path 'A'

XXIII

Path 'B'

XXIV

\[ \text{R} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{H3C} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{B=SNa} \]

\[ \text{R} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{H3C} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{CH2-O-S-CH3} \]
\[ \text{B=SNa} \]

XXI

Path 'B'

XXIV

\[ \text{Na2S·9H2O} \]
\[ \text{EtOH} \]

XXVIII

XXVI

XXVII

\[ \text{XXVIII} \]

\[ \text{XXVI} \]

\[ \text{XXVII} \]


\[ \text{Na2S·9H2O} \]
\[ \text{EtOH} \]

The formation of XXIII and XXIV from tetramesylate, XXI, could be visualized by the following mechanistic path.
Path "A" involves nucleophilic attack by the sulfide ion on the sterically hindered neopentyl carbon, whereas path "B" involves nucleophilic attack by the sulfide ion on the sterically less hindered mesylate sulfur. The formation of XXIV and XXIII in the relative ratios of 1:4 at 125° but 1:1 at 80° leads to the interesting observation that nucleophilic attack by sulfide ion on the sterically hindered site is favored at the higher temperature.

Interestingly, the isomeric bis-[(2,2-bis-methanesulfonylmethyl) propyl]-benzenes, XXIX, when treated with sodium sulfide nonahydrate in ethylene glycol and ethylene glycol monoethyl ether at 130-135° afforded the corresponding bisthietanes in yields ranging from 50 to 67%.9


\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 - \text{C} (\text{CH}_2\text{O}_3\text{SCH}_3)_2 \\
\text{R} \\
\text{CH}_2 - \text{C} (\text{CH}_2\text{O}_3\text{SCH}_3)_2 \\
\text{CH}_3 \\
\end{align*}
\]

XXIX

R = appropriate tetramethylphenylene diradicle for the o, m and p isomers.

In passing, mention may be made about two other methods available for the preparation of thietanes. One involves heating a 1,3-dibromide40


with sodium sulfide nonahydrate in ethanol and the other heating a cyclic
carbonate of a 1,3 diol with potassium thiocyanate. Neither of these methods affords better than a 60% yield and therefore did not look promising for the synthesis of bisthietane, XXIII.

\[
\begin{align*}
\text{H(c)} & \quad \text{H(d)} \\
\text{S} & \quad \text{H(c)} \\
\text{H(c)} & \quad \text{CH}_3 \\
\text{H(d)} & \quad \text{H(c)} \\
\end{align*}
\]

XXIII

\[
\begin{align*}
\text{H(e)} & \quad \text{H(f)} \\
\text{O} & \quad \text{H(e)} \\
\text{H(e)} & \quad \text{CH}_3 \\
\text{H(f)} & \quad \text{H(e)} \\
\end{align*}
\]

XXIV

**NMR Spectrum of the mixture containing XXIII and XXIV:**

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Coupling Constant $J$ (cps)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35</td>
<td>Singlet</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>2.42</td>
<td>Singlet</td>
<td>--</td>
<td>b</td>
</tr>
<tr>
<td>$\delta_B = 2.82$</td>
<td>AB quartet</td>
<td>-9 cps.</td>
<td>c and d protons</td>
</tr>
<tr>
<td>$\delta_A = 3.05$</td>
<td>AB type quartet</td>
<td>-5.5 cps.</td>
<td>e and f protons</td>
</tr>
</tbody>
</table>
Calculation of $J$, $\delta$ and relative intensity of the two components from the spectrum of the mixture (XXIII, XXIV)

By using equations (1), (2) or (3) and (4), mentioned in the Appendix, page 82, the following parameters were calculated.

**AB type quartet of methylene adjacent to the oxygen**

$$J_{AB} = -5.5 \text{ cps}^{42}$$

$$\delta_A - \delta_B = 7.74 \text{ cps}; \quad \delta_A = 4.38 \text{ ppm}; \quad \delta_B = 4.25 \text{ ppm}$$

$$\frac{I_2}{I_1} = \frac{I_3}{I_4} = 3.75$$


The relative intensity of the inner and outer pairs of lines were 3.75:1. This calculated ratio was in agreement with the observed intensity ratio of 3.55:1.

The error introduced by taking the midpoints of the doublets, for $\delta_A$ and $\delta_B$, when $J_{AB} / (\delta_A - \delta_B) = 0.71$ and $J_{AB} = 5.5 \text{ cps}$, was only 0.88 cps even though the intensity ratio of the doublet components were 3.75:1.

**AB type quartet of bisthietane (XXIII)**

$$J_{AB} = -9 \text{ cps}^{42}$$

$$\delta_A - \delta_B = 13.53 \text{ cps}; \quad \delta_A = 3.05 \text{ ppm}; \quad \delta_B = 2.82 \text{ ppm}$$

The parameters $J$, $\delta$ and relative intensity for the bisthietane, XXIII, calculated from the NMR spectrum of the mixture (XXIV, XXIII) and the pure sample were in agreement.
The observed increase in the geminal coupling constant on passing from cyclic sulfide, XXIII, to cyclic oxide, XXIV, is compatible with the lower electron negativity of sulfur and is in accordance with the observation\(^{43}\) that \(J_{\text{gem}}\) may be increased (i.e., made more positive) by an electronegative substituent attached to the same carbon as the geminally coupled protons.


Discussion of Significant Experimental Results in the Desulfurization of Bithiostane, XXIII

Desulfurization of XXIII generally afforded a mixture of the olefins, XVII, XVI, and 1,2-dineopentylethane (XVIII) and in a few cases also dineopentylacetylene (XXX). The relative proportions of these compounds in the reaction product varied with the activity of the catalyst, ratio of the catalyst to the bisthiostane and reaction time.

Optimum conditions for the formation of cis-1,2-dineopentylethylene, XVI

When Raney nickel catalyst,\(^{44}\) stored for a period of seven to ten days, after its preparation was used (cpd:catalyst = 1:20) and the reaction time was about five hours, the cis olefin, XVI, was always found by v.p.c. analysis to be the major component. In five runs the yield was between 66 and 72%. In one run when the ratio of the catalyst was increased (cpd : catalyst = 1:30), the yield of the cis olefin was cut

\(^{44}\)The preparation of the catalyst is described on page 71.
down to 33%. Also in two runs, when the catalyst (cpd : catalyst = 1:21) used was 2 and 6 days old and the reaction time was 6.5 hours, the cis olefin was obtained in 41 and 49% yield, respectively.

Optimum conditions for the formation of trans-1,2-dineopenty lethylene, XVII

In a run, when a sample of the catalyst stored for one month after its preparation was used (cpd : catalyst = 1:22) and the reaction time was extended to 16 hours, a product was obtained which by v.p.c. analysis was found to contain 37% of the trans olefin, XVII, and 40% of the cis olefin, XVI. The saturated compound, XVIII, accounted for the remaining 23% of the reaction product. The maximum yield of the trans olefin was observed only in this run.

Small amounts of reaction products were always absorbed strongly on the catalyst surface. The absorbed products were recovered by extracting the catalyst with pentane using a soxhlet extractor. The composition of these extracts from 3 runs were examined by v.p.c. analysis and found to contain about 40% of the trans olefin, XVII, 43% of the cis olefin, XVI, and 17% of the saturated hydrocarbon, XVIII. It is noteworthy that in these runs work-up of the filtrate after removal of the catalyst afforded products containing 15 to 17% of the trans olefin, XVII, 70 to 72% of the cis olefin, XVI, and 8 to 10% of the saturated hydrocarbon, XVIII. The relatively large amount (40%) of the trans olefin present in the product recovered from the catalyst compared to that (15 to 17%) present in the filtrate could be rationalized as follows. The cis olefin, XVI, has greater tendency to be absorbed on the catalyst surface than the trans olefin. The absorbed cis olefin could
either isomerize to the trans olefin or undergo hydrogenation to the saturated hydrocarbon, XVIII, depending upon the activity of the catalyst. In the present instance, both these processes have occurred to varying extent, increasing the content of the trans olefin and the saturated hydrocarbon in the product extracted from the catalyst.

Optimum conditions for the formation of 1,2-dineopentylethane, XVIII

The saturated hydrocarbon, XVIII, was formed in larger amount when the catalyst used was increased. The maximum yield, 37% (by v.p.c. analysis) was observed, when in a run, the catalyst (cpd : catalyst = 1:30) was 10 days old and the reaction time 5.5 hours. Also in another run a 23% yield (by v.p.c. analysis) of the saturated hydrocarbon, XVIII, was observed when the catalyst (cpd : catalyst = 1:22) was one month old and the reaction time extended to 16 hours.

Optimum condition for the formation of dineopentylacetylene, XXX

The formation of the acetylene was observed only in two runs, when catalyst \(^{45}\) of very low activity was used for the desulfurization.

\(^{45}\) The preparation of this catalyst is described on page 76.

In the best run, the bisthietane, XXIII, was treated with eighteen times its weight of the catalyst over a period of 4 hours to obtain a product containing 31% (by v.p.c. analysis) of the acetylene, XXX.
The following generalizations are made from the above observations in the desulfurization experiments

1. The formation of the cis olefin, XVI, is favored when the reaction time and the quantity of the catalyst are kept at a minimum.

2. Increase in the formation of the trans olefin, XVII, is observed when catalyst of low activity is used in excess over an extended period of time.

3. The saturated hydrocarbon, XVIII, is formed in increasing amounts when excess of active catalyst is used.

4. Dineopentyl acetylene, XXX, is formed only when catalyst of low activity is used and when both the amount of the catalyst and the reaction time are considerably decreased.

Anomalous reaction between the bisthietane, XXIII, and Raney nickel in presence of acetone

The reaction between XXIII and Raney nickel\(^{46}\) (cpd : catalyst = 1:24) in refluxing acetone afforded in 15% yield a colorless crystalline product, m.p. 105-107°. This compound analyzed well for C\(_{14}H_{18}S_2O_2\), had C=O stretching absorption at 5.9μ, and its NMR spectra supported structure XXXI for the compound.

\(^{46}\)Deactivated by refluxing in acetone for 1 hour.
NMR Spectrum of XXXI:

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant $J$ (cps)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.34</td>
<td>Singlet</td>
<td>6</td>
<td>--</td>
<td>$-\text{CH}_3$</td>
</tr>
<tr>
<td>2.46</td>
<td>Singlet</td>
<td>4</td>
<td>--</td>
<td>$-\text{CH}_2 - \text{C} \equiv \text{C}$</td>
</tr>
<tr>
<td>$\delta_B = 2.38$</td>
<td>AB type quartet</td>
<td>4</td>
<td>$J_{AB} = -17.5^{42}$</td>
<td>$H_A$ and $H_B$ protons of methylene adjacent to $C=O$</td>
</tr>
<tr>
<td>$\delta_A = 2.63$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_B = 3.16$</td>
<td>AB quartet</td>
<td>4</td>
<td>$J_{AB} = -11.5^{42}$</td>
<td>$H_A$, $H_B$ protons of methylene adjacent to sulfur</td>
</tr>
<tr>
<td>$\delta_A = 3.43$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By using equations (1), (2) or (3) and (4) mentioned in the Appendix, page 82, the following parameters were calculated.

AB quartet of methylene adjacent to carbonyl group

- $J_{AB} = -17.5$ cps
- $\delta_A - \delta_B = 14.92$ cps; $\delta_B = 2.38$ ppm; $\delta_A = 2.63$ ppm
- $\frac{I_2}{I_1} = \frac{I_3}{I_4} = 7.36$; the relative intensity of the inner and outer pairs of lines was 7.36:1.
Calculation showed that $\delta_A$ and $\delta_B$ lie nearer the strong central lines than the outer weak satellites. An error of 4.04 cps would be introduced if $\delta_A$ and $\delta_B$ were calculated from the midpoints of the doublets, when $J_{AB}/\delta_A - \delta_B = 1.17$ and $J_{AB} = 17.5$ cps.

A AB quartet of methylene adjacent to sulfur

$J_{AB} = -11.5$ cps

$\delta_A - \delta_B = 15.75$ cps; $\delta_B = 3.16$ ppm; $\delta_A = 3.43$ ppm

$\frac{I_2}{I_1} = \frac{I_2}{I_4} = 3.87$; i.e. 3.87:1.

An error of 1.88 cps would be introduced, if $\delta_A$ and $\delta_B$ were to be calculated from the midpoints of the doublets when $J_{AB}/\delta_A - \delta_B = 0.73$ and $J_{AB} = 11.5$ cps.

Mechanism of desulfurization with Raney nickel

In the desulfurization of bisthietane, XXIII, no evidence was found for the formation of any biscyclopropyl derivative, XXXII, and only compounds XVI and XVII were formed.

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_2\text{C} - \text{C} = \text{C} - \text{CH}_2 - \text{C} & \\
& \quad \text{CH}_3 & \\
& \quad \text{XXXII}
\end{align*}
\]

This observation rules out the possibility that in the desulfurization reaction simultaneous breaking off the two carbon-sulfur bonds to afford diradicals of the type XXXIII occur to any extent,
for if this occurred, cyclopropyl derivatives should have been formed. 
On the other hand, formation of cis olefin, XVI, and trans olefin, XVII, 
strongly suggests that stepwise breaking of the C-S bonds are more likely 
in desulfurization with Raney nickel.

Separation of Cis Olefin, XVI, Trans Olefin, XVII, 
Saturated Hydrocarbon, XVIII, and the Acetylene, 
XXX, by Preparative Gas Chromatography

The mixture obtained by desulfurization of the bisthietane, XXIII, 
was-subjected to preparative gas chromatography, on a carbowax column to 
separate the components. The cis olefin and the dineopentyl acetylene, 
XXX, were effectively separated from the other components. However, the 
trans olefin and the saturated hydrocarbon, XVIII, had the same retention 
times and hence could not be separated from one another on this column. 
All the four components of the mixture could be easily obtained in the 
pure form by preparative gas chromatography on a tetracyanoethylated 
pentaerythritol column.47 However, the maximum sample size separable on 

47 We thank Dr. Earl Taft of Wilkens Instrument and Research, Inc., 
California, for suggesting this column.

this column was limited to 25 μl. cis olefin, XVI, and acetylene, XXX, 
can be easily separated from trans olefin, XVII, and saturated hydrocarbon, 
XVIII, on a 100 μl. scale. But on this scale the saturated hydrocarbon
and the trans olefin cannot be separated since they have very close retention time. Work is in progress to find a better preparative column capable of separating on a larger scale.

**Assignment of Structure to the Isomeric Olefins**

**Structural proof of cis-1,2-dineopentylenethylene, XVI**

1. The infrared spectrum of XVI showed absorption at 1650 cm\(^{-1}\) due to C=C stretching vibrations,\(^{48}\) and absorption at 680 cm\(^{-1}\) due to \(\text{=C-H out of plane vibration}\).\(^{48}\) Also the absence of absorption at 970 cm\(^{-1}\), characteristic of trans olefins favors the cis structure for this olefin.

2. Near infrared spectrum of XVI, exhibited a combination band at 2.140\(\mu\) characteristic of cis unsaturation\(^{49,50}\) (\(\text{=C-H stretching vibration}\)).


3. **NMR Spectrum of the cis olefin XVI:**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant (J) (cps)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>Singlet</td>
<td>18</td>
<td>--</td>
<td>-(\text{C-CH}_3)</td>
</tr>
<tr>
<td>1.93</td>
<td>Two AB Quartets</td>
<td>4</td>
<td>(<em>\text{J}_{\text{vic}} = 4.5) cps (</em>\text{J}_{\text{al}} = 1.3) cps</td>
<td>(\text{CH}_2 - \text{C=})</td>
</tr>
<tr>
<td>5.55</td>
<td>Triplet of Triplets</td>
<td>2</td>
<td>(\text{J}<em>{\text{vic}} = 4.5) cps (\text{J}</em>{\text{al}} = 1.3) cps</td>
<td>(\text{C} = \text{H})</td>
</tr>
</tbody>
</table>

\(*\text{J}_{\text{vic}} = \text{vicinal coupling constant}; \text{J}_{\text{al}} = \text{allylic coupling constant.}\)
Structural proof of trans-1,2-dioctylvinylene, XVII

1. The infrared spectrum of XVII showed the absence of an absorption at 1650 cm\(^{-1}\) (due to C=C stretching vibration). The absence of this band in symmetric trans olefin is due to the fact the dipole moment of the molecule is zero and remains zero throughout the vibration.

2. The infrared spectrum showed strong absorption at 970 cm\(^{-1}\) (=C-H out of plane vibration), characteristic of trans olefins.

3. **NMR Spectrum of the trans olefin, XVII:**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Coupling Constant</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.89</td>
<td>Singlet</td>
<td>18</td>
<td>--</td>
<td>-CH(_3)</td>
</tr>
<tr>
<td>1.90</td>
<td>Two AB Quartets</td>
<td>4</td>
<td>(J_{vic} = 4.5) (\text{cps}) (J_{al} = 1.9) (\text{cps})</td>
<td>CH(_2) - C =</td>
</tr>
<tr>
<td>5.43</td>
<td>Triplet of Triplets</td>
<td>2</td>
<td>(J_{vic} = 4.5) (\text{cps}) (J_{al} = 1.9) (\text{cps})</td>
<td>H (\text{C} =)</td>
</tr>
</tbody>
</table>

The assignment of structure to the geometrical isomers was made on the basis of NMR data.\(^{51}\)

---


\(r\) = the distance between the mid-point of C-C bond and the olefinic proton.
The shielding equation given below would predict that the C-C bond (a) should shield proton b (proton cis to the neopentyl group) and deshield proton c (trans to the neopentyl group), since \( r' > r \) and \( \Theta > \Theta' \).

\[
\sigma_{av}(G) = \frac{(3 \cos^2 \Theta - 1)(\chi_L - \chi_T)}{3r^3}
\]


\( G = \) symmetrical group of electrons.
\( r = \) distance between the electrical center of gravity of \( G \) and the proton
\( \chi_L = \) longitudinal susceptibility.
\( \chi_T = \) transverse susceptibility.
\( \chi_L - \chi_T = \) measure of the diamagnetic anisotropy of \( G \).

The olefinic proton of trans isomer, XVII, resonates as a low field multiplet, centered at 5.43 ppm and that of the cis isomer, XVI, at 5.55 ppm.

\[ \Delta \delta_{ct} = \delta_{cis} - \delta_{trans} = 0.12 \text{ ppm} \]

Thus the olefinic proton of the trans isomer is shielded (i.e., shifted upfield) by 7 cps and that of the cis isomer is deshielded (i.e., shifted downfield) by 7 cps. The observed chemical shift of 0.12 ppm between the olefinic protons of the geometrical isomers is obviously due to the long range shielding effect associated with the diamagnetic anisotropy of the carbon-carbon single bond.

It may be noted that the methyl protons of neopentyl group of cis isomers, XVI, resonate at a higher frequency by 1.5 cps \(^{53}\) and methylene
protons by 2 cps than those of the trans isomer, XVII. This

53 These values were confirmed by scanning the spectrum four to five times on both samples of identical concentration.

paramagnetic shift is attributed to the steric interaction of the cis oriented bulky neopentyl groups, since asymmetrical distortion of the electron cloud due to Vander Waal's repulsion would decrease the effective shielding of the hydrogen nucleus. Other instances where steric interaction of the groups causes deshielding of the hydrogen nucleus have been reported. 54


It may be observed that the allylic coupling constant for the cis isomer (Jtransoid = 1.3 cps), is lower than the trans isomer (Jcisoid = 1.9 cps), in agreement with the general observation that Jcisoid is greater than Jtransoid. 54a


Structural proof of 1,2-dineopentylmethane, XVIII

Infrared spectrum:

<table>
<thead>
<tr>
<th>Absorption band</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principle absorption at 3.45 μ with</td>
<td>Asymmetrical and symmetrical stretching of C-H</td>
</tr>
<tr>
<td>shoulders at 3.40, 3.49 and 3.52 μ.</td>
<td>bonds of methyl and methylene groups.</td>
</tr>
<tr>
<td>7.20 and 7.35 (s) μ</td>
<td>C-H bending of t-butyl group.</td>
</tr>
<tr>
<td>6.80 (s) and 8.05 (m) μ</td>
<td>C-H bending of methylene group.</td>
</tr>
</tbody>
</table>
NMR Spectrum of XVIII:

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88</td>
<td>Singlet</td>
<td>18</td>
<td>- C -&lt;br&gt;[CH_3]</td>
</tr>
<tr>
<td>1.20</td>
<td>Singlet</td>
<td>8</td>
<td>- CH_2 -</td>
</tr>
</tbody>
</table>

Structural proof of dinlineopentylacetylene. XXX

The NMR spectrum of XXX is in agreement with the assigned structure.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>Singlet</td>
<td>18</td>
<td>- C -&lt;br&gt;[CH_3]</td>
</tr>
<tr>
<td>2.01</td>
<td>Singlet</td>
<td>4</td>
<td>- CH_2 - C=\equiv\ C</td>
</tr>
</tbody>
</table>

Attempted conversion of tetramesylate, XXI, to dinlineopentylacetylene, XXX

When tetramesylate, XXI, was treated with lithium aluminum hydride and lithium hydride mixture in refluxing ether, no reaction took place. When the reaction was carried out in refluxing tetrahydrofuran, bisdiol,\(^{55,56}\) XX, was obtained in 35% yield.

\(^{55}\) H. A. Karnes, M.Sc. thesis, Ohio State University, 1962. Formation of bisdiol has been observed on reduction of tetramethane-sulfonate of 1,4-tis[2,2-tis(hydroxymethyl)-propyl]-durene.

Attempted conversion of tetraiodide, XXII, to dineopentylacetylene, XXX

Reduction of tetraiodide, XXII, with lithium aluminum hydride in ether afforded 1,4-bis(1-methylcyclopropyl)-2-butylene, XXXII, in 80% yield instead of the anticipated acetylene, XXX. The near infrared spectrum of XXXII had $\lambda_{max}$ at 1.640 $\mu$ ($\epsilon = 1.22$).

Similar formation of a cyclopropyl ring has been reported (reference 9) on reduction of 1,4-bis[2,2-bis(iodomethyl)propyl]durene.


The NMR spectrum of XXXII also supported the assigned structure.

<table>
<thead>
<tr>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Multiplicity</th>
<th>Number of Protons</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>Multiplet</td>
<td>8</td>
<td>c and d</td>
</tr>
<tr>
<td>0.40</td>
<td>Multiplet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td>Singlet</td>
<td>6</td>
<td>a</td>
</tr>
<tr>
<td>2.13</td>
<td>Singlet</td>
<td>4</td>
<td>b</td>
</tr>
</tbody>
</table>

XXXII
Some Unsuccessful Attempts in the Preparation of Dineopentylacetylene, XXX

1. Reductive dehalogenation of the tetraiodide, XXII, could not be effected by treatment with lithium-tri-t-butoxyaluminoxyhydride in diglyme at 125° for 10 hr. The tetraiodide was recovered quantitatively.

2. Attempt to effect the reductive dehalogenation of the tetraiodide with phosphorous and hydriodic acid at 100° led to a viscous liquid containing iodine (sodium fusion test). The NMR spectrum of this liquid showed a doublet at 2.42 ppm (J = 7 cps; \(-\text{H}_2\text{C} - \text{C} =\)) and a triplet at 5.8 ppm (J = 7 cps; \(\text{H} - \text{C} =\)) indicating the presence of a methylene adjacent to an olefinic proton. Hence the addition of hydrogen iodide to the acetylenic bond was inferred. No attempt was made to isolate and identify the products.

3. Attempt to effect the reductive dehalogenation of the tetraiodide, XXII, by treatment with tri-n-butyltinhydride\(^5\) at 135-140° for 4 hr. led to a liquid b.p. 94-97° (33 mm.); nonhomogenous by v.p.c. analysis. The NMR spectrum of this liquid showed cyclopropyl protons resonating as high field multiplets centered at 0.24 ppm; 0.42 ppm and signal in the downfield centered at 5.4 ppm due to either an olefin or allenic proton. Hence in this reaction, besides the formation of cyclopropyl derivative, the reduction of the triple bond or tautomerism of the triple bond to an allene had occurred. No attempt was made to isolate and identify the products.

4. Reaction between 1,4-dichloro-2-butyne and t-butyl magnesium chloride afforded a liquid boiling over several degrees range. The NMR spectrum of the distillate showed olefinic and allenic protons appearing as low field multiplets in the region 4.3-5.3 ppm. Hence the addition of the Grignard reagent to the acetylenic bond and tautomerism of acetylene to an allene was inferred. No attempt was made to isolate and identify the products.

60 The addition of t-butyl lithium to diphenylacetylene has been reported by J. E. Mulvaney at the 148th National Meeting of the American Chemical Society, Chicago, September 1964.

5. An attempt was made to obtain dineopentylacetylene, XXX, from the bisthietane, XXIII, by the following sequence of reactions.

Bromination of the bisthietane, afforded a sticky material which without purification was treated with Raney nickel. The product obtained was a yellow liquid, b.p. 113-117° (20 mm.), nonhomogenous by v.p.c. analysis.
The NMR spectrum of the liquid showed olefinic proton resonating as a low field multiplet centered at $\delta = 5.5$ ppm. The presence of olefinic proton in the product suggested the possibility of structural rearrangement during bromination. Hence further work on this route was abandoned.
EXPERIMENTAL

1. Melting points: Melting points were determined in a stirred silicone bath equipped with a calibrated thermometer, or in a Fisher John's melting point block. All melting points are uncorrected.

2. Infrared spectra: Infrared spectra were obtained with a Perkin Elmer infraord spectrophotometer. When better resolution was desired the samples were run on a Perkin Elmer Model 21 Double Beam Spectrophotometer.

3. Nuclear magnetic resonance spectra: NMR spectra were determined on a Varian A-60 Spectrometer at the operating temperature of the instrument (≈40°C), using carbon tetrachloride as solvent (unless otherwise specified) and tetramethylsilane as internal reference. Parameter "S" has been used to express chemical shifts in parts per million downfield from the TMS signal (0 ppm). The coupling constants (J) mentioned are the coupling constants measured on the spectrum. Resonance areas were measured with an electronic integrator. The relative areas were determined from an average of at least five integrations for each sample. The NMR spectra of the more important compounds of this investigation have been compiled in the Appendix.

4. Near infrared spectra were recorded on a Cary 14 spectrometer.

5. Elemental analysis: The analyses marked "a" and "b" were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, and Microanalysis, Wilmington, Delaware, respectively.

6. Vapor phase chromatography: V.P.C. analyses were carried out on a Model 609, programmed temperature flame ionization gas chromatograph;
(F and M Scientific Corporation) equipped with a disc chart integrator and preparative work was done on Model A-700 automatic preparative gas chromatograph (Wilken Instrument and Research, Inc.).

7. The phrase "worked up in the usual manner" refers to the handling of the organic solutions as follows. The organic layer was washed successively with dilute hydrochloric acid, sodium bicarbonate, water and saturated sodium chloride followed by drying over anhydrous magnesium sulfate. The solvent was removed in a rotatory evaporator.
EXPERIMENTAL FOR PART I

Synthesis of Neopentylbenzene

Diethyl isopropylidenemalonate

This compound was prepared according to the procedure described in the literature. A. C. Cope and E. M. Hancock, J. Am. Chem. Soc. 60, 2645 (1938).

From 1000 g. (6.25 moles) of diethyl malonate, 540 g. (9.3 moles) of acetone, 800 g. (7.8 moles) of acetic anhydride and 120 g. of freshly fused zinc chloride was obtained 670 g. (53%) of diethyl isopropylidenemalonate, b.p. 110-112° (9 mm.), after fractionation through a 70 x 2.5 cm. column packed with glass helices.

Purification of cuprous chloride

This method was suggested by Dr. K. Greenlee, formerly of this department.

To a weighed sample of crude cuprous chloride (Baker analyzed) in a mortar was added 10% by weight of hydroxylamine hydrochloride. The two solids were rapidly ground until a uniform dark color was obtained and fumes of nitrous oxide (NO) were no longer apparent. A small amount of water was added to the solid to form a paste. The paste was filtered by suction under nitrogen. The solid was washed with a small amount of water (caution: too much of water causes reoxidation of the Cu(I) ions as noted by a color change to yellow). The sample was then washed well
with absolute alcohol, followed by washing with ether. Care was taken to avoid any contact with air during washing. The resulting colorless powder was stored in a vacuum dessicator until used. The entire operation was carried out under nitrogen.

**Diethyl (α, α-dimethyl phenethyl) - malonate, IV**

In the best run, to 154.5 g. (0.772 moles) of diethyl isopropylidenemalonate in 200 ml. of ether and 12.0 g. (8% by weight of the ester used) of purified cuprous chloride was added with stirring 116.4 g. (0.772 moles) of the Grignard reagent prepared in 97% yield from 100 g. (0.790 moles) of benzyl chloride, 20.0 g. (0.822 g. atom) of magnesium in 2290 ml. of ether. The addition was made dropwise at such a rate that ether was held at reflux. After addition, the reaction mixture was heated to reflux for two hours, cooled and decomposed with saturated ammonium chloride solution. The organic layer was worked up as usual and the residual liquid was distilled in a claisen flask. The distillate was fractionated through a 30 x 2.5 cm. column packed with glass helices to obtain 122.0 g. (54%) of IV, b.p. 163-165° (4 mm.). V.P.C. analysis on a 2' x 1/4", 10% SE-30 (silicone gum rubber) on 60/80 chromosorb P column showed this material to be homogenous.

Analysis calculated for C\text{17}H\text{24}O\text{4}: C, 69.8; H, 8.2

Found (a): C, 69.7; H, 8.0

I.R.: Strong absorption at 5.85\text{μ} (1709 cm\text{⁻¹}).

**NMR Spectrum of IV:**

\[ \delta = 1.083 \text{ ppm (6H), 1.20 (6H), 2.83 (2H), 3.20 (1H), 4.11 (4H), 7.16 (5H).} \]
(α, α-Dimethyl phenethyl) malonic acid, V

A solution of 87.0 g. (0.298 moles) of IV and 41.7 g. (0.745 moles) of potassium hydroxide in a mixture of 100 ml. of ethanol and 300 ml. of water was refluxed for 12 hr. Ethanol was removed by distillation and 100 ml. of benzene-ether mixture (1:1) was added to the residue. The alkali layer was separated and added dropwise with stirring to 62 ml. of cold concentrated hydrochloric acid. The solid that separated was filtered, washed with 50 ml. of water and dried. Recrystallization from benzene afforded 63 g. (93%) of V as colorless crystalline solid, m.p. 167-168° (melts with evolution of gas).

Neutral equivalent of V

The neutral equivalent of V was found to be 119, compared to the calculated value of 118.

Analysis calculated for C₁₃H₁₆O₄: C, 66.1; H, 6.8

Found (b): C, 66.0; H, 6.8

I.R.: Broad O-H stretching absorption in the region of 3.0-4.0μ (3333-2500 cm⁻¹) and two C=O absorptions at 5.76μ (1736 cm⁻¹) and at 5.85μ (1710 cm⁻¹).

N.M.R.: 0 = 1.083 ppm (6H); 2.83 (2H); 3.15 (1H); 7.24 (5H); 10.20 (2H).

4-Phenyl-3,3-dimethyl butyric acid, VI

The solid dicarboxylic acid, V, 54.0 g. was heated in an oil bath maintained between 175-177°. Evolution of carbon dioxide was observed at the melting point of the compound. The carbon dioxide liberated was measured with the aid of a "Gas Testmeter." After two hours, when the
calculated amount of carbon dioxide had been collected, heating was
stopped and the residual liquid was distilled in a claisen flask to
obtain 41.6 g. (95%) of VI as a colorless viscous liquid, b.p. 141-142°
(2.5-3.0 mm.).

**Neutral equivalent:** The neutral equivalent of VI was found to be 190.1
compared with the theoretical value of 192.0.

**Analysis calculated for C_{12}H_{16}O_{2}:** C, 75.0; H, 8.3

**Found (a):** C, 75.2; H, 8.5

**I.R.:** Broad absorption in the region of 3.0-4.0 μ and a strong absorp­
tion at 5.88 μ (1701 cm⁻¹).

**NMR:**

δ = 1.037 ppm (6H); 2.20 (2H); 2.66 (2H); 7.16 (5H); 12.03 (1H).

4-Phenyl-3,3-dimethylbutyroyl chloride, VII

A mixture of 25.0 g. (0.130 moles) of VI and 77.0 g. (0.651 moles)
of thionyl chloride in 100 ml. of benzene was heated by an oil bath at
85° for 10 hr. After removal of benzene and unreacted thionyl chloride
by distillation, the residue was distilled to obtain 25.0 g. (91%) of VII,
b.p. 113-113.5° (4.5-5.0 mm.).

**I.R.:** Strong absorption at 5.55 μ (1802 cm⁻¹). The broad absorption in
the region of 3.0-4.0 μ (3333-2500 cm⁻¹) was absent.

**NMR Spectrum:**

δ = 0.933 ppm (6H); 2.33 (2H); 2.68 (2H); 7.28 and 7.94 ppm (5H).
Rosenmund reduction of VII to 4-phenyl-3,3-dimethylbutyraldehyde, VIII

A 250 ml. three-necked flask equipped with ground joints was fitted with a stirrer, a reflux condenser and a gas inlet tube extending to a point just above the stirrer. The top of the condenser was connected by a rubber tube to a glass tubing extending to the bottom of an Erlenmeyer flask containing 100 ml. of water and a few drops of phenolphthalein indicator. A burette containing 0.3 N sodium hydroxide was arranged for delivery into the Erlenmeyer flask.

The apparatus was made free of moisture by evaporating 5 ml. of dry toluene with a flame under nitrogen atmosphere. A suspension of 0.7 g. of 5% palladium on barium sulfate catalyst in 100 ml. of dry toluene (dried over sodium wire) was heated at 110° (bath temperature) with stirring and bubbling nitrogen through the inlet tube for one half hour. Nitrogen stream was replaced by hydrogen for one half hour. The reaction mixture was cooled to 60°, 7.0 g. of the acid chloride, VII, added at once under nitrogen atmosphere and hydrogen was passed continuously through the stirred reaction mixture. The extent of reduction was followed by estimating the hydrogen chloride absorbed by the water in the Erlenmeyer flask by titration with sodium hydroxide. Evolution of hydrogen chloride was slow at 60° and the bath temperature was gradually increased to 95°. The evolution of hydrogen chloride was brisk when the bath temperature was between 90-95° and most of the reaction occurred in this temperature range. About 90% of the reaction was over in about 2.5 hr. The rate of hydrogen chloride evolution was slow towards the end.
Even after the addition of 0.1 g. of fresh catalyst and elevation of the temperature to 105°, further reduction occurred to the extent of only 2% in 1 hr. Hydrogen was replaced by nitrogen (to avoid reduction of aldehyde to alcohol) and heating was continued further for one half hour. After cooling, the reaction mixture was filtered through a sintered glass funnel and the catalyst was washed with hot toluene. The solvent was removed by distillation under reduced pressure in an atmosphere of nitrogen. The resulting residue was distilled under nitrogen to obtain 4.5 g. (77%) of a colorless liquid, b.p. 99-100° (3.5-4.0 mm). A small amount of viscous material was left behind in the distillation flask.

The infrared spectrum of this residue and that of the monoacid, VI, were identical. By hydrolyzing and titrating 0.11 g. of the distillate, unreacted VII was found to be present only to the extent of 0.2%. Hence the aldehydic content of the sample was estimated to be 99.8%.

During the course of the Rosenmund reduction samples of the effluent gas were withdrawn at different intervals of time and analyzed for carbon monoxide by gas chromatography on a 16' x 1/4" molecular sieve, type 5A (column temperature 80°; helium flow rate 30 ml./min.) column. The chromatogram showed no peak with retention time corresponding to that of carbon monoxide.

I.R.: Strong absorption at 5.80μ (1724 cm\(^{-1}\)). From 0.18 g. of VIII was obtained 0.21 g. (57%) of its 2,4-dinitrophenyl hydrazone derivative, X.

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\(^{64}\) G. Kyryacos and C. E. Boord, Analytical Chemistry, 22, 787 (1957).

---

\(^{65}\) No attempt was made to recover X quantitatively as more of X was present.
as yellow crystals, m.p. 134-135°, after two recrystallizations from ethanol-benzene mixture.

Analysis calculated for \( \text{C}_{16}\text{H}_{20}\text{N}_{4}\text{O}_{6} \): C, 60.7; H, 5.6; N, 15.7

Found (a): C, 60.7; H, 5.7; N, 16.0

NMR:

\( \delta = 0.98 \text{ ppm (6H)}; 2.24 (2H); 2.60 (2H); 7.26 (5H); 7.85 (1H); 8.20 (1H); 8.34 (1H); 8.86 (1H); 11.45 (1H). \)

Synthesis of neopentylbenzene, IX (Decarbonylation of VIII)

The following experiment describes the best of three runs.

Decarbonylation was effected in a 25 ml. claisen flask fitted with a solid receiver cooled by cold water. The carbon monoxide evolved was measured either by a "Gas testmeter" or by collection over water. The system was flushed with nitrogen, a mixture of 4.5 g. of VIII and 0.2 g. of 10% palladium on charcoal catalyst was placed in the claisen flask and heated in a salt bath. Gas evolution commenced at 160° (bath temperature) and was extremely rapid at 220°, where most of the gas was evolved at a constant rate. About 90% of the calculated amount of carbon monoxide was evolved in four hours and then the reaction became sluggish. Gas evolution became brisk after the addition of a small quantity of powdered soft glass. At the end of 4.5 hr. when the theoretical amount of carbon monoxide had been evolved, heating was stopped. The distillate, 3.6 g., collected in the solid receiver contained mere traces of VIII (practically no absorption at 5.80\( \mu \)) and was purified as described below. About 150 ml. of pentane, 50 ml. of water was added to the distillate. After stirring at room temperature for 24 hr., the aqueous layer was separated and extracted twice with 100 ml. of pentane. The combined pentane
solution was washed successively with 5% aqueous potassium carbonate, water, saturated sodium chloride and dried over anhydrous magnesium sulfate. Pentane was removed by careful distillation through 30 x 2.5 cm. vigreaux column and the residual liquid was distilled to obtain 3.4 g. (90%) of IX as colorless liquid, b.p. 186.0-187.5°. (Literature records 185.6-187.0°.)

V.P.C. analysis on a 2' x 1/4", 10% SE-30 on 60/80 chromosorb P column showed the liquid to be homogeneous.

I.R.: Absorption bands at 8.05, 12.95 and 13.90/μ. (Literature records bands at 8.02, 12.92 and 13.87/μ.)

NMR:
\[ \delta = 0.89 \text{ (9H)}; 2.43 \text{ (2H)}; 7.11 \text{ (5H) ppm.} \]

4-Phenyl 3,3-dimethyl butanol-1, XI

To a solution of 2.7 g. of lithium aluminum hydride in 150 ml. of tetrahydrofuran was added dropwise a solution of 13.6 g. of VI in 100 ml. of tetrahydrofuran. The mixture was refluxed for 10 hours, cooled and excess of lithium aluminum hydride was decomposed with 10 ml. of 10% sulfuric acid. After filtering the aluminum salts through hypo-flo supercel, tetrahydrofuran was removed from the filtrate by evaporation under reduced pressure. The residue was taken in 500 ml. of ether-benzene mixture and the organic extract was worked up in the usual manner. The residual liquid on distillation yielded 8.5 g. (67%) of XI as colorless liquid, b.p. 124.0-125.0° (5 mm.).
Attempted synthesis of neopentylbenzene, IX

A mixture of 5.0 g. of XI and 0.4 g. of 10% palladium on charcoal was heated in a salt bath. Gas evolution was very slow at 220° and was not brisk even at 290°. Even the addition of 0.3 g. of fresh catalyst and increase of bath temperature to 300° did not facilitate the reaction. After 7 hours of heating, the reaction mixture was cooled and filtered. The catalyst was washed with ether and the ether washings combined with the filtrate. Evaporation of the solvent and distillation of the residual liquid afforded 0.5 g. (12%) of IX and 2.0 g. (40%) of XI, b.p. 122-125° (5 mm.). Some tarry residue was observed in the distillation flask.
Synthesis of Cis- and Trans-1,2-Dineopentylethylene

Tetraethyl-4-octyne-2,2,7,7-tetracarboxylate, XIX

In a dry 1-l. three-necked flask equipped with a stirrer, condenser and addition funnel were placed 220 ml. of absolute ethanol. Sodium metal 15.5 g. (0.666 g. atoms) was added in small pieces at room temperature and the last pieces of sodium metal were dissolved by heating the solution at 80°. To the resulting solution of sodium ethoxide was added 170.0 g. (0.976 moles) of diethyl methylmalonate\(^{66}\) (Aldrich Chemical Co.). The color of the solution changed to yellow. The solution was heated at 80° for 3 hr., cooled to room temperature, and 40.0 g. (0.325 moles) of 1,4-dichloro-2-butyne (General Aniline Co.) was added dropwise over a period of 2 hours. The reaction was highly exothermic and caused an immediate precipitation of sodium chloride on addition of 1,4-dichloro-2-butyne. After the completion of addition, the deep yellow colored reaction mixture was stirred for one and one half hours. The reaction mixture (pH = 8) was neutralized (pH = 7) with dil. acetic acid. The precipitated sodium chloride was dissolved with a minimum amount of water and the organic material extracted with benzene-ether mixture. The organic layer was separated and the aqueous layer was extracted twice.

\(^{66}\)V.P.C. analysis on a 6' x 1/4", 20% SE-30 on 60/80 P column showed diethyl methylmalonate to consist of only one component.
with ether-benzene. The combined organic solution was worked up in the usual manner. The resulting yellowish-red residue was fractionated on a 30 x 2.5 cm. column packed with glass helices to yield 94.0 g. (72%) of XIX, b.p. 148.0-148.1° (0.5 mm.).

V.P.C. analysis on a 2' x 1/4", 10% SE-30 on 60/80 P column showed XIX to consist of only one component.

Analysis calculated for C_{20}H_{30}O_3: C, 60.3; H, 7.6

Found (a): C, 60.1; H, 7.4

I.R.: Strong absorption at 5.75μ (1739 cm\(^{-1}\)).

NMR:

\[ \delta = 1.23 \text{ ppm (12H); 1.40 (6H); 2.63 (4H); 4.13 ppm (8H)}. \]

2,2,7,7-Tetrakis (hydroxymethyl)-4-octyne, XX

a. In a 1-l. three-necked flask equipped with a stirrer, condenser and addition funnel were placed 500 ml. of dry ether and 28.6 g. (0.773 moles) of lithium aluminum hydride. The resulting mixture was stirred and refluxed under nitrogen for 6 hr. To the resulting slurry of lithium aluminum hydride was added dropwise over a period of 1.5 hours 38.4 g. (0.097 moles) of tetraester, XIX in 150 ml. of dry ether. The addition caused immediate precipitation of yellow solid. The reaction mixture was stirred with reflux for 12 hr., cooled and hydrolyzed with 140 ml. of 10% sulfuric acid. The resulting mixture was diluted with 1-l. of ethanol, filtered through fiberglass filter paper and the alumina salts washed with 500 ml. of ethanol. The filtrate (pH = 8) was neutralized with cold 10% sulfuric acid. The precipitates formed were filtered and the neutral filtrate was dried over anhydrous magnesium sulfate. Excess ethanol was stripped off and to the remaining residue
was added 600 ml. of benzene. About 500 ml. of benzene was distilled in order to remove last traces of water. The remaining solution on cooling afforded white crystalline product which was recrystallized from benzene and ethanol to yield 16.0 g. (72%) of XX, m.p. 149-150°.

Analysis calculated for C₁₂H₂₂O₄: C, 62.6; H, 9.6
Found (a): C, 62.8; H, 9.6

I.R.: Strong absorption at 3.05 μ (3280 cm⁻¹).

NMR; (5% solution in dimethylsulfoxide-D₆)
\[ \delta = 0.83 \text{ ppm (6H)}; 2.075 (4H); 3.30 (8H); 4.37 \text{ ppm (4H)} \]

b. To a slurry of 28.5 g. (0.772 moles) of lithium aluminum hydride in 500 ml. of dry ether was added dropwise over a period of 1.5 hours, 38.4 g. (0.097 moles) of tetraester, XIX, in 150 ml. of ether. After stirring with reflux for 12 hours, the reaction mixture was hydrolyzed with 140 ml. of 10% sulfuric acid and the aluminum salts were dissolved by the addition of 1-l. of water. The solution was made neutral with 5% sodium bicarbonate, saturated with solid sodium chloride and subjected to continuous extraction with ether. The white crystalline product that was obtained afforded on crystallization from benzene-ethanol mixture 19.2 g. (86%) of XX, colorless crystals, m.p. 150-151°.

When the above experiment (a) was repeated using tetrahydrofuran as a solvent instead of ether, XX, m.p. 149-151°, was obtained in 70% yield, whose NMR was in agreement with the required structure.

2,2,7,7-Tetakis (hydroxymethyl)-4-octyne tetramethanesulfonate, XXI

In a 1-l. three-necked flask equipped with a condenser, addition funnel and stirrer were placed 350 ml. of chloroform (A.R.) and 29.0 g. (0.126 moles) of XX. The heterogeneous mixture was cooled to -10° and
and 104.0 g. (0.908 moles) of methanesulfonyl chloride was added at once. To the stirred mixture was then added dropwise 109.9 g. (0.908 moles) of collidine at 0-5° over a period of 2 1/4 hr. Upon completion of addition of collidine, the heterogenous mixture turned into a light yellow homogenous solution which was allowed to stir at 0° for 2 hr. and then the mixture was brought to room temperature. Upon warming to room temperature, the light yellow mixture turned bright yellow and then slowly to black. The reaction mixture was stirred at room temperature for 12 hr. To the dark colored mixture was added 250 ml. of water and the colloidal sulfur filtered through fiberglass filter paper. The chloroform layer was separated and the aqueous layer extracted twice with 300 ml. portion of chloroform. The combined chloroform extract was washed with 6% hydrochloric acid and worked up in the usual manner. The residual liquid was triturated with ether and the brown solid was treated with decolorizing charcoal (Darco G-60) and recrystallized from chloroform-methanol mixture to obtain 63.0 g. (92%) of XXI, m.p. 121-122°.

Analysis calculated for C_{16}H_{30}O_{12}S_4: C, 35.4; H, 5.5; S, 23.6

Found (a): C, 35.6; H, 5.7; S, 23.5

I.R.: No absorption at 3.05 μ.  

NMR Spectrum: (CDCl₃)  
δ = 1.15 ppm (6H); 2.35 (4H); 3.05 (12H); 4.15 (8H).

2,2,7,7-Tetakis(iodomethyl)-4-octyne, XXII

In a 1-l. three-necked flask equipped with stirrer and condenser were placed 400 ml. of ethyl cellulosolve (monoethyl ether of ethylene glycol), 206.0 g. (1.373 moles) of sodium iodide (Baker analyzed) and 62.0 g. (0.114 moles) of tetramesylate, XXI. The heterogenous mixture
was heated under an atmosphere of nitrogen. Upon heating at 110-120° for
an hour, tetramesylate, XXI, went into solution and a light yellow
homogenous mixture was obtained. On further heating a precipitate of
sodium methanesulfonate started appearing. The heterogenous mixture was
heated for 24 hours at 125° (bath temperature). The reaction mixture
turned from yellow to dark reddish brown. To the cooled reaction mix­
ture was added 200 ml. of water and extracted with 500 ml. of ether-
benzene mixture. The aqueous layer was extracted twice with 200 ml.
portion of ether-benzene. The combined organic solution was washed with
sodium thiosulfate and worked up in the usual manner. The resulting
brown residue on cooling afforded light brown solid. The crude product
was crystallized from benzene-methanol mixture to obtain 70.0 g. (91%) of
XXII, m.p. 63-64°.
Analysis calculated for C₁₂H₁₆I₄: C, 21.5; H, 2.7; I, 75.8
Found (a): C, 21.7; H, 2.6; I, 75.8

NMR Spectrum:

δ = 1.19 (6H); 2.39 (4H); 3.36 (8H) ppm.

2,3'- (2-Butynylene)bis(3-methylthietane), XXIII

To 800 ml. of freshly distilled Ethyl Cellosolve under nitrogen
was added 43.0 g. (0.180 moles) of sodium sulfide nonahydrate (crystal­
lized twice from ethanol and dried over phosphorous pentoxide). The
mixture was heated for 10 minutes at 70° and the resulting yellow colored
solution was cooled to 50°.

In a 2-l. three-necked flask fitted with a stirrer, condenser and
dropping funnel were placed 30.0 g. (0.045 moles) of tetraiodide, XXII,
and 800 ml. of freshly distilled ethylene glycol monoethyl ether. The
resulting mixture was heated to 110° under nitrogen atmosphere and Ethyl Cellosolve-sodium sulfide nonahydrate solution was added dropwise over a period of 1 hr. maintaining the reaction temperature between 110° and 120°. After addition, the pale brown reaction mixture was heated at 124-125° for 6 hr., cooled and about 1500 ml. of Ethyl Cellosolve was removed in vacuo. To the dark brown colored residue was added 500 ml. of ether, 100 ml. of water and the organic layer was separated. The aqueous layer was extracted twice with 200 ml. portions of ether. The combined organic solution was washed with sodium thiosulfate and worked up in the usual manner. The resulting residue on distillation afforded 8.6 g. (85%) of XXIII, b.p. 129-131° (0.3 mm.).

Analysis calculated for C_{12}H_{18}S_{2}: C, 63.7; H, 7.9; S, 28.3

Found (a): C, 63.6; H, 7.7; S, 28.0

V.P.C. analysis on a 2' x 1/4", 10% SE-30 on 60/80 P column, showed this compound to consist of only one component.

NMR:

\[ \delta = 1.35 \text{ ppm (6H)}; 2.41 (4H); \delta_B = 2.83; \delta_A = 3.05 (8H), \text{ ppm.} \]

(See Discussion.)

Attempted conversion of tetramesylate, XXI, into dineopentylacetylene, XXX

A mixture of 0.21 g. of lithium aluminum hydride and 0.06 g. of lithium hydride was placed under an atmosphere of nitrogen in a dry two-necked flask equipped with a condenser and a magnetic stirrer. To the mixture was added 70 ml. of tetrahydrofuran (dried over lithium aluminum hydride) and heated at reflux for an hour. A solution of 1.0 g. (0.0018 moles) of XXI in 30 ml. of tetrahydrofuran was added dropwise at such a rate as to maintain moderate reflux. After refluxing for 6 hours, the reaction mixture was decomposed with 10% sulfuric acid and extracted with
ether. The aqueous layer was neutralized with sodium bicarbonate, saturated with sodium chloride and subjected to continuous extraction with ether. The product obtained was crystallized from benzene-ethanol mixture to yield 0.15 g. (35%) of tetralcohol, XX, as colorless crystals, m.p. 149-151°.

Attempted preparation of 3,3'-(2-butynylene)bis(3-methylthietane), XXIII
(Reaction between tetramesylate, XXI, and sodium sulfide nonahydrate)

To 200 ml. of ethanol at 70° was added 17.7 g. (.074 moles) of sodium sulfide nonahydrate (Baker reagent, recrystallized from ethanol and dried over phosphorous pentaoxide). The resulting solution was heated at 80° for 1/2 hr. and then cooled to 50°.

In a 750 ml. two-necked Erlenmeyer flask equipped with a magnetic stirrer, condenser and addition funnel were placed 240 ml. of absolute ethanol and 10.0 g. (0.018 moles) of tetramesylate, XXI. The resulting mixture was heated to reflux and ethanol-sodium sulfide solution added dropwise over a period of 1/2 hr. in an atmosphere of nitrogen. The tetramesylate, XXI, went into solution after 3 hr. of reflux and sodium methanesulfonate started precipitating. The resulting light brown colored mixture was refluxed for 24 hours. After cooling and removal of sodium methanesulfonate deposit, the solution was concentrated in vacuo and the residue taken up in ether. The ether layer was washed with dilute hydrochloric acid and then worked up in the usual manner. The resulting residue on distillation yielded 2.9 g. (70%) of a material boiling over the range 130-140° (0.7 mm.).

The v.p.c. analysis of this material on a 2' x 1/4", 10% SE-30 on 60/80 P column showed the presence of two components in the relative ratios of 1:1.
When reaction was carried out using sodium sulfide nonahydrate (Baker analyzed) without further purification by recrystallization from ethanol, no product was formed and tetramesylate, XXI, was quantitatively recovered.

**Attempted preparation of XXIII**

To 160 ml. of ethylene glycol at 160° in a 250 ml. Erlemeyer flask equipped with a magnetic stirrer and a nitrogen inlet tube was added 17.7 g. (0.0738 moles) of sodium sulfide nonahydrate (Baker analyzed reagent, crystallized from ethanol). The resulting solution was maintained at about 180° with stirring and bubbling of nitrogen until evolution of water ceased and then cooled to 80°.

In a 500 ml., two-necked Erlemeyer flask equipped with a magnetic stirrer, condenser and addition funnel were placed 10.0 g. (0.0185 moles) of tetramesylate, XXI, and 260 ml. of distilled Ethyl Cellosolve (ethylene glycol monoethyl ether). The resulting mixture was heated at 120° and the ethylene glycol-sodium sulfide solution added dropwise under an atmosphere of nitrogen. The resulting reddish-brown solution was heated for 2 hours at 123-124° and cooled. Ethyl Cellosolve was removed in vacuo and to the remaining residue was added ether. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined organic layer was washed with dilute hydrochloric acid and then worked up in the usual manner. The remaining residue was distilled to obtain 1.2 g. (28%) of a material boiling over the range 136-141° (0.8 mm.). This fraction did not give satisfactory analysis for the bisthietane, XXIII.

**Analysis calculated for C₁₂H₁₈S₂**:  C, 63.7; H, 7.9; S, 28.3

**Found (a)**:  C, 64.7; H, 8.4; S, 27.3
According to v.p.o. analysis on a 2' x 1/4", 10% SE-30 on 60/80 P column, this material contained two components in the relative ratios of 1:4.

**NMR Spectrum:**

\[ \delta = 1.35; 2.42; \delta_B = 2.82; \delta_A^1 = 3.05; \delta_B^1 = 4.25; \delta_A^2 = 4.38 \text{ ppm} \]

(See Discussion.)

**Cis 1,2-dineopentylethylene, XVI**

The maximum yield of cis 1,2-dineopentylethylene obtained was in the following experiment.

In a 500 ml. three-necked flask equipped with a condenser cooled by ice water and a stirrer (turbor stirrer) was placed 165.0 g. of Raney nickel-Wg \(^{67,68}\) (cpd:Raney Ni = 1:20) and 90 ml. of methanol (A.R.). A solution of 8.3 g. (0.0367 moles) of bisthietane, XXIII, in 50 ml. of methanol was added all at once to the Raney nickel, the system flushed with nitrogen and closed with the help of stoppers. Upon stirring the contents became very hot and at the end of one half hour the exothermic reaction subsided. After stirring for 5 hr. at room temperature, the reaction mixture was filtered through Hypo-flo Supercel. \(^{69}\) The Raney nickel-Wg was prepared according to the procedure described in Organic Syntheses Collective, Vol. III, p. 181, with slight modifications. (1) The reaction temperature during the addition of Raney nickel alloy to the alkali solution was maintained between 35\(^\circ\) to 40\(^\circ\) instead of a maximum of 25\(^\circ\). (2) The catalyst was washed thirty-six times with 5-1. portions of distilled water over a period of 27 hr.

\(^{67}\) Hypo-flo Supercel is an inert cellulose filtering aid.
nickel cake was washed with 400 ml. of pentane. The filtrate (a) and the Raney nickel cake (b) were worked up separately.

a. After addition of 5 ml. of water, the two layers of the filtrate were separated. The lower aqueous methanol layer was extracted twice with 100 ml. portion of pentane and the combined pentane solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Pentane was distilled off very carefully at atmospheric pressure through a 30 cm. vigreux column. The liquid residue was distilled, using a dry ice acetone bath for cooling the receiver, to obtain 4.7 g. (77%)\(^7\) of a colorless liquid, b.p. 100-103\(^\circ\) (78 mm.).

\(^7\)Caution should be exercised in working up the reaction product as these hydrocarbons are highly volatile. The yield varied from a maximum of 77% to a minimum of 56% depending upon the room temperature.

V.P.C. analysis of this liquid on 8' x 1/4", 30% carbowax 20M on 60/80 chromosorb P column showed the presence of three components in the relative ratios of 8.3:24:1 in the order of their increasing retention times.

The components were separated by preparative gas chromatography on a 20' x 3/8", 30% carbowax 20M on 60/80 P column, using on-column injection and programming the "A-700" from 100-145\(^\circ\) (helium flow rate 133 ml./min. and sample size 75 \(\mu\)l.). The two major components were collected. The component A having retention time of 21 minutes was formed in smaller amount and the component B having retention time of 24 minutes was formed in larger amount.
Physical properties of component B (cis-1,2-dineopentylethylene, XVI)

1. Component B was homogenous as indicated by v.p.c. analysis on 8' x 1/4", 30% carbowax 20M on 60/80 P and also on a 100' squalane capillary column.

2. Mass spectra showed component B to be pure.

Our thanks to Dr. Mynard Hamm of the Continental Oil Co., Ponca City, Oklahoma, for the mass spectral analysis.

3. NMR Spectrum showed component B to be homogenous.

\[ \delta = 0.91 (18H); 1.93 (4H); 5.55 (2H) \text{ ppm.} \]

4. Near infrared spectrum of component B exhibited a combination band at 2.140, characteristic of cis unsaturation.49,50

5. Infrared spectrum: Absorption band at 1650 cm\(^{-1}\) (6.6\(\mu\); C=C stretching)\(^{48}\) and 680 cm\(^{-1}\) (14.7\(\mu\); =C-H out of plane vibration).\(^{48}\)

Analysis calculated for C\(_{12}\)H\(_{24}\): C, 85.6; H, 14.4

Found (b): C, 85.8; H, 14.4

V.P.C. analysis of five runs showed that component B (cis-1,2-dineopentylethylene, XVI) was present in the range of 66 to 72% in the filtrate when the reaction was carried out under identical conditions using the same batch of the catalyst\(^{67,68}\) of comparable activity.

Physical properties of component A

1. V.P.C. analysis on 8' x 1/4", 30% carbowax 20M on 60/80 P column gave only one peak but 100' squalane capillary column showed it to contain two components in the relative ratios of 1:1.3.

2. NMR: Component A was found to be nonhomogenous and to contain two components in the relative ratios of 1:1.4. These two
components were identified to be the saturated hydrocarbon, XVIII, and trans-1,2-dineopentylethylene, XVII, respectively.

3. I.R.: Strong absorption at 970 cm\(^{-1}\) (10.3\(\mu\) ; =C-H out of plane vibration).\(^4\)

4. Mass spectrum:\(^7\) Component A was nonhomogenous.

b. Work up of Raney nickel cake

Raney nickel cake was extracted with pentane by using soxhlet extractor. Pentane solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of solvent carefully using a 30 cm. vigreaux column and distillation of the residue afforded 0.6 g. (10%) of a colorless liquid, b.p. 102-104° (79 mm.). The infrared spectrum of this liquid was identical to that of the liquid obtained from the filtrate. But the former exhibited relatively a strong absorption at 970 cm\(^{-1}\).

V.P.C. analysis of this liquid on an 8' x 1/4", 30% carbowax 20M on 60/80 P column showed the presence of two major components in the relative ratios of 1.1:1.0 in the order of their increasing retention times.

Comparison of v.p.c. retention times, infrared and NMR spectra showed these components to be identical with components A and B obtained from the filtrate.

Trans-1,2-dineopentylethylene, XVII

The experimental procedure and work up described under the preparation for the cis isomer, XVI, was also followed for the preparation of this trans isomer.
By stirring 8.3 g. of bisthietane, XXIII, and 181.0 g. of Raney nickel\(^{67,72}\) (ratio 1:22) in 140 ml. of methanol for 16 hr.\(^{73}\) at room temperature was obtained 4.5 g. (74%) of liquid, b.p. 99-102° (76-77 mm.).

Prom this experiment inference should not be drawn that 16 hr. is the required time for obtaining maximum yield of trans isomer. Reaction times lower than 16 hr. are likely to give better yield of trans isomer, XVII, since the possibility of getting saturated analog, XVIII, over a longer period of time will be increased.

V.P.C. analysis of this liquid on a 20' x 3/8", 30% tetracyanoethylated pentaerythritol on 60/80 P (column temperature 100° and helium flow rate 90 ml./min.) column showed the presence of three components in the relative ratios of 1.0:1.60:1.74 with retention times 19, 21 and 25 minutes, respectively. The components were separated by preparative gas chromatography on a 20' x 3/8", 30% tetracyanoethylated pentaerythritol on 60/80 P column using on-column injection and isothermal conditions (column temperature 100°, helium flow rate 90 ml./min. and sample size 25µl.). The relative order of retention times were saturated hydrocarbon, XVIII, trans olefin, XVII, and cis olefin, XVI.

Physical properties of XVIII, 1,2-dineopentylethane

1. Low melting solid, m.p. 25-26° (volatile).

2. NMR Spectrum:
\[ \delta = 0.88 (18H); 1.20 (8H) \text{ ppm.} \]

3. Infrared: Absorption band at 3.45µ (shoulders at 3.40; 3.49 3.52µ); 6.80; 7.20; 7.35 and 8.05µ.
Physical properties of XVII, trans-1,2-dineopentylethylene

1. Analysis calculated for C_{12}H_{24}: C, 85.6; H, 14.4
   Found (b): C, 85.6; H, 14.6

2. I.R.: Strong absorption at 10.3 μ (970 cm⁻¹; C=H out of plane vibration).48

3. N.M.R.: Showed it to be homogenous.
   δ = 0.89 (18H); 1.90 (4H); 5.43 (2H) ppm.

V.P.C., I.R. and N.M.R. analyses showed that the trans olefin, XVII, was present relatively in larger amount (~40%) in the product obtained from the Raney nickel cake than in the product obtained from the filtrate (15-17%).

XVI was identified by infrared and N.M.R. spectra to be cis-1,2-dineopentylethylene.

1,2-Dineopentylacetylene, XXX

a. Experimental procedure and work up described under the cis isomer, XVI, was also followed in the present instance. By stirring, 8.2 g. of bisthietane, XXIII, and 148.0 g. of Raney nickel74 (ratio 1:18) in 145 ml. of methanol for 4 hr. at room temperature was obtained 1.2 g. (20%) of colorless liquid, b.p. 100-103° (80 mm.) and 4 g. (50%) of the

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74 The catalyst used was much less active than that used in the previous two runs. The Raney nickel-W2 was prepared according to the procedure described in Organic Syntheses Collective, Vol. III, p. 181, with the following modifications. (1) The reaction temperature during the addition of Raney nickel alloy to the alkali solution was maintained between 35° to 40°, instead of a maximum of 25°. (2) The catalyst was washed well 52 times with 5-l. portions of distilled water over a period of 40 hr.

unreacted bisthietane, XXIII, was recovered. The liquid was analyzed by
v.p.c. on a 20' x 3/8" 30% tetracyanoethylated pentaerythritol on 60/80 P column (column temperature 100° and helium flow rate 90 ml./min.). The chromatogram showed the presence of 4 components, XVIII, XVII, XVI and XXX, having retention times 19, 21, 25 and 40 minutes in the relative ratios of 1:2:7:4:4. Preparative gas chromatography was used to separate these four components (column temperature 100°, helium flow rate 90 ml./min.). The components XVIII, XVII and XVI having retention times 19, 21 and 25 minutes were identified by I.R., NMR spectra to be 1,2-dineopentylethane, trans-1,2-dineopentylethylene and cis-1,2-dineopentylethylene.

NMR Spectrum of XXX, 1,2-dineopentylacetylene:

\[ \delta = 0.98 (18H); 2.01 (4H) \text{ ppm.} \]

b. 1,2-Dineopentylacetylene was also obtained in another run.

By stirring 8.5 g. of bisthielane, XXIII, with 173.0 g. of Raney nickel\(^{77,75}\) (ratio 1:20) in 140 ml. of methanol for 5 hr. and 30 minutes at room temperature was obtained 2.8 g. (45%) of a colorless liquid, b.p. 100-103° (78 mm.) and 3.0 g. (35%) of unreacted bisthielane, XXIII. The v.p.o. analysis of this liquid on 20' x 3/8", 30% tetracyanoethylated pentaerythritol on 60/80 P (column temperature 100°, helium flow rate 90 ml./min.) column showed the presence of four components, XVIII, XVII, XVI and XXX, having retention times 19, 21, 25 and 40 minutes in the ratios of 1:2:6:4:1:1.
Desulfurization of XXIII with Raney nickel in acetone (Formation of 3,8-bis(mercaptomethyl)-3,8-dimethyl-5-(decynedioic acid, bis γ-thiolactone, XXXI)

In a 500 ml. two-necked Erlenmeyer flask equipped with a magnetic stirrer and condenser were placed 72.0 g. of Raney nickel (mp: Raney Ni, 1:24). After washing by decantation with 200 ml. of acetone, the catalyst was suspended in 100 ml. of acetone, refluxed for 1 hr. under nitrogen and cooled to room temperature. About 60 ml. of acetone was removed by decantation and 3.0 g. of bisthietane, XXIII, in 40 ml. of acetone was added. After stirring at room temperature for 30 minutes, the mixture was heated to reflux for 3 hr. under nitrogen. The reaction mixture was cooled and filtered through Hypo-flo Supercel. The Raney nickel was washed with 200 ml. of hot pentane. About 25 ml. of water was added to the filtrate and the pentane layer was separated. The aqueous layer was extracted twice with 50 ml. of pentane. The combined pentane solution was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. Pentane was removed on a 30 cm. vigreaux column at atmospheric pressure. When the volume of the residue was about 5 ml. a solid separated and was filtered. The solid was recrystallized from chloroform to obtain 0.5 g. (15%) of a crystalline colorless compound, m.p. 105-107°. This compound contained sulfur (sodium-fusion test) and analyzed for C₁₄H₁₈S₂O₂.

Analysis calculated for C₁₄H₁₈S₂O₂: C, 59.6; H, 6.4; S, 22.7; O, 11.3

Found (b): C, 59.8; H, 6.4; S, 22.6; O, 11.2.
I.R.: Strong absorption at 5.90 μ (1695 cm⁻¹).

NMR Spectrum:

\[ \delta = 1.34 \text{ (6H)}; 2.46 \text{ (4H)}; \delta_B, 2.38; \delta_A, 2.63 \text{ (4H)}; \delta_B, 3.16; \delta_A, 3.43 \text{ (4H)} \text{ ppm. (See Discussion.)} \]

Synthesis of 1,4-bis(1-methylcyclopropyl)-2-butyne, XXXII

Method A:

To a suspension of 4.4 g. of magnesium in 125 ml. of ether was added with stirring over a period of 2 hr. 5.0 g. (0.007 moles) of the tetraiodide, XXII, in 150 ml. of ether. The reaction was initiated with a few drops of ethylene bromide. After stirring at room temperature for 6 hr., the brownish black reaction mixture was decomposed with saturated ammonium chloride and the precipitate formed was dissolved by the addition of 50 ml. of water. The ethereal layer was washed successively with sodium thiosulfate solution, water, saturated sodium chloride and dried over anhydrous magnesium sulfate. Ether was removed by distillation at atmospheric pressure using a 30 cm. vigreaux column and the residue was distilled to obtain 1.0 g. (83%) of a colorless liquid, b.p. 96.0-96.5° (35 mm.).

V.P.C. analysis of this liquid on a 2' x 1/4", 10% SE-30 on 60/80 chromosorb P (column temperature 100°) column, showed it to be at least 98% pure.
Analysis calculated for $C_{12}H_{18}$: C, 86.8; H, 11.1

Found (b): C, 87.6; H, 11.2

Satisfactory analysis could not be obtained as this compound has a great tendency to decompose and turn into deep yellow on standing even in a sealed tube. NMR spectrum of the liquid, XXXII, immediately after its preparation agreed with the assigned structure. But NMR spectrum of the liquid, XXXII, stored over a period of one month after its preparation showed additional signals resonating near methyl and methylene ($CH_2 - C\equiv C -$) protons of XXXII. The cyclopropyl protons appeared as usual as high field multiplets centered at 0.24 and 0.40 ppm. This liquid (one month old) also showed signal resonating in the down-field region (~4.3 ppm).

I.R.: Strong absorption at 1010 cm$^{-1}$ (9.9 $\mu$).

Near I.R.: $\lambda_{max}^{CCl_4} = 1.640 \mu$; $\epsilon = 1.22$ (cyclopropyl).

NMR Spectrum:

$\delta = 0.23; 0.40$ (8H) ppm; $1.10$ (6H); $2.13$ (4H) ppm.

Reductive cleavage of XXII with lithium aluminum hydride

Method B:

To a solution of 1.0 g. of lithium aluminum hydride in 70 ml. of ether was added dropwise 2.0 g. (.0029 moles) of tetraiodide, XXII, in 100 ml. of ether. The reaction mixture was held at reflux for 8 hr. with stirring. Excess lithium aluminum hydride was destroyed with dilute sulfuric acid, the mixture filtered through Hypo-flo Supercel and the ether layer worked up in the usual manner. The liquid on distillation afforded 0.4 g. (82%) of a colorless liquid, b.p. 100-101$^\circ$ (38 mm.). V.P.C. analysis of this liquid on a 2' x 1/4", 10% SE-30 on 60/80 P (column temperature 100$^\circ$) showed it to be homogenous. Comparison of v.p.c. retention times, infrared, near infrared, and NMR spectra showed it to be identical with the compound XXXII obtained by Method A.
Calculation of Chemical Shift (δ), Coupling Constant and Relative Intensity of AB System\textsuperscript{78,79}

\textsuperscript{78} L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 1959, p. 89.

\textsuperscript{79} N. S. Bhacca, D. H. Williams, Applications of NMR Spectroscopy in Organic Chemistry, 1964, p. 42.

The AB spectrum consists of four lines, two for the A proton and two for the B proton, and is a function of the ratio $J_{AB}/\delta_A - \delta_B$. As $J/\delta_A - \delta_B$ increases, the center of gravity (i.e., the position from which we compute $\delta$) of each band moves towards its inner component. In order to compute accurate chemical shifts ($\delta$) in AB system, we have to know the center of gravity corresponding to each value of $J/\delta_A - \delta_B$. The four lines of the AB spectrum are labelled as $V_1$, $V_2$, $V_3$ and $V_4$ in the order of increasing frequency (i.e., increasing separation from the line of tetramethylsilane).

The spacing between the two lines for either part is equal to the coupling constant.

\[ V_4 - V_3 = V_2 - V_1 = J_{AB} \]

\[ Q = V_3 - V_1 = V_4 - V_2 \]

If we designate the spacing between 1 and 3 (or 2 and 4 lines) as $Q$, then the chemical shift between proton A and B is given by

\[ \delta_A - \delta_B = \sqrt{Q^2 - J_{AB}^2} \]

or

\[ \delta_A - \delta_B = \sqrt{(V_4 - V_1)(V_3 - V_2)} \]
The actual values of $\delta_A$ and $\delta_B$ are found by adding and subtracting $1/2(\delta_A - \delta_B)$ to and from the midpoint of the AB spectrum, respectively.

Relative intensity of lines 1 and 2 (or 3 and 4) for a large $J/\delta$ ratio is given by

$$\frac{I_2}{I_1} = \frac{I_3}{I_4} = \frac{V_4 - V_1}{V_3 - V_2}$$

\[ (4) \]
Figure 1
Figure 2. Chemical shift, $\delta$

Chemical structure with labels for different functional groups and peaks on the graph.