GENERAL INTRODUCTION
Molecules containing two nitrogen atoms joined together and with one of these nitrogen atoms attached to a single carbon atom, are referred to as diazoalkanes \( (R_2C\ N\ H) \). Many extensive reviews of this subject have appeared in the previous decade\(^1\)\(^2 \) in addition to several since 1970\(^3\)\(^4\)\(^5\)\(^6 \). There has been much interest in the chemistry of diazoalkanes for many years because of their usefulness as intermediates, and more recently as a consequence of work on the reactivity and structure of carbenes \( (R_2C\ :\ ) \).\(^7\)\(^8\)\(^9 \)

Many diazo-compounds form carbenes on photolysis, thermolysis and on catalytic decomposition (specially when copper and its salts are used):

\[
\begin{align*}
R_1\ C\ N_2\ (h\nu, \ \nabla \text{ or cat.}) & \rightarrow R_1\ C\ : + N_2 \\
R_2
\end{align*}
\]

Since these fission reactions proceed easily in most cases, diazoalkanes are the most important sources of carbenes.\(^10\)\(^11 \)

Diazomethane is the simplest diazoalkane and as such has served as the prototype for many studies, both experimental and theoretical. From a classical point of view, it may be considered as a resonance hybrid of a variety of planar forms.
\[
\begin{align*}
\text{CH}_2 &= \text{N} \equiv \text{N} \quad \leftrightarrow \quad \text{CH}_2 &= \text{N} \equiv \text{N} \\
\quad \leftrightarrow \quad \text{CH}_2 &= \text{N} \equiv \text{N} \quad \leftrightarrow \quad \text{CH}_2 &= \text{N} \\
\end{align*}
\]

Consequently, diazomethane can be thought of possessing the properties of a carbene source, an acid, a base, an electrophile, a nucleophile or a 1,3-dipole.\(^5\)

Electron diffraction studies\(^{12}\) indicate the C-N\(_2\) moiety to be linear and microwave spectroscopy\(^{13}\) and the low dipole moment of diazomethane\(^{14}\) support the resonance hybrid formation. Simple HMO\(^{15}\) calculation predicts value of bond lengths and dipole moment in close agreement with those experimentally observed.

The thermal stability of diazoalkane depends markedly on the nature of substituents. Conjugating substituents increase stability irrespective of whether they are electron releasing or electron attracting. Diazomethane and diazoethane are gases under normal atmospheric conditions, decomposing readily under the influence of rough surfaces. Diazoalkanes having carbonyl, aryl, nitrile or other conjugating substituents are much more stable, and may be handled conveniently as pure liquids or solids.

**Decomposition of diazoalkanes to olefins and Azines:**

The decomposition of aliphatic diazo-compounds in the absence of reaction partners can lead to azines(1) and to alkenes (2):
It is usually assumed that carbenes are formed as intermediates in these reactions,\textsuperscript{5,16-21} but this route is not invariably the only possible one.\textsuperscript{5,22} Formation of azines and olefins is a characteristic\textsuperscript{23} of relatively stable diazo-compounds, e.g.:

Diazodiphenylmethane $\rightarrow$ Tetraphenylethylene
9-Diazofluorene $\rightarrow$ 9, 9'-Bifluorenylidene
1-Diazoethanol acetate $\rightarrow$ 2-Octene-2,3-diol diacetate
$\alpha$-Diazoketones $\rightarrow$ 1,2-Diacetylenes.

Diazomethane decomposes merely to polymethylene.\textsuperscript{11}

Azines are often formed by heating diazo-compounds in the absence of catalysts, particularly on the preparative scale. It is possible to prepare unsymmetrical azines from a mixture of two different diazo-compounds; 70-90\% in yield of the azine has been prepared when one of the components was diazodiphenylmethane.\textsuperscript{22,24} Heating aliphatic diazo-compounds in inert solvents in presence of copper salts gives olefins in high yield. This way 9,9'-bifluorenylidene (91\%) and tetraphenylethylene in 86\% yield has been obtained from 9-diazofluorene\textsuperscript{25} and diazodiphenylmethane,\textsuperscript{25,26} respectively.
Photolysis of diazoalkanes has been studied much less as compared to the thermal decomposition since the former proceeds less cleanly. A communication, however, reports a similar product, i.e. 80-90% azine in the decomposition of diazodiphenylmethane in benzene brought about by thermal and photolytic methods.

**Reaction of diazoalkanes with C = C double bond systems producing cyclopropanes:**

The reaction of diazo-compounds with olefins carried out photochemically or in the presence of catalyst results in the elimination of nitrogen and the corresponding cyclopropanes are formed.

\[
\begin{align*}
\text{R}_1 & \quad \text{C = C} \quad \text{R}_2 \\
\text{R}_1 & \quad \text{N}_2 + \quad \text{C = C} \quad \text{R}_2 \quad \xrightarrow{\text{N}_2} \\
\text{R}_1 & \quad \text{R}_2
\end{align*}
\]

When halides of zinc or alkylaluminum are used as catalysts, there are indications for the intermediate formation of organo-metallic compounds. When the reaction is carried out in the presence of copper or copper salts, it is assumed that carbenoid mechanism operates. Unequivocal support for the importance of carbene-copper complexes in the product-determining stages of the reaction has come from observations that a chiral Cu (II) complex promotes the decomposition of
ethyl-diazoacetate in the presence of styrene giving cyclopropanes which are optically active.\textsuperscript{32} Cu (I) halidetrialkyl phosphate complexes promote cyclopropane formation with stereoselectivity determined by the nature of the alkyl groups of the phosphate.\textsuperscript{33}

**Acid induced Decomposition of Diazoalkanes**

The chemistry of aliphatic diazo-compounds has undergone something of a revival in recent years. The primary interest has been in carbenes and in 1,3-dipolar additions, but much of the renewed activity in diazoalkane chemistry has been in the field of acid-induced decomposition.

In the presence of strong acid, diazodiphenylmethane reacts under conditions in which thermal and photolytic reactions are not operating but different route of decomposition takes place to yield a quite different pattern of products. In alcoholic solvents, the benzhydryl ether of the solvent predominates, but small quantities of tetraphenylethylene (TPE) are also formed. In aprotic solvents, the product is tetraphenylethylene (TPE). For reactions with undissociated acids in alcoholic solvents, a large fraction of the benzhydryl ester of the acid is produced in addition to the ether; in aprotic solvents, formation of the ester is nearly quantitative.\textsuperscript{34,35} All of these products may be considered to derive from an intermediate carbonium ion, as is depicted in scheme 1.
The first systematic investigation involving both kinetic and product studies of the acid catalysed decomposition of diazodiphenylmethane was carried out by Roberts and his collaborators\textsuperscript{37-39} using ethanol as a solvent. They had concluded that decomposition of the diazoalkane by strong acids involved rate determining proton transfer to the \(\alpha\)-carbon atoms. The diazonium ion then loses nitrogen to form benzhydryl cation, which reacts with the diazo precursor to give tetraphenylethylene, or with protic solvent (ROH) to give benzhydrol or benzhydryl ethers. For both strong and weak acids, deuteriation of the solvent was found to depress the reaction rate and kinetic isotope effects of \(K_H/K_D\) = 3.5 and 3.6 were obtained for acetic and benzoic acids respectively.\textsuperscript{38} This observation gave a clear indication of proton transfer as the rate determining step.

Identical mechanism as postulated for strong acid catalysed decomposition, was postulated for catalysis by weak acids, except that a major product was the benzhydryl
ester of the weak acid, however, such scheme failed to answer an important observation. It was found that, in the decomposition with undissociated acids, addition of the salt of the acid had no effect on the product ratio of ester and ether. This implies that the ester could not have arisen by free competition for a carbonium ion between the acid anion and the solvent.

This was confirmed by Roberts himself; in the ethanalysis of benzhydryl chloride, the presence of carboxylate anions, at the same concentration as in the diazodiphenylmethane reaction, did not significantly divert the benzhydryl cation from reaction with the solvent. Subsequently, it was shown that the product ratio was also insensitive to changes in reaction temperature, and moderate changes in the reactivity of the catalysing acid. These results imply that the ester is not formed from dissociated anions of the acid and the product-partitioning occurs via steps of low activation energy.

The first improvement of the initially proposed mechanism by Roberts came from Roberts himself, in which he supposed that two competing processes were taking place during the decomposition, the first being the straight-forward reaction already described and the second being the direct formation of the ester via a cyclic transition state.
A more rational explanation was presented at a later stage by Miller and O’Ferrall in terms of competing ion-pair return reaction. A similar formulation was suggested by Chapman and his associates.

The scheme depicts that the first intermediate is a diazonium ion pair which loses nitrogen unimolecularly without dissociation with the result that a carbonium ion-ammonium pair is formed. This carbonium ion-pair can,
in turn, either collapse to form benzhydryl ester, or it can dissociate to yield a free carbonium ion which reacts with solvent to form benzhydryl ether. There is always the possibility that the ester may undergo solvolyis at a rate comparable with that for the decomposition of diazodiphenylmethane itself, as is seen for the reaction of undissociated hydrogen chloride in ethanol.\(^{36,37}\) For the reaction of free hydrogen ions, no ion-pairs can be formed and benzhydryl ethyl ether can be speculated as the only product. The formation of ion-pair suggested by C. O’Ferrall as depicted in scheme-3 is definitely the most convincing and this was formulated on the basis of the evidence\(^{42}\) presented (e.g., the isotope effect, using \(\text{HCO}_2\text{H} (D)\) in ethanol was the same for the formation of ether and ester, whereas a different effect might be expected for the product formed by a cyclic route).

Direct proof of the intervention of ion-pairs was obtained by Diaz and Weinstein\(^{43}\) from the reaction of diazodiphenylmethane with \(\text{D}^{18}\)-labelled \(p\)-nitrobenzoic acid in ethanol. Competition between ion-pair return, dissociation, and ethanolyis of \(\text{D}^{13}\)-labelled benzhydryl \(p\)-nitrobenzoate had previously been investigated by Goering and Levy\(^{44}\) after having compared the rates of \(\text{D}^{18}\)-scrambling and acid production. Employing the similar techniques, Diaz and Weinstein\(^{43}\) showed that same ion-pair or host ion-pairs, were involved in decomposition of the diazo-compound :
More searching examination of Scheme 3 suggests alternatives to the proposed paths leading to the products. Thus, the carbonium ion precursor of the benzhydryl ether might be formed not from dissociation of carbonium carboxylate ion-pairs but by nitrogen loss from already dissociated diazonium ions. The most important parameter which decides this, is the lifetime of the diazonium ion, which in turn is probably determined by the stability of the carbonium ion formed from it. It is, therefore, apparent that stable carbonium ion is conducive to a short-lived diazonium ion and vice-versa. Therefore, if appreciable dissociation occurs at the diazonium ion stage for a carbonium ion as stable as the benzhydryl cation, for less stable carbonium ions, such dissociation should be complete, and no indication of ion-pair collapse should be found among the products. Indeed, there is evidence that
even primary diazonium ions reacting under highly polar solvent conditions yield a significant product fraction from carbonium ion pair collapse. In the benzhydryl case, therefore, dissociation of diazonium ion-pairs is highly unlikely.

**Reactions in Aprotic Solvents:**

Lentell and Callister made extensive studies of the reaction of diazodiphenylmethane with hydrogen ions in acetonitrile. One factor leading to different behaviour of acids in hydroxylic and aprotic solvents pertains to the variation in acid strength. Thus, toluenesulphonic acid which behaves as a strong acid in ethanol, is weak in acetonitrile. But perchloric acid is known to be fully ionised in acetonitrile and clean second order kinetics was observed when it induced the decomposition of diazodiphenylmethane. Electron-donating substituents were shown to accelerate the reaction and, in the absence of added nucleophiles, tetraphenylethylene was found to be the sole product. Addition of water diverted the product to benzhydryl alcohol at the expense of the reaction rate getting slower. Replacement of $\text{H}_2\text{O}$ by $\text{D}_2\text{O}$ gave a kinetic isotope effect $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = 3.3$, but had no effect on the product proportions.

Lentell and Callister concluded that the proton transfer leading to the formation of benzhydryldiazenium ion is rate-determining and that the benzhydryl cation
participates in subsequent rapid steps for the available nucleophiles and also the parent diazoalkane molecule according to the scheme 4:

\[
\text{Ph}_2\text{CN}_2 \xrightarrow{H^+} \text{Ph}_2\text{CHCN}_2 \xrightarrow{} \text{Ph}_2\text{CH}^+ \\
\xrightarrow{K_x} \text{Ph}_2\text{CN}_2 + \text{H}_2\text{O} \xrightarrow{} \text{Ph}_2\text{CH}^+ + \text{H}^+ \\
\text{Ph}_2\text{C} = \text{CPh}_2 + \text{N}_2 + \text{H}^+ \\
\text{Ph}_2\text{CHOH} + \text{H}^+ \\
\text{(Scheme 4)}
\]

In a subsequent paper, Bethell and Callister\textsuperscript{66} investigated the decomposition of diazodiphenylmethane with toluenesulphonic acid in acetonitrile. This acid being non-ionizable in acetonitrile, reacts to form benzhydryl toluenesulphonate, which subsequently interposes a slow solvolysis to form tetraphenylenethylene provided excess diazodiphenylmethane is present. An interesting feature in this investigation pertains to the role of added water towards the reaction rate and the product distribution. The addition of water has two effects; it facilitates the solvolysis of the ester and it enhances the ionization of the acid. An increase in reaction rate without a change of mechanism was attributed to the first factor, i.e. enhanced ionization was thought to bring about the decomposition with the proton transfer, yielding the same products, but without the formation of the ester as an intermediate. An important finding was that \(K_x/K_y\) for
the product-partitioning is independent of whether or not the benzhydryltoluenesulphonate is an intermediate. This gave an unequivocal evidence of the fact that partitioning occurs at the state of the carbonium ion and not of the diazonium ion. Scheme 4 may be extended to incorporate the behaviour of toluenesulphonic acid (Scheme 5). Comparison with scheme 3 indicates that, despite strong superficial differences, the mechanisms are similar whether the medium is acetonitrile or ethanol.

\[
\begin{array}{c}
\text{Ph}_2\text{CH}_2\text{OTs} \\
\uparrow \\
\text{Ph}_2\text{CHN}_2^+ \text{OTs} \xrightarrow{\text{N}_2} \text{Ph}_2\text{CH}^+\text{OTs} \\
\text{Ph}_2\text{CH}_2 \\
\text{H}_2\text{C} = \text{C Ph}_2 \\
\text{Ph}_2\text{CHOH}
\end{array}
\]

(Scheme 5)

In a recent paper, E.T. Blues and Coworkers have reported the reactions of diazophenylmethane with p-toluenesulphinic acid in a host of non-hydroxylic solvents. The reaction shows rate-determining proton transfer \((K_a/K_D) = 3.0\) in dichloromethane, benzene, acetonitrile, dioxan and dimethylsulphoxide. The fastest rates are found in the dipolar aprotic DMSO and this is attributed to dedimerization of the acid which is not
solvated by its conjugate base in the solvent. Both sulphinate (2) and sulphone (1) are observed among the products, but the sulphone (1) is the sole product in more dissociating DMSO.

\[
\text{ARSO}_2\text{H} + \text{Ph}_2\text{C} = \text{N} \quad \longrightarrow \quad \text{Ph}_2\text{C} = \text{N}^+ \cdot \text{O}_2\text{S} \text{ Ar}
\]

\[
\text{Ph}_2\text{C} = \text{O}_2\text{S} \text{ Ar} \quad \longleftrightarrow \quad \text{Ph}_2\text{C}^+ \cdot \text{O}_2\text{S} \text{ Ar}
\]

\[
\text{Ph}_2\text{C} = \text{SO}_2\text{Ar} \quad \text{Ph}_2\text{CHO}_2\text{SO}_2\text{Ar}
\]

(1) (2)

**Redox reactions of diazocarboxyls:**

Diazoalkanes are slowly oxidized by oxygen. It has been demonstrated that formaldehyde is formed on passing air through irradiated ethereal solutions of diazomethane; under the same conditions diazodiphenylmethane forms benzophenone.\(^{23}\) Oxidation of diazoketones can occur as a side reaction during rearrangements.\(^{48}\)

There is a vigorous reaction on treating diazoalkanes with ozone. Ozonization of solutions of diazodiphenylmethane, 9-diazofluorene, or 2-diazoo-2-phenyl acetophenone (azibenzil) forms the corresponding carbonyl compounds in almost quantitative yields.\(^{49,50}\) The mono-substituted diazocompounds, (diazoephethylmethane, ethyl diazoacetate, 2-diazoacetophenone, 4'-chloro-2-diazoacetophenone) on ozonization involve reactions in which the C=H bond adjacent to the diazo group may be attacked as well as the C = N bond.\(^{49,50}\)
Treatment with tert-butyl hypochlorite is a convenient method for the conversion of 2-diazo-1, 3-dicarbonyl compounds into 1,2,3-tricarbonyl compounds.\textsuperscript{51,52} For example, reacting 2-diazo-1, 3-indandione with tert-butyl hypochlorite in ethanol yields 2,2-dithoxy-1, 3-indandiones, which is converted into ninhydrin by treatment with aqueous sulfuric acid\textsuperscript{52}:

\[
\frac{(\text{CH}_3)_3\text{C}Cl/\text{H}_2\text{C}=\text{OH}}{95-100^\circ} \xrightarrow{\text{H}_2\text{SO}_4} \text{ product}
\]

\textit{Oxidation of 9-diazofluorene with per acids or with dibenzoyl peroxide mainly gives fluorenone but the occurrence of insertion and dimerization reactions has also been noted.}\textsuperscript{53} The relative ratios of the products formed, depend on the peroxy compound used for oxidation.

\textit{Oxidation of 9-diazofluorene with leadtetraacetate has been shown to give dimethyl fluorene-9, 9-diacetate in high yield.}\textsuperscript{54}
During the past ten years, some interesting investigations have been made in the electro chemical behaviour of several diazo-compounds. Jugelt's group has made extensive studies on the anodic oxidation of a variety of diazo-compounds in acetonitrile. For example diazodiphenylmethane and its substituted derivatives undergo a reversible one-electron oxidation at a rotating platinum disk electrode which involves an initial formation of short lived intermediate, presumably the corresponding radical cation.\textsuperscript{55} Similarly anodic oxidation of other diazo-compounds (1-3), in acetonitrile has been shown to proceed by initial formation of a radical cation intermediate.\textsuperscript{55-57}

\begin{align*}
\text{ArC Ar'}^+ & \quad \text{ArC COAr'}^+ & \quad \text{ArC CO}_2\text{Et}^+ \\
\begin{array}{ccc}
\| & \| & \\
R_2 & R_2 & R_2 \\
(1) & (2) & (3)
\end{array}
\end{align*}

The oxidation potentials of each compound were found to be linearly correlated with Hammett $\sigma^+$ and $\sigma$.\textsuperscript{56,57} Furthermore, the rates of reaction of members of a given class of diazo-compound with benzoic acid were found to be linearly correlated with their oxidation potentials.\textsuperscript{55-57} For example, the rates of reaction of substituted diazodiphenylmethane (1) with benzoic acid were found to obey the following relationship:

$$
\log K_R = -6.13 E_{1/2R} + 5.59
$$

where $K_R$ and $E_{1/2R}$ are the rate of reaction and oxidation potential, respectively of a given diazo-compound. Similar correlations were observed for other classes of diazo-compounds,
e.g. 2 and 3. The success of such correlations was ascribed to the fact that both processes occur at the diazo group, the position of highest electron density.

**Initiation:**

\[ (C_6H_5)_2CH_2 \overset{-e^-}{\longrightarrow} (C_6H_5)_2CH^+ N_2^+ \]

(1) \hspace{1cm} (2)

**Propagation:**

(1) + (2) \[ \overset{-N_2}{\longrightarrow} (C_6H_5)_2CH - \overset{c}{\longrightarrow} (C_6H_5)_2CH^+ \]

N_2^+

(3)

(1) + (3) \[ \overset{-N_2}{\longrightarrow} (C_6H_5)_2CH - \overset{c}{\longrightarrow} (C_6H_5)_2CH^+ (2) \]

(4)

**Termination:**

(2) + H_2O \[ \overset{-N_2}{\longrightarrow} (C_6H_5)_2CHOH \]

(5)

(3) + (5) \[ \overset{-N_2}{\longrightarrow} 4 \cdot (C_6H_5)_2CHOL \]

(2) + (5) \[ (C_6H_5)_2CH - \overset{c}{\longrightarrow} (C_6H_5)_2CH^+ \]

N_2^+

\[ \overset{-N_2}{\longrightarrow} \overset{c}{\longrightarrow} C_6H_5CO(C_6H_5)_3 \]

(Scheme 6)

The radical cations from oxidation of diazocompounds decompose in complex fashion. Diazodiphenylmethane (1) gives tetraphenylethylene (4) as a major product along with
benzophenone, benzpinacolone and benzhydrol.\textsuperscript{56} An important mechanistic clue was provided by coulometric experiments, which demonstrate that the anodic process involves a chain reaction: at an initial concentration of diazodiphenylmethane of 0.05 M, 25 molecules of diazodiphenylmethane react for every electron passed; when the initial concentration of diazodiphenylmethane is 0.004 M, only seven molecules of diazodiphenylmethane react per electron. The products were rationalized as in scheme.\textsuperscript{56,58}

A different anodic pathway appears to take place when the diazo group is alpha to a carbonyl group\textsuperscript{59 (6)} or one of its phosphorus analogues\textsuperscript{60 (7)}. With such compounds,

(6) \quad \begin{array}{c}
\text{R} \quad \text{C} \quad \text{CR} \\
\text{R} \quad \text{N} \quad \text{R}
\end{array}
\quad \quad \quad \quad (7) \quad \begin{array}{c}
\text{R} \quad \text{C} \quad \text{P} \quad \text{R'} \\
\text{R} \quad \text{N} \quad \text{R''}
\end{array}

R = \text{aryl or OR}, \quad R'' = \text{OR}

a complex set of products is formed, some of which apparently arise by coupling of two molecules of substrate at the para position. This was established by permanganate oxidation of the neutral fraction from the electrochemical reaction, after removal of acidic materials. For example,
anodic oxidation of benzoylphenyl diazomethane (8) in acetonitrile containing lithium perchlorate and Sodium bicarbonate afforded benzoic acid (27%), benzilic acid (trace), benzil (9%), benzoic, benzaldehyde and a neutral fraction which afforded diphenic acid (17%) and benzoic acid (35%). Upon treatment with permanganate the coupling was rationalized as illustrated in scheme 7. All of the observed products can be rationalized in terms of intermediates (9) and (12) (which could also be written as a quinoid structure), though other mechanisms could be imagined. There are, however, many precedents for para coupling of anodically generated radical cations. The difference between the anodic behaviour of aryldiazo compounds, e.g. (1) and species such as (8), appears to lie on the site at which the corresponding radical cations couple: Coupling of two (2) species occurs at the diazo carbons, while with (9) coupling is between two para sites. Apparently the electron-withdrawing carbonyl and phosphoryl groups in (6) and (7), respectively, inhibit coupling at the diazo carbon.

\[ \text{C}_6\text{H}_5\text{COC}_N_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{COC}_N_2\text{C}_6\text{H}_5^+ \]  
(8)

\[ 2 \times (9) \rightarrow \text{C}_6\text{H}_5\text{CO} \text{C} = \text{C}_6\text{H}_5^+ \]  
(9)

\[ (10) \xrightarrow{2\text{H}^+} \text{C}_6\text{H}_5\text{COC}_N_2 \]  
(10)

\[ (11) \]
(Scheme 7)

The anodic conversion of the diazo group to an n-hydroxycarbonyl radical\textsuperscript{60} [ cf. the conversion of (11) to (12) ] can not only explain the formation

\[
-C-N_2^- \rightarrow -C-N_2^+ \rightarrow -C- \overset{\text{H}_2\text{O}}{\text{\Large$\rightarrow$}} -C- \overset{-2\text{H}^+}{\text{\Large$\rightarrow$}} -C-
\]

of benzoin and benzil from oxidation of (7), but also explains the anodic conversion of dinzoketone (13) to the dicarboxylic acid (16) along with a trace of diketone (15).\textsuperscript{62}

(Scheme 8)
appears to be the only aliphatic diazoketone whose anodic electrochemistry has been examined. The generality of the conversion exemplified by (13) — (16), and its possible synthetic utility as a means of carbon—carbon bond cleavage alpha to the carbonyl group aliphatic ketones (via the corresponding diazoketone) remain to be established.

Elofson and Coworkers\(^63\) carried out the electrochemical oxidation of diazomethane in sulfolane medium. These workers suggested a mechanism involving successive generation of diazomethane radical cation, methylene radical cation and finally methyl cation. In presence of pyridine, the product was \(\beta\)-methyl pyridinium perchlorate possibly derived from nucleophilic attack upon the diazomethane radical cation by pyridine. They proposed that the nitrogen moieties of diazoalkanes are reasonably stable in sulfolane solution.

**AIM OF THE PRESENT INVESTIGATION**

Oxidative decomposition of diazoalkanes, particularly diazodiphenylmethane by electron transfer oxidants in homogeneous solution has been relatively little studied up till now and it is surprising that this area has remained neglected. The first two chapters of this thesis describe several important aspects of oxidations of diazodiphenylmethane and 9-diazofluorene with some electron transfer oxidants and high potential quinones.
The author has demonstrated the utility of organic electron acceptors — the radical cation salts (Tris-p-bromophenylammoniumyl hexachloroantimonate and thianthreneium pentachloroantimonate) as potential oxidants in bringing about the decomposition of the aforesaid diazoalkanes in a manner analogous to anodic oxidation pathways. Oxidation with stable radical cation salts holds great promise for consideration as analogues of anodic process in that a good comparison can be made between anodic oxidations and chemical electron transfer oxidations in homogeneous solution. The author has presented a detailed account of the kinetics and mechanism of decomposition of diazodiphenylnmethane induced by tris-(p-bromophenyl)ammoniumyl hexachloroantimonate and thianthreneium pentachloroantimonate. A rapid electron abstraction from the diazoalkane takes place in the beginning and cation radical intermediates are generated from the diazoalkane. The decomposition is effected in a chain process in which the chain carriers are radical cations.

Second chapter presents mechanistic studies on the reaction of (1) 2,3-dichloro-5,6-dicyano-p-benzoquinone (DQ), (2) chloranil and (3) Tetracyanoethylene with diazodiphenylnmethane and 9-diazofluorene.

Oxidation by quinones commonly assumed to proceed by hydride transfer mechanism involves, in some cases, oxidation by electron transfer. Many reactions which take
place between donor and acceptor type of reagents involve the charge transfer complexes as reactive intermediates. There are very few reports which mention the subsequent reaction of these charge-transfer complexes involving cation and anion radicals. The work on complete electron transfer with 2,3-dichloro-5, 6-dicyano-p-benzoquinone, leading to unambiguous formation of radical cations from suitable substrates, appears to have remained unexplored. It is with this outlook that the author has attempted to explore some of the electron transfer reactions between high potential quinones and diazoalkanes, the latter serving as electron donors. Some mechanistic aspects of such reactions have been presented in the second chapter. This chapter also includes some studies pertaining to the interaction of diazoalkanes with tetracyanoethylene.

Some acid induced reactions involving the decomposition of diazodiphenylmethane have been studied both from the standpoint of kinetics and mechanism. This work has been presented in the third chapter. Reactions have been carried out both in dipolar aprotic solvent acetonitrile and in ethanol between diazodiphenylmethane and some mono carboxylic acids particularly heterocyclic acids.

A brief investigation of the reaction of diazodiphenylmethane and 9-diazofluorene with picryl-sulphonic acid has also been carried out to determine the nature of the intermediates.
The last phase of the work is concerned with the decomposition of diazodiphenylmethane with dicarboxylic acids.

All along the studies described in this thesis, it has been the main aim of the author to identify and compare the nature and reactivity of various intermediates derived from diazoalkanes.
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