Oxidative cleavage of carbon-carbon triple bond – a review

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Oxidation of phenylacetylene with molecular oxygen led to the formation of 10 oxygen containing products along with dimerisation, oligomerisation and polymerisation products. Benzaldehyde, benzoic acid and benzoic anhydride are the main oxidation products. The autoxidation of diphenylacetylene gives benzil as the main product and its yield increases upon use of di-tertiary-butylperoxide as initiator. Examination of the crude oxidation mixtures of 1-phenylalk-1-yynes revealed the presence of corresponding a-dicarbonyl compounds in small quantities along with typical products like benzil, benzoic anhydride and phenyl benzoate. Similar oxidation of 1-phenylalkan-1,2-diones also yielded benzoic acid and the lower carboxylic acids as in the case of the corresponding 1-phenyl-1-alkynes and the oxidation is faster than the corresponding acetylenes. a-Dicarbonyl compounds undergo photochemical dissociation to free radicals in diffuse daylight but a thermal dissociation under the experimental conditions is not noted. Phenylglyoxal is regarded as one of the intermediates of phenylacetylene autoxidation. The formation of benzoic acid in all cases and considerable amounts of benzil from 1-phenyl-propane-1,2-dione and 1-phenyl-butane-1,2-dione in the thermal decomposition at 130° in presence of dibenzoyl peroxide, diacetyl peroxide or di-tertbutyl peroxide using chlorobenzene as solvent show that the reactions of the type Ph-CO-CO-R + X" ~ Ph-CO" + R-CO-X (with X" = R'-0" or R'-C0-0") take place during the course of autoxidation of a-diketones. The products expected from the reaction of the short lived intermediate ketocarbenes with oxygen i.e. a-dicarbonyl compounds and lower carboxylic acids, especially benzoic acid were not detected in the thermal and photochemical decomposition of a-diazoacetophenone, a-diazopropiophenone, a-diazobutyrophenone and a-diazo-desoxybenzoin. This shows that the oxidative scission of the C=C bond proceeds via the corresponding a-dicarbonyl compounds as intermediates and not via the corresponding oxirenes or the valence isomeric ketocarbenes.

It is well known that the autoxidation of acetylenic hydrocarbons preferably affords products of the attack at α-position to the C=C bond. Mayo and Sickle 8,9 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 bond and its decomposition products namely acetylenic alcohols and ketones. Argument either for the attack of oxygen on C=C bond or for the formation of the oxidative cleavage products of 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.

Oxidation of isomeric octynes

The autoxidation of all the four isomers of n-octyne 8 yielded as expected, the corresponding α-hydroperoxy-acetylenes and their decomposition products along with 2-7% α,β-unsaturated ketones, 5-10% carboxylic acids and 6-12% saturated ketones (Scheme 1). 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 α-position to the C=C bond was observed.

α,β-Unsaturated ketones were considered as the rearrangement products of the intermediate oxirenes and their valence isomers, ketocarbenes. Oxirenes can be formed for n-octyne in a way similar to the formation of oxirene/epoxide 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 valence isomeric ketocarbenes. The shift of a hydride in the two isomeric ketocarbenes leads to the formation of the α,β-unsaturated ketones 12 (Scheme 2). If there are no hydrogen atoms in α-position to the carbene centre, Wolff rearrangement to a ketene 13 takes place.

Oxidation of 1-phenylalk-1-yynes

The autoxidation of 1-phenylalk-1-ynes 14, (1-phenylprop-1-yne, 1-phenylbut-1-yne and 1-phenyl-3-
methylbut-1-yne) forms oxidative cleavage products of C=C bond and the rearrangement products through the intermediate oxirenes and/or their valence isomers, ketoarbenes. LiAlH₄ reduction of the oxidates furnished 2-phenylpropan-1-ol, 2-phenylbutan-1-ol and 3-methyl-2-phenylbutan-1-ol along with benzyl alcohol. They are the reduction products of 2-phenylpropanoic acid, 2-phenylbutanoic acid, 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 (Scheme 3). Further, 1-phenylethan-1-ol, 1-phenylpropan-1-ol and 2-methyl-1-phenylpropan-1-ol are the reduction products of 1-phenylethan-1-one, 1-phenylpropan-1-one and 2-methyl-1-phenylpropan-1-one respectively which are derived from autoxidation of the corresponding ketenes.³⁵,³⁶

Again, 1-phenylbut-1-en-3-ol obtained from 3-methyl1-phenylbut-1-yne is likely to be the reduction product of 1-

Scheme 1. Liquid-phase oxidation of the isomeric octynes with molecular oxygen at 85°.

Scheme 2. Formation of α,β-unsaturated ketones in the autoxidation of the isomeric octynes.

Scheme 3. Wolff rearrangement of the ketocarbenes corresponding to the oxirenes in the autoxidation of the 1-phenylalk-1-ynes.
Rao et al.: Oxidative cleavage of carbon-carbon triple bond – a review

The oxidation rates and the yields of the corresponding α-hydroperoxyacetylenes and their consecutive products in the order from 1-phenylprop-1-yne, 1-phenylbut-1-yne to 3-methyl-1-phenylbut-1-yne. The yields of the oxidative cleavage products of the C=C 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\(^\text{17}\). Phenylacetylene\(^\text{18}\) was subjected to autoxidation at 110° until the absorption of oxygen amounted to 25 mmol per 100 mmol of the starting hydrocarbon. Ten oxygen containing products, namely, benzaldehyde, phenylacetaldehyde, acetophenone, phenol, benzoic acid, phenylacetic acid, benzil, phenyl benzoate and benzoic anhydride were characterized (Scheme 5) 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\(^\text{19,20}\) of phenylacetylene. Acid anhydride isolated and characterized is considered as one of the most important products in the autoxidation of acetylenic hydrocarbons.

Benzil was found to be the main product along with the traces of benzoic acid in the oxidates of diphenylacetylene\(^\text{21}\). The yield of benzil increased when di-tert-butyl peroxide was used as initiator (Scheme 6). No traces of diphenylacetic acid or benzophenone, which are to be expected as oxidative products of the corresponding diphenylketene formed via oxirene were found in the reaction mixtures.

Reexamination\(^\text{21}\) of the crude oxidation mixtures of 1-phenylprop-1-yne, 1-phenylbut-1-yne and 1-phenyl-3-methylbut-1-yne established besides acetylenic alcohols, acetylenic ketones, the presence of the corresponding α-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 bonds in considerable

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Scheme 4. Formation of 1-phenylbut-1-yn-3-one from 3-methyl-1-phenylbut-1-yne.

Scheme 5. Pathways of formation of several products of phenylacetylene oxidation.
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 bond taking place during the autoxidation of acetylenic hydrocarbons, different possible reaction pathways were considered (Scheme 7).

The peroxy vinyl radical formed by the addition of a propargyl peroxyradical, to the C≡C bond can react further with oxygen giving rise to a peroxo-alkylperoxy radical which in turn adds to a molecule of alkyne to deliver a vinyl radical 3 with two peroxide functions. The radical 3 can react further with oxygen and acetylene molecules simultaneously giving radicals of the type 3a with \( n > 1 \). Cleavage of peroxide bonds in 3 and 3a resulted in the formation of oxirene an \( \alpha \)-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.

Formation of the acid anhydride\(^1\),\(^2\),\(^22\),\(^23\) or the \( \alpha \)-dicarboxyl compound\(^{24}\) and their reaction products can be expected as shown in the Scheme 8. Ketocarbenes, which can be formed from acetylenes via oxirenes can react with oxygen to give rise to carbonyl oxides\(^{25}-29\). These can react further, resulting, in the formation of ozone and the corresponding \( \alpha \)-dicarboxyl compound\(^{24}\) (in its triplet form) or transfer an atom of oxygen to the ketocarbenes forming two molecules of the \( \alpha \)-dicarboxyl compound\(^{30}\). A reaction between the carbonyl oxides and the starting acetylenes with the formation of the \( \alpha \)-diketones and the corresponding oxirenes similar to the formation of oxiranes can also be taken into consideration. The ketocarbone formation from acetylenes via oxirenes is established in several reactions. Formation of carbene from phenylacetylene via oligomerisation and C≡C bond scission\(^{31},^{32}\) at a mixed-metal centers are reported. Radical formation by singlet
methylenic with acetylenes are also discussed\textsuperscript{33,34}.

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$_2$ to form dioxetene\textsuperscript{35-39} directly or from the excited singlet-triplet complex states (Scheme 9). 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 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{40,41}.

Unstrained cyclic acetylenes i.e. 1,7-cyclododecaadiyne and 1,8-cyclotetradecadiyne did not react with ground state triplet or singlet oxygen. Dioxetene and its opening to α-dicarbonyl compounds\textsuperscript{42} were formulated via radical cation in photo-oxygenation via electron transfer in the presence of 9,10-dicyanoanthracene.

\textbf{Scheme 8.} Oxirenes or α-ketocarbenes as intermediates.

\textbf{Scheme 9.} Dioxetenes as intermediates.

Photosensitized oxidation of acetylenes to α-dicarbonyl compound leading to the corresponding carboxylic acid\textsuperscript{43} is also known. One step synthesis of α-diketones\textsuperscript{44} from
alkynes with ruthenium tetroxide as catalyst has been developed. Direct anodic oxidation of acetylenes in non-aqueous solvents giving α, β-unsaturated γ-diketones has also been formulated.

Oxidation of 1-phenylalkane-1,2-diones

To test the applicability of the Scheme 7, α-diketones 1-phenylpropane-1,2-dione, 1-phenylbutane-1,2-dione and 3-methyl-1-phenylbutane-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 during 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 to the amount obtained from the corresponding α-diketones.

Majzus and Zaikov showed the formation of the two acyl radicals through thermal decomposition of C-C single bond present between the two carbonyl groups in the liquid phase oxidation of butane-2,3-dione at 85° as the initiation step which required 148 kJ mol\(^{-1}\) of activation energy (Scheme 10). An analogous mechanism was also formulated for the oxidation of cyclohexanone to \(\varepsilon\)-caprolactone. On the other hand the formation of two acyl radicals required an activation energy of the order of 250 kJ mol\(^{-1}\) in gas phase oxidation.

\[
\begin{align*}
\text{CH}_3\text{CO-CH}_2\text{CH} & \rightarrow 2\text{CH}_3\text{CO} \quad E_A = 148 \text{ kJ mol}^{-1} \\
\text{CH}_3\text{CO-CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{CO-CH}_2\text{CO} + \text{CH}_3 \\
\text{CH}_2\text{CO-CH}_2\text{CO} & \rightarrow \text{CH}_2\text{CO-CH}_3 + \text{RO'} \\
\end{align*}
\]

Liquid-phase oxidation of butan-2,3-dione

\[
\begin{align*}
\text{CH}_3\text{CO-CH}_2\text{CH}_3 & \rightarrow 2\text{CH}_3\text{CO} \quad E_A = 250 \text{ kJ mol}^{-1} \\
\text{CH}_3\text{CO-CH}_2\text{CH}_3 + R' & \rightarrow \text{CH}_3\text{CO} + \text{CH}_2\text{CO-R} \quad E_A = 26 \text{ kJ mol}^{-1} \\
\end{align*}
\]

Gas-phase decomposition of butan-2,3-dione

Scheme 10

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

Photo-oxidation\(^{55-58}\) 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 photo-chemistry of benzocyclobutenedione\(^{59}\). Photo-oxidation of α-diketones in the presence of olefins 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. Photo-chemistry of α-diketones\(^{64}\) delivers a variety of products.

The thermal dissociation of α-diketones using 1-phenylpropane-1,2-dione and benzil as initiators of the autoxidation of cumene at 75° in chlorobenzene was investigated as solvent according to the generally accepted Batesman equation\(^{65}\). The dependencies of the rate of oxygen uptake on the concentration of cumene as substrate and α-diketones as initiators were found in accordance with the Bateman equation.

Because the correlations 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 \(\lambda_{\text{max}} = 407 \text{ nm}; \varepsilon_{\text{max}} = 9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\), 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° as a thermal reaction. It is possible only as a photochemical reaction.

The oxidation studies of both 1-phenylalk-1-yne 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\(^{21}\) formed was not altered.

Benzil was characterized in the oxidates of the α-diketones obtained both in the 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 alkoxo or alkyl peroxy radical.
Reaction of acyloxy and alkoxy radicals

To prove the possibility of $S_2$ reactions at the C–C bond between the two carbonyl groups of $\alpha$-diketones, dibenzoyl peroxide, diacetyl peroxide and di-tert-butyl peroxide were thermally decomposed at 130° in the presence of benzil, 1-phenylpropane-1,2-dione and 1-phenylbutane-1,2-dione using chlorobenzene as solvent. In all cases benzoic acid was formed. Moreover, considerable amounts of benzil were obtained from 1-phenylpropane-1,2-dione and 1-phenylbutane-1,2-dione. With the formulation of Majzus, 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 (Scheme 11).

Dissociation of $\alpha$-diketones to acyl radicals, possible only as a photochemical reaction:

\[
\text{Ph–CO–CO–R} \xrightarrow{\text{hv}} \text{Ph–CO} + \text{R–CO}
\]

Reaction of $\alpha$-diketones with free radicals:

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

($X = R^*$; $R–O^*$; $R–O–O^*$)

Free-radical chain mechanism of the $\alpha$-diketone oxidation:

\[
\begin{align*}
\text{Ph–CO–O–O} & \rightarrow \text{Ph–CO–O} + \text{R–CO–R} \\
\text{Ph–CO–O} + \text{Ph–CO–CO–R} & \rightarrow \text{Ph–CO} + \text{Ph–CO–O–O–CO–R}
\end{align*}
\]

Dimerization of benzoyl radicals to benzil (chain termination):

\[
2\text{Ph–CO} \rightarrow \text{Ph–CO–CO–Ph}
\]

Scheme 11. Oxidation of phenylalkan-1,2-diones: formation of acid anhydrides and of benzil.

During the decomposition of di-tert-butyl peroxide in the presence of $\alpha$-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 $\alpha$-diketones is a tert-butyl ester which under the conditions of the reaction or during gas chromatographic analysis decomposes to benzoic acid and isobutene.

Tertiary butoxy radicals decompose very fast according to

It is concluded that the formation of benzoic anhydride

\[
\begin{align*}
\text{CH}_3 & \xrightarrow{\text{CO} + \text{CH}_3} \text{CO} + \text{CH}_3 \\
\text{CH}_3 & \xrightarrow{\text{O} + \text{CH}_3} \text{CO} + \text{CH}_3
\end{align*}
\]
in the reaction products of alkoxy radicals is not possible. 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\(^{67-69}\) leading to the formation of diphenyl.

Phenylglyoxal could not be traced in the oxidates of phenylacetylene\(^{18}\) since it undergoes oxidation several times faster than the corresponding hydrocarbon. The oxidation products of phenylacetylene namely benzoic anhydride, benzaldehyde, benzoic acid, benil, benzenophene and phenyl benzoate could also be characterized in the oxidates of phenyl glyoxal\(^{70}\). 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 benzenophene 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.

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

Reactions of this type are known from gas-phase decomposition \(\alpha\)-diketones\(^{50-52}\). Further reaction of benzenophene with one of the peracids formed during the oxidation of phenylglyoxal i.e. phenylglyoxylic peracid or perbenzoic acid yields phenylbenzoate\(^{71-74}\). The formation of phenyl radicals is possible both via decarbonylation of benzoyl and decarboxylation of benzoyloxy radicals

\[
\begin{align*}
\text{Ph} - \text{CO} & \rightarrow \text{Ph}^* + \text{CO} \\
\text{Ph} - \text{CO} - \text{O}^* & \rightarrow \text{Ph}^* + \text{CO}_2
\end{align*}
\]

Some other radical reactions\(^{75-77}\) related with acetylenes have been discussed recently.

**Studies concerning \(\alpha\)-diazoketones:**

\(\alpha\)-Diazocarbonyl compounds are very reactive substances and undergo Wolff rearrangement under catalytic, thermal or photochemical conditions\(^{78,79}\). Wolff\(^{80,81}\) and Schroeter\(^{82,83}\) formulated a one step mechanism while Kaplan and coworkers\(^{84,85}\) discussed a synchrone mechanism. Kinetic studies\(^{86-88}\) and the influence of substituents\(^{89}\) on the elimination of nitrogen and the migrating capability of the aryl or alkyl groups argue against the synchrone mechanism. Tomioka\(^{90,91}\) 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 \(\alpha\)-oxocarbene-ketene-reaction sequence of the Wolff rearrangement is the occurrence of a ketocarbene interconversion via intermediate oxirene\(^{92-97}\). Lemal and coworkers\(^{98}\) reported that the species originally assigned as the \(\alpha\)-ketocarbene is actually the \(\alpha\)-ketodiazirine, an isomer of the starting \(\alpha\)-diazoketone. Tanaka et al.\(^{99}\) could not obtain any detectable traces of the corresponding \(\alpha\)-diketones and acid-anhydrides. Energy barrier calculations for relative stabilities in rare gas matrices and structural stud-
Oxidative cleavage of carbon-carbon triple bond -- a review

Studies concerning the reaction of ketocarbenes with molecular oxygen:

It was shown that the oxidative cleavage of the C≡C bond during the autoxidation of acetylenic hydrocarbons proceeds via the corresponding α-diketones. Different possibilities for the formation of α-dicarbonyl compounds, acid anhydrides and their consecutive products, carboxylic acids from ketocarbenes were formulated (Scheme 8). To test these assumptions, α-diazoacetophenone, α-diazoacrylonitrile, α-diazobutyrophenone and α-diazodesoxybenzoin were subjected to photolysis and photo-oxidation in benzene and cyclohexane at 40° for about 10 h. Thermal oxidation and thermolysis were carried out at 75° for about 15 h in benzene in the case of α-diazoacetophenone and at 110° for about 12 h 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 bond during the autoxidation 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-diazoketones in the presence and in the absence of oxygen. Formation of different products of α-diazoketones can be explained as shown below in Schemes 13–15.

Decomposition of α-diazoketones yields a singlet ketocarbone which is transformed in some cases into the more stable triple 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-diazoketones. Secondly, if possible as in the case of α-diazoacrylonitrile and α-diazobutyrophenone, the stabilization of the ketocarbenes takes place mainly through hydrogen atom shifts under the formation of α,β-unsaturated ketones. 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, dimerization etc. The ketocarbenes from α-diazoacetophenone showed the C–H bond insertion reactions with benzene and cyclohexane resulting in the formation of 1-oxo-1,2-diphenylethane and 2-cyclohexyl-1-oxo-1-phenylethane.

Scheme 13. Decomposition of α-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\textsuperscript{122}. Most of the products discussed can be explained on the basis of singlet ketocarbone. 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. Formation of phenylbenzoate in photochemical and thermal oxidations in considerable amounts from \(\alpha\)-diazodesoxybenzoin leads one to consider the Baeyer-Villiger type oxidation\textsuperscript{123} which can take place with the \(\alpha\)-ketocarbonyl oxide of the ketocarbene or with diphenycarbonyl oxide\textsuperscript{124} in photochemical oxidation. The direct rearrangement of the intermediate carbonyl oxides to esters\textsuperscript{125–128} is also well known. Minor quantities of phenol formed in thermal and photochemical oxidations of \(\alpha\)-diazodesoxybenzoin in benzene can be attributed due to the intermediate arene oxide\textsuperscript{129}. The pathway for the formation of \(\alpha\)-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.

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