CHAPTER 2

OXIDATIVE CLEAVAGE OF CARBON-CARBON TRIPLE BOND
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It is well known that the autoxidation of acetylenic hydrocarbons preferably affords the products of the attack at α-position\(^1\) to the C≡C triple bond. Mayo and Sickle\(^2\) and Ivanov and Chirko\(^3-6\) engaged in studies on the autoxidation of some acetylenic hydrocarbons could account for the formation of a hydroperoxide at α-position to the C≡C triple bond and its decomposition products namely, acetylenic alcohols and ketones. Argument either for the attack of oxygen on C≡C triple bond or for the formation of the oxidative cleavage products of C≡C triple bond was not considered. Several kinetic studies by Howard and Ingold\(^7\) reveal that the oxidizabilities of acetylenic hydrocarbons are a little higher than the oxidizabilities of the corresponding comparable olefins. In the case of 2-methylalk-3-ynes where two non equal α-positions to the C≡C triple bond were present, the tertiary C-H bond was easily attacked than the secondary or primary C-H bonds.

2.1 Oxidation of isomeric octynes

The autoxidation of all the four isomers of n-octyne\(^8\) yielded as expected,

\[ \text{Scheme 1: Liquid-phase oxidation of the isomeric octynes with molecular oxygen at 85°C} \]
the corresponding \( \alpha \)-hydroperoxyacetlenes and their decomposition products along with 2-7\% \( \alpha,\beta \)-unsaturated ketones, 5-10\% carboxylic acids and 6-12\% saturated ketones. In the case of oct-2-yne, a secondary C-H bond is 8 times easily attacked than a primary C-H bond. No considerable difference between the reactivities of different secondary C-H bonds present in \( \alpha \)-position to the \( C\equiv C \) triple bond was observed.

\( \alpha,\beta \)-unsaturated ketones were considered as the rearrangement products corresponding to the intermediate oxirenes and/or their valence isomers, ketocarbenes.

\[
\begin{align*}
R^1CH_2C\equiv CCH_2R^2 & \quad \text{R} & \quad R^1CH_2C\equiv CCH_2R^2 \\
R^1CH_2C\equiv CCH_2R^2 & \quad \text{R} & \quad R^1CH_2C\equiv CCH_2R^2 \\
R^1CH_2C\equiv CCH_2R^2 & \quad \text{R} & \quad R^1CH_2C\equiv CCH_2R^2 \\
R^1CH_2C\equiv CCH_2R^2 & \quad \text{R} & \quad R^1CH_2C\equiv CCH_2R^2 \\
R^1CH_2C\equiv CCH_2R^2 & \quad \text{R} & \quad R^1CH_2C\equiv CCH_2R^2
\end{align*}
\]

**Scheme 2:** Formation of \( \alpha,\beta \)-unsaturated ketones in the autoxidation of the isomeric octynes

Oxirenes can be formed from n-octynes. The formation of oxirene is similar to the formation of oxirane/expoxide in olefine oxidation through the mechanism of Twigg\(^9\) and Mayo\(^10,11\). Oxirenes are very unstable intermediate products and exist in equilibrium with the two isomeric ketocarbenes. The shift of a hydride in the two isomeric ketocarbenes
leads to the formation of the \( \alpha, \beta \)-unsaturated ketones\(^{12} \). If there are no hydrogen atoms in \( \alpha \)-position to the carbene centre, Wolff rearrangement to a ketene\(^{13} \) takes place.

### 2.2 Oxidation of enynes

Ivanov and Chirko studied the autoxidation of some conjugated enynes\(^{14,15} \). Cyclopentenyl and cyclohexenyl acetylenes afforded the corresponding hydroperoxides (I & III) and the epoxides (II & IV)

![Chemical structures](image)

An attack on \( \text{C} \equiv \text{C} \) triple bond was not observed in both the cases. Analogue results were obtained in the case of the autoxidation of 2,3,6-trimethyl-hept-2-en-4-yn and 5-cyclohexyl-2,3-dimethyl-hept-2-en-4-yn. In each case, the main products were the tertiary hydroperoxides with the hydroperoxy group at \( \alpha \)-position to the \( \text{C} \equiv \text{C} \) triple bond. By higher degrees of turnovers, an attack on the \( \text{C} = \text{C} \) double bond could be detected but not on \( \text{C} \equiv \text{C} \) triple bond.

The conjugated enynes were found to undergo oxidation unexpectedly faster. Formation of a mixture of the two hydroperoxides\(^{16} \) in the oxidation of 6-methyl hept-1-en-4-yn was reported by Cirko et al.

![Chemical structures](image)

Surprisingly, the allyl isomeric hydroperoxide which could be possible as cis and trans forms could not be found.
2.3 Oxidation of 1-phenylalk-1-ynes

The autoxidation of 1-phenylalk-1-ynes\textsuperscript{17}, (1-phenylprop-1-yne, 1-phenylbut-1-yne and 1-phenyl-3-methylbut-1-yne) lead to the formation of the oxidative cleavage products of C≡C triple bond and the rearrangement products corresponding to the intermediate oxirenes and/or their valence isomers, ketocarbenes.

\begin{center}
\begin{tikzpicture}
\node (O2) at (0,0) {$\text{O}_2$};
\node (Ph) at (1,0) {Ph};
\node (C≡C-R) at (2,0) {C≡C-R};
\node (O) at (2,1) {$O$};
\node (Ph-CO) at (3,0) {Ph-C=O};
\node (Ph-COH) at (4,0) {Ph-C-OH};
\node (Ph-C-R) at (1,-1) {Ph-C-R};
\node (Ph-CO-R) at (2,-1) {Ph-C=O-R};
\node (Ph-C-C-R) at (3,-1) {Ph-C-C-R};
\node (Ph-C-C-O) at (4,-1) {Ph-C-C-O};
\node (Ph-CH-COOH) at (1,-2) {Ph-CH-COOH};
\node (Ph-CH-CH₂OH) at (1,-3) {Ph-CH-CH₂OH};
\node (Ph-C-O) at (4,-2) {Ph-C-O};
\node (Ph-CH-OH) at (4,-3) {Ph-CH-OH};
\node (R) at (2,-2) {R};
\node (LIAH₄) at (1,-2) {LIAH₄};
\node (LIAH₄) at (4,-2) {LIAH₄};
\draw[->] (O2) -- (Ph);
\draw[->] (Ph) -- (C≡C-R);
\draw[->] (C≡C-R) -- (O);
\draw[->] (O) -- (Ph-CO);
\draw[->] (Ph-CO) -- (Ph-COH);
\draw[->] (Ph-C-R) -- (Ph-C-C-R);
\draw[->] (Ph-C-C-R) -- (Ph-C-C-O);
\draw[->] (Ph-CH-COOH) -- (LIAH₄);
\draw[->] (Ph-CH-CH₂OH) -- (LIAH₄);
\draw[->] (Ph-C-O) -- (LIAH₄);
\draw[->] (Ph-CH-OH) -- (LIAH₄);
\end{tikzpicture}
\end{center}

**Scheme 3:** Wolff rearrangement of the ketocarbenes corresponding to the oxirenes in the autoxidation of the 1-phenylalk-1-ynes

LiAlH₄ reduction of the oxidates furnished 2-phenylpropan-1-ol, 2-phenylbutan-1-ol and 2-phenyl-3-methylbutan-1-ol along with benzyl alcohol. They are the reduction products of 2-phenylpropanoic acid, 2-phenylbutanoic acid and 3-methyl-2-phenylbutanoic acid and benzoic acid. Formation of the first three acids can possibly be
explained as the hydration products of the corresponding ketenes. Hydration of ketenes\textsuperscript{18,19} is the only general method of generation of the corresponding carboxylic acids. Unfortunately, the second step of ketonization of enol, is usually much faster than ketene

\[
\text{R}^1\text{C}≡\text{C}≡\text{O} + \text{H}_2\text{O} \rightarrow \text{R}^1\text{C}≡\text{C}≡\text{OH} \rightarrow \text{R}^1\text{C}≡\text{C}≡\text{O}
\]

reaction with water.

Further, 1-phenylethan-1-ol, 1-phenylpropan-1-ol and 1-phenyl-3-methylpropan-1-ol are the reduction products of 1-phenylethan-1-one, 1-phenylpropan-1-one and 1-phenyl-3-methylpropan-1-one respectively. The formation of these ketones was considered due to the autoxidation of the corresponding ketenes\textsuperscript{20,21}.

Again, 1-phenyl-but-1-ene-3-ol obtained from 3-methyl-1-phenylbut-1-yne is likely to be the reduction product of 1-phenylbut-1-yn-3-one formed through the decomposition of the hydroperoxide.

**Scheme 4**: Formation of 1-Phenylbut-1-yn-3-one form 1-Phenyl-3-methylbut-1-yne

The oxidation rates and the yields of the corresponding α-hydroperoxyacetylenes and their consecutive products increase in the order from 1-phenylprop-1-yne, 1-phenylbut-1-yne to 1-phenyl-3-methylbut-1-yne. The yields of the oxidative cleavage products of the C≡C triple bond decrease in the order mentioned. The yields of the
rearrangement products corresponding to oxirenes and/or their valence isomers, ketocarbenes or the corresponding ketenes decrease. This variation is due to the difference in the reactivities of the primary, secondary and tertiary C-H bonds present in the compounds examined.

Phenylacetylene has been mainly the subject of kinetic and polymeric investigations. Phenylacetylene was subjected to autoxidation at 110°C until the absorption of oxygen amounted to 25 mmol per 100 mmol of the starting hydrocarbon.

Scheme 5: Pathways of formation of several products of phenylacetylene oxidation

Ten oxygen containing products, namely, benzaldehyde, phenylacetaldehyde, acetonophenone, phenol, benzoic acid, phenylacetic acid, benzophenone, benzil, phenyl benzoate and benzoic anhydride were characterized along with 1, 4-diphenylbut-1-yn-3-ene, a dimerization product of phenylacetylene and 1,3, 5 triphenylbenzene, a trimerization product of phenylacetylene reported earlier as a product of the thermal oligomerization of phenylacetylene. Acid anhydride isolated and characterized is considered as one the most important products in the autoxidation of acetylenic hydrocarbons. The acid anhydride was also identified in the oxidation of hept-3-ynes.
Benzil was found to be the main product along with the traces of benzoic acid in the oxidates of diphenylacetylene\textsuperscript{27}. The yield of benzil increased when di-tert-butyl peroxide was used as initiator.

Scheme 6: Autoxidation of diphenylacetylene

No traces of diphenylacetic acid or benzophenone, which are to be expected as consecutive products of the corresponding diphenylketene formed via oxirene could be found in the reaction mixtures.

Re-examination\textsuperscript{27} of the crude oxidation mixtures of 1-phenylprop-1-yn e, 1-phenylbut-1-yn e and 1-phenyl-3-methylbut-1-yn e established besides acetylenic alcohols, acetylenic ketones, the presence of the corresponding \(\alpha\)-diketones in minor quantities, benzil, benzoic anhydride and phenylbenzoate in considerable amounts. Autoxidation of acetylenic hydrocarbons examined involved the oxidative cleavage products of the C=C bond in considerable amounts. In the case of 1-phenylalk-1-ynes, the amount of benzoic acid and the corresponding lower carboxylic acids was about 40-50\% of the total products. To understand the oxidative scission of C=C triple bond taking place during the autoxidation of acetylenic hydrocarbons, different possible reaction pathways were considered.
2.4 α-diketones as intermediates

![Diagram of α-diketones as intermediates]

**Scheme 7: α-Diketones as intermediates**

The peroxy vinyl radical formed by the addition of a propargyl peroxyradical, to the acetylenic C≡C triple bond can react further with oxygen giving rise to a peroxy-alky peroxy radical which in turn adds to a molecule of acetylene to deliver a peroxy radical with two peroxide functions. The radical 3 can react further with oxygen and acetylene molecules simultaneously giving radicals of the type 3a with n > 1. The zipper like fragmentation of the radical 3 and respectively 3a resulted in the formation of oxirene along with a peroxy-alkoxy radical, which undergoes a simultaneous breakage of C=C double bond present between the two oxygen functions and the peroxide O-O bonds, resulting in the formation of an α-dicarbonyl compound and an alkoxy radical.
The ratio of the cleavage products depends on the size of the decomposing radical. The \(\alpha\)-dicarbonyl compounds are further oxidized to mixed acid anhydrides subsequently furnishing benzoic acid and the lower carboxylic acids.

2.5 Oxirenes and/or \(\alpha\)-ketocarbenes as intermediates

Formation of the acid anhydride\(^{23,28,29}\) or the \(\alpha\)-dicarbonyl compound\(^{30}\) and their consecutive products can be expected as shown in scheme 8.

\[
\text{Scheme 8: Oxirenes or } \alpha\text{-ketocarbenes as intermediates}
\]

Ketocarbenes, which can be formed from acetylenes via oxirenes can react with oxygen to give rise to carbonyl oxides\(^{31-35}\). These can react further, resulting, in the formation of ozone and the corresponding \(\alpha\)-dicarbonyl compound\(^{30}\) (in its triplet form) or transfer an atom of oxygen to the ketocarbene forming two molecules of the
α-dicarbonyl compound\textsuperscript{36}. A reaction between the carbonyl oxides and the starting acetylenes with the formation of the α-diketones and the corresponding oxirenes similar to the formation of oxiranes can also be taken into consideration. The ketocarbene formation from acetylenes via oxirenes is established in several reactions. Formation of carbene from phenylacetylene via oligomerisation and C≡C bond scission\textsuperscript{37,38} at a mixed-metal centers are reported. Radical formation by singlet methylene with acetylenes are also discussed\textsuperscript{39,40}.

2.6 Dioxetenes as intermediates

The cyclic seven membered strained acetylenes possess an exceptionally small C-C≡C bond angle of 146°. The singlet ground state acetylene reacts with triplet O\textsubscript{2} to from dioxetene\textsuperscript{41-45} directly or from the excited singlet-triplet complex states. The zwitter ion formed after the spin flip can give rise to dioxetene or the ground state acetylene along with singlet oxygen. Now the dioxetene so formed undergoes the opening of the double bond to form the corresponding α-diketone which in turn reacts to produce the oxidative cleavage products of C≡C triple bond of acetylenic hydrocarbons. The spin and flip processes normally occur when the energy barrier is very low. The opening of the dioxetene ring to form α-diketone in thermal reactions is prohibited\textsuperscript{46,47}.
Scheme 9: Dioxetenes as intermediates

Unstrained cyclic acetylenes i.e. 1,7-cyclododecadiyne and 1,8-cyclo-tetradecadiyne did not react with ground state triplet or singlet oxygen. Dioxetene and its opening to \( \alpha \)-dicarbonyl compounds\(^{48} \) was formulated via radical cation in photo-oxygenation via electron transfer in the presence of 9,10-dicyanoanthracene.
Photosensitized oxidation of acetylenes to α-dicarbonyl compound leading to the corresponding carboxylic acid\textsuperscript{49} is also known. One step synthesis of α-diketones\textsuperscript{50} from alkynes with ruthenium tetroxide as catalyst is known. Direct anodic oxidation\textsuperscript{51} of acetylenes in non-aqueous solvents giving α, β-unsaturated γ-diketones has also been formulated.

2.7 Oxidation of 1-phenylalkane-1, 2-diones

To find the probability of the scheme 7, the α-diketones corresponding to the acetylenes i.e. 1-phenylpropane-1,2-dione, 1-phenylbutane-1,2-dione and 1-phenyl-3-methylbutane-1,2-dione subjected to oxidation yielded the oxidative cleavage products of C-C triple bond i.e. benzoic acid and the lower carboxylic acids in individual cases as in the case of the corresponding acetylenes. Some other products like benzil, benzoic anhydride and phenyl benzoate obtained in the oxidation of acetylenes were also formed by the oxidation of the α-diketones. The amount of the oxidative cleavage products of acetylenes is comparable with the amount obtained from the corresponding α-diketones.

Majzus and Zaikov\textsuperscript{52,53} showed the formation of the two acyl radicals through thermal decomposition of C-C single bond present between the two carbonyl groups in
\[
\text{CH}_3\text{CO} - \text{CO} - \text{CH}_3 \rightarrow 2\text{CH}_3\text{CO}^- \quad E_A = 148 \text{ kJ mol}^{-1}
\]

\[
\text{CH}_3\text{CO} - \text{CO} - \text{CH}_3 + \text{R} - \cdot \cdot \rightarrow \text{CH}_3\cdot \text{C} - \text{CO} - \text{CH}_3
\]

\[
\downarrow \quad \text{O} - \cdot \cdot - \text{O} - \cdot \cdot - \text{R}
\]

\[
\text{CH}_3\text{CO} - \text{O} - \text{CO} - \text{CH}_3 + \text{RO}^*
\]

\[
\text{CH}_3\text{CO} - \text{CO} - \text{CH}_3 \rightarrow 2\text{CH}_3\cdot \text{CO}^{+} \quad E_A = 250 \text{ kJ mol}^{-1}
\]

\[
\text{CH}_3\text{CO} - \text{CO} - \text{CH}_3 + \text{R}^* \rightarrow \text{CH}_3\cdot \text{CO} + \text{CH}_3\cdot \text{CO} - \text{R} \quad E_A = 26 \text{ kJ mol}^{-1}
\]

**Scheme 10**: Gas-Phase decomposition of butan-2,3-dione

The liquid phase oxidation of butane-2,3-dione at 85°C as the initiation step which required 148kJ/mol\(^{-1}\) of activation energy. An analogous mechanism was also formulated for the oxidation of cyclohexanone\(^{54}\) to ε-caprolactone. On the other hand, the formation of two acyl radicals required an activation energy of the order of 250kJ/mol\(^{-1}\) in gas phase oxidation\(^{55-59}\).

Goldman et al.\(^{60}\) observed that the reaction of ROOH (R=H; Me\(_3\)C; C\(_{13}\)H\(_{27}\)CO) with 8,9-hexadecanoidione proceeded via reversible addition of the peroxide to the diketone and the decomposition of the adduct to give C\(_7\)H\(_{15}\)COOH and/or (C\(_7\)H\(_{15}\)CO)\(_2\)O as the major products along with C\(_7\)H\(_{15}\)CO\(_2\)OMe\(_3\) or C\(_{13}\)H\(_{27}\)COOH.

Photo-oxidation\(^{61-64}\) of camphorquinone, benzil, acenaphthenequinone and phenanthrenequinone yielded the corresponding acid anhydrides. The fission of the OC—CO bond as the primary process was concluded in the photochemistry of benzocyclobutenedione\(^{65}\). Photo-oxidation of α-diketones in the presence of olefins\(^{66-68}\) suggests that α-diketones are not really the sensitizers of the olefin epoxidation but are
themselves oxidized together with olefins. The acyl peroxy radicals formed by acyl radicals with molecular oxygen are the real epoxidizing agents\(^{69}\). Photochemistry of \(\alpha\)-diketones\(^{70}\) delivers a variety of products.

The thermal dissociation of \(\alpha\)-diketones using 1-phenylpropane-1,2-dione and benzil as initiators of the autoxidation of cumene at 75°C in chlorobenzene was investigated as solvent according to the generally accepted Batesman equation\(^{71}\). The dependencies of the rate of oxygen uptake on the concentration of cumene as substrate and \(\alpha\)-diketones as initiators were found in accordance with the Bateman equation.

**Determination of the rate of initiation of 1-phenyl propane-1, 2-dione**

*(in diffuse daylight)*

\[
\begin{align*}
W_0 &= \frac{k_p}{\sqrt{k_i}}[RH]_0 \sqrt{w_i} \\
k_p &= \sqrt{w_i} = 6.9767 \times 10^{-7} \\
\frac{k_p}{\sqrt{w_i}} &= 6.9767 \times 10^{-7} \\
\sqrt{w_i} &= 6.9767 \times 10^{-7} \\
&= 3.77^{-1} \\
w_i &= 1.850.10^{-4} \\
w_i &= 3.4247.10^{-9} \text{ mol L}^{-1} \text{ sec}^{-1}
\end{align*}
\]

\[\tan \alpha = \frac{k_p}{\sqrt{k_i}} \sqrt{w_i} \]

\[w_0 = 2k_i f(I) \]

\[2k_i = k_p \]

\[k_i = \frac{w_i}{(I)} = 3.4247.10^{-9} \]

\[\frac{(I)}{1.1464.10^{-2}} = 2.9871.10^{-2} \text{ sec}^{-1} \]
Because, the correlations\textsuperscript{27} were unexpectedly bad and α-diketones under examination were yellow and absorb at shorter wavelengths in visible spectrum for e.g. 1-phenylpropane-1,2-dione has $\lambda_{\text{max}} = 407\text{nm}$; $\varepsilon_{\text{max}} = 9$ lmol\textsuperscript{-1}.cm\textsuperscript{-1}, the oxidation experiments were carried out in the dark. No oxygen uptake could be detected. This means that a dissociation of α-diketones to acyl radicals does not take place at about 100°C as a thermal reaction. It is possible only as a photochemical reaction.

The oxidation studies of both 1-phenylalk-1-ynes and their corresponding α-diketones carried out in diffuse daylight were repeated in two cases in darkness. As expected the rate of 1-phenylbut-1-yne was not altered but more 1-phenylbutane-1,2-dione could be detected in the oxidation mixture. On the other hand, the oxidation of 1-phenylbutane-1,2-dione proceeded considerably slower in the dark than in diffuse daylight, but the nature of the products\textsuperscript{27} formed was not altered.

Benzil was characterized in the oxidates of the α-diketones obtained in the experiments carried under the conditions of darkness and in diffuse daylight. Therefore, one must consider that benzoyl radicals are not only formed by the dissociation of the C–C single bond present between the two carbonyl functions, which takes place only as a photochemical reaction but also by another type of reaction i.e. Ph-CO-CO-R + X$^*$ → Ph-CO$^*$ + R-CO-X, where X$^*$ must be expected as alkoxy or alkyl peroxy radical.

\subsection*{2.8 Reactions of acyloxy and alkoxy radicals}

To prove the possibility of S$_2$ reactions at the C–C bond between the two carbonyl groups of α-diketones, dibenzoyl peroxide, diacetyl peroxide and di-tert-butyl peroxide were thermally decomposed at 130°C in the presence of benzil, 1-phenyl-propane-1,2-dione and 1-phenyl-butane-1,2-dione using chlororobenzene as solvent. In all cases
benzoic acid was formed. Moreover, considerable amounts of benzil were obtained from 1-phenyl-propane-1,2-dione and 1-phenyl-butane-1,2-dione. With the formulation of Majzus\textsuperscript{52,53}, it is not possible to explain the formation of benzil. Formation of acid anhydrides, mixed acid anhydrides, the corresponding acids and benzil can be represented as follows\textsuperscript{72}.

Dissociation of α-diketones to acyl radicals is possible only as a photochemical reaction:

\[ \text{Ph} - \text{CO} - \text{CO} - \text{R} \xrightarrow{\text{h}_\text{u}} \text{Ph} - \cdot \text{CO} + \text{R} - \cdot \text{CO} \]

Reaction of α-diketones with free radicals:

\[ \text{Ph} - \text{CO} - \text{CO} - \text{R} + \text{X}^* \rightarrow \text{Ph} - \cdot \text{CO} + \text{R} - \cdot \text{CO} - \text{X} \]

\((X = R^*; R = O^*; R = O - O^*)\)

Free-radical chain mechanism of the α-diketone oxidation:

\[ \text{Ph} - \cdot \text{CO} + \text{O}_2 \rightarrow \text{Ph} - \text{CO} - \text{O} - \cdot \text{O} \]

\[ \text{Ph} - \cdot \text{CO} - \cdot \text{O} + \text{Ph} - \text{CO} - \text{CO} - \text{R} \rightarrow \text{Ph} - \cdot \text{CO} + \text{Ph} - \text{CO} - \text{O} - \text{O} - \text{CO} - \text{R} \]

\[ \text{Ph} - \cdot \text{CO} - \cdot \text{O} - \text{O} - \text{CO} - \text{R} \rightarrow \text{Ph} - \cdot \text{CO} - \text{O} - \text{CO} - \text{R} + \text{R} - \cdot \text{CO} - \cdot \text{O} \]

\[ \text{Ph} - \cdot \text{CO} - \cdot \text{O} + \text{Ph} - \text{CO} - \text{CO} - \text{R} \rightarrow \text{Ph} - \cdot \text{CO} + \text{Ph} - \text{CO} - \text{O} - \text{CO} - \text{R} \]

\[ \text{R} - \cdot \text{CO} - \cdot \text{O} + \text{Ph} - \text{CO} - \text{CO} - \text{R} \rightarrow \text{Ph} - \cdot \text{CO} + \text{R} - \cdot \text{CO} - \text{O} - \text{CO} - \text{R} \]

Dimerization of benzoyl radicals to benzil (chain termination)

\[ 2\text{Ph} - \cdot \text{CO} \rightarrow \text{Ph} - \text{CO} - \text{CO} - \text{Ph} \]

**Scheme 11:** Oxidation of phenyl-\text{\textlakran-1, 2-diones: formation of acid anhydrides and of benzil

During the decomposition of di-\text{\textlakran-butyl peroxide in the presence of α-diketones, benzoic acid was formed as the main product, but no benzoic anhydride could be found. This is plausible because the product primarily formed from tert-butoxy radicals and α-diketones is a tert-butyl ester which under the conditions of the reaction or during gas chromatographic analysis decomposes to benzoic acid and isobutane.**
Tertiary butoxy radicals decompose rapidly to

\[
\begin{align*}
\text{CH}_3\text{C-O}^* & \rightarrow \text{CH}_3\text{C-O} + \text{CH}_3^* \\
\text{CH}_3\text{C-O}^* & \rightarrow \text{CH}_3\text{C-O}\cdot
\end{align*}
\]

It is concluded that the formation of benzoic anhydride in the reaction products of alkoxy radicals is not possible.

\[
\begin{align*}
\text{H}_2\text{C-C-O-O-C-CH}_3 & \xrightarrow{\Delta} 2\text{H}_2\text{O-C-O}^* \\
\text{H}_2\text{C-C-O-O-C-CH}_3 & \xrightarrow{\Delta} 2\text{H}_2\text{O-C-O}^* \\
\text{H}_2\text{C-C-O-O-C-CH}_3 & \xrightarrow{\Delta} 2\text{H}_2\text{O-C-O}^* \\
\text{H}_2\text{C-C-O}^* + \text{Ph-C-C-R} & \rightarrow \text{Ph-C-O}^* + \text{H}_2\text{C-C-C-O-C-R} \\
\text{O-C-O}^* + \text{Ph-C-C-R} & \rightarrow \text{Ph-C-O}^* + \text{O-C-C-O-C-R} \\
\text{H}_2\text{C-C-O}^* + \text{Ph-C-C-R} & \rightarrow \text{No acid anhydride}
\end{align*}
\]

**Scheme 12:** Decomposition of diacetyl peroxide, dibenzoyl peroxide and di-tertiary butyl peroxide in the presence of \(\alpha\)-diketones

Benzaldehyde found in most of the cases can be considered as the product of H-abstraction by benzoyl radicals, probably from reaction products with relatively weak C-H bonds. In the decomposition of dibenzoyl peroxide, the benzoyloxy radicals primarily formed are very quickly decarboxylated to phenyl radicals\(^{73-75}\) leading to the formation of diphenyl.
Phenylglyoxal could not be traced in the oxidation mixture of phenylacetylene\textsuperscript{33} since it undergoes oxidation several times faster than the corresponding hydrocarbon. The oxidation products of phenylacetylene namely benzoic anhydride, benzaldehyde, benzoic acid, benzil, benzophenone and phenyl benzoate could also be characterized in the oxidates of phenyl glyoxal\textsuperscript{76}. Therefore, phenylglyoxal is considered as one of the intermediates in the autoxidation of phenylacetylene.

The formation of phenylglyoxylic acid is a typical reaction of phenylglyoxal as an aldehyde. The formation of benzophenone points to the presence of phenyl radicals in the reaction mixture. These radicals can react with the starting compound leading to the formation of benzophenone

\[
\text{Ph—CO—CHO + Ph}^* \rightarrow \text{Ph—CO—Ph + H—}^*\text{CO}
\]

Reactions of this type are known from gas-phase decomposition of \(\alpha\)-diketones\textsuperscript{56-58}. Further reaction of benzophenone with one of the peracids formed during the oxidation of phenylglyoxal i.e. phenylglyoxylic peracid or perbenzoic acid yields phenylbenzoate\textsuperscript{77-80}. The formation of phenyl radicals is possible both via decarboxylation of benzoyl and decarboxylation of benzoyloxy radicals

\[
\text{Ph—}^*\text{CO} \rightarrow \text{Ph}^* + \text{CO}
\]

\[
\text{Ph—CO—O}^* \rightarrow \text{Ph}^* + \text{CO}_2
\]

Some other radical reactions\textsuperscript{81-83} related with acetylenes have been discussed recently.

2.9 Studies concerning \(\alpha\)-diazoketones

\(\alpha\)-Diazocarbonyl compounds are very reactive substances and undergo Wolff rearrangement under catalytic, thermal or photochemical conditions\textsuperscript{84,85}. Wolff\textsuperscript{86,87} and Schroeter\textsuperscript{88,89} formulated a one step mechanism while Kaplan and coworkers\textsuperscript{90,91}
discussed a synchrone mechanism. Kinetic studies\textsuperscript{92-94} and the influence of substituents\textsuperscript{95} on the elimination of nitrogen and the migrating capability of the aryl or alkyl groups argue against the synchrone mechanism. Tomioka\textsuperscript{96,97} postulated a concerted mechanism starting from the S-Z conformer and a non concerted mechanism starting from S-E conformer on the basis of the product ratios. An argument for the α-oxocarbene-ketene-reaction sequence of the Wolff rearrangement is the occurrence of a ketocarbene interconversion via intermediate oxirene\textsuperscript{98-103}. Several unresolved problems\textsuperscript{104} regarding WR were addressed. Lemal and coworkers\textsuperscript{105} reported that the species originally assigned as the α-ketocarbene is actually the α-ketodiazirine, an isomer of the starting α-diazoketone. Tanaka et al could not obtain any detectable traces of the corresponding α-diketones and acid-anhydrides. Energy barrier calculations for relative stabilities in rare gas matrices and structural studies\textsuperscript{107-113} are considered to draw several conclusions.

Oxirenes are shown as intermediates in the oxidation of acetylenes by peracids\textsuperscript{101,114-118}.

2.10 Studies concerning the reaction of ketocarbenes with molecular oxygen

It was shown that the oxidative cleavage of the C≡C triple bond during the autoxidation of acetylenic hydrocarbons proceeds via the corresponding α-diketones\textsuperscript{27}. Different possibilities for the formation of α-dicarboxyl compounds, acid anhydrides and their consecutive products, carboxylic acids from ketocarbenes were formulated (scheme-8). To test these assumptions, α-diazoacetophenone, α-diazopropiophenone, α-diazobutyrophene and α-diazodesoxybenzoin were subjected to phototysis and photo-oxidation in benzene and cyclohexane at 40°C for about 10 hours. Thermal
oxidation and thermolysis were carried out at 75°C for about 15 hours in benzene in the case of α-diazoacetophenone and at 110°C for about 12 hours in chlorobenzene in all other cases. Thermolysis and photolysis were carried in an atmosphere of pure argon. From the results, it is clear that no noticeable amounts of the expected α–diketones, acid anhydrides or the carboxylic acids, the main products of the oxidative scission of the C≡C triple bond during the autooxidation of acetylenic hydrocarbons could form via the corresponding oxirenes. Obviously, the reaction of α-ketocarbenes with molecular oxygen can be neglected under the experimental conditions. This statement is confirmed by the fact that there is no substantial difference between the composition of the products formed from the α-diazo ketones in the presence and in the absence of oxygen. Formation of different products of α-diazo ketones can be explained as shown below in Schemes 13-15.

Decomposition of α-diazo ketones yields a singlet ketocarbene, which can be transformed in some cases into the more stable triplet form. In the photochemical decomposition, both singlet and triplet ketocarbenes were shown as primary reaction intermediates. Ketocarbenes, the primary energy-rich fragments can stabilize via different competing reactions. Firstly, the stabilization occurs through nucleophilic migration of an aryl or alkyl group to the electron deficient centre leading to the formation of ketene. The ketenes so formed can yield the corresponding carboxylic acids by hydration and lower ketones by oxidation. These products were characterized in all the four cases of α-diazo ketones. Ketenes are highly versatile synthetic intermediates and unlike most unsaturated compounds, they undergo thermal [2+2] as well as [2+4] cycloadditions readily. Secondly, if possible as in the case of α-diazopropiophenone and α-diazobutyrophenone, the stabilization of the ketocarbene takes place mainly
through hydrogen atom shifts under the formation of \(\alpha,\beta\)-unsaturated ketones\(^{12}\). Thirdly, the stabilization of the ketocarbenes can take place through intra or intermolecular insertion into the C-H bonds. When the intramolecular reactions are difficult or impossible, the ketocarbenes tend to enter into intermolecular reactions i.e. insertion into the C-H bonds of the solvents, azine formation\(^{133}\), dimerisation\(^{134}\) etc. The ketocarbenes from \(\alpha\)-diazoacetophenone showed the C-H bond insertion reactions\(^{119}\) with benzene and cyclohexane resulting in the formation of 1-oxo-1,2-diphenylethane and 2-cyclohexyl-1-oxo-1-phenylethane.

\[
\begin{align*}
\text{Ph} & \quad \text{C} \quad \text{CHN}_2 \quad \rightarrow \quad \text{Ph} \quad \text{C} \quad \text{O} \quad \rightarrow \quad \text{Ph} \quad \text{C} \quad \text{C} \quad \text{Ph} \\
\text{Ph} & \quad \text{C} \quad \text{CH} \quad \text{N} \quad \text{N} \quad \text{CH} \quad \text{C} \quad \text{Ph} \\
\text{Ph} & \quad \text{C} \quad \text{CH} \quad \text{N} \quad \downarrow \quad \text{N}_2 \\
\text{Ph} & \quad \text{C} \quad \text{CH} \quad \text{C} \quad \text{O} \\
\text{Ph} & \quad \text{C} \quad \text{CH} \quad \text{O} \\
\text{Ph} & \quad \text{C} \quad \text{CH} \quad \text{OH} \\
\text{Ph} & \quad \text{C} \quad \text{CH}_3
\end{align*}
\]

Scheme 13: Decomposition of \(\alpha\)-diazoacetophenone
1,4-Diphenylbut-2-ene-1,4 dione formed from α-diazoacetophenone can be treated as a dimerisation product of the ketocarbene. Dimerisation of the intermediate ketocarbenes seems to be a very improbable reaction from a kinetic point of view because of the low concentration of the ketocarbenes in the reaction mixtures. More probable is the reaction of a singlet ketocarbene with the starting diazoketone which can deliver both the azine if the ketocarbene attacks the nitrogen centre of the diazo compound and the olefin if the ketocarbene attacks the carbon centre of the diazo compounds. Most of the products discussed can be explained on the basis of singlet ketocarbene. Nevertheless, the reaction of abstraction of hydrogen by the triplet ketocarbene to form the corresponding saturated monoketone in small quantity was observed in all the cases.
Scheme 15: Decomposition of α-diazodesoxybenzoin

Formation of phenylbenzoate in photochemical and thermal oxidations in considerable amounts from α-diazodesoxybenzoin leads one to consider the Baeyer-Villeger like oxidation\textsuperscript{136} which can take place with the α-ketocarbonyl oxide of the ketocarbene or with diphenycarbonyl oxide\textsuperscript{137} in photochemical oxidation. The direct rearrangement of the intermediate carbonyl oxides to esters\textsuperscript{138-141} is also well known. Minor quantities of phenol formed in thermal and photochemical oxidations of α-diazodesoxybenzoin in benzene can be attributed due to the intermediate arene oxide\textsuperscript{142}. 
The pathway for the formation of α-dicarbonyl compounds via dioxetenes proposed in the case of highly strained cyclic acetylenes (scheme 9) is not considered for acyclic acetylenes as chemiluminescence or the evidence for singlet oxygen formation was not observed by any group.

2.11 Spectroscopy of matrix isolated reactive intermediates

At 77K, photolysis of the two isomeric diazonaphthalenones yielded indenoketene which was characterized\textsuperscript{143} by UV absorption bands at 310nm and 250nm and IR peaks at 2130cm\(^{-1}\) and 2115cm\(^{-1}\). A direct identification of the carbonyl oxide was achieved in the case of cyclopentadienyldiene through argon matrix\textsuperscript{144} isolation. Carbonyl oxide was characterized by argon matrix\textsuperscript{31}, IR, UV and isotope \(^{18}\)O\(_2\) labelling.

Chapmann et al\textsuperscript{29} showed that diazoketones produced α-ketocarbenes in matrix isolated in argon at 10-15 K. The identification of α-ketocarbenes was carried out with UV-Vis, Infrared and Electron Spin Resonance spectroscopy.

Photolysis of matrix isolated α-diazoketones monitored by FT-IR spectroscopy\textsuperscript{111} revealed

(i) ketenes were always more abundant than the α,β-unsaturated ketones

(ii) oxirenes were detected as minor, but well identified reaction products stable at temperature less than 25K and

(iii) with matrix doped with CO, the reaction diverted towards ketoketene assumed due to trapping ketocarbene by CO molecules.

The two experimental techniques used to study the isomerisation of ketene lead to the detection of carbon monoxide photofragments following near-UV excitation of C\textsubscript{13} isotopomers\textsuperscript{145} of ketene.
\[ ^{12}\text{CH}_2^{13}\text{CO} + \text{hv} \rightarrow ^{12}\text{CH}_2 + ^{13}\text{CO} \]

\[ ^{13}\text{CH}_2^{12}\text{CO} + \text{hv} \rightarrow ^{13}\text{CH}_2 + ^{12}\text{CO} \]

\[ ^{12}\text{CH}_2 + ^{13}\text{CO} \]

The laser excitation at 308 nm generates diazoketocarbene \(^{111}\) in the case of 1,3-bis (diazo) indane-2-one and ketocarbene in the case of 2-diazoindan-1-one respectively. At 77K, photolysis of the two isomeric diazonaphthalenones yielded indenoketene which was characterized \(^{146}\) by UV absorption bands at 310nm and 250nm and IR peaks at 2130cm\(^{-1}\) and 2115cm\(^{-1}\).

The IR spectroscopy of ketenes generated photochemically has been studied extensively in cryogenic matrices \(^{147}\) and by laser flash photolysis with time resolved-infrared detection \(^{148,149}\). Hitherto unknown triplet \(\alpha\)-ketocarbene was characterized by means of transient absorption spectroscopy \(^{150}\) and characteristic reactivity. A likely ring contraction to form the corresponding ketene and formation of the triplet carbene are competing reactions.

Supersonic expansion and matrix isolation spectroscopy are the two major experimental techniques to prepare cold, isolated molecules \(^{151}\). The basic difference between the two techniques is that the supersonic jet is a gas phase technique, while matrix isolation is a condensed phase method. It was shown that the more strained bond makes a greater contribution to the Cotton effect \(^{152}\) of the \(\pi-\pi^*\) transition in the absence of additional substitution in cyclic dialkylketenes.

The Haton products arising in the near UV \(^{153}\) (193.3-213.3 nm) photodissociation of jet-cooled CH\(_2\)CO molecules were investigated by photofragment translational spectroscopy (PTS). The spectra of the primary H+HCCO products were shown to span all energetically accessible product internal energies, peaking in the range 1200-1500 cm\(^{-1}\) at all excitation wavelengths.
2.12 Thermal Oxidation of 1-Phenyl-hept-1-yne

1-Phenyl-hept-1-yne was subjected to autoxidation at 115°C in a closed oxidation apparatus at 35 Kg/cm² O₂ pressure for about 15 hours. A dark brown thick liquid (foul smelling) obtained was extracted with acetone and is subjected to GC and GC/MS analyses. The GC pattern of the oxidate is given in fig.1.

From the gas chromatogram, it is observed that leaving the peaks at retention times of 1.05 (due to acetone used as solvent to extract the oxidation mixture from the reactor) and 18.35 min. (1-phenyl-hept-1-yne, the starting hydrocarbon left), four major oxidation products are present in the oxidation mixture. These are identified from the GC/MS and MS spectral data given in table 1. The GC/MS and MS spectra are given in 2 and 3-7 fig. respectively.

**Table 1: Identification of the oxidation products of phenylethyl-1-yne**

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min.)</th>
<th>Compound*(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.19</td>
<td>Butanoic acid</td>
</tr>
<tr>
<td>2</td>
<td>17.35</td>
<td>1-phenyl-hept-1-yne</td>
</tr>
<tr>
<td>3</td>
<td>18.48</td>
<td>Pentanoic acid</td>
</tr>
<tr>
<td>4</td>
<td>22.21</td>
<td>1-phenyl-hexan-1-one</td>
</tr>
<tr>
<td>5</td>
<td>33.52</td>
<td>Benzoic acid</td>
</tr>
</tbody>
</table>

*\(^a\) The retention time and the identification of the compound is based on the GC/MS spectral analysis

1-phenyl-hept-1-yne was also subjected to autoxidation at 100°C in chlorobenzene as solvent in an open oxidation apparatus for about 60 hours with oxygen flow kept at 5 L/hour. The results of the GC and GC/MS analysis of the oxidation mixtures under ambient conditions are recorded in the table 2 and 3. The GC pattern of the oxidate is given in fig.8. The GC/MS and MS spectra are given in fig. 9 and 10-15 respectively.
Chromatogram Plot

File: C:\GCQ\DATA\704
Date: Jun-26-2006 15:00:36
Comment: 1-Phenyl-1-heptyne Oxidation (GLT) on Innowax cap EI+
Scan No: 1575 Retention Time: 26:10 RIC: 56829 Mass Range: 37 - 350
Plotted: 22 to 2131 Range: 1 to 3149 100% = 6567551

Fig. 2
Background Subtract

File: C:\GCQ\DATA\704
Date: Jun-26-2006 15:00:36

Comment: 1-Phenyl-1-heptyne Oxidation (GLT) on Innowax cap EI+

Average of: 974 to 978 Minus: 949 to 953

100 % 42

100 % 60

100 % 72

100 % 45

100 % 55

100 % 72

100 % 50

100 % 57

100 % 67

100 % 77

100 % 86

100 % 89

100 % 91

100 % 104

100 % 109

100 % 114

100 % 118

100 % 127

100 % 133

Date: July 1st, 2006 4:30pm GCQ Data Processing, Finnigan Corporation

Fig. 3
Background Subtract

File: C: \ GCQ \ DATA \ 704
Date: Jun - 26 - 2006 15:00:36

Comment: 1-Phenyl -1-heptyne Oxidation (GLT) on Innowax cap EI+
Average of: 1123 to 1127 Minus: 1114 to 1118

100 %

100% = 9516

Fig. 5
Spectrum Plot
File: C:\GCQ\DATA\704
Date: Jun -26- 2006 15:00:36
Comment: 1-Phenyl-1-heptyne Oxidation (GLT) on Innowax cap EI+
# Peaks: 288 Base Pk: 105 Ioniz: 19628 us Int: 14594 100.00% = 14594

100 %

INT

77
45
55
94
132
157

119
175
190 212 232 254 277 310 330 345

120 140 160 180 200 220 240 260 280 300 320 340 360

Date: July 1st, 2006 4:30pm GCQ Data Processing, Finnigan Corporation

Fig. 6
Table 2: Chromatographic investigation of the products of the thermal oxidation of 1-phenylhept-1-yne under ambient pressure

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min.)</th>
<th>Area</th>
<th>Height</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.128</td>
<td>136822</td>
<td>2445</td>
<td>0.1755</td>
</tr>
<tr>
<td>2</td>
<td>12.31</td>
<td>355803</td>
<td>10267</td>
<td>0.4563</td>
</tr>
<tr>
<td>3</td>
<td>13.848</td>
<td>63360</td>
<td>1192</td>
<td>0.0813</td>
</tr>
<tr>
<td>4</td>
<td>16.269</td>
<td>64490</td>
<td>1518</td>
<td>0.0827</td>
</tr>
<tr>
<td>5</td>
<td>20.154</td>
<td>29738</td>
<td>783</td>
<td>0.0381</td>
</tr>
<tr>
<td>6</td>
<td>21.617</td>
<td>15028</td>
<td>588</td>
<td>0.0913</td>
</tr>
<tr>
<td>7</td>
<td>22.829</td>
<td>18210</td>
<td>530</td>
<td>0.0234</td>
</tr>
<tr>
<td>8</td>
<td>24.188</td>
<td>38445</td>
<td>1300</td>
<td>0.0493</td>
</tr>
<tr>
<td>9</td>
<td>25.713</td>
<td>244298</td>
<td>9786</td>
<td>0.3133</td>
</tr>
<tr>
<td>10</td>
<td>29.211</td>
<td>332801</td>
<td>11031</td>
<td>0.4268</td>
</tr>
<tr>
<td>11</td>
<td>30.542</td>
<td>94232</td>
<td>2487</td>
<td>0.1209</td>
</tr>
<tr>
<td>12</td>
<td>32.824</td>
<td>74199976</td>
<td>1223653</td>
<td>95.1601</td>
</tr>
<tr>
<td>13</td>
<td>35.183</td>
<td>23460</td>
<td>823</td>
<td>0.0301</td>
</tr>
<tr>
<td>14</td>
<td>36.164</td>
<td>123575</td>
<td>4297</td>
<td>0.1585</td>
</tr>
<tr>
<td>15</td>
<td>37.66</td>
<td>27047</td>
<td>943</td>
<td>0.0347</td>
</tr>
<tr>
<td>16</td>
<td>39.428</td>
<td>75072</td>
<td>2032</td>
<td>0.0963</td>
</tr>
<tr>
<td>17</td>
<td>41.233</td>
<td>20171</td>
<td>411</td>
<td>0.0259</td>
</tr>
<tr>
<td>18</td>
<td>43.503</td>
<td>2111337</td>
<td>44897</td>
<td>2.7077</td>
</tr>
</tbody>
</table>

Table 3: Identification of the oxidation products of phenylhept-1-yne

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min.)</th>
<th>Compound$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.15</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>2</td>
<td>29.31</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>3</td>
<td>29.43</td>
<td>1-phenyl-hex-1-yne</td>
</tr>
<tr>
<td>4</td>
<td>33.05</td>
<td>Dimerization product$^b$</td>
</tr>
<tr>
<td>5</td>
<td>34.23</td>
<td>4-methyl-1-phenylhex-1-yn-3-one</td>
</tr>
<tr>
<td>6</td>
<td>36.51</td>
<td>1-phenylhexan-1-one</td>
</tr>
<tr>
<td>7</td>
<td>41.42</td>
<td>2-chloro-1,1'-biphenyl</td>
</tr>
<tr>
<td>8</td>
<td>46.51</td>
<td>1-phenyl-hept-1-yn-3-one</td>
</tr>
</tbody>
</table>

$^a$ The retention time and the identification of the compound is based on the GC/MS spectral analysis. The mass spectra of chlorobenzene and naphthalene are given elsewhere for the purpose of comparison.

$^b$ The product is considered to be probably formed due to the dimerisation of 1-phenyl-hept-1-yne during the GC/MS analysis.
Chromatogram Plot

File: C:\GCQ\DATA\590  Date: Jan-31-2006  10:08:14
Comment: Sample-2 from (GLT) on Innowax cap EI+
Scan No: 1678  Retention Time: 28:01  RIC: 121321  Mass Range: 30 - 349
Plotted: 358 to 3008  Range: 1 to 3355  100% = 76809799

Fig. 9
Spectrum Plot

File: C:\GCQ\DATA\590 Date: Jan-31-2006 10:08:14
Comment: Sample-2 from (GLT) on Innowax cap EI+
Scan No: 1982 Retention Time: 33:05 RIC: 72116331 Mass Range: 30 - 349
# Peaks: 292 Base Pk: 287 Ioniz: 59 us Int: 5307437 100.00% = 5307437

Fig. 11
Spectrum Plot

File: C:\GCQ\DATA\590  Date: Jan-31-2006  10:08:14
Comment: Sample-2 from (GLT) on Innowax cap  EI+
Scan No: 2208  Retention Time: 36:51  RIC: 3736267  Mass Range: 31 - 349
# Peaks: 268 Base Pk: 105  Ioniz: 479 us  Int: 1041720   100.00% = 1041720

Fig. 13
Spectrum Plot

File: C:\GCQ\DATA\590  Date: Jan-31-2006  10:08:14
Comment: Sample-2 from (GLT) on Innowax cap  EI+
Scan No: 2498  Retention Time: 41:42  RIC: 2684260  Mass Range: 30 - 349
# Peaks: 281  Base Pk: 188  Ioniz: 728 us  Int: 1033978  100.00% = 1033978

Fig. 14
Spectrum Plot

File: C:\GCQ\DATA\590  Date: Jan-31-2006 10:08:14
Comment: Sample-2 from (GLT) on Innowax cap  EI+
# Peaks: 294  Base Pk: 129  Ioniz: 119 us  Int: 6709740  100.00% = 6709740

Fig. 15
2.13 Photochemical Oxidation of 1-Phenyl-hept-1-yne

100 mmol of 1-phenylheptyne analyzed by gas chromatography was subjected to photooxidation in a photochemical reactor in chlorobenzene as solvent for about 30 hours with 5 L/h O₂ using medium pressure mercury lamp. The oxidation mixture obtained as dark brown liquid on concentration was subjected to GC/MS analysis. The identification of the oxidation products is based on the comparison of the mass spectra with those of the authentic specimen. Some products are also established on the basis of the fragmentation pattern. The GC pattern of the oxide is given in the fig.16. The GC/MS and MS spectra are given in fig. 17 and 18-29 respectively. The results are compiled in table 4.

Table 4: Identification of the photo-oxidation products of phenylhept-1-yne

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention time (min.)</th>
<th>Compounda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.49</td>
<td>1,4-dichlorobenzene</td>
</tr>
<tr>
<td>2</td>
<td>18.11</td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>3</td>
<td>22.54</td>
<td>1-phenylheptane</td>
</tr>
<tr>
<td>4</td>
<td>27.56</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>5</td>
<td>28.26</td>
<td>1-phenylhexyne</td>
</tr>
<tr>
<td>6</td>
<td>32.16</td>
<td>1-phenylheptyne</td>
</tr>
<tr>
<td>7</td>
<td>33.46</td>
<td>1-phenyl-4-methylhex-1-yn-3-one</td>
</tr>
<tr>
<td>8</td>
<td>35.56</td>
<td>4-phenyl-3-butyn-2-one</td>
</tr>
<tr>
<td>9</td>
<td>36.23</td>
<td>1-phenyl-1-hexanone</td>
</tr>
<tr>
<td>10</td>
<td>41.28</td>
<td>2-chloro-1,1'-biphenyl</td>
</tr>
<tr>
<td>11</td>
<td>46.54</td>
<td>1-phenyl-hept-1-yn-3-one</td>
</tr>
<tr>
<td>12</td>
<td>47.10</td>
<td>3-chloro-1,1'-biphenyl</td>
</tr>
</tbody>
</table>

a) The retention time and the identification of the compound is based on the GC/MS spectral analysis
Spectrum Plot

File: C: \GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT) on Innowax cap  EI+
Scan No: 646  Retention Time: 10:49  RIC: 49919  Mass Range: 30 - 349
# Peaks: 308 Base Pk: 146  Ioniz: 19902 us Int: 11970  100.00% = 11970

Fig. 18
File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT )on Innowax cap  EI+
Scan No: 1088  Retention Time: 18:11  RIC: 32658  Mass Range: 31 - 348
# Peaks: 307 Base Pk: 105  Ionz: 19397 us Int: 6384  100.00% = 6384

Fig.19
Spectrum Plot

File: \GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT) on Innowax cap EI+
Scan No: 1703  Retention Time: 28:26  RIC: 440840  Mass Range: 31 - 349
# Peaks: 287  Base Pk: 143  Ioniz: 3908 us  Int: 72612  100.00% = 72612

Fig. 22
Spectrum Plot

File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT )on Innowax cap  EI+
Scan No: 1933  Retention Time: 32:16  RIC: 514613  Mass Range: 30 - 349
# Peaks: 302  Base Pk: 143  Ioniz: 3497 us  Int: 59139  100.00% = 59139

100%

INT

39 51 63 79 91 102 157 172 217 240 259 274 301 316 344

Fig. 23
Spectrum Plot

File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT) on Innowax cap EI+
Scan No: 2023  Retention Time: 33:46  RIC: 958762  Mass Range: 31 - 349
# Peaks: 288  Base Pk: 129  Ioniz: 1937 us  Int: 101364  100.00% = 101364

Fig. 24
Spectrum Plot

File: C:\GCQ\DATA\587  Date: Jan-30-2006 13:08:51
Comment: Sample-7 from (GLT) on Innowax cap EI+
Scan No: 2153  Retention Time: 35:56  RIC: 1131108  Mass Range: 30 - 349
# Peaks: 280 Base Pk: 129  Ioniz: 1568 us  Int: 589721  100.00% = 589721

Fig. 25
Spectrum Plot

File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT)on Innowax cap EI+
Scan No: 2485  Retention Time: 41:28  RIC: 2084662  Mass Range: 30 - 349
# Peaks: 261 Base Pk: 188  Ioniz: 934 us  Int: 794275  100.00% = 794275

Fig. 27
File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT )on Innowax cap EI+
Scan No: 2810  Retention Time: 46:54  RIC: 1728293  Mass Range: 31 - 349
# Peaks: 285 Base Pk: 129  Ioniz: 1028 us  Int: 635715  100.00% = 635715

Fig. 28
Spectrum Plot

File: C:\GCQ\DATA\587  Date: Jan-30-2006  13:08:51
Comment: Sample-7 from (GLT) on Innowax cap EI+
Scan No: 2826  Retention Time: 47:10  RIC: 1066822  Mass Range: 31 - 349
# Peaks: 285  Base Pk: 188  Ioniz: 1714 us  Int: 349925  100.00% = 349925

Fig. 29
Autoxidation at 115°C in a closed oxidation apparatus at 35 Kg/cm² O₂ pressure for about 15 hours resulted in the formation of the products due to the C-C bond cleavages of the side chain which is not observed either in the experiment under ambient or photochemical conditions. The C ≡ C triple bond cleavage leading to the formation of benzoic acid is also more pronounced compared to the ones under the other two conditions. The formation of 1-phenyl-1-hexanone which is considered as the oxidation product of the relatively stable intermediate ketene is more in the experiments carried out under UV-light irradiation. It is observed that under the ambient conditions the C-H bond activation particularly at the α-position to the C ≡ C triple bond is more compared to the rest. From the results it is assumed that the thermal oxidation under ambient conditions mainly leads to the formation of the α-hydroperoxide and its decomposition products while at higher temperatures and pressures both the hydroperoxide decomposition and the C ≡ C triple bond cleavage products along with the C-C cleavage products form.
References


