THE CHEMISTRY OF ENYNES

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A modified method for the alkylation of enynes with a terminal triple bond is presented. The alkylation can be accomplished in good yields for 2-methyl-1-buten-3-yne and 1-ethynyl cyclohexene. Triple bonds of enynes, 1-(3-Methyl-3-buten-1-ynyl)cycloheptanol, 1-ethynylcyclohexene and 6-hydroperoxy-1-ethynylcyclohexene are selectively reduced by diimide. Double bonds of enynes can be selectively epoxidized with dimethyldioxirane. Intramolecular cyclization of enyne hydroperoxides via a free radical routes, (generated from N-bromo succinimide), via cationic routes (via bromination) or via anionic routes (catalization by tetrabutyl ammonium fluoride) failed to produce cyclic peroxide products. Instead, complex reactions occurred which lead to the formation of multiple products. The co-oxidation of 1,2 dicarboxy methyl acetylene gave a vinyl sulfide product.
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I. Introduction

This research focuses on exploring the chemistry of conjugated enynes. This is done in order to design a synthesis of vinyl peroxides via enyne chemistry. Vinyl peroxides are compounds with a peroxide bond adjacent to a carbon-carbon double bond. These unusual species may find applications in polymer chemistry. In addition to their polymer applications, they may possess potent oxidative properties and can serve as oxygen atom transfer agents. They have been claimed as reactive intermediates in some reactions but have never been isolated, even though several attempts at their syntheses were attempted. The main drawback for the isolation of vinyl peroxides is related to the inherent instability of the O-O bond directly attached to the vinyl bond. The electron rich \( \pi \) bonds of vinyl groups will destabilize the O-O bond by increasing the repulsion of the oxygen lone pairs. However, there are many examples of compounds that have the peroxide moiety adjacent to a carbon-oxygen or carbon-nitrogen double bond, particularly for cyclic peroxides. The key must lie in flanking the vinyl carbons with electron withdrawing groups to reduce the electron density of the \( \pi \) bond and thereby lone pair repulsion will be minimized. Our main strategy for the synthesis of vinyl peroxides is via intramolecular cyclization of an enyne hydroperoxide as shown below (equation (1) and (2)).
Hydroperoxide 1 could give rise to a vinyl peroxide upon electrophilic or nucleophilic cyclization reactions. In both cases, the lone pair repulsion of O-O bond could be decreased by distributing the electron cloud over the conjugated diene.
II. Review of the Literature

Reactions in Which Vinyl Peroxides are Claimed as Intermediates

Industrial interest in the use of organic peroxides began in the early 1900's when it was found that benzoic peroxide was an effective bleaching agent for edible oil. The continued growth of free radical polymerization stimulated the development of many organic peroxide products to meet a variety of needs. Today, organic peroxides are used as initiators in free-radical polymerization processes, crosslinking agents for polyolefines, vulcanizing agents for elastomers, curing agents for polyester resins, bleaching agents and epoxidizing reagents.7-10

The particular use of vinyl peroxides is not very clear, because they have never been isolated, as we stated above. However, according to their structure, vinyl peroxides can be promising monomers for photodegradable polymers. Some special vinyl peroxides such as diaryl peroxides once were thought to be present in solutions. For example, 4 was proposed11 for the dimer of the radical from "β-dinaphtol", and 5 was adopted for the product from 9-substituted 10-hydroxyphenanthrenes,12-13,14 614 and 715 was adopted for the products from monocyclic phenols.
However, later some extensive work\textsuperscript{16-19} on the oxidation of 2, 4, 6-trisubstituted phenols had shown that the dimers of the aryloxy radicals from these compounds are cyclohexadienonyl phenyl ethers \textsuperscript{9} and not aryl peroxides.
In the light of this, it would seem likely that the structures 4 to 7 are incorrect, and should also be replaced by non-peroxidic formulae.\textsuperscript{20}

Because O-O bonds are weak (around 34 kcal/mol) and because a vinyl group would further destabilize the O-O bonds, it is very difficult to generate a vinyl peroxide. For example, from the literature survey, the most stable vinyl peroxide is o-xylylene peroxide 11, synthesized by Jimmie. This compound appeared as a reactive intermediate, its life time was only twenty seconds.\textsuperscript{21}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=1cm]{figure11.png}};
\end{tikzpicture}
\end{center}

\textbf{(11)}

\textbf{The Chemistry of Enynes}

Enynes are derivatives of vinylacetylene. The first preparation of vinylacetylene was by exhaustive methylation of tetramethyl-1,4-butene.\textsuperscript{22} Today, enynes have a great value in polymer industry. Enynes have two unsaturated bonds increasing the possibility of undergoing intramolecular cyclizations, thus we chose enynes as the starting material to synthesize vinyl peroxide.
1. The Alkylation of Enynes

Low molecular weighted enynes are usually too volatile to be handled. Conjugated enynes with terminal acetylenic carbons can be alkylated very easily. Thus, one can increase the molecular weight and therefore the boiling point of the enyne via simple alkylation reactions. In practice by far the most important process for alkylation involves enynes as nucleophile since the acidity of the alkyne proton (Pka is around 2.5)\(^{23}\) allows the ready formation of alkynide ions. These are excellent nucleophiles and they readily undergo alkylation with appropriate electrophiles. The alkylation of alkynide ions is a reaction of considerable synthetic use and has been extensively reviewed.\(^{24-27}\)

One of the most important reactions in acetylene chemistry is the reaction of lithio alkynes with carbonyl compounds.\(^{27}\)

\[
\text{Li} \quad \begin{array}{c}
\equiv \\
R^1 \\
\equiv \\
R^2 \\
\equiv \\
R^3 \\
\end{array} + \quad \begin{array}{c}
\text{O} \\
R^4 \\
\equiv \\
R^5 \\
\equiv \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\equiv \\
\text{OH} \\
R^4 \\
R^5 \\
\equiv \\
R^3 \\
\end{array} 
\]

(12) (13) (14)

Another convenient alkylation of lithio alkynes is the reaction with alkyl bromide.\(^{28}\)
2. The Reduction of Enynes by Diimide

Of the widely diverse methods of reduction of carbon-carbon double and triple bonds, the reduction by diimide appears to be the most versatile.\textsuperscript{29} The reduction of carbon-carbon double and triple bonds by diimide occurs with complete stereoselectivity and stereospecificity, and can be effected in the presence of a variety of reactive functional groups.

Norin and Unelius\textsuperscript{30} did a series of reductions of enynes with diimide and found that the double bond is selectively reduced, the main products being acetylenic compounds.

3. The Epoxidation of Enynes by Dioxirane

Epoxides (oxiranes) are compounds which contain a saturated three-membered ring having one oxygen atom and two carbon atoms.
They are widely distributed in nature and are of industrial, mechanistic and biochemical interest.\(^{31}\)

The epoxidation reagent we used in this experiment, dimethyl dioxirane, is an efficient oxygen transfer reagent. It is quite selective in its reactivity, mild toward the oxidized product and conveniently prepared from commercially available materials. It possesses catalytic activity, and is recyclable and environmentally agreeable.\(^{32}\) Though as early as 1899 Baeyer and Villiger\(^ {33}\) had already postulated a dioxirane intermediate, only sporadic mention of the dioxiranes is to be found as elusive reaction intermediates in oxidation reactions prior to 1970s.\(^ {34-35}\) The historical advance was made by Suenram and Lovas.\(^ {36}\) In their experiments, the parent dioxirane could be detected in the gas-phase ozonolysis of ethylene, and the existence of dioxirane rigorously established. Once dioxiranes became accepted as relatively stable entities, numerous oxidations were performed in situ for synthetic purposes.\(^ {34-35}\) Now the widely used isolated dimethyl dioxirane is in a solution of ca. 0.1 M of the compound in acetone solution, which was first proposed by Murray and Jayaraman.\(^ {37}\) Of course, this solution is not as good as a pure product; however, efforts\(^ {38}\) to separate dioxirane have been so far unsuccessful.

Alkynes may be oxidized to diketones, but the oxidation at a carbon-carbon triple bond involving electrophilic attack by the dioxirane reagent occurs much less readily than a carbon-carbon double bond.\(^ {39}\)
Intramolecular Cyclization of Acetylenic Hydroperoxide

1. The Cyclization Via Radical Reaction

There are many methods to produce cyclic peroxides. One of the most frequently used methods is to accomplish a cyclization via free radical route.40

\[
\begin{align*}
\text{O-} & \quad \text{R'} \quad \text{O-} \\
\text{O} & \quad \text{O} \\
\text{OOH} & \quad \text{O} & \quad \text{X'} \quad \text{O} & \quad \text{X} \\
(19) & & (20)
\end{align*}
\]

For example, N-bromo succinimide has been applied to numerous synthetic problems.41-42 Its reaction is accelerated by chemical initiators and light. If an acetylene group is substituted for the vinyl group, the free radical cyclization may work, then vinyl peroxides would be obtained.

\[
\begin{align*}
\text{O-} & \quad \text{R'} \quad \text{O-} \\
\text{O} & \quad \text{O} \\
\text{OOH} & \quad \text{O} & \quad \text{Br} & \quad \text{R'} \\
(1) & & (21)
\end{align*}
\]

2. The Cyclization Via Bromination

Another method for the synthesis of cyclic peroxides used quite often is the cyclization via bromination. Petrov43-44 had
studied halogenation of enynes, and the addition to the conjugated system leads mainly to 1,4 allene product, i.e., 23.

\[
\begin{align*}
\text{Br}_2 & \quad \text{Br} \quad \text{Br} \quad \text{Br} \\
\text{Br} & \quad \text{Br} \quad \text{Br} \quad \text{Br}
\end{align*}
\]

(9)

(22) \quad \rightarrow \quad (23) \quad + \quad (24)

However, by attaching some bulky groups on the ene carbons, then the bromine attack occurs in a 1,2 sense to give 26.45-46

\[
\begin{align*}
\text{Br}_2 & \quad \text{Br} \quad \text{Br} \\
\text{Br} & \quad \text{Br} \quad \text{Br} \quad \text{Br}
\end{align*}
\]

(10)

(25) \quad \rightarrow \quad (26)

Though bromine is a homogeneous molecule, it acts under specific conditions as an ionic and an electrophilic compound in the addition reaction to unsaturated bonds.47 The addition reaction to olefins takes place by formation of a bridged intermediate:48

\[
\begin{align*}
\text{R}_1 \quad \text{R}_3 & \quad \text{Br} \quad \text{R}_2 \quad \text{R}_4 \quad \text{Br} \quad \text{R}_1 \quad \text{R}_3 \\
\text{R}_1 \quad \text{R}_3 & \quad \text{Br} \quad \text{R}_2 \quad \text{R}_4 \quad \text{Br} \quad \text{R}_1 \quad \text{R}_3
\end{align*}
\]

(11)

(27) \quad \rightarrow \quad (28)

An ionic mechanism of the bromination of alkyl-substituted acetylenes has also been postulated to involve a bridged, rate determining, transition state leading to a bromonium ion intermediate.49
For enynic hydroperoxides, the hydroperoxoyl group may attack the bromonium ion intermediate. If the double bond were brominated, the following intramolecular cyclization may occur.

If the triple bond were brominated, a vinyl peroxide may form via a intramolecular cyclization.
3. Tetrabutyl Ammonium Fluoride Catalyzed Cyclization

Pless\textsuperscript{50} found that tetrabutyl ammonium fluoride (TBAF) has a remarkable capacity to promote intramolecular cyclization. He pointed out that even in a solution of low polarity such as THF, the TBAF would be completely dissociated. The "naked" fluorine anion could act like a strong base and weak nucleophile at the same time facilitating certain types of base catalyzed cyclizations. Thus, in the presence of TBAF, the acetylenic hydroperoxide may undergo the following intramolecular cyclization to form a five membered ring or a six membered ring by attacking 1-acetylenic carbon with the anionic oxygen.

\[
\text{F}^- \xrightarrow{\text{H}} \begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{R}^3
\end{array}
\end{array} \xrightarrow{\text{O}^- \text{O}^{'}} \begin{array}{c}
\begin{array}{c}
\text{R}^3
\end{array}
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\begin{array}{c}
\text{R}^3
\end{array}
\end{array}
\text{ (15)}
\]

or

\[
\text{F}^- \xrightarrow{\text{H}} \begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{R}^3
\end{array}
\end{array} \xrightarrow{\text{O}^- \text{O}^{'}} \begin{array}{c}
\begin{array}{c}
\text{R}^3
\end{array}
\end{array} \xrightarrow{\text{H}^+} \begin{array}{c}
\begin{array}{c}
\text{R}^3
\end{array}
\end{array}
\text{ (16)}
\]
Cooxidation

The process of co-oxidation is the simultaneous oxidation of an olefin and a mercaptan with molecular oxygen. Griesbaum observed that phenylacetylene could be cooxidized with thiophenol to give phenyglyoxal hemithioacetals.\textsuperscript{51} The proposed intermediate for this conversion is a vinylhydroperoxide $37$. Decomposition via a sigmatropic pathway\textsuperscript{52} or a homolytic pathway\textsuperscript{1} then lead to the formation of hemithioacetal $38$.

\begin{equation}
\begin{array}{c}
\text{phenylacetylene} \\ RSH, O_2
\end{array} \rightarrow \begin{array}{c}
\text{vinylhydroperoxide} \\ (37)
\end{array} \rightarrow \begin{array}{c}
\text{phenyglyoxal} \\ (38)
\end{array}
\end{equation}

This reaction may potentially lead to a stable vinyl peroxide intermediate if electron withdrawing substituents flank the triple bond. Our interest lies in attaching some electron withdrawing groups on the acetylene to trap the intermediate $37$. 
III. Results and Discussion

The Chemistry of Enynes

We initiate a study of conjugated enynes in order to devise synthetic schemes towards vinyl peroxides. Our experiments in this respect include alkylation, reduction, epoxidation and cyclization of enynes.

1. The Alkylation of Enynes with Terminal Triple Bond

The methodology of the cross coupling of monosubstituted acetylenes with ketones has been extensively investigated.\textsuperscript{27,53-55} We performed alkylations of 1-ethynylcyclohexene 39 with cyclohexenone 40 and 2-methyl-1-buten-3-yne 42 with cycloheptanone 43 using a slight modification of reported procedures.

\begin{center}
\begin{align*}
\text{(39)} & \xrightarrow{tBu-Li} \text{(39)}' & \text{(40)} & \xrightarrow{Li} \text{(41)} & \text{(40)}' & \xrightarrow{HO} \text{(41)}
\end{align*}
\end{center}
The product of reaction (18), 1-(2-Cyclohexenylethynyl)-2-cyclohexenol 41, is a new compound isolated in 70% yield. The $^{13}$C NMR shows resonances at $\delta=85.0$ ppm and $\delta=90.0$ ppm (all the spectra mentioned are attached to the thesis as appendices), that represent the two acetylenic carbons of a disubstituted acetylene. The IR shows the characteristic OH stretching frequency at 3381 cm$^{-1}$. All these data confirm the structure of 41. The product of the reaction (19), 1-(3-Methyl-3-buten-1-ynyl) Cycloheptanol 44, is also a new compound. The $^{13}$C NMR shows an internal triple bond (two resonances at $\delta=86.0$ and $\delta=92.7$ ppm). The IR (3280 cm$^{-1}$) and $^1$H NMR ($\delta=2.12$ ppm, s, 1H) demonstrate the presence of tertiary OH group. The yield of this reaction was 80%. We also did an alkylation reaction of enyne 42, according to Chong and Wong's procedure$^{28}$, with benzyl bromide in methyl sulfoxide. This reaction did not give enyne 46, instead gave enyne 47. The product of the first alkylation step, (4-methyl-4-penten-ynyl)benzene 46, has two very reactive protons at $\alpha$-position, and both of them were substituted by benzyl groups.
The reason for this result lies in the fact that both of the conjugated enyne and phenyl groups increase the acidity of the \( \alpha \)-protons of 46 so greatly that their acidity exceeds the acidity of the acetylenic proton. Therefore, the enyne 46 is deprotonated faster than enyne 42 and the reaction was happened in spite of the one-to-one ratio of the starting materials. The product of this reaction, (1-1-Dibenzyl-4-methyl-4-penten-2-ynyl)benzene 47, is a new compound also. The \(^1\)H NMR shows one vinyl group (\( \delta = 5.14 \) ppm, d of d, 2H), one methyl group (\( \delta = 1.89 \) ppm, s, 3H) and fifteen phenyl protons (\( \delta = 7.0-7.3 \) ppm, m, 15H). The \(^{13}\)C NMR shows an internal triple bond (\( \delta = 90.1 \) and \( \delta = 91.4 \) ppm) and one tetra-alkylated carbon (\( \delta = 46.0 \) ppm). The combination of \(^1\)H NMR (\( \delta = 3.17 \) ppm, d of d, 4H) and the \(^{13}\)C NMR (\( \delta = 48.6 \) ppm) shows two symmetric methylene groups. The yield of the reaction was 61%.
2. Reductions of Enynes with Diimide

We did reduction experiments with diimide for three different enynes: 1-(3-Methyl-3-buten-1-ynyl)cycloheptanol 44, 1-ethynylcyclohexene 39 and 6-hydroperoxy-1-ethynylcyclohexene 48.

Compound 48 was generated according to a procedure developed by Lu.2

![Chemical structures](44), (39), (48)

\[
(39) + \text{singlet O}_2 \rightarrow (48) \quad (21)
\]

The diimide used in these experiments was generated by the acid-catalyzed hydrolysis of the dipotassium salt of azodiformate.56 The reductions were done according to the procedure described by Norin and Rikard.30
In the reported experiments, diimide showed a selective preference for the reduction of double bond of a conjugated enyne. Our experiments showed that diimide prefers to attack triple bonds rather than double bonds. The $^{13}$C NMR for 49 lacks the
characteristic triple bond carbons ($\delta=65$-$95$ ppm), but shows two more vinyl carbons and altogether shows four vinyl carbons ($\delta=113.3$, $\delta=127.3$, $\delta=138.2$ and $\delta=145.3$ ppm). When combined with the $^1$H NMR ($\delta=4.95$ ppm, d, 2H; $\delta=5.74$ ppm, d, 1H; $\delta=5.56$ ppm, d, 1H), we know that there must be one vinyl, two monosubstituted vinyl and one disubstituted vinyl carbons. Hence, the data clearly indicates a diene structure for compound 49, 1-(3-Methyl-1,3-butadienyl) cycloheptanol. The GC-Mass confirms the structure by showing a molecular weight of 180. The yield of this new compound was 44%.

The products of the reaction shown in equation (23) have been previously described in the literature. An integration of three characteristic resonances, $\delta=5.67$ppm which belongs to 1-vinyl cyclohexene 50, $\delta=5.30$ppm which belongs to 1-ethyl cyclohexene 51 and $\delta=6.10$ppm which belongs to the starting material 39 (see $^1$H NMR offered by this work), shows that the amount of the three compounds was in the ratio of 1:1:1.

The reduction of 48 (equation (24)) gave 6-Hydroperoxy-1-ethylcyclohexene 52 as the main product in a 42% yield. The $^1$H NMR shows an ethyl group ($\delta=1.02$ ppm, t, 3H). The $^{13}$C NMR shows two vinyl carbons ($\delta=127.8$ and $\delta=135.6$ ppm). Combined with $^1$H NMR ($\delta=4.38$ ppm, s, 1H), we know that the new product only has one unsaturated bond. A KI test gives a positive result, which means the hydroperoxyl group was not affected by diimide.

The results of these reductions tell us that for these enynes, the triple bonds are selectively reduced.
3. Epoxidation of Enynes by Dimethyl Dioxirane

The oxidation of conjugated enynes with dimethyl dioxirane (DMD) was also investigated. The procedure we used in this work was modified on the basis of the one described by Murray and Jeyaraman.37

When enyne 39 was reacted with excess DMD (0.1 M solution in acetone), epoxide 54 was obtained in 90% yield. The 1H NMR of the product in the reaction (25) shows that the olefinic proton absorption at δ=6.17 ppm which belongs to the starting material disappeared. A new signal appeared at δ=3.35 ppm, and this is the absorption range for proton attached to epoxyl groups. The GC-Mass spectrum shows a increase in molecular weight of 16 units. The 13C NMR does not show any vinyl carbons, but shows two resonances at δ=59.4 and δ=49.4 ppm respectively, which are within the range for the absorptions of epoxide groups. Thus another new compound, 1,2-Epoxy-1-ethynylcyclohexane 54 was obtained and it’s structure confirmed.

Similarly, enyne 44 gave 1-(3-Methyl-3,4-epoxy-1-butynyl) cycloheptanol. When we added excess DMD (0.1 M solution in
acetone) to 44, the $^1$H NMR shows that the two olefinic proton absorptions at $\delta=5.21$ and $\delta=5.27$ ppm which belong to the vinyl group of the starting material disappeared, two new absorptions appeared at $\delta=2.8$ and $\delta=3.0$ ppm, which are within the range for the absorptions of protons attached to an epoxide group. Thus we assign the structure of this compound as 55. It is another new compound, and the yield was 45%.

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{HO-} & \quad \text{HO-} \\
\text{HO} & \quad \text{HO} \\
\text{\(\text{C}_6\text{H}_{12}\) + O-O} & \quad \text{\(\text{C}_6\text{H}_{12}\) + O-O} \\
\text{44)} & \quad \text{53)} \\
\text{\(\rightarrow\)} & \quad \text{\(\rightarrow\)} \\
\text{55)} & \quad \text{55)}
\end{align*}
\]

\[(26)\]

For the acetylenic hydroperoxide 48, the oxidation with DMD did not produce any products. When we added excess DMD (in 0.1 M solution of acetone) to a CH$_2$Cl$_2$ solution containing 48, there was no change for the 6-hydroperoxy-1-ethynylcyclohexene within 24 hours.

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{HO-} & \quad \text{HO-} \\
\text{HO} & \quad \text{HO} \\
\text{\(\text{C}_6\text{H}_{12}\) + O-O} & \quad \text{\(\text{C}_6\text{H}_{12}\) + O-O} \\
\text{48)} & \quad \text{53)} \\
\text{\(\rightarrow\)} & \quad \text{\(\rightarrow\)} \\
\text{No significant change} & \quad \text{No significant change} \\
\text{55)} & \quad \text{55)}
\end{align*}
\]

\[(27)\]

The reasons for nonreactivity of hydroperoxide 48 is not clear at this point.
Intramolecular Cyclization of Acetylenic Hydroperoxide

A radical induced cyclization of hydroperoxide 48 was next attempted. The hydroperoxyl radical was generated via reaction of 48 with N-bromo succinimide.

The reaction was very complex. Nine spots were detected via TLC. For these reasons this approach was abandoned.

The bromination of 48 was also attempted in the hope of capturing one of the bromonium ion intermediates with the adjacent hydroperoxy group, for example:
Unfortunately, this reaction also gave a very complicated mixture of products (11 spots shown by TLC) and there was no main product detected.

We also tried the cyclization of 48 with tetrabutyl ammonium fluoride (TBAF) according to the procedure described by Y. Ito.\textsuperscript{59} In these reactions, one equivalent of 6-hydroperoxy-1-ethynylcyclohexene 48 and one equivalent of TBAF were reacted in the hope of obtaining peroxide 59. However, no reaction occurred between these reagents.

\[
\begin{array}{c}
\text{H} \\
\text{O-O} \\
\text{\text{48}} \\
\end{array}
\xrightarrow{\text{TBAF}}
\begin{array}{c}
\text{F}^+ \\
\text{H} \\
\text{O-O} \\
\text{\text{59}} \\
\end{array}
\]

(30)

**Cooxidation of Dimethyl Acetylenedicarboxylate**

Since the strategy to synthesize vinyl peroxides via intramolecular cyclization was not successful, we tried cooxidation of dimethyl acetylenedicarboxylate 60. The purpose was to trap the intermediate vinyl peroxide shown in equation (17) by attaching two strong electron withdrawing groups to the alkyne. However, when alkyne 60 was co-oxidized, ester 62 was obtained as a main product.
The $^{13}$C NMR of 62 shows two carbonyl carbons at $\delta=164.5$ and $\delta=165.2$ ppm. The $^1$H NMR shows five phenyl protons ($\delta=7.32-7.45$, m, 5H) and one olefinic proton ($\delta=6.4$ ppm, sharp singlet, 1H). The combination of $^{13}$C ($\delta=52.4$ and $\delta=52.1$ ppm) and $^1$H NMR ($\delta=3.80$ ppm, s, 3H and $\delta=3.34$ ppm, s, 3H) shows two methoxy groups. The GC-Mass shows a typical mono-sulfur compound which has a molecular weight of 252, a 13.8% of M+1 and a 6.88% of M+2 molecular weight. These values are very close to theoretical M+1 (14.6%) and M+2 (5.2%) molecular weights of a monosulfur containing compound. It is another new compound, thiophenyl methyl maleate 62. The yield of this reaction was 28%. The yield is very low only because it is very difficult to separate the main product from the impurities, hence we lost most of the main product in purification.

\[
\begin{align*}
\text{(60)} & \quad \text{CH}_3\text{O} \quad \text{CH}_3\text{O} \\
+ \quad \text{PhSH} & \quad \text{O}_2, \text{hv} \\
\text{PhS} & \quad \text{H} \\
\text{(61)} & \quad \text{(62)}
\end{align*}
\]
IV. CONCLUSIONS

Modified methods for the alkylation of 1-alkynes and for the epoxidation of double bonds were developed giving good yields. Conjugated cyclohexene enynes and cycloheptanol enynes are reduced by diimide preferentially at triple bond. Dimethyl dioxirane reacts with the double bond on enynes to give epoxy acetylenes. Acetylenic hydroperoxides undergo complex reactions with bromonium ion or bromine radical sources. Acetylene dicarboxylates gave a vinyl sulfide product when co-oxidized.
V. Experimental

Melting points are uncorrected and obtained using a Gallenkamp Melting Point Apparatus. The infrared spectra were recorded on an MB 120 Bomen FT-IR or a Nicolet 510 FT-IR spectrometer. The NMR spectra were recorded using a 250 MHz Bruker FT-NMR spectrometer, Model WM 250, or a 80 MHz Bruker NMR spectrometer, Model WM 80. The GC-Mass data were obtained using a Varian GC-Mass spectrometer, Model HP 5995. The HPLC data were obtained using a Shimadzu LC-6AD Liquid chromatography and Shimadzu SPD-6AV Ultraviolet-visible Spectrophotometric Detector with Alltech Adsorbosphere C8 Columns. The elemental analyses were performed by Atlantic Microlab Inc. All chromatography was done via a flash chromatography using Silica Gel (Merck, grade 60,230-400, mesh, 60 A) or on a Chromatotron (Harrison Model 8924). The chemical reagents, 1-ethynylcyclohexene, 2-methyl-1-buten-3-yne, cyclohexenone, cycloheptanone, benzyl bromide, dimethylacetylene dicarboxylate, thiophenol, N-bromosuccinimide, tetrabutyl ammonium fluoride, azodicarbonamide, oxone, sec-butyllithium and methylolithium solutions were purchased from the Aldrich Chemical Company.
**Purification of Reagents**

*Methylene Chloride:* Methylene chloride was purified by first refluxing it with phosphorous pentoxide for 30 minutes, followed by distillation (b.p. 40 °C). The methylene chloride was collected over oven dried molecular sieves (Ref.\(^6\) b.p. 40 °C).

*Tetrahydrofuran:* Tetrahydrofuran was purified by refluxing with sodium and benzophenone until a characteristic blue color was evident in the solvent. The solvent was kept in contact with the sodium until distilled (b.p. 65 °C, Ref.\(^6\) b.p. 65.4 °C)

*Ethyl ether:* Ethyl ether was purified by washing with water, drying for 24 hours with CaCl\(_2\), filtering and drying further by adding sodium. The ether is stored in a dark cool place, until distilled (b.p. 34 °C) from sodium before use (Ref.\(^6\) b.p. 34.6 °C).

*Methanol:* Methanol was purified by fractional distillation (b.p. 65 °C). Drying with CaO and through 4A molecular sieves, then distilled (Ref.\(^6\) b.p. 64.5 °C).

*Chloroform:* Chloroform was purified by washing with water to remove the EtOH, drying with CaCl\(_2\), refluxing with P\(_2\)O\(_5\) , and distilling(b.p. 61 °C). The distilled CHCl\(_3\) should be stored in the dark to avoid photochemical formation of phosgene.(Ref.\(^6\) b.p. 61.2 °C).
**Carbon Tetrachloride:** Carbon Tetrachloride was purified by shaking with concentrated H₂SO₄ until there is no further coloration, then washed with water, dried with MgSO₄ and distilled (b.p. 77 °C; Ref.61 b.p. 76.8 °C).

*n-Hexane:* the n-Hexane was purified by distilling (b.p. 68 °C; Ref.61 b.p. 68.7 °C).

**Preparation of Reagents**

1. **The Preparation of Potassium Azodicarboxylate**

   (I-QW-56)

   Potion by potion, 10 g (86.2 mMol) of solid azodicarbonamide was added to 70 mL of cold (5°C) aqueous solution of potassium hydroxide (40% by weight) over one hour. The reaction mixture was stirred between 0-8°C during the addition and for 5 hours after the addition, then the bright yellow dipotassium azodicarboxylate was filtered off using a Buchner funnel. The solid product was washed 20 times with dry methanol (precooled to 0 °C), and then was dried on a rotary evaporator, obtaining 7.53 g (38.8 mMol) in 45.0% yield (Ref.62)

2. **The Preparation of Dimethyldioxirane** (I-QW-47)

   The procedure was based on the procedure used by Murray and Jeyaraman37. A mixture containing 240 mL of water, 150 mL of acetone and 430 g of sodium bicarboxylate was put into a five liter,
five neck, round bottom flask. The flask was equipped with a mechanical stirrer, a solid addition funnel and a dropping funnel. An air condenser was also attached to the flask via one of the necks. The other end of the air condenser was connected to a 100 mL receiving flask immersed in a Dewar containing Dry Ice. The receiving flask was a two neck round bottom flask. The air condenser was introduced in through one neck and the other neck was attached to the bottom of a Dry Ice condenser. The top of the Dry Ice condenser was connected to a series of traps immersed in Dewars containing Dry Ice. Nitrogen was passed through the reaction flask while 900 g of solid peroxymonosulfate (oxone) was added via a solids addition funnel. Simultaneously, a mixture of 480 mL of water and 300 mL of acetone was added dropwise. The mixture was stirred vigorously at room temperature, throughout the reaction period until all the oxone and acetone/water were added. After 15 minutes of reaction time, a slight vacuum was applied to the reaction assembly. The volatile product, which was recovered as 0.1 M dimethyldioxirane solution in acetone was sealed in a one necked flask and stored below -20 °C.

3. Preparation of 6-Hydroperoxy-1-ethynylcyclohexene (1-QW-64.1)

A solution of 150 mL of carbon tetrachloride, 3.0 g (28.3 mMol) of 1-ethynylcyclohexene was irradiated with a 400 watt sodium lamp in the presence of tetraphenylporphine (TPP) as sensitizer. The reaction was carried out under an oxygen atmosphere for 48 hours at
-10 °C. The progress of the reaction was monitored by proton NMR. The reaction mixture was put on a rotary evaporator to get rid of the solvent, then it was purified via a low temperature column chromatography (Silica gel, 5-10% ethylacetate in hexane solvent system) obtaining 1.41 g (10.2 mMol) of pure product as a pale yellow oil in 36% yield. The structure was determined by comparing NMR spectrum with that reported in the literature.\(^2\) \(^1\)H NMR (250MHz, \(\delta=\text{ppm}, \ J=\text{Hz}, \text{CDCl}_3, \text{TMS}\) 8.51, s, (1H), 6.49, t, (1H), 4.50, t, (1H), 2.91, s, (1H), 1.59-2.21, m, (6H).

**Synthetic Preparations**

1. Preparation of 1-(2-Cyclohexenylethynyl)-2-cyclohexenol (41), (II-QW-25.3)

   A mixture containing 80 mL of dry THF and 4.0 g (37.7 mMol) of 1-ethynlycyclohexene was put into a 250 mL 3-necked round bottom flask and stirred magnetically at -78 °C under a nitrogen atmosphere. Twenty-nine mL of 1.3 N solution of sec-butyllithium (37.7 mMol) in THF was injected into the mixture slowly through a septum inlet. About 40 minutes after the injection was completed, another solution containing 3.62 g (37.7 mMol) of cyclohexenone and 80 mL of dry THF was dropped in over a one hour period, then kept stirring for one more hour, then slowly raised the temperature to room temperature and kept stirring for another hour. The working up was done as follows. First, 50 mL of water was dropped into the product mixture, the mixture was put on a rotary evaporator. When
most of the THF in the mixture was gone, the crude product was extracted using 3X50 mL of ether. The ether then was dried with a small amount of magnesium sulfate, and was driven off on a rotary evaporator, which left the crude product only. Purification of the crude product via a column chromatography (Silica gel, 0-5% ethylacetate in hexane solvent system) gave 41 as pure product in a 70% yield (5.366 g, 26.56 mMol). $^1$H NMR (250 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS ) 6.05, m, sharp, (1H), 5.74, m, sharp, (2H), 3.39, s, broad, (1H), 1.87-2.09, m, (8H), 1.71-1.80, m, (2H), 1.54-1.65, m, (4H). $^{13}$C NMR (25 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 134.3, 130.8, 128.4, 120.0, 90.0, 85.0, 65.0, 37.7, 28.8, 25.2, 24.3, 21.9, 21.1, 18.9. IR (neat, cm$^{-1}$) 3635-3135, 3030, 2935, 2861, 2835, 2664, 2215, 1648, 1448, 1349, 1320, 1216, 1054, 957.8, 919.1, 843.4, 737.1.

2. Preparation of 1-(3-Methyl-3-buten-1-ynyl) Cyclo-heptanol (44), (II-QW-31.2)

A mixture containing 60mL of dry THF and 5.0 g (75.76 mMol) of 2-methyl-1-buten-3-yne was put into a 250 mL 3-necked round bottom flask and stirred magnetically at -78 °C under a nitrogen atmosphere. Fifty-eight mL of 1.3 N solution of sec-butyllithium (75.4 mMol) in THF was injected into the mixture slowly through a septum inlet. About 40 minutes after the injection was completed, another solution containing 8.48 g (75.76 mMol) of cycloheptanone and 80 mL of dry THF was drooped in over one hour, the solution was kept stirring for an additional hour. The temperature was then raised to room temperature and kept stirring for another hour. The
work up was done in the same way stated above, obtaining a pure product as a pale yellow oil, in a 80% yield (10.83 g, 60.84 mMol) after a Kugelrohr distillation at 100 °C and 1 mmHg. $^1$H NMR (250 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 5.24, d, (2H), 2.12, s, overlap, (1H), 1.99-2.07, m, overlap, (2H), 1.89, s, overlap, (3H), 1.81-1.86, m, overlap, (2H), 1.53-1.72, m, (8H). $^{13}$C NMR (25 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 126.3, 121.2, 92.7, 86.0, 71.2, 42.9, 27.6, 23.3, 22.1. IR (neat, cm$^{-1}$) 3035-3500, 2937, 2872, 2818, 1615, 1462, 1299, 1191, 1048, 905.3, 729.4. GC-MASS 178 (6.8%), 163 (39%), 145 (14%), 135 (30%), 122 (19%), 121 (base, 100%), 108 (29%), 107 (34%), 95 (16%), 93 (65%), 91 (37%), 79 (61%), 77 (44%), 67 (22%), 66 (20%), 65 (35%), 63 (16%), 55 (64%), 53 (27%), 51 (22%), 43 (26%), 41 (59%). Melting Point: 39.0-40.0 °C.

3. Preparation of (1-1-Dibenzyl-4-methyl-4-penten-2-ynyl)Benzene (47), (II-QW-19.1)

Through a septum inlet, a mixture containing 40 mL of dry THF and 1.0 g (15.2 mMol) of 2-methyl-1-buten-3-yne were injected into a 250 mL 3-necked round bottom flask, which was equipped with a magnetic stirrer and a dropping funnel. The contents of the flask were cooled to 0 °C by means of an ice bath and were stirred under a nitrogen atmosphere. After 15 minutes, again through the septum inlet, 11 mL of 1.4 N (15.4 mMol) methyllithium in dry THF was slowly injected into the solution. Fifteen minutes after the injection was completed, a solution containing 2.59 g (15.2 mMol) benzyl bromide and 50 mL of dry dimethylsulfoxide (DMSO) stored
inside the dropping funnel previously was added over one hour. The entire contents were stirred under the same conditions for 2.5 hours, then the reaction temperature was raised to room temperature and the contents were stirred for an additional hour. The reaction mixture was put into a rotary evaporator to remove THF, then filtered in small amount of silica gel with hexanes as washing solvent to get rid of DMSO. The hexanes were driven off on a rotary evaporator. After a purification of the crude product with a column chromatography (Silica gel, 100% hexane solvent system), 47 was obtained in a 61% yield (1.0336 g, 3.076 mMol). $^1$H NMR (250 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 7.32-7.35, m, (3H), 6.95-7.15, m, (12H), 5.19, d, (1H), 5.09, d, (1H), 3.17, d, (4H), 1.80, s, (3H). $^{13}$C NMR (25 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 142.2, 137.3, 130.7, 128.8, 127.8, 127.4, 127.2, 126.4, 126.2, 120.4, 120.2, 91.4, 90.1, 48.6, 46.0, 23.5. IR (neat, cm$^{-1}$) 3087, 3063, 3030, 2949, 2924, 2854, 1800-2500, 1602, 1495, 1454, 1373, 1341, 1290, 1079, 1032, 909.7, 765.7, 741.7, 698.8, 653.3, 543.4, 475.0.

4. Preparation of 1-(3-Methyl-1,3-butadienyl) Cyclo-heptanol (49), (II-QW-61.2)

To a well-stirred mixture of 60 mL of dry methanol and 2.0 g (11.2 mMol) of 1-(3-methyl-3-buten-1-ynyl) cycloheptanol, 6.546 g (33.7 mMol) of potassium azodicarboxylate was added at room temperature under a nitrogen atmosphere. When the solid was well-distributed inside the mixture, a solution of 4.045 g (67.4 mMol) of glacial acidic acid in 50 mL of methanol was added dropwise. After
the addition was completed, the reaction was continued for about 2 hours, until the bright yellow color of potassium azodicarboxylate completely disappeared. The work up was done as follows, the reaction mixture was put on a rotary evaporator until most of the methanol had evaporated, then 50 mL of ether was added to the rest of the solution and was washed with 50x3 mL of water. The ether then was dried with a small amount of magnesium sulfate, filtered and was evaporated on a rotary evaporator. The crude product was purified by column chromatography (Silica gel, 10% ethylacetate in hexane solvent system ); obtaining 0.91 g (4.95 mMol) of 49 in a 44.0% yield. $^1$H NMR (250 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 5.74, d, (1H), 5.56, d, (1H), 4.95, d, (2H), 2.93, s, (1H), 1.88, s, (3H), 1.40-1.88, m (12H). $^{13}$C NMR (25 MHz, $\delta$=ppm, J=Hz, CDCl$_3$, TMS) 145.3, 138.2, 127.3, 113.3, 76.5, 42.7, 29.2, 23.5, 22.0. IR (neat, cm$^{-1}$) 3572, 3475, 3093, 3000, 2940, 2869, 1628, 1461, 1379, 1342, 1268, 1198, 1071, 1041, 899.5, 863.6, 765.8. GC-MASS 180 (2.8%), 162 (27%), 119 (35%), 109 (43%), 107 (15%), 106 (50%), 105 (base, 100%), 95 (48%), 93 (35%), 92 (24%), 91 (92%), 82 (14%), 81 (32%), 80 (15%), 79 (47%), 77 (43%), 67 (45%), 65 (25%), 55 (41%), 53 (28%), 51 (19%), 43 (34%), 41 (90%).

5. Reduction of 1-Ethylcyclohexene (I-QW-66)

To a well-stirred mixture of 20 mL of dry methanol and 0.5 g (4.717 mMol) of 1-ethynylcyclohexene, 2.29 g (11.79 mMol) of potassium azodicarboxylate was added at room temperature under a nitrogen atmosphere. When the solid was well-distributed inside
the mixture, a solution of 0.708 g (11.80 mMol) of glacial acidic acid in 10 mL of methanol was added dropwise. After the addition was complete, the reaction was continued for 2 hours, until the bright yellow color of potassium azodicarboxylate completely disappeared. After a work up (as stated in reaction 4), 0.64 g of crude product mixture was obtained. NMR analysis of the mixture showed the presence of 1-vinylcyclohexene 50, 1-ethylcyclohexene 51, and the starting material, 1-ethynylcyclohexene 39, in a 1:1:1 ratio. 

1H NMR (250 MHz, δ=ppm, J=Hz, CDCl3, TMS) 6.20, 2x2, (1H), 6.10, m, (1H), 5.67, s, (1H), 5.30, m, (1H), 4.97, d, (1H), 4.80, d, (1H), 2.71, s, (1H), 1.84-2.08, m, (12H), 1.47-1.60, m, (12H), 0.91, t, (3H). Which were for

| Compound (50):57 | 6.23, 2x2, (1H), 5.66, m, (1H), 4.96, d, (1H), 4.81, d, (1H), 1.5-2.4, m, (8H) |
| Compound (51):58 | 5.30, m, (1H), 0.91, t, (3H), 1.5-1.92, m, (8H) |
| Compound (39): | 6.10, m, (1H), 2.72, s, (1H), 2.02-2.08, m, (4H), 1.54-1.60, m, (4H). |

6. Preparation of 6-Hydroperoxy-1-ethylcyclohexene (52), (I-QW-97.3)

A solution containing 50 mL of methanol, 1.0 g (7.2 mMol) of 6-hydroperoxy-1-ethynylcyclohexene and 7.03 g (36.2 mMol) of potassium azodicarboxylate was placed in a 250 mL 3-necked round bottom flask, and the round bottom flask was fitted with a sealed mechanical stirrer and a dropping funnel. After the solid salt was
well-distributed inside the mixture, a solution of 4.344 g (72.4 mMol) of glacial acidic acid in 50 mL of methanol was added dropwise. After the addition was completed, the reaction was continued for about 2 hours, until all of the bright yellow color of potassium azodicarboxylate completely disappeared. The work up was done by putting the reaction mixture on a rotary evaporator until most of the methanol had gone, then adding 50 mL of methylene chloride to the rest of the solution. The mixture then was washed with 50x3 mL of water and was dried with a small amount of magnesium sulfate. Last, the methylene chloride was driven off on a rotary evaporator. The crude product was purified via a low temperature column chromatography (Silica gel, 5-10% ethylacetate in hexane solvent system ) and 0.404 g (3.0 mMol) of pure product was obtained as a pale yellow oil in 41.6% yield. \(^{1}H\) NMR (250 MHz, \(\delta=ppm\, J=Hz, CDCl_3, TMS\) ) 8.45, s, (1H), 5.72, s, (1H), 4.38, s, (1H), 1.85-2.38, m, (4H), 1.49-1.83, m, (4H), 1.02, t, (3H). \(^{13}C\) NMR (25 MHz, \(\delta=ppm, J=Hz, CDCl_3, TMS\) ) 135.6, 127.8, 80.5, 27.2, 26.3, 25.1, 17.2, 12.3. IR (neat, cm\(^{-1}\) ) 3120-3620, 2964, 2933, 2877, 2836, 1655, 1460, 1440, 1377, 1261, 1064, 958.1, 815.9. GC-MASS 142 (6.4%), 124 (11%), 99 (11%), 98 (28%), 96 (16%), 86 (16%), 85 (base, 100%), 83 (16%), 82 (12%), 81 (11%), 79 (14%), 72 (26%), 71 (22%), 70 (12%), 69 (35%), 68 (13%), 67 (52%), 58 (16%), 57 (89%), 54 (44%), 52 (18%), 43 (13%), 42 (94%), 41 (17%), 40 (69%).
7. Preparation of 1,2-Epoxy-1-ethynylcyclohexane (54), (I-QW-73.1)

A solution containing 40 mL of methylene chloride and 1.0 g (9.43 mMol) of 1-ethynylcyclohexene was put into a 250 mL 3-necked round bottom flask stirred magnetically at -78 °C. Through a dropping funnel which was cooled with dry ice, 188 mL of 0.1 N (18.8 mMol) dimethyloxirane in acetone was added to the solution over a period of 2 hours. After the addition was complete, the resulting mixture was stirred for 1 hour, then the reaction temperature was raised to -10 °C and the mixture was stirred for two more hours. After all these steps were completed, the flask with the reaction mixture inside was sealed and put into a freezer overnight. The solution was evaporated on a rotary evaporator the next day to drive off the solvent, then it was purified via column chromatography (Silica gel, 10% ethylacetate in hexane solvent system), obtaining 0.5157 g (4.23 mMol) of pure major product in a 90% yield. \(^1\)H NMR (250 MHz, \(\delta=ppm\), J=Hz, CDCl\(_3\), TMS) 3.35, s, (1H), 2.34, s, (1H), 1.88-1.92, m, (4H), 1.34-1.44, m, (4H). \(^13\)C NMR (25 MHz, \(\delta=ppm\), J=Hz, CDCl\(_3\), TMS) 83.9, 70.1, 59.4, 49.4, 29.1, 23.7, 19.0, 18.5. IR (neat, cm\(^{-1}\)) 3277, 2988, 2928, 2861, 2674, 2118, 1435, 1345, 1190, 648, 506, GC-MASS 122 (19%), 107 (base, 100%), 94 (32%), 93 (19%), 91 (36%), 79 (56%), 78 (85%), 77 (61%), 66 (38%), 65 (39%), 63 (18%), 62 (11%), 57 (12%), 55 (13%), 53 (46%), 52 (30%), 51 (44%), 50 (30%), 42 (21%), 41 (33%).
8. Preparation of 1-(3-Methyl-3,4-epoxy-1-butynyl)cycloheptanol (55), (I-QW-65.1)

A 250 mL 3-necked round bottom flask, was surrounded by a dry ice-acetone bath and provided with a magnetic stirrer, a thermometer and a dropping funnel cooled with dry ice. A solution of 1.4 g (7.86 mMol) of 1-(3-methyl-3-buten-1-ynyl)cycloheptanol dissolved in 50 mL of methylene chloride was added to the reaction flask and cooled to -78 °C. To this, was added with stirring, 150 mL of 0.1 N (15 mMol) dimethyldioxirane in acetone over a period of 2 hours, via a dropping funnel. After the addition was complete, the resulting mixture was stirred for 1 hour, then the reaction temperature was raised to -10 °C, and the mixture was stirred for two more hours. After all these steps were completed, the flask with the reaction mixture inside was sealed and put into a freezer overnight. The solution was evaporated on a rotary evaporator the next day, recovering 1.53 g of an oil. This oil was purified via column chromatography (Silica gel, 20% ethylacetate in hexane, solvent system), obtaining 0.6931 g (3.57 mMol) of 55 in a 45% yield. ¹H NMR (250 MHz, δ=ppm, J=Hz, CDCl₃, TMS) 3.00, d (1H), 2.76, d (1H), 2.23, s (1H), 2.03-1.51, m (15H). IR (neat, cm⁻¹) (?) 3200-3600, 2854, 2777, 2132, 1598, 1379, 1367, 1306, 1260, 1187, 986.8, 948.4, 833.1, 790.9, 725.6.
9. Preparation of Thiophenyl methyl maleate (62), (II-QW-51.3)

A solution containing 1.0 g (7.04 mmol) of dimethylacetylene-
dicarboxylate and 50 mL of heptane was saturated with oxygen (bubbled through slowly at room temperature), then 0.775 g (7.04 mmol) of thiophenol was added dropwise into the reaction vessel. The mixture was stirred for 10 hours and followed by TLC until most of the enyne had reacted. The solution was evaporated on a rotary evaporator, recovering 1.52g of a green oil. This oil was purified via a column chromatography (Silica gel, 10% ethylacetate in hexane solvent system), obtaining 0.5013 g of 62 in 28% yield. $^1$H NMR (250 MHz, δ=ppm, J=Hz, CDCl₃, TMS) 7.44-7.45, m, (2H), 7.32-7.35, m, (3H), 6.38, s, (1H), 3.80, s, (3H), 3.34, s, (3H). $^{13}$C NMR (250 MHz, δ=ppm, J=Hz, CDCl₃, TMS) 165.2, 164.5, 149.4, 133.1, 131.9, 128.8, 128.6, 118.8, 52.4, 52.1. IR (neat, cm⁻¹) 1734, 1713, 1583, 1476, 1435, 1323, 1258, 1204, 1049, 1022, 893, 849, 770, 748, 708, 692. GC-MASS 254 (M⁺2, 6.88%), 253 (M⁺1, 13.8%), 252 (Base, 100%), 221 (26%), 193 (45%), 192 (68%), 161 (80%), 150 (18%), 149 (24%), 134 (52%), 109 (22%), 77 (%29), 69 (19%), 65 (24%), 59 (49%), 51 (35%).

10. The Attempted Preparation of 1,2-Epoxy-6-hydro-peroxy-1-ethynylcyclohexane by Oxidation with Dimethyl-dioxiran (II-QW-1)

A solution containing 50 mL of methylene chloride and 1.2 g (8.70 mMol) of 6-hydroperoxy-1-ethynylcyclohexane was put into a
250 mL 3-necked round bottom flask stirred magnetically at -78 °C. Through a dropping funnel which was cooled with dry ice, 87 mL of 0.1 N (8.70 mMol) dimethyldioxirane in acetone was added over a period of 2 hours. After the addition was complete, the resulting mixture was stirred for 1 hour, then the reaction temperature was raised to -10 °C, and the mixture was stirred for two more hours. After all these steps were completed, the flask with the reaction mixture inside was sealed and put into a freezer overnight. The solution was evaporated on a rotary evaporator the next day. Analysis of the 1H NMR showed that the starting material had not reacted.

11. The Attempted Cyclization of Hydroperoxide 48 via Radical Routes (I-QW-77, I-QW-78)

Two reactions were carried out at the same time under the same conditions except that one of them was protected from light by the means of covering the reactor with aluminum foil, but the other was not. In both cases, a solution containing 0.691 g (5.01 mMol) of 6-hydroperoxy-1-ethynylcyclohexene, 3.357 g (20.04 mMol) of N-bromosuccinimide, 120 mL of methylene chloride and 30 mL of methanol was put into a 250 mL 3-necked round bottom flask. The reaction solution was stirred magnetically at 0 °C under a nitrogen atmosphere. After 24 hours the TLC showed that the starting material had been consumed, however, seven new spots appeared and the NMR spectra of the reaction mixtures were complex.
12. The Attempted Cyclization via Bromination of 6-Hydroperoxy-1-ethynylcyclohexene (I-QW-49)

A solution of 234 mg (1.46 mMol) of bromine in 40 mL of methylene chloride was added to a mixture containing 200 mg (1.45 mMol) of 6-hydroperoxy-1-ethynylcyclohexene, 202 mg (1.45 mMol) of potassium carbonate and 40 mL of methylene chloride. The reaction mixture was stirred at -78°C under a nitrogen atmosphere. The reaction was monitored by TLC. After 5 hours, the solvent was evaporated and 563 mg of a brown oil was obtained. The TLC showed 11 spots and the NMR spectrum was very complex.

13. The Attempted Cyclization of Hydroperoxide 48 via TBAF Catalysis (I-QW-58.1 and I-QW-60.4)

A mixture containing 100 mL of dry THF, 138 mg (1 mMol) of 6-hydroperoxy-1-ethynylcyclohexene and 1 mL of 1 M solution of tetrabutyl ammonium fluoride (TBAF) in THF was placed in a 100 mL round bottom flask. The reaction mixture was kept under a nitrogen atmosphere and was stirred magnetically at 0 °C or room temperature for 12 hours respectively. The work up was done as follows: the reaction mixture was put on a rotary evaporator, when most of the THF was evaporated, 50 mL of methylene chloride was added. The solution then was washed with 50 mLx3 of water and dried with a small amount of magnesium sulfate. The methylene chloride was evaporated on a rotary evaporator. The crude product was purified via low temperature column chromatography (Silica
gel, 5-10% ethylacetate in hexane solvent system). The NMR of the crude product indicates that the hydroperoxide failed to react under these conditions in both the cases (Only the crude $^1$H NMR for I-QW-60.4 was offered).
VI. APPENDIX

1-(2-Cyclohexylethylnyl)-2-cyclohexenol
1-(2-Cyclohexylethynyl)-2-cyclohexenol

\[
\text{HO} \\ \equiv
\]

\[
\text{C}_6\text{H}_{12} = \text{C}_6\text{H}_{12} \\
\text{C}_6\text{H}_{12} \equiv \text{C}_6\text{H}_{12}
\]
1-(2-Cyclohexylethynyl)-2-cyclohexenol

Wavenumber (cm⁻¹)

3871.3 2931.8 2834.9 2861.4 1627.2 1584.8 1456.2 1319.7 1073.7 957.8 757.85

Transmittance (T)
1-(3-Methyl-3-buten-1-ynyl) Cycloheptanol

\[
\text{1H, 1H, 1H, 1H, 2H, 2H, 3H, 8H}
\]

\[
\text{10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, 0.0, -1.0}
\]
1-(3-Methyl-3-buten-1-ynyl) Cycloheptanol

PPM

-321

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180 160 140 120 100 80 60 40 20 0 -20 -40
1-(3-Methyl-3-buten-1-ynyl) Cycloheptanol

Scan 591 (11.365 min) of IIQW3102.D
1-(3-METHYL-3-ENE-1-BUTYNYL)-1-CYCLOHEPTANOL

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Scan 591 (11.365 min) of IIQW3102.D
1-(3-Methyl-3-buten-1-ynyl) Cycloheptanol

![Chemical Structure](image)

**Wavenumber (cm⁻¹)**

4000 3500 3000 2500 2000 1500 1000 500

**Transmittance**

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(1-1-Dibenzyl-4-methyl-4-penten-2-ynyl)benzene
(1-1-Dibenzyl-4-methyl-4-penten-2-ynyl)benzene
6-Hydroperoxy-1-ethynylcyclohexene
1-(3-Methyl-1,3-butadienyl) cycloheptanol
1-(3-Methyl-1,3-butadienyl) cycloheptanol
1-(3-Methyl-1,3-butadienyl) cycloheptanol

Scan 687 (11.719 min) of 11046102.D
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1-(3-Methyl-1,3-butadienyl) cycloheptanol
Product mixture for reaction (23)

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\text{Cyclohexene} + \text{H-N=N-H} & \rightarrow \text{Cyclohexene} + \text{Cyclohexane} \\
(39) & \quad (17) & \quad (50) & \quad (51) \\
\text{Reaction (23)}
\end{align*}
\]
6-Hydroperoxy-1-ethylcyclohexene

Scan 563 (11.618 min) of IO98703.0

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6-Hydroperoxy-1-ethylcyclohexene
1,2-Epoxy-1-ethynyl cyclohexane
1,2-Epoxy-1-ethynyl cyclohexane

Scan 208 (4.364 min) of IQU73001.D

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1-(3-Methyl-3,4-epoxy-1-butynyl) cycloheptanol

\[
\text{HO} - \equiv - O
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- **GB:** 0.0
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- **CY:** 0.0
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- **F2:** -1.358P
- **HZ/CM:** 119.849
- **PPM/CM:** 479
- **SR:** 2846.55

**Chemical Shifts:**
- 4.48, 4.48, 4.35, 5-6.41
Thiophenyl methyl maleate

\[
\text{CH}_3\text{O}-\text{PhS}-\text{CH} = \text{OCH}_3
\]

Thiophenyl methyl maleate 62
Thiophenyl methyl maleate

CH$_3$O

O

O

PhS

H

PPM

180 160 140 120 100 80 60 40 20 0 -20 -40

PPM
Thiophenyl methyl maleate

\[
\begin{array}{c}
\text{CH}_3\text{O} \\
\text{PhS} \\
\text{H} \\
\text{O} \\
\text{OCH}_3
\end{array}
\]

Nicolet Instrument Corporation

Nicolet DX v5.25

Thiophenyl methyl maleate

\[
\text{CH}_3\text{O} &= \text{C} = \text{C} = \text{OCH}_3 \\
\text{PhS} &= \text{H}
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Scan 920 (18.020 min) of I1QWG103.D

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VII. REFERENCES


7. Tobolsky, A. V.; Mesrobian, P. B.; Organic Peroxides, Interscience, New York, 1954, Chapter 1


11. Pummerer, Rieche, Ber., 1926, 59, 2161

12. Goldschmidt; Schmidt; Ber., 1922, 55, 3197

13. Goldschmidt; Vogt; Bredig; Ann., 1925, 445, 123

73
14. Dimroth; Neubauer; Chem. Ber., 1957, 90, 2058
15. Pummerer; Schmidutz; Seifert; Chem. Ber., 1952, 85, 535.
16. Muller; Schick; Scheffler; Chem. Ber., 1959, 92, 474
17. Cook; Depatie; J. Org. Chem., 1959, 24, 1356
18. Muller; Ley; Scheffler; Mayer, Chem. Ber., 1958, 91, 2682
22. Willstatter; Wirth, Ber., 1913, 46, 535

74
33. Baeyer, A.; Villiger, V.; Chem. Ber., 1899, 32, 3625
34. Curci, R.; in Advances in Oxygenated Process; Baumstark, A. L. Ed.; JAI: Greenwich, CT, 1990; Vol.2, Chapter 1
41. Djerassi,C.; Chem. Rev.; 1948, 43, 271
42. Horner; L. E.; Winkelmann; H.; Angew. Chem., 1959, 71, 349
44. Petrov, A. A.; CA, 1959, 53, 4109f
   CA, 1957, 51, 9469f

75


