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# Mass Spectrometry of Diazo Compounds

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## I. INTRODUCTION

Since the publication of the first paper on the mass spectrometry of diazomethane in 1954, more than 50 publications dealing with diazoketones, diazoalkanes, diazonium salts, diazoesters, quinondiazides, diazoamides, diazoimines, diazo-sulfones, and organometallic diazo compounds have appeared. These compounds were studied by EI, CI, FAB, and other mass spectral techniques. Similarities between fragmentations in an ion source and thermolysis, photolysis, and acid-catalyzed reactions in solution have been reported. These observations have permitted results obtained from mass spectrometry to be used to predict the behavior of diazo compounds in solution. Diazo compounds have been used as models to aid the investigations of a range of reduction processes in an ion source using different ionization modes.

## II. DIAZOALKANES AND DIAZONIUM SALTS

The mass spectrometric study of diazoalkanes is hindered because of (i) instability of the compounds and (ii) the potential for explosion.

In 1954 Langer *et al.* (1) recorded the first mass spectrum of diazomethane (see Table I) at 75 °C and 75 eV in order to measure the values of appearance energy (AE) for  $C^+$ ,  $CH^+$ , and  $CH_2^+$  cations. They have also determined the heat of formation of diazomethane to be 2.0 eV.

The results of this work have been criticized by Paulett and Ettinger (2). In particular they expressed doubt about the possible formation of the abundant fragments at  $m/z$  26–28 and the absence of  $CHN_2^+$  and  $CH_2^+$  fragments. The authors proposed that the sample of diazomethane used (1) had already undergone considerable thermal decomposition at the temperature employed and that  $CH_2$  radicals had recombined on the walls of the reaction vessel. As a result, Langer *et al.* (1) may have been observing a composite spectrum of  $N_2$  (from thermal decomposition), ethylene (from radical recombination), and diazomethane. Furthermore, errors in the calculation of the heat of formation were noted. For example, a molecular model of a cyclic structure of diazomethane (diazirine) has

**Table I.** Mass spectrum of diazomethane (1).

Ion	Abundance	Ion	Abundance
42	1.0	25	6.2
29	2.4	24	2.0
28	100	14	2.0
27	50	13	0.7
26	44	12	0.2

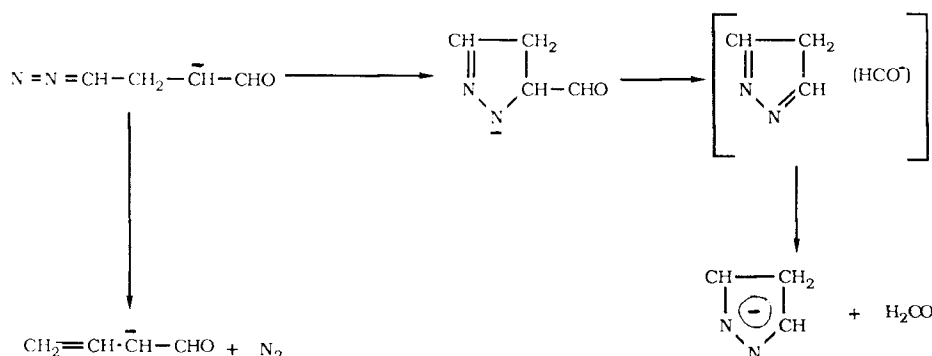
been used in the calculations, although the linear structure of diazomethane had already been well accepted.

Paulett and Ettinger (2) obtained the spectra of diazomethane and diazirine (Table II) after taking particular care to prevent thermal decomposition. The  $M^{+\cdot}$  of diazomethane is intense but the base peak is due to  $CH_2^{+\cdot}$ . The authors also measured several important parameters. The ionization energy (IE) of diazomethane was determined to be  $9.03 \pm 0.05$  eV [cf. previous results by Herzberg, 9.0 eV (3); and Lossing, 9.13 eV (3); and Berkowitz and Wexler (4),  $9.2 \pm 0.3$  eV] and that of diazirine to be  $10.18 \pm 0.05$  eV. The appearance energy (AE) of  $CH_2^{+\cdot}$  ion for diazomethane is  $12.3 \pm 0.1$  eV and that of diazirine is  $11.0 \pm 0.1$  eV. The energy of the C—N bond in a neutral molecule of diazomethane is 1.9 eV and in the molecular ion is 3.27 eV. This increase in bond energy was attributed to the stabilization of the molecular ion because of removal of an antibonding electron from the neutral. The doubly charged ions ( $m/z$  20–21) observed in the mass spectrum of diazomethane support the conclusion about the enhanced stability of the ion over the neutral molecule. Paulett and Ettinger (5) later revised these earlier values (2) for the heats of formation of diazomethane and diazirine to 13.6 and 11.2 eV, respectively.

The gas-phase negative ion chemistry of diazomethane has been investigated by DePuy *et al.* (6) by using the flowing afterglow (FA) and selected ion flow tube techniques. The gas-phase acidity of diazomethane was determined to be  $\Delta G_{\text{acid}}^0(\text{CH}_2\text{N}_2) = 365 \pm 3$  kcal/mol and the electron affinity of the diazomethyl

**Table II.** Mass spectra of diazomethane and diazirine (4).

$m/z$	Diazomethane	Diazirine
43	2.2	0.8
42	96.5	48.1
41	8.4	10.7
40	5.8	2.1
29	3.4	1.9
28	50	8.5
27	10.7	6.6
26	4.2	2.3
21	2.8	
20.5	0.6	
20	0.1	
15	2.9	1.9
14	100	100
13	32	23
12	13	11

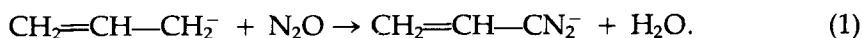


1a  $\text{CH}_2\text{N}_2$ ; 1b  $\text{CH}_2=\text{CH}-\text{CHN}_2$ ; 1c  $\text{CH}_3-\text{CH}=\text{CH}-\text{CHN}_2$ ; 1d  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CHN}_2$ ; 1e  $\text{PhCHN}_2$ ; 1f  $\text{CH}_2=\text{CH}-\text{C}(=\text{CH}_2)-\text{CHN}_2$

Scheme I

radical was estimated to be  $2.0 \pm 0.3$  eV. The reactions of the diazomethyl anion with  $\text{CS}_2$ ,  $\text{COS}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , and with  $\alpha,\beta$ -unsaturated aldehydes and ketones were studied. Exothermic addition reactions lead to energetic product ions, which fragment by loss of nitrogen. The resulting carbene anions undergo further reactions, either internally or by reactions with the neutral reagents. Diazomethane also can be reduced by hydride transfer to produce an  $[\text{M} + \text{H}]^-$  ion, which is likely to be the  $\text{CH}_2\text{NNH}^-$  anion. Michael addition of the diazomethyl anion to the unsaturated aldehydes and ketones results in further cyclization and loss of a nitrogen molecule or of an aldehyde to form a pyrazole anion (Scheme I).

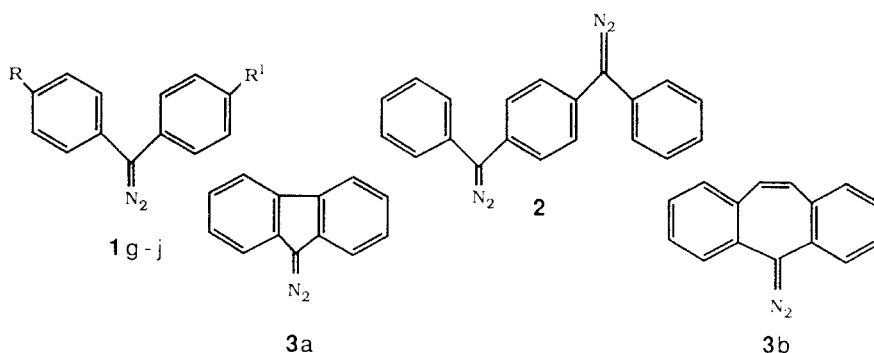
The addition reactions of the  $[\text{M} - \text{H}]^-$  ions of diazoalkanes 1b–f were studied by DePuy in a FA apparatus earlier (7). The corresponding diazo anions were generated *in situ* from simple basic anions,



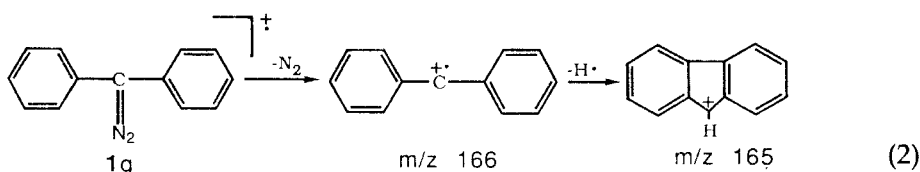
The reaction with  $\text{CO}_2$  simply forms an adduct, but the more highly exothermic additions to  $\text{COS}$  and  $\text{CS}_2$  lead both to addition and to addition followed by fragmentation [loss of  $\text{N}_2$ , formation of  $\text{SCN}^-$  (for  $\text{CS}_2$ )].

The mass spectra of diphenyldiazomethane and its derivatives has been reported (8,9). The abundance of the molecular ion of 1g is only 0.81% of the base peak  $\{[\text{M} - \text{N}_2 - \text{H}]^+ (m/z 165)\}$ .<sup>\*</sup> The dominant fragmentation process is the loss of a nitrogen molecule, a reaction analogous to those observed in photolysis and thermolysis experiments. It is proposed that the radical cation ( $m/z 166$ ) loses a hydrogen atom with cyclization to form the fluorenyl cation ( $m/z 165$ ) [Eq. (2)]. The further fragmentation of the latter ion is identical to that of the  $[\text{M} - \text{H}]^+$  ion of fluorene.

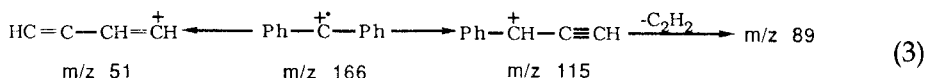
<sup>\*</sup>The weak intensity of  $\text{M}^+$  might be a consequence of thermal decomposition (cf. Refs. 1–4).



**Figure 1.** (g) R = R<sup>1</sup> = H; (h) R = OCH<sub>3</sub>, R<sup>1</sup> = H; (i) R = R<sup>1</sup> = OCH<sub>3</sub>; (j) R = NO<sub>2</sub>, R<sup>1</sup> = H.



The ratios of intensities of ions at  $m/z$  166 and 165 ( $J_{165}/J_{166} = A$ ) depend on the applied electron voltage. When the ion at  $m/z$  166 has insufficient energy it does not transform to the fluorene structure. Below 12 eV,  $A = 0.2$ . This is analogous to the results of thermolysis and photolysis experiments, i.e., processes that provide the neutrals with a small excess of energy. An increase in electron energy to 50 eV increases  $A$  to 1.7. This value remains constant with increasing energy. The formation of ions at  $m/z$  164, 163, and 139 is rationalized by losses of H<sup>•</sup>, H<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>, respectively, from the fluorenyl cation. Aromatic ring cleavage produces the fragments at  $m/z$  115 and 51 [Eq. (3)]. The latter process is substantiated by observation of the corresponding metastable peaks. The authors connect the higher abundance of an ion at  $m/z$  51 with the further decomposition of the alternative fragment leading to an ion at  $m/z$  89.



Diphenyldiazomethane itself and several of its derivatives have been studied (9). All the samples (1–3) (see Fig. 1) produce molecular ions (~10% of the base peak).

The authors did not pay much attention to secondary processes, since they concentrated on the formation of  $[M - N_2]^{++}$  ions. Electron donating groups (1h,i) increase the abundance of  $[M - N_2]^{++}$  peaks to 100%. These ions lose a hydrogen atom or radical R to form the corresponding fluorenyl cation. The assignment of the fluorenyl structure was made according to the high intensities of the corresponding ions and the identity of spectra of 1g with those of fluorene and diphenylketene in the mass region 60–165. This assignment would be more reliable

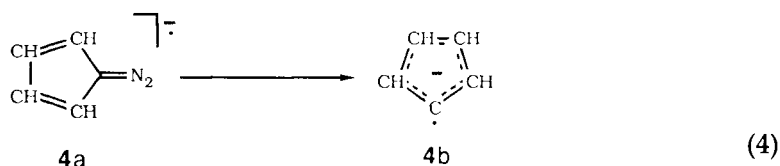
if CA MIKE spectra of the corresponding ions for diazocompounds **1g-j** and fluorene could be substantiated.

While the presence of electron-donating groups leads to the stabilization of  $[M-N_2]^{++}$  ions, the presence of an electron-accepting  $NO_2$  group (**1j**) leads to elimination of  $NO_2$  from the  $[M-N_2]^{++}$  ions.

Analogous processes involving consecutive losses of a nitrogen molecule and a hydrogen atom are noted for the cyclic structures **3a** and **3b**.

The base peak in the very simple spectrum of the bis-diazoketone **2** is due to the  $[M-56]^+$  ion. The authors describe it as corresponding to  $[M-2N_2]^{++}$ , emphasizing that it should contain the carbene and the radical-cation carbene units.

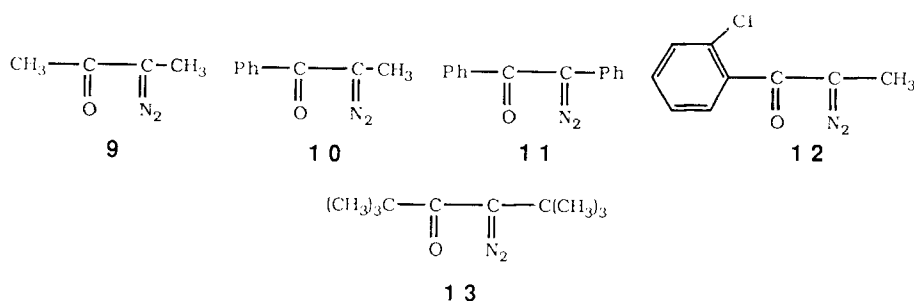
Finally a certain similarity in the behavior of the compounds studied under EI, photolysis, and thermolysis conditions was mentioned (9). At the same time the authors note that they were unable to establish a detailed mechanism for the loss of a nitrogen molecule from the  $M^{++}$ .



The cyclopentadienylidene anion radical **4b** was generated [Eq. (4)] by dissociative attachment of diazocyclopentadiene **4a** in a FA apparatus (10). The proton affinity of the carbene species was determined to be  $377 \pm 2$  kcal/mol and its heat of formation  $\Delta H_f \geq 67.7 \pm 3$  kcal/mol, data that support the results of protonation studies. The  $S_N2$  reactions of **4b** with methyl halides and its nucleophilic Michael addition reactions with activated olefins were studied. The reactivity of **4b** as a base towards proton donors, especially ROH, permitted the authors to propose the structure of a  $\pi$ -delocalized anion ( $\sigma^1\pi^2$ ) electronic configuration for this anion radical.

Diazonium salts are thermally very labile. That is why it is very difficult to record the mass spectra of these compounds using conventional mass spectrometric methods. Several commercially available compounds have been investigated (11) using the water thermospray technique. All spectra exhibit the diazonium cation as the base peak. Other major fragment ions also present are  $[\text{Cat}-N_2]^+$ ,  $[\text{Cat}-N_2+2H]^+$ , and  $[\text{Cat}-N_2+H_2O]^+$ . The fragmentation of diazonium cations is found to be dependent on the temperature of the capillary and jet chamber. Schmelzeisen-Redeker *et al.* (11) emphasize the difficulty of the mass spectrometric analysis of these compounds using other methods of ionization, including fast atom bombardment (FAB). However, Ambroz *et al.* (12) have managed to obtain FAB spectra of a group of diazonium salts using the 3-nitrobenzyl alcohol (NBA) matrix. In the majority of the cases  $\text{ArN}_2^+$  ions are responsible for the base peak. Intense peaks due to  $\text{Ar}^+$  and  $[M+\text{ArN}_2]^+$  ions are also noted. Peaks due to solvated ions are more prominent in the mass spectra of monosubstituted arene diazonium salts than in those of trisubstituted compounds, while



**Figure 4**

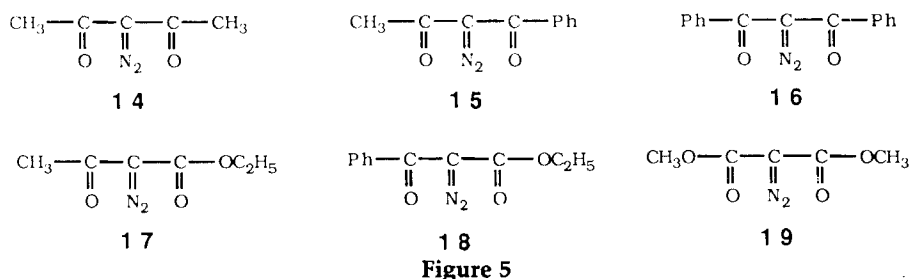
siderably higher than the total abundance of the fragments  $[\text{M}-\text{N}_2]^{++}$  and  $[\text{M}-\text{N}_2-\text{CO}]^{++}$ . The authors did not pay attention to this fact, although these results demonstrate the notable strength of the C—N bond.

Later Foffani published a series of papers (15–17) where on the basis of IR, UV, and MS data together with dipole moment measurements, the structures of a variety of diazoketones have been proposed for both gas and condensed phases. The paper (17) deals with the mass spectrometry of compounds 5 and 8–13 (see Fig. 4).

Foffani *et al.* used the measured values of the IE to draw conclusions concerning the molecular structures of the compounds. The highest occupied molecular orbital in a diazoketone molecule is either that of the C—N bonding or the N—N antibonding orbital (17). The IE of the diazomethane molecule containing only the  $\pi$  system of the diazo group is 9.02 eV, that is, in the middle of the range of that parameter for diazoketones (Table III). The maximum values of the IE are found for compounds 5 and 9 with small differences in the energies of the  $\pi$  system. Substitution of a hydrogen atom for the *tert*-butyl group (a substituent possessing a strong positive inductive effect) decreases that value to 8.6 eV. A significant decrease in IE is noted in cases where an aromatic system is connected with the carbonyl group and an alkyl or aryl substituent (not a hydrogen) is connected to the diazo portion. Foffani *et al.* (17) propose a *pseudo-trans* conformation, with the benzene ring and the diazo group slightly out of the plane of the carbonyl group. This distortion does not prevent an interaction of  $\pi$  electrons of these systems, but it does eliminate steric hindrance. The symmetry and energy conditions are also favorable for such an interaction. For example, the IE for the

**Table III.** Values of the ionization energies for diazoketones (14).

Compound	IE
5	9.37
8	9.12
9	9.15
10	8.28
11	8.10
12	8.55
13	8.6

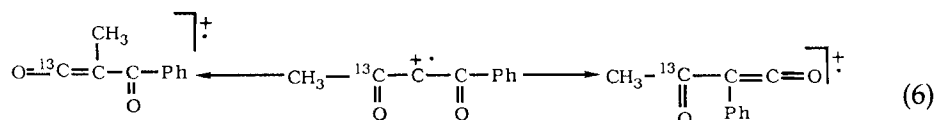


benzene ring ranges around 9 eV, that is, near that for the diazo group (17). An *ortho* substituent in the aromatic ring (e.g., compound 12) takes it further out of that plane, thus preventing interaction with the diazocarbonyl group. As a result, the IE increases.

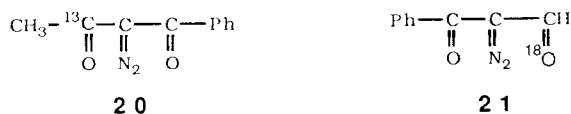
The possibility of the application of the AE values of the  $[\text{M}-\text{N}_2]^{++}$  ions in order to estimate the ability of the diazo group to dissociate was also discussed (17). However, since the AE values are virtually equal for all the compounds studied (sometimes even lower than the IE of the corresponding diazoketone), it can be concluded that thermal decomposition contributes considerably to the formation of these ions (17).

The Wolff rearrangement initiated by EI has been a subject of investigations carried out by Zeller *et al.* (18–22). Besides the diazoketone 11 and the 1,3-diazocarbonyl compounds 14–16, the diazoesters 17–19 have also been studied (18) (see Fig. 5).

First it was suggested (18) that the loss of CO by  $[\text{M}-\text{N}_2]^{++}$  of 11, 14–17 indicates the operation of the Wolff rearrangement. The labeled compound 20 (see Fig. 6) was synthesized to study the migratory attitude of different groups. The abundances of the  $[\text{M}-\text{N}_2-\text{CO}]^{++}$  and  $[\text{M}-\text{N}_2-^{13}\text{CO}]^{++}$  ions in its mass spectrum are equal to each other. This fact led the authors to propose that the methyl and phenyl groups had the same migratory ability,

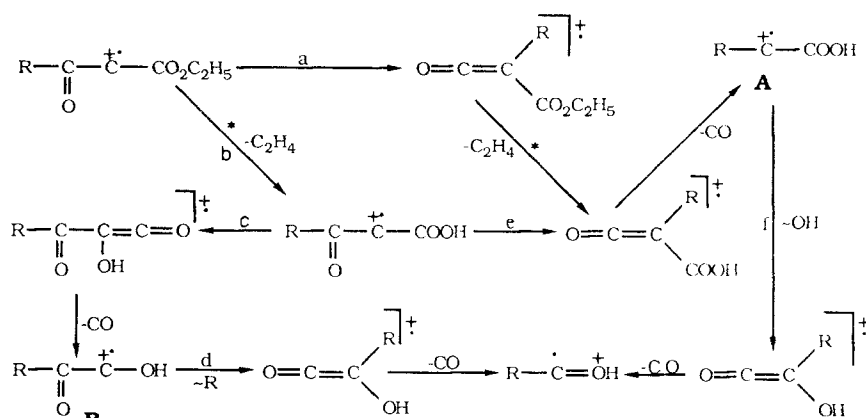


The substitution of one of the carbonyl functions for an ester group (18) leads to more complicated fragmentation patterns. The authors note that the Wolff rearrangement takes place for the compounds 17 and 18 but following the McLafferty rearrangement (the loss of  $\text{C}_2\text{H}_4$ ). Three different pathways for the transformation of  $[\text{M}-\text{N}_2]^{++}$  ions were proposed (Scheme II).



**Figure 6**





Scheme II

The authors did not discuss any further decompositions (e.g., fragmentations of the  $[M-N_2-CO]^{++}$  ions); however, the published mass spectra (18) suggest that a rearrangement process analogous to the Wolff rearrangement may take place (ions A or B in Scheme II). As a result, one more molecule of CO is lost (pathways d or f). It would be possible to answer the question as to which of the two possible structures A or B is more favorable if a compound labeled by  $^{13}C$  in the acetyl group was available. Such an experiment was not carried out.

The absence of the  $[M-N_2-CO]^{++}$  peak in the mass spectrum of dimethyl diazomalonate 19 led the authors to propose that an alkoxy group does not migrate under EI conditions (18). This fact distinguishes EI from thermally or photo-induced rearrangements (21,23,24).

A paper (19) dealing mainly with thiadiazoles (sulfur analogs of diazoketones) has been published. The primary act of decomposition of the  $M^{++}$  is loss of a nitrogen molecule to form an  $[M-N_2]^{++}$  ion. These compounds are mentioned in reviews on heterocycles (25). Thus the fragmentation patterns of thiadiazoles are not discussed here. Nevertheless, it is worthwhile mentioning that Zeller (19) proposes a mechanism of stabilization of the  $[M-N_2]^{++}$  ions as a result of the Wolff rearrangement involving thioketene formation. Several workers (26–29) propose other possible structures of  $[M-N_2]^{++}$  ions, particularly for thiadiazoles with heteroatomic groups in side chains.

The migratory attitude of different groups in the Wolff rearrangement initiated by EI, heating, or photons has been reported (20) and appears to be dependent on the initiation method.

For thermolysis  $H > p-CH_3O-C_6H_4 > Ph > CH_3 > p-O_2N-C_6H_4$ , and for photolysis  $H, CH_3 > p-CH_3O-C_6H_4 > Ph > p-O_2N-C_6H_4$ .

The analysis of the mass spectra demonstrates the equal probability for H,  $CH_3$ , or Ph (compounds 20 and 21) (see Fig. 6) group to migrate (20). The absence of selectivity may be rationalized in terms of the wide range of internal energies of  $[M-N_2]^{++}$  ions. The small differences in energies characteristic for softer methods like thermolysis or photolysis make these methods quite selective. In contrast, excitation of molecules by EI leads to fast but unselective processes.

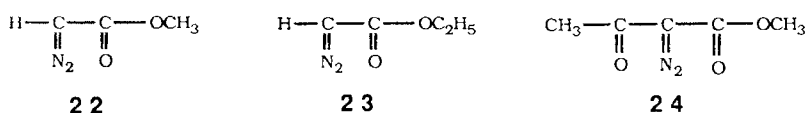


Figure 7

It was also stressed (20) that under conditions of thermolysis and photolysis not all the reacting molecules undergo the Wolff rearrangement. Oxirane structures and adducts with solvents are formed as well.

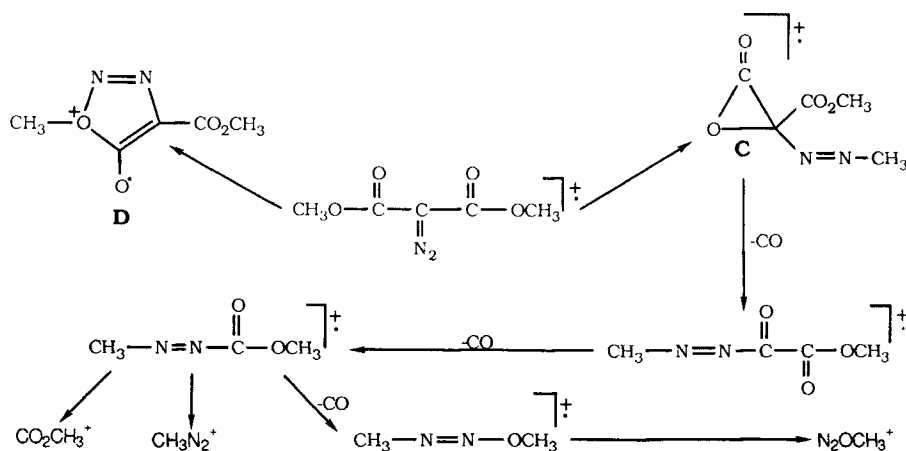
The diazoesters **19**, **22–24** (see Fig. 7), and the diazoketone **14** have been studied (30,31). By applying high-resolution mass spectrometry, low-energy electrons, and defocusing techniques, the authors managed to note and rationalize several peaks of low intensity that had not been reported earlier (18).

The authors concentrated on the absence of  $[\text{M} - \text{N}_2]^+$  peaks in the mass spectra of the diazoesters. This observation contradicts the results of Zeller (18), who may have observed the  $\text{M}^{++}$  of ketenes, formed by thermolysis followed by ionization. One other notable discrepancy is concerned with the spectrum of the diazoketone **14**. Although the  $[\text{M} - \text{N}_2]^{++}$  peak was observed in both cases, Wulfmann *et al.* (30), using high-resolution measurements, showed that the further loss of 28 mass units was not due to CO loss, but to loss of ethylene. Such results produce certain doubts on all earlier conclusions (18–21) concerning the Wolff rearrangement and demand verification. The presence of the peaks due to  $\text{CN}_2^+$ ,  $\text{CH}_3\text{N}_2^+$ ,  $\text{CHN}_2^+$ , ions, etc., in the spectra of diazoesters studied proves the strength of the C—N bond.

Consecutive losses of three CO molecules are noted for compound **19**. Since there are only two CO groups in the intact molecule, the loss of a third molecule has been rationalized on the basis of a rearrangement process involving methyl and methoxyl group migrations. This proposal is supported by elimination of a  $\text{CH}_3\text{N}_2$  radical from the  $[\text{M} - 2\text{CO}]^{++}$  ion and formation of the  $\text{CH}_3\text{ON}_2^+$  fragment from the  $[\text{M} - 3\text{CO}]^{++}$  ion. The losses of  $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{O}$ , and  $\text{CO}_2$  from the  $\text{M}^{++}$  also were not mentioned by Zeller (18).

The authors proposed that the decompositions of the  $\text{M}^{++}$  of **19** occur through an  $\alpha$ -lactone intermediate **C** (30), as noted in Scheme III. The oxodiazole structure as proposed as an alternative for the linear form as early as 1900 by Wolff (32) might rationalize the formation of  $\text{N}_2\text{O}^+$  and  $\text{N}_2\text{OCH}_3^+$  ions, although the relatively low intensities of those ions are consistent with the lack of importance of the pathway.

Significant attention is paid to the elucidation of the nature of intermediates for the reactions of diazoketones in solution (30). With reference to their own results and to other data (33,34), the authors reject the carbene character of these intermediates. In the authors' opinion the retention of  $\text{N}_2$  when bombarded with electrons of 300, 960, and 1656 kcal/mol should cast considerable doubt as to the ability of photons in the energy range about 80–150 kcal/mol to generate nitrogen-free species such as carbenes. This conclusion is not convincing, since small excesses in internal energy due to photon or thermal excitement in solution may cause selective processes resulting in definite bond cleavages, for example, the



Scheme III

loss of the nitrogen molecule. On the other hand, highly energetic molecular ions in different electronically excited states may decompose with the rupture of any bond.

The formation of the  $M^{\cdot-}$  of **23** under FA conditions was reported by McDonald and Kasem Chowdhury (35). The ion-molecule reactions of that anion radical with 30 neutral substrates were examined. Using bracketing methods, the proton affinity [PA ( $\text{EtO}_2\text{CCHN}_2^{\cdot-}$ ) =  $355 \pm 4$  kcal/mol] and the electron affinity [EA ( $\text{EtO}_2\text{CCHN}_2$ ) = 19.7 kcal/mol] were derived. Both associative and dissociative electron transfers are observed in the reactions of **23** with certain perhalomethanes together with halogen atom abstraction from  $\text{BrCCl}_3$ . While no reaction is observed with  $\text{CH}_3\text{CHO}$  or  $(\text{CH}_3)_2\text{CO}$ , the molecular anion of **23** reacts with certain other ketones and esters ( $\text{CF}_3\text{CO}_2\text{R}$ ) mainly to yield enolate anions of the  $\beta$ -keto esters,  $\text{EtO}_2\text{CCH}=\text{C}(\text{R})-\text{O}^{\cdot-}$ . The authors propose that those enolates are formed by nucleophilic addition of C of the  $M^{\cdot-}$  of **23** to the carbonyl group of the neutral substrate, followed by loss of  $\text{N}_2$  and radical  $\beta$ -fragmentation.

In contrast to the results from the flowing afterglow studies, ethyl diazoacetate **23** produces the abundant carboethoxycarbene anion radical ( $\text{EtOCOCH}^{\cdot-}$ ) under low-pressure FTMS conditions (36). Failure to lose  $\text{N}_2$  from the molecular anion of **23** in FA (35) experiments permitted the authors (36) to conclude that collisional stabilization in the FA system was efficient. However, under the low-pressure conditions ( $10^{-7}$  Torr) prevailing in the trap cell of a Fourier transform mass spectrometer collisional stabilization of an excited  $M^{\cdot-}$  is less likely than unimolecular  $\text{N}_2$  loss. According to the reactions observed, the  $\text{EtOCOCH}^{\cdot-}$  ion should possess two resonance structures (see Fig. 8).

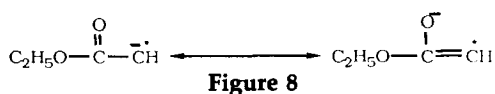
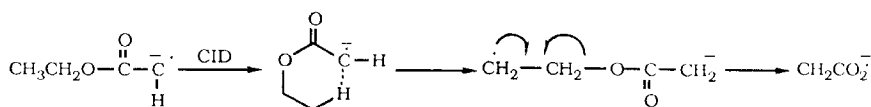
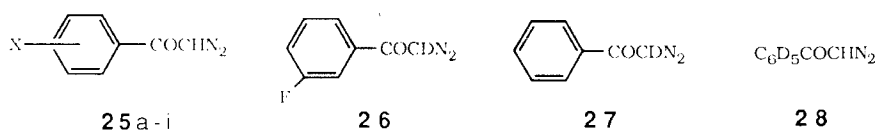


Figure 8



Scheme IV

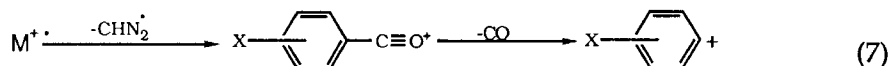
Collision-induced dissociation studies demonstrate that  $\text{EtOCOCH}^{\bullet-}$  eliminates  $\text{C}_2\text{H}_4$  via a six-membered transition state, yielding the  $\text{C}_2\text{H}_2\text{O}_2^{\bullet-}$  anion (Scheme IV). The reactions of  $\text{EtOCOCH}^{\bullet-}$  with carbonyl compounds, olefins, and some other species were also studied. The proton affinity of  $\text{EtOCOCH}^{\bullet-}$  was found to be  $377 \pm 2$  kcal/mol, and  $\Delta H_f(\text{EtOCOCH}^{\bullet-})$  was estimated to be  $-48.5 \pm 3$  kcal/mol.



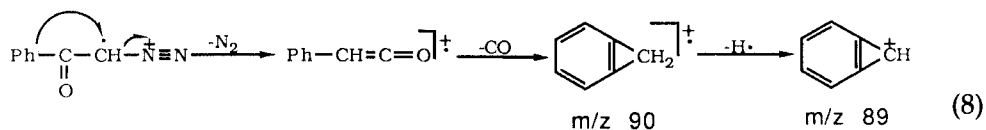
**Figure 9.** (a)  $\text{R} = \text{H}$ ; (b)  $\text{R} = p\text{-CH}_3\text{O}$ ; (c)  $\text{R} = p\text{-C}_2\text{H}_5\text{O}$ ; (d)  $\text{R} = p\text{-CH}_3$ ; (e)  $\text{R} = m\text{-CH}_3$ ; (f)  $\text{R} = p\text{-F}$ ; (g)  $\text{R} = m\text{-F}$ ; (h)  $\text{R} = m\text{-Cl}$ ; (i)  $\text{R} = m\text{-Br}$ .

EI and metastable ion spectra together with high-resolution mass spectrometry and labeling techniques have been used for the analysis of substituted diazoacetophenones **25–28** (37) (see Fig. 9).

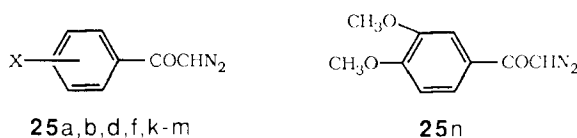
All the compounds are characterized by very abundant molecular ions. In each case the  $\text{M}^{+\bullet}$  undergoes  $\alpha$ -fission to produce a benzoyl cation,



Benzoyl ions from all compounds are of moderate to strong intensity, and there is no simple relationship between the intensity of the oxonium ion and the electronic nature of the substituent. All the compounds also undergo a rearrangement sequence that involves stepwise loss of  $\text{N}_2$ ,  $\text{CO}$ , and a hydrogen atom. This sequence is supported by the corresponding metastable ions and by an increase in the relative abundances of  $[\text{M}-\text{N}_2]^{+\bullet}$  and  $[\text{M}-\text{N}_2-\text{CO}]^{+\bullet}$  ions with the decreasing electron energy. However, the relative intensity of a fragment at  $m/z$  89 in **25a** decreases with decreasing electron energy; this observation is rationalized (37) in terms of the absence of any rearrangements accompanying the loss of a hydrogen atom from  $m/z$  90,



The authors emphasize that it is difficult to propose a satisfactory seven-membered monocyclic structure for an ion at  $m/z$  90, and since benzocyclopropene is



**Figure 10.** (k) R = *p*-Cl; (l) R = *p*-Br; (m) R = *p*-NO<sub>2</sub>.

a known stable compound (38) and cyclopropenyl cations are stable as well, it is probable that both ions have the bicyclic structures of the type mentioned above.

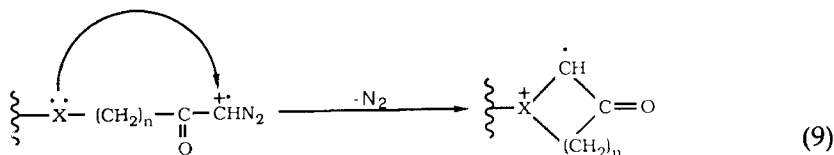
An analysis of the labeled compounds 26–28 demonstrates that hydrogen atom elimination occurs through different complex mechanisms. For example, in the case of 27 the  $[\text{M}-\text{N}_2-\text{CO}]^{++}$  ion loses H $\cdot$  and D $\cdot$  in the ratio 3:2 despite the fact that the H:D ratio in this ion is 4:1 and that the primary kinetic isotope effect should favor hydrogen loss. In the case of 28, the  $[\text{M}-\text{N}_2-\text{CO}]^{++}$  ion loses H $\cdot$  and D $\cdot$  in the ratio 1:2. These results demonstrate that a hydrogen atom is lost mainly from the original diazocarbonyl portion and imply that the benzocyclopropene structure proposed in Ref. (37) is (at least) not the only possible structure for these ions.

A high-resolution mass spectrometry study reveals that the spectrum of 25c is further complicated by the loss of ethylene from the  $[\text{M}-\text{N}_2]^{++}$  ions. This process is followed by the usual CO loss.

Other diazoacetophenones 25 (see Fig. 10) have also been analyzed (39).

The proposed fragmentation scheme is in good agreement with that proposed earlier (37). The authors connect the formation of an ion  $\text{ArC}\equiv\text{CH}^{+}$ , not previously noted, with isomerization of some of the  $\text{M}^{++}$  into an oxadiazole structure (cf. Refs. 30 and 31) with further loss of N<sub>2</sub>O.

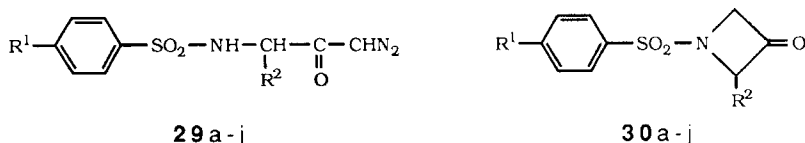
Several papers (40–54) discuss the mass spectrometry of more complex diazoketones. The presence of a heteroatom in alkyl diazoketones capable of eliminating a nitrogen molecule through anchimeric assistance of the heteroatom leads to instability of the  $\text{M}^{++}$ . The resulting  $[\text{M}-\text{N}_2]^{++}$  ions are stabilized by intramolecular cyclization [Eq. (9)]. This leads to suppression of the Wolff rearrangement.



Such processes initiated by EI or CI (reagent gas isobutane or methane) appear to be similar to those of the corresponding acid-catalyzed reactions in solution (40–42).

In the majority of these studies (43–54), the mass spectra of diazoketones have been compared with the spectra of the corresponding products of their cyclization in solution.

In the presence of concentrated sulfuric acid 1-diazo-3-sulfonylamino-*propan*-



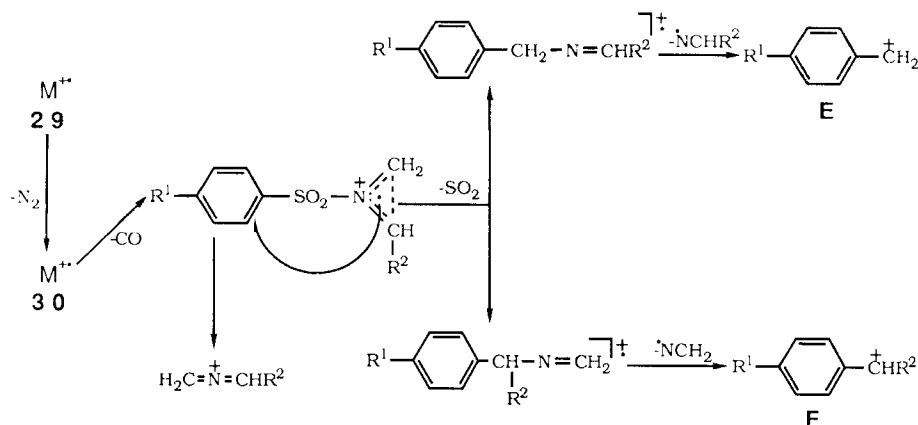
**Figure 11.** (a)  $\text{R}^1 = \text{R}^2 = \text{H}$ ; (b)  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{H}$ ; (c)  $\text{R}^1 = \text{OCH}_3$ ,  $\text{R}^2 = \text{H}$ ; (d)  $\text{R}^1 = \text{Cl}$ ,  $\text{R}^2 = \text{H}$ ; (e)  $\text{R}^1 = \text{NO}_2$ ,  $\text{R}^2 = \text{H}$ ; (f)  $\text{R}^1 = \text{NHCOCH}_3$ ,  $\text{R}^3 = \text{H}$ ; (g)  $\text{R}^1 = \text{R}^2 = \text{CH}_3$ ; (h)  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{C}_2\text{H}_5$ ; (i)  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{CH}_2\text{Ph}$ ; (j)  $\text{R}^1 = \text{NHCOCH}_3$ ,  $\text{R}^2 = \text{CH}_3$ .

2-ones **29a-j** are transformed into the corresponding N-sulfonylazetidinones-3 (**30a-j**) (see Fig. 11) (55).

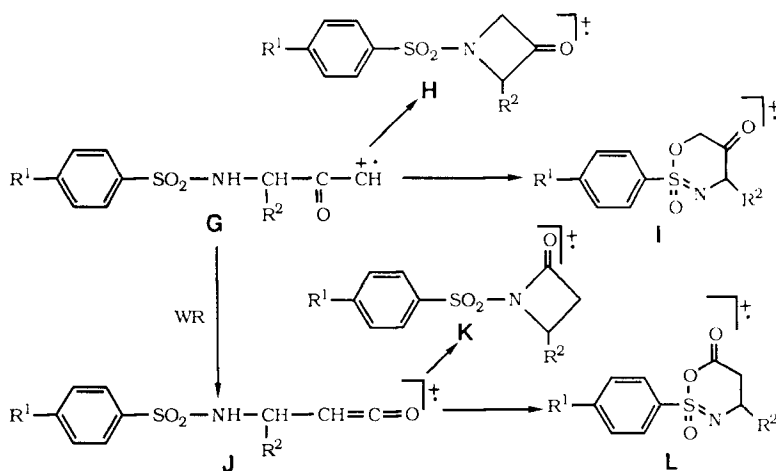
The mass spectra of compounds **29** and **30** demonstrate a similar array of fragments (Scheme V). However, there are notable differences in the abundances of these common fragments. The base peak in all the spectra is due to the  $\text{CH}_2=\text{N}=\text{CHR}^2$  ion (24–80 % of total ion current for **30** and 13.8–61.5 % for **29**). The only peak absent in the spectra of azetidinones is the  $[\text{M}-\text{CHCON}_2]^+$  ion, which either results from the  $\text{M}^{++}$  or the unisomerized structure of the  $[\text{M}-\text{N}_2]^+$  ion of **29** (40–43). Its abundance does not exceed 1–2 %. Another process stressed by the authors is a rearrangement with elimination of  $\text{SO}_2$ . The structures of the ions E and F are supported by accurate mass measurements.

Any substituent in the benzene ring increases the abundances of the E and F ions. This observation led the authors to suggest a radical attack on the benzene ring. There are several possible structures for the  $[\text{M}-\text{N}_2]^+$  ions.

To rationalize the fragmentation pattern (e.g.,  $\text{CH}_2=\text{N}=\text{CHR}^2$  ion formation) it is necessary to postulate some sort of isomerization of the primary ions G (Scheme VI). The 2-azetidinones (structure K) are known to decompose mainly by the loss of a ketene molecule (56). Elimination of a ketene molecule or  $\text{CO}_2$



**Scheme V**



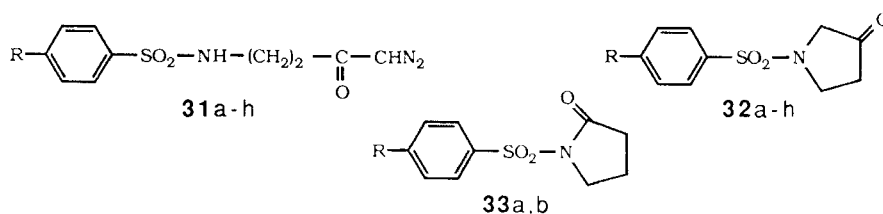
Scheme VI

molecule should be a feature of structure **L** (57). Such processes are not observed in the case of the compounds **29**. Since the most common process of fragmentation of ketenes demands the rupture of the bond  $\beta$  to the double C—C bond (58), ion **J** should yield  $[J - R^2]^+$  or  $[R^2 - CH=CH - CO]^+$  fragments. Such fragments are of small abundance in the spectra of **29**. As a result, structures **J**, **K**, and **L** are eliminated by the authors (43). Participation of the sulfo group with formation of heterocycle **I** is also rejected on the basis of the increased abundances of the fragments  $ArSO_2^+$ ,  $ArSO^+$ ,  $ArS^+$ ,  $ArO^+$  in the spectra of the diazoketones **29**. On the other hand, the fragmentation pattern may be easily rationalized by using structure **H** for the  $[M - N_2]^+$  ions. Thus it was concluded that  $[M - N_2]^+$  ions exist in the **H** and to a lesser extent in the **G** form (43). In later publications (40–42) it was emphasized that the cyclization process takes place directly in the  $M^{++}$  ions while the nitrogen atom of the amino group actually pushes the nitrogen molecule out. Thus the Wolff rearrangement is suppressed in such systems.

The 1-diazo-4-arylsulfonylbutanones-2 (**31a–h**) and the products of their cyclization, *N*-substituted 3-pyrrolidinones (**32a–h**), have been studied (44). The diazoketones **31** are easily transformed into heterocycles **32** in solution by reaction with acetic acid (59), while photoexcitation induces the Wolff rearrangement with further cyclization into 2-pyrrolidinones (**33**) (see Fig. 12) (60).

Compounds **31** and **32** have very similar fragmentation patterns. The  $m/z$  values of all the fragments are the same and their relative abundances are similar. The analysis of possible structures of the  $[M - N_2]^+$  ions, (analogous to the analysis mentioned above for the diazoketones **29**) suggested that a considerable proportion of the ions possessed the pyrrolidinone structure **32**. That is, the same cyclization reaction takes place in solution and in the ion source of a mass spectrometer. The Wolff rearrangement is suppressed. Some fraction of the  $M^{++}$  of **31** must decompose without cyclization, since it loses a  $COCHN_2$  radical.

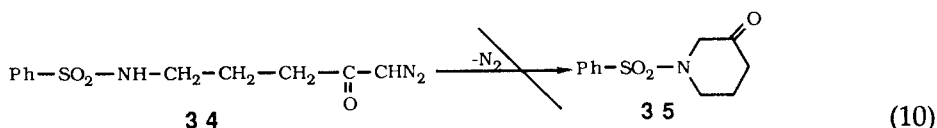
The compounds **31a,b** and **32a,b** were reinvestigated (45) using a more reliable method of proving the structures (CA MIKES). The results obtained are in total



**Figure 12.** (a)  $R = H$ ; (b)  $R = CH_3$ ; (c)  $R = OCH_3$ ; (d)  $R = Cl$ ; (e)  $R = Br$ ; (f)  $R = COCH_3$ ; (g)  $R = NO_2$ ; (h)  $R = NHCOCH_3$ .

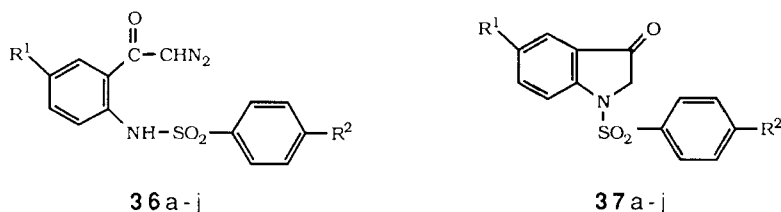
agreement with the previous conclusions (40–42,44) concerning the cyclization of the  $[M-N_2]^{++}$  ions of the diazoketones **31** into the  $M^{++}$  of pyrrolidinones **32**. The near-thermalization of energies of the  $[M-N_2]^{++}$  ions and of the  $M^{++}$  of the corresponding pyrrolidines due to the CA technique leads to even more similar spectra than in the case of stable ions (i.e., those that do not decompose before reaching the detector) (44).

Increasing the chain length of **31** by one more  $CH_2$  group should allow cyclization to the stable piperidone **35**. However, there are no ions characteristic of the piperidone structure in the mass spectrum of **34**. All attempts to cyclize this diazoketone in solution using various acids also failed [Eq. (10)]. These observations reiterate the similar behavior of the diazoketones in acid-catalyzed reactions in solution and under EI or CI conditions in the gas phase.



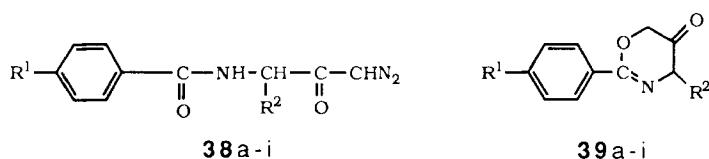
An absolute coincidence of EI and CI mass spectra was noted for the diazoacetophenone derivatives **36** and indoxyl derivatives **37** (46).

Thus the molecular ions of **36** transform quantitatively into indoxyls **37**  $M^{++}$  while decomposing by loss of  $N_2$  (see Fig. 13). Analysis of the fragmentation pattern led the authors (46) to reject all the other possible structures of the  $[M-N_2]^{++}$



**Figure 13.** (a)  $R^1 = R^2 = H$ ; (b)  $R^1 = H, R^2 = CH_3$ ; (c)  $R^1 = H, R^2 = OCH_3$ ; (d)  $R^1 = CH_3, R^2 = H$ ; (e)  $R^1 = OCH_3, R^2 = H$ ; (f)  $R^1 = R^2 = CH_3$ ; (g)  $R^1 = OCH_3, R^2 = CH_3$ ; (h)  $R^1 = OCH_3, R^2 = Cl$ ; (i)  $R^1 = Cl, R^2 = OCH_3$ ; (j)  $R^1 = Br, R^2 = OCH_3$ .





**Figure 14.** (a)  $R^1 = R^2 = H$ ; (b)  $R^1 = CH_3$ ,  $R^2 = H$ ; (c)  $R^1 = OCH_3$ ,  $R^2 = H$ ; (d)  $R^1 = Cl$ ,  $R^2 = H$ ; (e)  $R^1 = Br$ ,  $R^2 = H$ ; (f)  $R^1 = NO_2$ ,  $R^2 = H$ ; (g)  $R^1 = H$ ,  $R^2 = CH_3$ ; (h)  $R^1 = H$ ,  $R^2 = C_2H_5$ ; (i)  $R^1 = H$ ,  $R^2 = Bz$ .

ions, e.g., ketene or oxindole. Therefore the presence of an *ortho* substituent in the diazoacetophenone leads to a dramatic change in the decomposition mechanism of the molecular ion. The intramolecular cyclization process completely suppresses the Wolff rearrangement (13,37,39). The diazoketones **36** easily produce indoxyls **37** in solution. This rearrangement occurs when a solution of the diazo compound passes through a column packed with  $SiO_2$  or  $Al_2O_3$ . The eluent contains a mixture of **36** and **37** in the ratio ca. 1:1 (61).

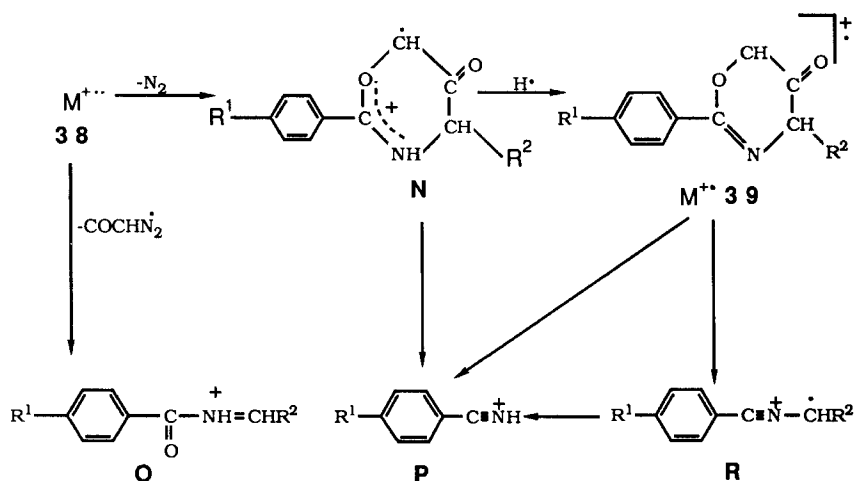
In the case of 1-diazo-3-arylaminopropan-2-ones (**38**) the oxygen atom of the carbonyl group is able to compete with the nitrogen atom of the amino group during nucleophilic attack on carbon  $C_1$  (47).

As a result, the 1,3-oxazin-5-ones (**39**) are the only cyclic products (yields ca. 40%) following interaction of diazocompounds **38** with sulfuric acid (62) (see Fig. 14). The mass spectra of both types of compounds have been reported (47). The  $m/z$  values of all the fragments are the same for each pair of compounds **38** and **39**. The only exception is associated (as usual) with the  $[M - CHCON_2]^+$  ions, which arise from the unisomerized  $M^{++}$  or  $[M - N_2]^{++}$  ions (40–46). However, in this case the relative abundances of the common fragments are absolutely different (see Table IV). For example, fragment **R** dominates the mass spectra of oxazinones, but it is 20–40 times less abundant for the corresponding diazoketones. The authors (40,47) proposed that the cyclization process proceeds through intermediate structure **N**, which may then transform into the molecular ion of **39** (Scheme VII).

Such a structure can explain the formation of all the secondary fragments. To

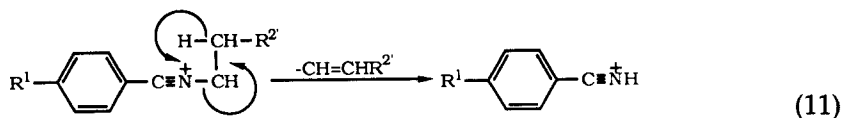
**Table IV.** Abundances of the fragments **R**, **O**, **P** in the mass spectra of **38** and **39**.

R1	R2	<b>R</b>		<b>O</b>		<b>P</b>	
		38	39	38	39	38	39
H	H	0.9	20.6	2.1		8.0	1.0
CH <sub>3</sub>	H	0.5	9.5	0.8		5.9	0.6
OCH <sub>3</sub>	H	0.7	18.4	0.6		6.3	1.1
Cl	H	0.9	14.1	0.7		5.4	0.4
Br	H	0.5	14.2	2.0		10.0	2.2
NO <sub>2</sub>	H	1.0	8.1	1.4		4.5	1.8
H	CH <sub>3</sub>	0.2	5.7	7.5		6.0	11.9
H	C <sub>2</sub> H <sub>5</sub>	0.1	0.9	4.1		3.2	13.0
H	Bz			2.4		2.2	10.6



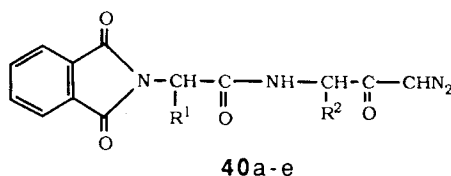
Scheme VII

support their proposal the authors discuss the formation of ions **P**, whose abundance in the case of the diazoketones is approximately an order of magnitude higher than for the corresponding heterocycles **39**. Formation of **P** from **N** needs only a simple rupture of the C—N and C—O bonds, while a hydrogen migration from positions 4 or 6 of the oxazinone ring is necessary for the pathway **(39) → P**. The latter process is unfavorable unless  $R^2 = \text{alkyl}$  (e.g., for compounds **39g-i**). In this case the mechanism changes and **P** is formed by a process analogous to the secondary fragmentation of amines [Eq. (11)] (42).



Thus, the authors (42,47) propose that the major part of the  $[M - N_2]^{++}$  ions of **38** possess structure **N**. A small proportion of the  $[M - N_2]^{++}$  ions rearrange to the  $M^{++}$  of 1,3-oxazin-5-one. In addition, a portion of the molecular ions of **29** decompose without any rearrangement. The similarity between the intramolecular cyclization in the liquid and gas phases is stressed, even though decomposition of the intermediate **N** in the gas phase proceeds at a faster rate than does transformation into the molecular ion of the oxazinones.

The fragmentations of phthaloyldipeptide derivatives of diazomethane **40** (Fig. 15) suggest the possibility of minor cyclization into 1,3-oxazin-5-ones by a mechanism similar to the one described for 1-diazo-3-arylamino-2-ones **38** (48). Attempts to synthesize the corresponding oxazines in solution were not successful. However, the NMR spectra of the reaction mixtures indicate formation of cyclic structures with signal shifts and multiplicities very close to those of 1,3-oxazin-5-ones **39**.



**Figure 15.** (a)  $R^1 = R^2 = H$ ; (b)  $R^1 = CH_3$ ,  $R^2 = H$ ; (c)  $R^1 = CH_2Ph$ ,  $R^2 = H$ ; (d)  $R^1 = R^2 = CH_3$ ; (e)  $R^1 = CH_3$ ,  $R^2 = CH_2Ph$ .

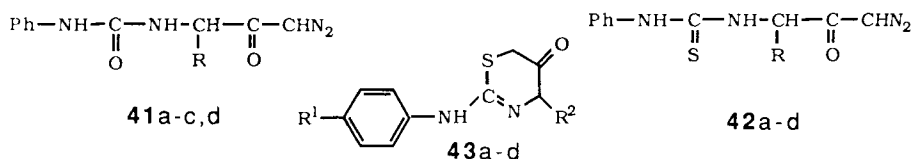
The ureidoalkyldiazoketones and thioureidoalkyldiazoketones **41** and **42** (49) have very complex mass spectra. A variety of possible structures for the  $[M - N_2]^{++}$  ions were considered. Thiazinones **43** were also studied (see Fig. 16).

Detailed fragmentation schemes are suggested as a result of this investigation. The sulfur atom is more convenient for the initiation of cyclization than oxygen, and cyclic structures of the  $M^{++}$  of thiazinones **43** [or at least of an intermediate similar to **N** (see above)] constitute at least part of the  $[M - N_2]^{++}$  ions of **42**. In the case of **41** a lesser amount of  $[M - N_2]^{++}$  ions possess an oxazinone structure. It is also impossible to totally exclude the Wolff rearrangement as a possible pathway of transformation. The reaction of the thio compounds **42** with acids produces the expected 1,3-thiazin-5-ones (**43**) in an approximate yield of 30–40% (63). In contrast, in the case of diazo compounds **41** it was found that the corresponding 1,3-oxazin-5-ones are unstable. However, the formation of these compounds as minor products was indicated by an NMR study (42).

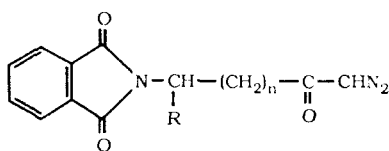
The results of CI experiments (compounds **29–43**) led to similar conclusions concerning the intramolecular cyclization process (40–49). However, the lack of fragmentation in the case of CI, unless the ionization process is followed by collision activation (45), makes the interpretation of the results more difficult.

There are no fragments in the mass spectra of phthalimidoalkyl- $\alpha$ -diazoketones **44** (Fig. 17), other than those resulting either from unisomerized  $M^{++}$  or the product of the Wolff rearrangement (50). (Nevertheless the  $M^{++}$  of **44** are unstable and are detected only in the case of **44g**.) The main fragmentation pathways are initiated by rupture of the C—C bond  $\alpha$  to the carbonyl group in the side chain or by loss of a nitrogen molecule. The latter process is accompanied by the Wolff rearrangement (Scheme VIII).

The fragmentation pattern is similar for compounds **44h–l** ( $n > 0$ ). The abundant peak at  $m/z$  84 is detected for the compounds **44j–l**. High resolution mass spectrometry suggests that  $m/z$  84 contains a diazo group ( $C_3H_4N_2O$ ). The formation



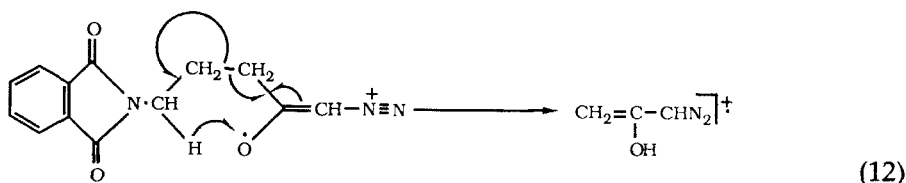
**Figure 16.** (a)  $R = H$ ; (b)  $R = CH_3$ ; (c)  $R = C_2H_5$ ; (d)  $R = CH_2Ph$ .



44 a-l

**Figure 17.** (a)  $R = H, n = 0$ ; (b)  $R = CH_3, n = 0$ ; (c)  $R = C_2H_5, n = 0$ ; (d)  $R = iso-C_3H_7, n = 0$ ; (e)  $R = iso-C_4H_9, n = 0$ ; (f)  $R = sec-C_4H_9, n = 0$ ; (g)  $R = Bz, n = 0$ ; (h)  $R = Ph, n = 1$ ; (i)  $R = H, n = 1$ ; (j)  $R = H, n = 2$ ; (k)  $R = H, n = 3$ ; (l)  $R = H, n = 4$ .

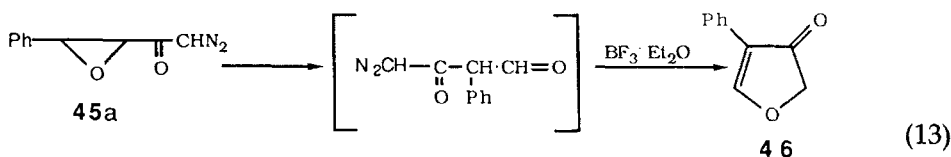
of such a fragment may be rationalized by a six-center reaction, e.g., Eq. (12) for **44j**.



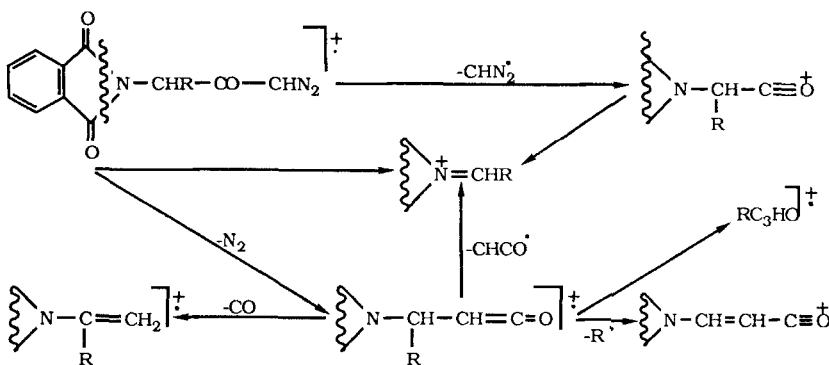
(12)

Attempts to achieve cyclization of these diazocompounds in solution also failed (42,50,51). The cause of such behavior may be connected with the decreased ability of the phthalimide nitrogen to donate its electrons for the anchimerically assisted expulsion of the nitrogen molecule and the necessity of opening of the phthalimide ring for the formation of a new stable heterocyclic system.

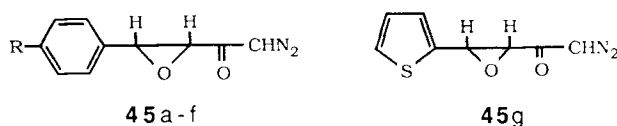
It was shown in 1974 that in the presence of  $BF_3 \cdot Et_2O$  1-diazo-3,4-epoxy-4-phenylbutan-2-one (**45a**) underwent aryl migration followed by cyclization to form the furan system **46** [Eq. (13)] (64,65).



(13)



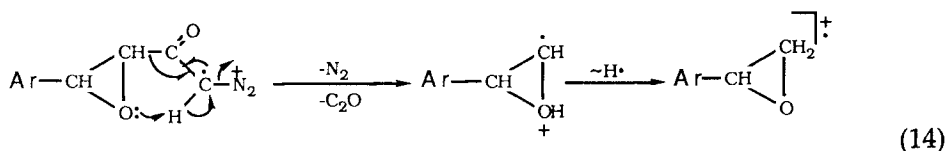
Scheme VIII



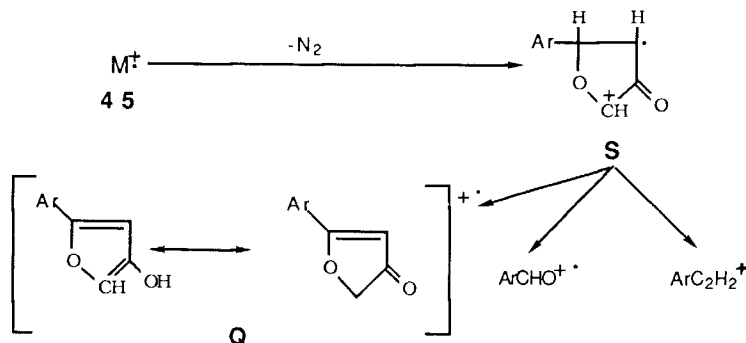
**Figure 18.** (a) R = H; (b) R = CH<sub>3</sub>; (c) R = OCH<sub>3</sub>; (d) R = NO<sub>2</sub>; (e) R = F; (f) R = Cl.

The mass spectra of the compounds 45a-g (Fig. 18) were studied later (51,52).

Transformation of the arylepoxy unit into some other structure is suggested by the dramatic differences observed in the spectra of the compound 45 and arylepoxides (66) or arylepoxyketones (67). Formation of a furan system under EI conditions is therefore proposed. The fragmentation pattern suggested that the usual cyclization process leading to the formation of 3-hydroxy-5-arylfurans **Q** was operative. A major peak in the spectra of compounds 45 (6–17% of total ion current) is produced by the ArCHO<sup>+</sup> ion (ArCO<sup>+</sup> is also pronounced). This is not characteristic of either a linear structure (66,67) or structure 46. On the other hand, formation of ArCHO<sup>+</sup>, together with formation of the ion ArCH=CH<sup>+</sup>, may be rationalized on the basis of an intermediate structure **S** (Scheme IX). ArCH<sup>+</sup> and ArC<sup>+</sup> ions (which are abundant in the mass spectra of epoxy compounds) are absent in the spectra of 45. The formation of the ion [M - N<sub>2</sub> - C<sub>2</sub>O]<sup>+</sup> occurs, since the oxygen atom can attack as both a nucleophile and a base [Eq. (14)].



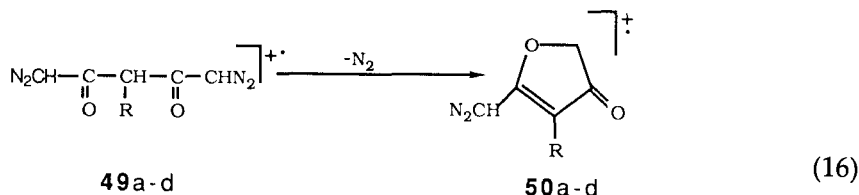
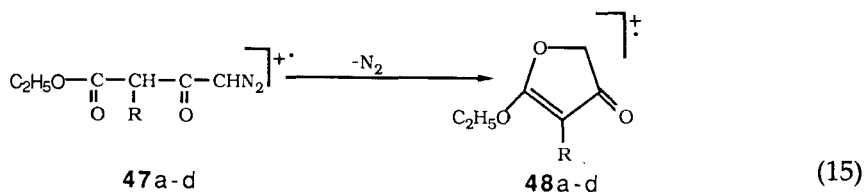
Nevertheless, the possibility that the Wolff rearrangement produces a portion of the [M - N<sub>2</sub>]<sup>+</sup> ions cannot be totally excluded (51,52). Remarkably, the M<sup>+</sup> of the fluorine derivative 45e decomposes mainly without cyclization.



Scheme IX

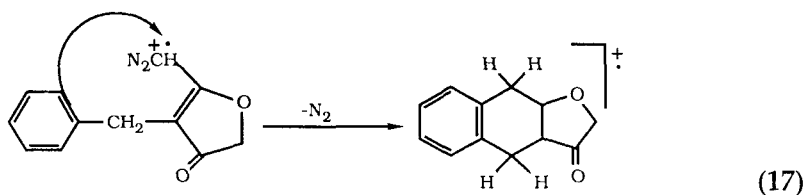
An experiment to induce cyclization with formation of the furans **Q** in solution has been undertaken (42). Each of the acids used ( $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ) produces two isomeric heterocycles in roughly a 1:1 ratio. A gas chromatography/mass spectrometry (GC/MS) analysis showed the isomeric compounds to be 4- and 5-aryl-3-hydroxyfuran. Hence, in these cases mass spectrometry may be used as a tool to predict the results of chemical reactions in solution (42).

Other furan systems form from diazoketones (42). On the basis of EI, metastable ion spectra, and high-resolution mass spectrometry data it was shown that the  $\text{M}^{+\bullet}$  of **47** loses a nitrogen molecule (because of anchimeric assistance) with subsequent transformation into the molecular ion of the heterocycles **48** [Eq. (15)]. Analogous reactions resulting in the formation of furans **50** were noted for the bisdiazoketones **49** [Eq. (16)].



(a)  $\text{R} = \text{H}$ , (b)  $\text{R} = \text{CH}_3$ , (c)  $\text{R} = \text{C}_2\text{H}_5$ , (d)  $\text{R} = \text{CH}_2 \text{ Ph}$ .

The  $[\text{M} - \text{N}_2]^{+\bullet}$  ions of compounds **49** are quite abundant. The 100-fold decrease in the intensity of that ion [as well as other peculiarities of secondary fragmentation pathways of the  $[\text{M} - 2\text{N}_2]^{+\bullet}$  ions in the case of the benzyl derivative **49d** (e.g., formation of the  $[\text{M} - 2\text{N}_2 - \text{H}_2]^{+\bullet}$ ) suggest (42) that  $\pi$ -electrons of the benzene ring can anchimerically assist in the ejection of a nitrogen molecule [Eq. (17)].



Possible anchimeric assistance involving the  $\pi$ -electrons of the benzene ring in the fragmentation of diazoketones also has been reported (53). This work deals with the analysis of possible structures for the  $[\text{M} - \text{N}_2]^{+\bullet}$  ions of **51**. EI mass spectra as well as MI and CA spectra of those compounds were studied.

Although the major fragmentation pathways of **51** involve the consecutive loss

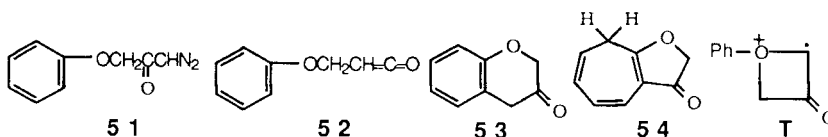


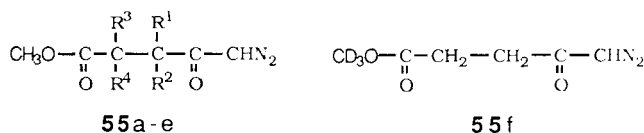
Figure 19

of  $N_2$  and CO molecules, the CA MIKE spectra of the  $[M - N_2]^{++}$  of **51** and the  $M^{++}$  of **52** appear to have several notable differences. Although the Wolff rearrangement occurs, some of the  $[M - N_2]^{++}$  ions have other structures. Since **51** transforms in solution into the cyclic structures **53** and **54**, it was proposed that the formation of these structures under EI should also be considered. Unfortunately the authors did not have a sample of **54** and were unable to produce **T** (which was thought to be formed under EI, following the elimination of  $N_2$ ) independently. Nevertheless, reliable evidence was obtained concerning the possible structures of the  $[M - N_2]^{++}$  ions. These results imply that the unimolecular reactivity of the  $M^{++}$  of **51** under EI followed the same routes which occur during thermal, photochemical, and catalytic reactions of the neutral substrate in the condensed phase. Although the Wolff rearrangement still occurs, this reaction competes with Friedel-Crafts (compound **53**), carbene addition (**54**), and oxygen anchimeric assistance (T) processes, all of which lead to cyclic products (see Fig. 19).

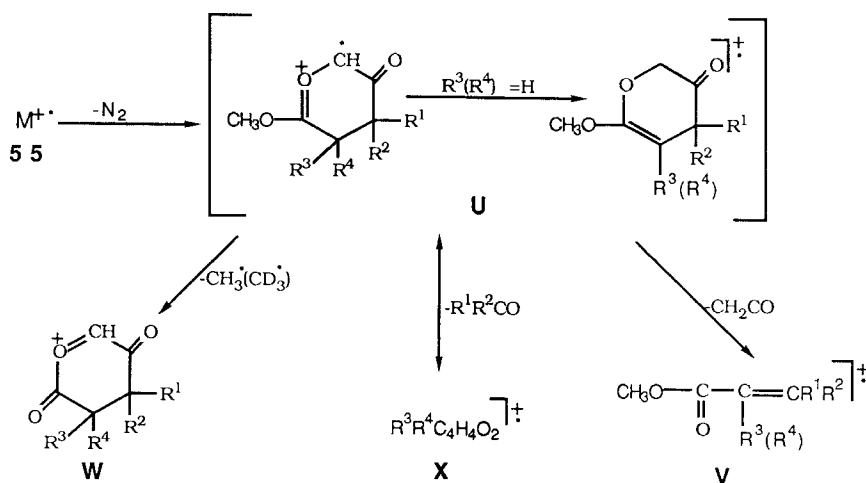
To predict the possible transformations of 1-diazo-4-methoxycarbonylbutan-2-ones (**55a-f**) (Fig. 20), their EI mass spectra have been studied (54). The complexity of the spectra led the authors to measure the accurate masses of more than 70 ions, many of which appeared to be doublets.

The fragmentation scheme has been reported (54). The mass spectra of the compounds **55** are devoid of a molecular ion, but there are several fragments containing the diazo group (e.g.,  $[M - OCH_3]^+$ ,  $COCHN_2^+$ ). The product of the McLafferty rearrangement (when  $R^3$  or  $R^4 = CH_3$ ) with the retention of the diazocarbonyl portion is also noted.

The existence of cyclic oxolanone structures **U** may be supported by the formation of several secondary ions (Scheme X). The most important are the retro Diels-Alder processes (**V** and **X**) and the  $CH_3$  radical loss (**W**). However, a possibility of a number of other structures of  $[M - N_2]^{++}$  ions cannot be eliminated. For example, the Wolff rearrangement may still account for the structure of a



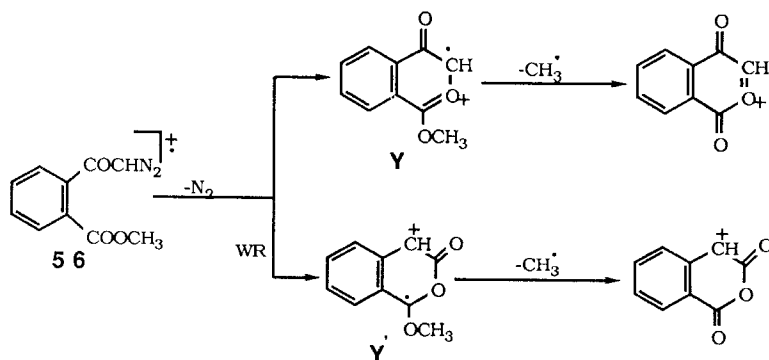
**Figure 20.** (a)  $R^1 = R^2 = R^3 = R^4 = H$ ; (b)  $R^1 = CH_3$ ,  $R^2 = R^3 = R^4 = H$ ; (c)  $R^1 = R^2 = CH_3$ ,  $R^3 = R^4 = H$ ; (d)  $R^3 = R^4 = CH_3$ ,  $R^1 = R^2 = H$ ; (e)  $R^1 = R^3 = CH_3$ ,  $R^2 = R^4 = H$ .



portion of the  $[M - N_2]^{++}$  ions. Thus, the authors concluded that although the elimination of  $N_2$  with formation of the oxolanone rings could take place in acid-catalyzed reactions in solution, their yield would not be high because of different competitive reactions [the last experiments in solutions brought to a mixture of more than 10 products (68)], and analogously there are numerous fragmentation routes.

A hypothesis was developed to explain the remarkable similarity in the behavior of the diazoketones studied (40–54) in the gas and condensed phases (40–42,51). It is assumed that the charge and an unpaired electron in the  $M^{++}$  of diazoketones should be on the  $CN_2$  group in the ground state (17). That is, the same charge localization followed by the anchimerically assisted loss of the  $N_2$  molecule and formation of heterocycles using electron impact ionization or protonation by acids in solution (59,61–63) should produce the same effect.

The molecular ion of 56 is unstable and the mass spectrum is characterized by

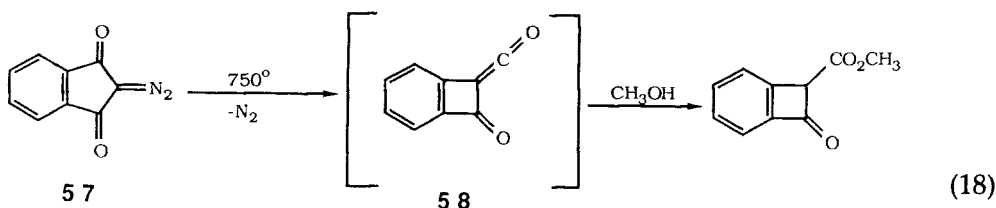




abundant peaks formed by  $[M - N_2]^{++}$  and  $[M - CHN_2]^+$  ions (69). The high abundance of the  $[M - N_2]^{++}$  fragment is rationalized in terms of intramolecular cyclization. Further  $CH_3$  group elimination supports the formation of ions **Y** or **Y'** (Scheme XI). However, the appearance of the 1,4-isochromandiones in acid-catalyzed reactions in solution (70), suggested by analogy that the ion **Y** was a more probable structure.

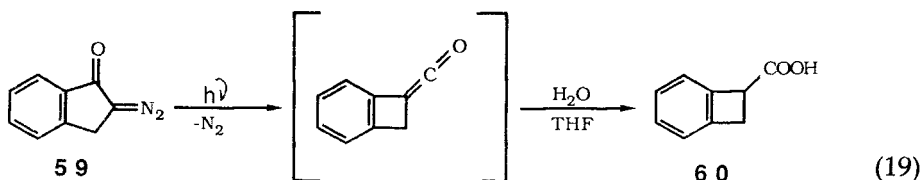
#### IV. CYCLIC DIAZOKETONES AND DIAZOQUINONES

Similarities between the EI-induced fragmentation and photolytic and thermolytic reactions of several cyclic diazocompounds have been reported (71–73). When subjected to pyrolysis, 2-diazoindane-1,3-dione **57** transforms into the ketotetene intermediate **58**. The reaction of **58** with  $CH_3OH$  gives 2-carbomethoxybenzocyclobutenone (71); that is, ring contraction through the Wolff rearrangement takes place [Eq. (18)].



The fragmentation pattern of **57** under EI conditions suggests that loss of  $N_2$  involves a Wolff rearrangement with formation of the  $M^{++}$  of **58** (72), which loses two molecules of CO followed by  $C_2H_2$ .

The photolysis of 2-diazoindanone-1 (**59**) in aqueous tetrahydrofuran gives benzocyclobutene-1-carboxylic acid **60** resulting from the addition of water to the ketene (73). The fragmentation pattern of **59** is characterized by the consecutive losses of  $N_2$ , CO, and  $C_2H_2$  molecules. These processes may be rationalized in terms of the Wolff rearrangement [Eq. (19)], but it is also possible that the loss of CO may take place without any rearrangement of the  $[M - N_2]^{++}$  ions (72).



The decomposition pathways of **61–68** (Fig. 21) also have been reported (72). Besides the loss of CO, the  $[M - N_2]^{++}$  ions of **61** also eliminate a  $CH_3$  radical. The base peak in the spectrum is due to the ion  $[M - N_2 - CO - H]^+$ .

Comparison of the EI and metastable ion spectra, together with the ratio of abundances of the singly and doubly charged metastable ions for **62** and anthracene, shows that the ions  $[M - N_2 - CO]^{++}$  of **62** may have the structure of the

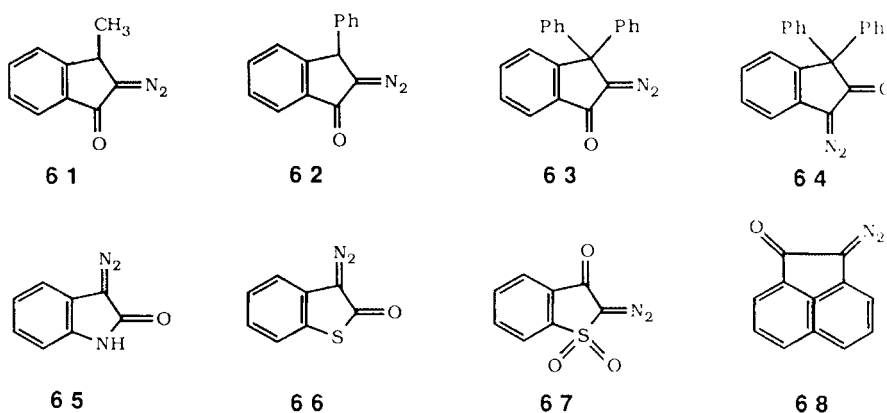
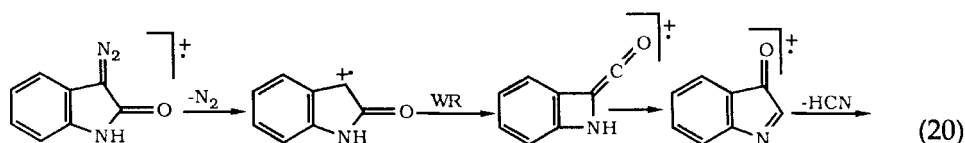


Figure 21

$M^{++}$  of anthracene (72). Nevertheless the authors refrain from offering a simple proposal.

The spectra of the isometric compounds **63** and **64** are very similar; the only significant difference being the more pronounced loss of the Ph group from the  $[M - N_2]^{++}$  ions in the case of **64**. The resulting ion at  $m/z$  205 fragments by losing CO.

The spectrum of diazooxindole **65** shows competitive losses of CO and HCN by the  $[M - N_2]^{++}$  ions. This suggests that in addition to the Wolff rearrangement, other rearrangements may stabilize the  $[M - N_2]^{++}$  species. The processes of Eq. (20) have been proposed (72):



Under electron impact 3-diazo-2-ketothianaphthane **66** sequentially loses  $N_2$  and CO molecules. The product ion at  $m/z$  120 then decomposes by the loss of  $C_2H_2$  or CS.

The absence of the  $[M - N_2]^{++}$  peak is a feature of the spectrum of **67**. The low eV spectrum of **67** similarly shows no  $[M - N_2]^{++}$  peak, although the peak due to  $[M - N_2 - CO]^{++}$  ions persists even at ca. 13 eV. Perhaps, then,  $N_2$  and CO molecules are lost simultaneously.

The molecular ion of 2-diazoacenaphthen-1-one **68** loses  $N_2$  followed by CO. A similar fragmentation pattern is observed for 10-diazophenanthren-9-one **69**.

The EI spectra of **69** and **70** were studied earlier by Kinson and Trost (74). In both cases consecutive losses of  $N_2$  and CO molecules were noted. The resulting ion (base peak) competitively loses a hydrogen atom and a  $C_2H_2$  molecule. The possibility of the Wolff rearrangement was investigated by generating the corresponding ketene ions independently from compounds **71** and **72** (see Fig. 22).

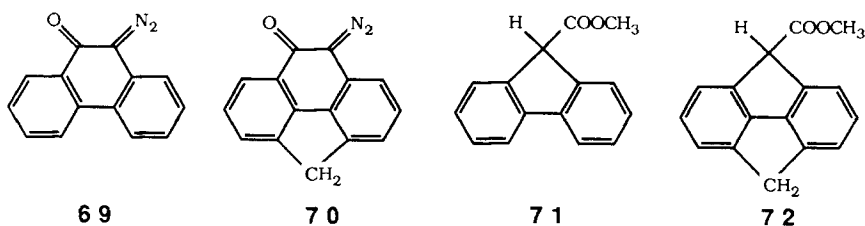
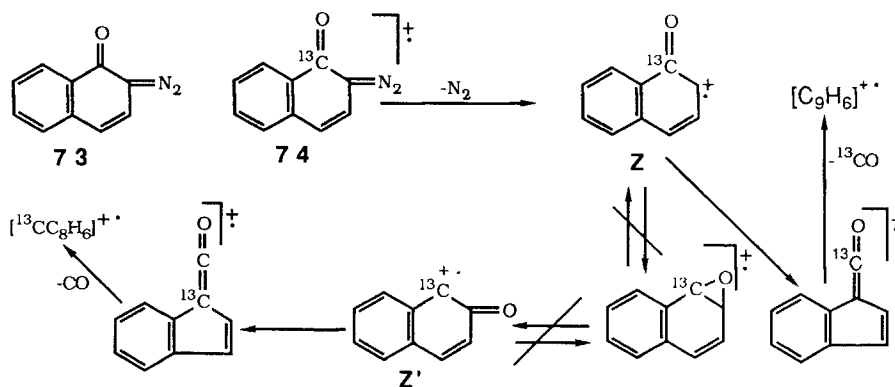


Figure 22

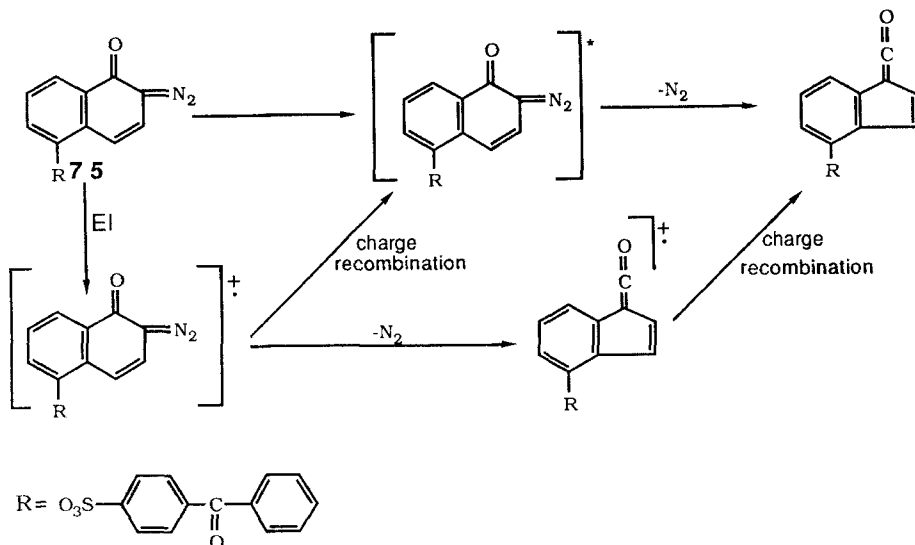
Metastable peak characteristics serve as a fingerprint for ions of identical structure and energy (75), thus these parameters were measured for the process of CO elimination from the appropriate ions of 69–72. Each ester-diazoketone pair has metastable peaks with identical height-width ratios, implying that the  $[M - N_2]^{++}$  ions derived from the diazoketones have the ketene structure, i.e., the Wolff rearrangement is operative. High relative abundances of the metastable peaks due to  $N_2$  loss are interpreted in terms of a concerted nitrogen elimination together with the Wolff rearrangement.

Zeller (22) has studied the EI-induced Wolff rearrangement for naphthalene-2,1-diazooxide 73. The data obtained were compared with the available results for thermolysis and photolysis (21). The molecular ion undergoes consecutive loss of  $N_2$ , CO, and  $C_2H_2$ . The base peak in the spectrum is due to an  $[M - N_2 - NO]^{++}$  ion. The label in compound 74 is lost following CO elimination. Thus Zeller proposed that the Wolff rearrangement was the only way that  $[M - N_2]^{++}$  ions could be stabilized. If an alternative oxirene structure was present, even as an intermediate, the consequent opening of the ring would yield both structures Z and Z', together with partial retention of the label following loss of CO (Scheme XII).

Since the EI and photochemical results differ, either the  $[M - N_2]^{++}$  ions may have insufficient energy to isomerize to the oxirene structure, or, alternatively, the Wolff rearrangement takes place simultaneously with the nitrogen molecule



Scheme XII

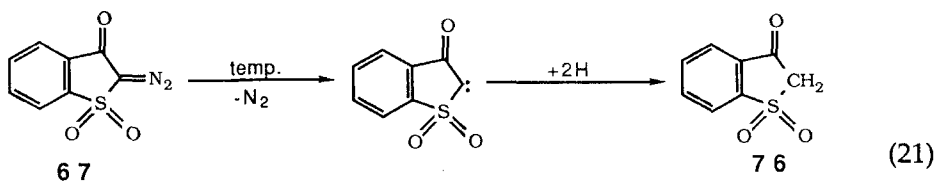


Scheme XIII

loss (22). The former explanation seems to be less probable because of the wide range of energies of ions in EI mass spectrometry. No comment has been made (22) concerning the possibility that direct loss of the CO molecule comes from the unisomerized  $[M - N_2]^{++}$  species. Such a process is impossible for linear diazoketones but quite probable for cyclic compounds.

The EI-induced Wolff rearrangement of **75** in the solid state (Scheme XIII) has been described (76). By use of a specially designed experimental apparatus it has been shown that the diazoketone transforms into ketene with loss of  $N_2$ . Several possible mechanisms have been suggested, but the authors indicate that differentiation between those mechanisms requires further experimentation.

The molecular ion of 3-ketothianaphthene-1,1-dioxide **76** appears following thermal decomposition of **67** (72) [Eq. (21)]. The abundance of this ion increases when the sample is heated in a reservoir. The low eV spectrum of **67** does not show any  $[M - N_2]^{++}$  peak, although the peak due to the  $M^{++}$  of **76** persists even at ca. 13 eV.



An analogous process is observed in the case of other diazo compounds (18,72,74).

The EI spectra of **69**, **77**, and **78** have been reported (77). Molecular ions are detected for all three samples, producing the base peak for **77** and **78**. Other abundant peaks are due to losses of 26, 27, and 28 mass units. In the absence of high-resolution data the authors suggest that these particles are CN, HCN, and

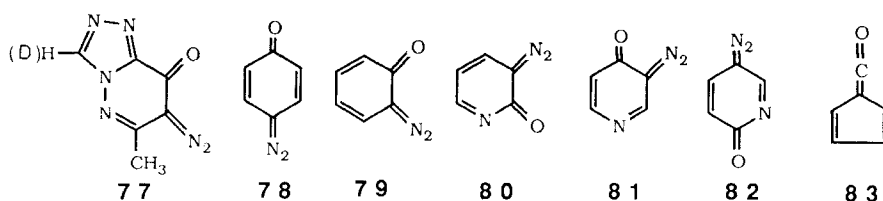
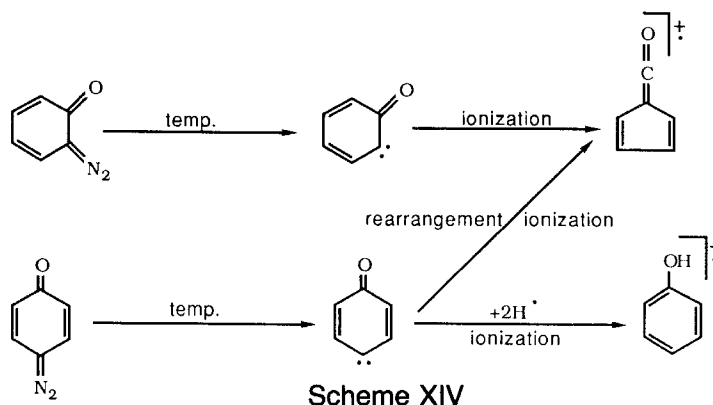


Figure 23

$N_2$  or CO, respectively. On the basis of this assumption they explain the fragmentation mechanisms. For example, formation of the ion at  $m/z$  66 in the spectrum of 78 is rationalized by the deprotonated pyrrole structure formed following consecutive losses of CN and CO. The same scheme is suggested for compound 69. To elucidate the fragmentation processes for 77, the spectrum of a D-labeled derivative (position 3 of the triazole ring) was studied. This experiment indicated that the triazole ring was retained during "HCN" loss. In addition, two  $^{15}N$  compounds (both nitrogen atoms of the diazo group alternatively) were analyzed. None of the mentioned fragments contain any label. Nevertheless, the authors concluded that there was an equilibrium between the linear and diazine structures of the diazo group. In fact, the results obtained (77) indicate the absence of the nitrogen atoms of the diazo group in each of the three fragments. Incorrect conclusions were also made concerning the fragmentation patterns of compounds 69 and 78.

A thorough investigation of compounds 78–82 (Fig. 23) was carried out by Thorstad, Undheim, and Hvistendahl (78–81). The first step of the electron impact decomposition of these compounds is loss of  $N_2$ . The same process occurs thermally. The elimination of  $N_2$  is followed by the Wolff rearrangement and CO loss. The Wolff rearrangement is proposed for all of the compounds studied. This process is more favorable for *ortho*-quinones, because in the case of the *para*-quinones a preliminary hydrogen migration is necessary. In addition, the *ortho* isomer loses  $N_2$  through essentially a thermal process. In contrast, the *para* isomer loses  $N_2$  on EI. The IE measurements support the last conclusion. The AE of the  $[M - N_2]^{++}$  ion for the *ortho* isomer is 9.05 eV, which is quite close to the IE of fulvenone-6 83 (8.95 eV); the product of the Wolff rearrangement for quinone-diazides. With increasing temperature AE decreases and approaches the IE value for 83. For the *para* isomer 78 the AE is 9.6 eV (55 °C), and so EI is a major contributor towards formation of the  $[M - N_2]^{++}$  species (78). An increase of temperature from 55 to 200 °C decreases the AE of the  $[M - N_2]^{++}$  ion from 9.6 to 9.1 eV, which then remains constant as the temperature is increased further. Thus, it is claimed that the thermal loss of the  $N_2$  molecule arises from a Wolff rearrangement followed by ionization of fulvene. Analogous conclusions were made for pyridine derivatives 80–82. It was also suggested that the *ortho* isomer is more "quinoid" than the *para* isomer (Scheme XIV) (cf. Ref. 82).

$[M - 26]^{++}$  ions are detected in the spectra of compounds 78–82. High-resolution measurements show that these are  $[M - N_2 + 2H]^{++}$  ions. The authors (78,79) could not detect any metastable peak supporting the formation of these ions, and pro-



pose the following (Scheme XIV). This scheme is in agreement with the proposals of Ref. (72) and not with conclusions of Ref. (77).

Both isomers produce ketocarbenes following thermally induced  $N_2$  loss (83–85). The *ortho*-carbene undergoes the Wolff rearrangement directly; the *para*-carbene requires a preliminary rearrangement. As a result, the lifetime of the *para*-carbene is the longer of the two, and being quite reactive, it can pick up hydrogen atoms from the environment (cf. Ref. 72). The rate of this reaction is temperature dependent. While the temperature of samples is of minor importance, an increase of the source temperature increases the abundance of the product ion considerably. It is proposed that the reaction takes place on the walls of the source. The longer lifetime of *para*-ketocarbenes gives higher peak abundances compared with those of the *ortho* isomer. Analogous conclusions are made for pyridines 80–82 (80,81).

One experimental observation remains unresolved (79). The injection of  $D_2O$  into the ion source during the analysis of 78 shifts the  $m/z$  value of the phenol ion by only one amu.

Reduction of ketocarbenes in an ion source has been independently studied for substituted diazonaphthalenones 84, 85 (Fig. 24) using EI, CI (86), and FAB (87).

All these compounds provide a molecular ion of medium abundance. The fragmentation schemes proposed were aided by high-resolution mass spectrometry and metastable studies. The main decomposition pathway involves  $N_2$  molecule loss followed by the Wolff rearrangement and loss of CO. The spectra of compounds 84 and 85 are more complex because of interference from other fragmentation pathways involving substituents.

In the cases of 84b and 85b an abundant fragment at  $m/z$  300 (due to  $[M-26]^+$  ions) is observed (86). These ions ( $[M-N_2+2H]^{++}$  species as shown by high-resolution mass spectrometry studies) decompose further with formation of secondary fragments ( $m/z$  207,  $m/z$  143, etc.). Analogous processes are also observed for benzophenone derivatives. The abundance of the  $[M-N_2+2H]^{++}$  ion is higher in the case of 4-substituted compounds and increases in the sequence *ortho* <

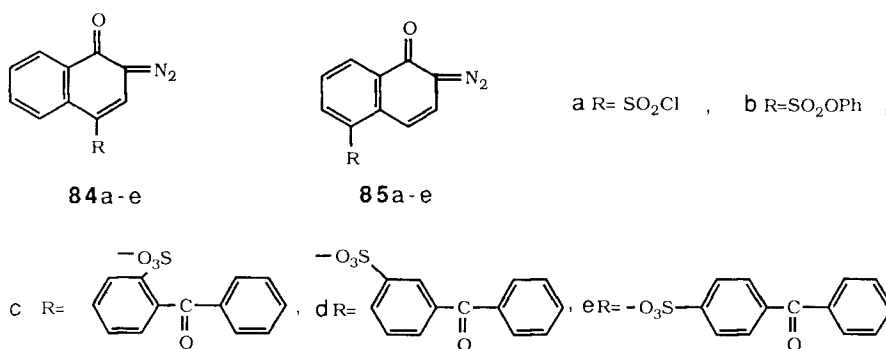
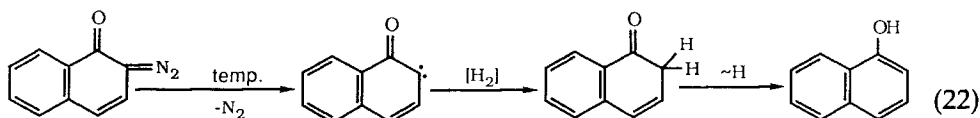


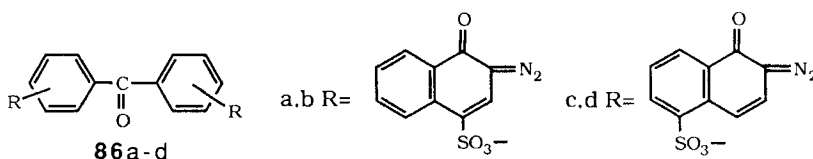
Figure 24

*meta* < *para*. The CI mass spectra of the target compounds were recorded using methane as reagent gas. In these cases  $[M-26]^+$  ions are even more pronounced; in a proton-rich environment this process effectively suppresses the usual elimination of N<sub>2</sub>. It is proposed that a reduction process takes place on the surface of the glass tip of the direct insertion probe (86). To confirm this hypothesis, experiments were conducted with several representative compounds in which the probe tip surfaces were saturated with D<sub>2</sub>O, as well as a mixture of D<sub>2</sub>O and D<sub>2</sub>PO<sub>4</sub><sup>-</sup>. A shift of the  $[M-26]^+$  ions to  $[M-24]^+$  and  $[M-25]^+$  is observed. Deuterium isotope incorporation is evident also for the ions associated with the process of the formation of the  $[M-26]^+$  ions. Nevertheless the authors mention that the results are not simple. For example, there are no shifts noted for **85a**. Linked scans indicate that there is no relationship between an M<sup>++</sup> and  $[M-N_2+2H]^+$  ions under the experimental conditions used (cf. Ref. 78). The authors propose that the  $[M-26]$  species probably form during the thermal degradation step, and that the  $[M-N_2]$  neutral species become hydrogenated by interaction with hydrogen atoms from the probe tip surface. They also speculate that thermal decomposition may proceed via a carbene intermediate. Hydrogenation of carbene leads to a naphthol structure following H-migration in the  $\beta$ -ene-ketone [Eq. (22)]. In a hydrogen-rich environment (e.g., under CI conditions) the process is further enhanced. These proposals are in agreement with earlier conclusions (cf. Refs. 78–81).



Since there are similarities between photolytic, thermolytic, and EI-induced reactions of diazoketones, it is suggested (86) that mass spectrometry may be used as a screening method for the prediction of chemical reactions (cf. Refs. 40–54).

Compounds **84–86** (see Fig. 25) were analyzed by FAB using both glycerol and 3-nitrobenzyl alcohol (NBA) as matrices (87). Of most interest is the process of

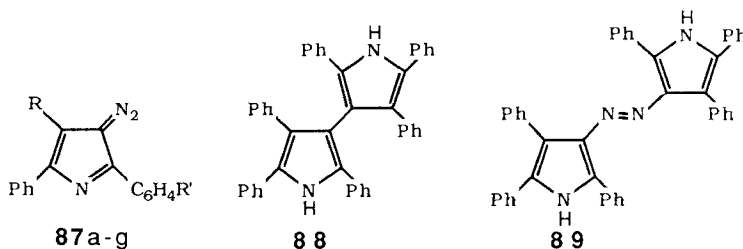


**Figure 25.** (a), (c) [2,2']diester; (b), (d) [4,4']diester.

the reduction-producing  $[\text{MH} - 26]^+$  ions. In all cases this process competes with the usual fragmentation via the Wolff rearrangement. In the case of **86** (using glycerol as matrix) the Wolff rearrangement is totally suppressed. Glycerol is a better matrix for reduction, although the spectra are more pronounced with NBA, because of increased solubility in the latter matrix. The  $[\text{M} - 26]^+$  species are formed much more readily from the 4- than from the 5-isomer in the case of **84b** and **85b** in glycerol. An explanation involving electronic stability is proposed. In the 4-isomer, the lone pair of electrons (from the carbene center) may be shifted to the sulfone oxygens, leaving an electron deficient site at carbon 2. Reduction may then take place at this position. If a similar mechanism is invoked for the 5-substituted isomer, the aromaticity of the adjacent ring would be affected. The preference of the single hydrogen reduction in case of the NBA matrix is connected with the lower reducing potential of NBA (Scheme XV).

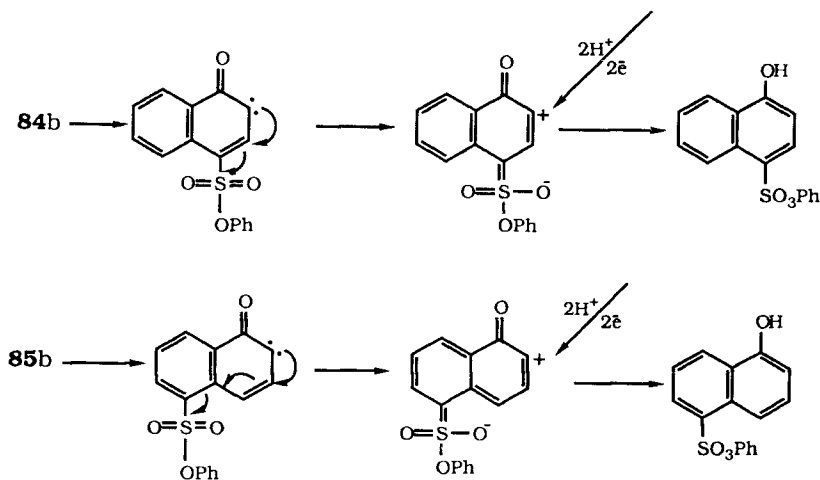
As the compounds studied (**86,87**) are used in lithographic systems, the authors conclude that the application of the similar FAB process may be useful for clarification of mechanisms of lithographic processes. For example, if the reduction product is formed in the photochemical process, it is reasonable to assume that the carbene-initiated reaction of the imaging dyes would be quenched, thus leading to inefficient quantum yields.

The EI mass spectra of 2,5-diaryl- and 2,4,5-triaryl-3-diazopyrroles **87** (Fig. 26) has been reported (88). Molecular ions are quite abundant, and elimination of  $\text{N}_2$  is the main fragmentation process. The loss of  $\text{N}_2$  is EI-induced and is not thermal (shown by metastable and temperature variation experiments). The  $[\text{M} - \text{N}_2]^{++}$  ions lose  $\text{PhCN}$  to form the base peak of the spectrum [Eq. (23)].



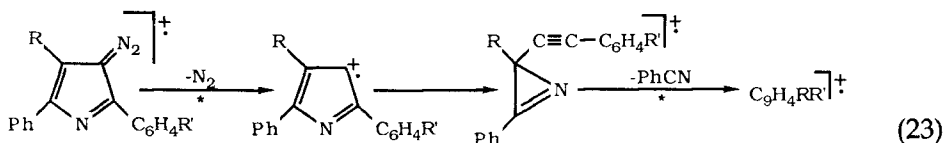
**Figure 26.** (a) R = Ph, R<sup>1</sup> = H; (b) R = Ph, R<sup>1</sup> = *p*-CH<sub>3</sub>; (c) R = Ph, R<sup>1</sup> = *p*-OCH<sub>3</sub>; (d) R = Ph, R<sup>1</sup> = *o*-OCH<sub>3</sub>; (e) R = Ph, R<sup>1</sup> = *m*-OCH<sub>3</sub>; (f) R = R<sup>1</sup> = H; (g) R = H, R<sup>1</sup> = *p*-CH<sub>3</sub>.





Scheme XV

The similarity between this process and thermal or photochemical processes has been demonstrated. A fragmentation process producing a new heterocycle is proposed for the compound **87d** with the *ortho* substituent R'. [M - 26]<sup>+</sup> peaks due to [M - N<sub>2</sub> + 2H]<sup>+</sup> ions are observed (cf. Refs. 74-78, 86, and 87).



Experiments involving saturation of the probe surface with deuterium support the conclusions (86,87). When the mass spectrum of **87a** is run at a probe temperature of 180 °C, the peak at [M - N<sub>2</sub> + 2H]<sup>+</sup> becomes dominant, whereas at 240 °C peaks at *m/z* 588 and 616 (attributable to the molecular ions of cross-linked compounds **88** and **89**) are also observed.

The mass spectrum of **90** (Fig. 27) has been described (89). The principal fragmentation pathway involves the losses of N<sub>2</sub> and CO. The base peak is produced by an [M - N<sub>2</sub> - CO - CH<sub>3</sub>]<sup>+</sup> ion. The abundance of the M<sup>+</sup> is 24%. The other processes involve elimination of different hydrocarbon neutrals from the two *t*-butyl groups.

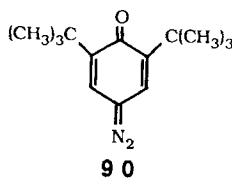


Figure 27

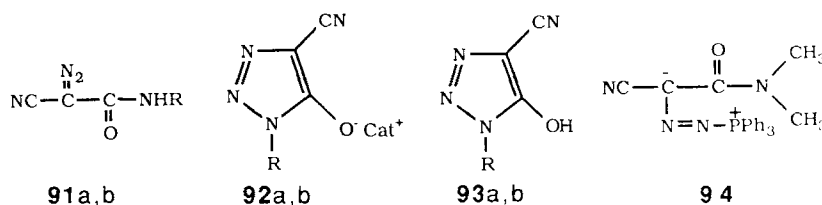


Figure 28. (a) R = H; (b) R = CH<sub>3</sub>.

## V. DIAZOAMIDES, DIAZOIMINES, AND DIAZOSULFONES

Diazoketones possess a linear structure and diazothiketones a cyclic one, but diazoamides may exist in interconvertible linear and cyclic forms (90–92). Mass spectrometric studies of 1,2,3-triazoles (cyclic isomers of linear diazoamides) have been reviewed with other nitrogen heterocycles (e.g., Ref. 25); linear diazoamides are covered in this review.

Diazoamides **91**, in ethanol or water solution in the presence of NaOC<sub>2</sub>H<sub>5</sub>, NH<sub>3</sub>, or (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N undergo cyclization with the formation of triazolates **92** (**93**). Addition of acid leads to triazoles **93** (see Fig. 28).

The EI spectra of these compounds have been reported (**94**). The aim of the work was to test the possibility of cyclization of diazoamides **91** into the isomeric triazoles **93** under EI conditions. The spectra of **92** and **93** are very similar: NH<sub>3</sub> or CH<sub>3</sub>NH<sub>2</sub> is eliminated from the Cat<sup>+</sup> portion of **92** to give the M<sup>++</sup> of **93**. On the other hand, the spectra of the isomers **91** and **93** are different. High-resolution measurements aided these studies. Two different fragmentation schemes were proposed. The Wolff rearrangement with migration of the amino group is characteristic for the [M–N<sub>2</sub>]<sup>++</sup> ions of diazoamides. In the case of **91a** these ions lose CO, HCO, or HCN fragments, while for **91b**, CH<sub>2</sub>NH and CH<sub>3</sub> fragments are also lost. The M<sup>++</sup> may also decompose, forming RHNCO<sup>++</sup>, NCCHN<sub>2</sub><sup>++</sup> and C<sub>2</sub>N<sub>3</sub><sup>+</sup> fragments. The same fragmentation scheme is observed for **94**; this compound does not transform into triazoles in solution. [It is also shown (**94**) that the adducts of diazoamides **91** with PPh<sub>3</sub> fragment under the EI with the rupture of the N–P bond and formation of M<sup>++</sup> of diazoamides, which fragmentation is entirely similar to that of authentic diazoamides **91**.] The similarity between the decomposition processes of **94** and **91** indicate that they fragment without cyclization (**94**). In addition, a hypothesis was advanced concerning a possible analogy between negative ion mass spectra and base-catalyzed reactions of cyclization of diazoamides. Thus the resonance electron capture spectra of compounds **91**, **93**, **95**, and **96** were recorded (**95**).

The dissociative resonance capture of electrons by the molecules of these compounds take place in four different ranges of electron energies. The highest abundances of ions are observed in the first range (electron energies ca. 0.1–0.2 eV). The yield of ions when electrons of 1.5, 5.0, and 7.5 eV are used is 2–3 orders of magnitude lower. The molecular radical anions of all the compounds are unstable and are not observed. The secondary fragments are connected mainly with [M–N<sub>2</sub>]<sup>–</sup> ions and their abundances are very close for both isomers. On the

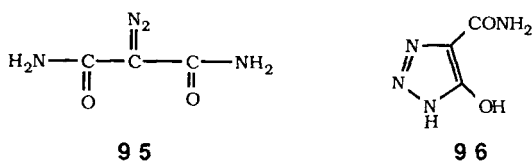


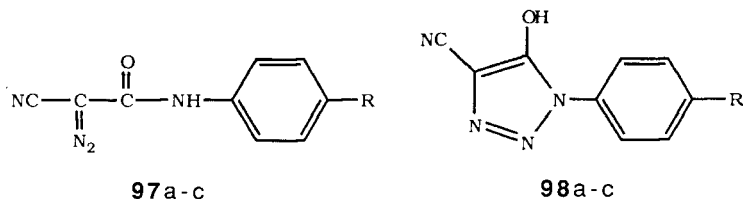
Figure 29

other hand, the abundances of ions connected directly with  $\text{M}^{--}$  ( $\text{HC}_2\text{N}^-$ ,  $\text{CN}^-$ ,  $[\text{M}-\text{H}]^-$ ) differ greatly for the corresponding pairs of isomers. Thus the different structures of  $\text{M}^{--}$  and common structures of  $[\text{M}-\text{N}_2]^{--}$  ions for the isomers **91** and **93** have been proposed. In the case of **95** and **96** (Fig. 29) the spectra are identical, but all the ions are connected with the primary  $[\text{M}-\text{N}_2]^{--}$  fragment. Thus, it is impossible to define a structure of  $\text{M}^{--}$ . To prove the hypothesis concerning the probability of the analogous behavior of diazoamides in base-catalyzed and negative ion mass spectral conditions, compounds with more stable molecular anions need to be studied (95).

The cyclization of aryl derivatives **97** into triazoles **98** (see Fig. 30) takes place more readily than for their alkyl analogs **91** (96). This reaction may be induced by acids, bases, or even by changing the solvent. The EI mass spectra of **97** and **98** indicate that the molecular ions of the isomers transform to a common structure. As the array of fragments and their abundances is the same for all three pairs of isomers, the authors provide a common comprehensive scheme of fragmentation which is aided by high-resolution mass spectrometry data and metastable ion studies. The B/E linked scan spectra of the  $\text{M}^{++}$  and  $[\text{M}-\text{N}_2]^{++}$  ions of the corresponding isomers are also identical.

The authors suggest that the loss of  $\text{NCO}$  and  $\text{NHCO}$  from the  $[\text{M}-\text{N}_2]^{++}$  ions cannot be rationalized on the basis of azirine or ketenimide structures (94,97,98). Perhaps a more complex rearrangement with participation of the benzene ring takes place.

The replacement of an aryl by a cyclohexyl group leads to the corresponding isomers **99** and **100** (Fig. 31), whose spectra differ. Although the dominant fragmentation pathways are almost the same, the abundances of fragments with the same compositions are substantially different. The B/E spectra of the  $\text{M}^{++}$  and  $[\text{M}-\text{N}_2]^{++}$  ions are different. The elimination of  $\text{N}_2$  is a dominant process in the metastable  $\text{M}^{++}$  spectra for triazoles **100**, while the geometry of the amide **99**

Figure 30. (a)  $\text{R} = \text{H}$ ; (b)  $\text{R} = \text{CH}_3$ ; (c)  $\text{R} = \text{OCH}_3$ .

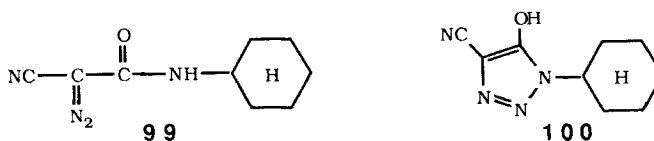
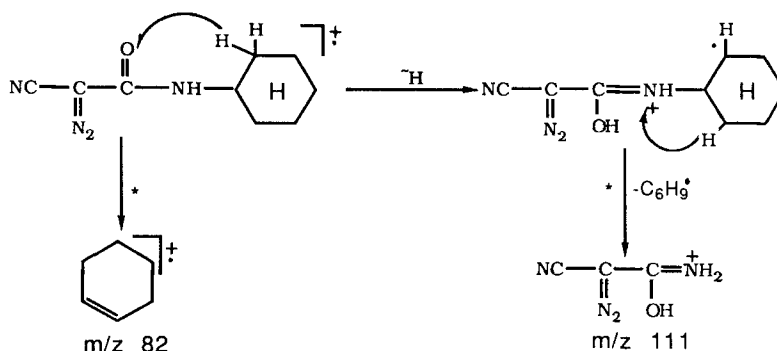


Figure 31

makes the process leading to  $m/z$  82 and 111 more favorable (Scheme XVI). Thus, the common structure does not form in these cases.

IE data have been used to describe the different behavior of alkyl and aryl substituted compounds (94,96). The IE of the  $N_2CHCO$  radical is known to be 8.1 eV (13). The exchange of a hydrogen atom for the cyano group usually causes an increase of an IE value by 0.4–0.5 eV (99), so that the IE of the  $N_2C(CN)CO$  radical should be ca. 8.5–8.6 eV. The IE of the  $C_6H_{11}NH$  radical is 9.3 eV, while that of  $PhNH$  is 8.3 eV; hence in the case of aryl substituted diazoamides the unpaired electron and the positive charge should be preferentially localized on the arylamino group, and in the case of alkyl-substituted compounds on the diazocarbonyl function. Thus the difference in charge localization may be responsible for the differences in the fragmentation of these classes of compounds.



Scheme XVI

Maquestiau *et al.* (100) have described the fragmentation patterns of  $\alpha$ -diaziminines **101** (Fig. 32). They suggest that the loss of  $N_2$  is accompanied by the Wolff rearrangement to form ketenimine **102** [Eq. (24)]. The isomerization of the primary cation-radical of the carbene is indicated by the absence of the  $[M - N_2 - CH]^+$  or

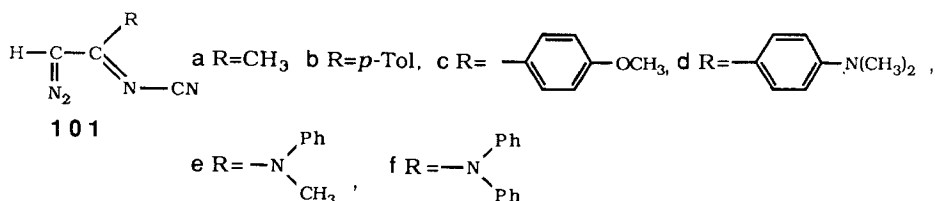
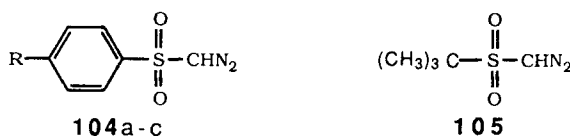
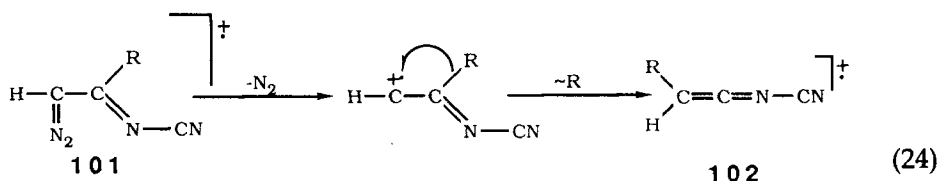


Figure 32

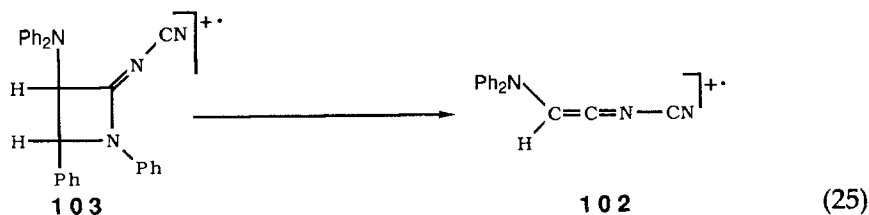


**Figure 33.** (a)  $\text{R} = \text{CH}_3$ ; (b)  $\text{R} = \text{OCH}_3$ ; (c)  $\text{R} = \text{O}_2\text{N}$ .

$[\text{M}-\text{N}_2-\text{CN}, -\text{CH}]^+$  fragments in the CA MIKE spectra of the  $[\text{M}-\text{N}_2]^{++}$  ions. On the other hand, the consecutive elimination of two CN or CN and HCN species by the  $[\text{M}-\text{N}_2]^{++}$  ions supports the proposed ketenimine structure. The ions formed in the ion source and in the field-free region of a triple sector instrument possess the same structures in these cases.



The similar CA MIKE spectra of the  $[\text{M}-\text{N}_2]^{++}$  ions from compound **101f** and of the  $\text{M}^{++}$  of **102** (generated by the retro-Diels-Alder reaction of the  $\text{M}^{++}$  of **103**) suggest the operation of a process similar to the Wolff rearrangement [Eq. (25)].



However, in the case of **101f** the  $\text{Ph}_2\text{N}$  group migrates. Aryl- or alkyl-substituted  $[\text{M}-\text{N}_2]^{++}$  ions may be stabilized because of interaction with the imino group. For example, formation of an azirine ion could induce consecutive elimination of CN and HCN. To test this supposition it is necessary to generate an azirine ion independently or to study the spectrum of a compound labeled with  $^{13}\text{C}$  in the  $\text{CN}_2$  group.

The diazosulfones **104** and **105** (Fig. 33) were analyzed by EI mass spectrometry (101). A fragmentation scheme has been proposed on the basis of high-resolution mass spectrometry data and metastable studies. All the compounds give molecular ions of moderate intensity, but no  $[\text{M}-\text{N}_2]^{++}$  ions are present. However, metastable transitions for the losses of SO,  $\text{SO}_2$ , and CO from the  $[\text{M}-\text{N}_2]^{++}$  ions are detected. This implies that the  $[\text{M}-\text{N}_2]^{++}$  ions, although formed, are unstable and decompose with a rate constant  $>10^5$ . The losses of SO and  $\text{SO}_2$  are connected with the sulfene formed as a result of the Wolff rearrangement. However, fragmentation along the route involving exclusively a sulfene intermediate does not



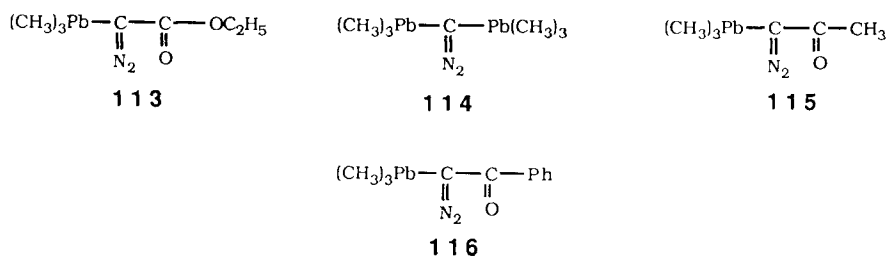
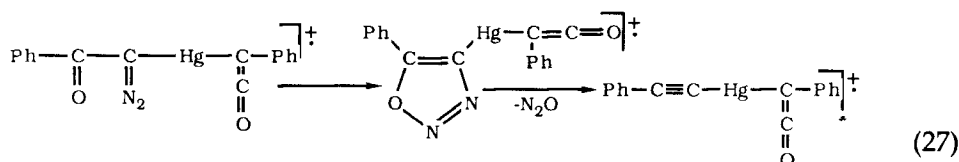


Figure 35

are the only ions present. The formation of the latter may be rationalized by  $\text{N}_2\text{O}$  loss from the ketene  $[\text{M}-\text{N}_2]^+$  ions. That means that the isomerization into the oxadiazole structure needs to be considered [Eq. (27)] (cf. Refs. 30 and 39).



Fragmentation of **110** involves losses of  $\text{N}_2$  and  $\text{C}_2\text{H}_4$  molecules as well as of alkoxy radicals, a reaction characteristic of diazoesters (18–21). The  $[\text{M}-\text{N}_3]^+$  ions seem to be questionable, as are the  $[\text{M}-\text{N}]^+$  ions, in the spectra of **111** and **112** (102). Again, the samples could have some impurities. The Wolff rearrangement may be proposed as a convenient mechanism of decomposition of molecular ions of **111** and **112**.

There are three separate groups of peaks in the mass spectrum of **113** (Fig. 35): (i) consecutive losses of  $\text{CH}_3$  groups; (ii) consecutive losses of  $\text{CH}_3$  groups from the  $(\text{CH}_3)_3\text{Pb}^+$  ion; and (iii) fragmentation of the  $\text{HC}(\text{N}_2)\text{COOC}_2\text{H}_5^+$  ion.

Since the diazo group is present in many fragments the "remarkable" strength of the C—N bond was mentioned (cf. Refs. 30 and 31).

In the original paper (103) the mass spectrum of **114** showed no molecular ion, but an array of peaks due to the  $\text{Pb}_2(\text{CH}_3)_{6-n}^+$  and  $\text{Pb}(\text{CH}_3)_{3-m}^+$  ions ( $n=0-6$ ,  $m=0-3$ ). In later work (104) a revised spectrum showed  $\text{M}^{++}$  (30%), and a full series of  $[(\text{CH}_3)_{6-n}\text{Pb}_2\text{CN}_2]^+$  fragments ( $n=0-6$ ), with abundances much higher than that observed for the  $\text{Pb}_2(\text{CH}_3)_{6-y}^+$  series. This reiterates the stability of the C—N bond (30).

Besides containing a  $\text{M}^{++}$  of medium abundance, the usual fragment due to  $\text{N}_2$  loss followed by the Wolff rearrangement, and consecutive losses of the  $\text{CH}_3$  groups, the mass spectra of the compounds **115** and **116** showed an array of ions due to ion-molecule reactions in the ion source. The structures of these ions were proposed.

## VII. CONCLUSION

In conclusion, diazo compounds have been shown to be a very interesting class of organic compounds for mass spectrometric analysis, and they definitely require

further study. Even the Wolff rearrangement, mentioned in almost all the publications dealing with diazo compounds, often remains without reliable proof. The possibility of predicting the results of chemical reactions in solution using mass spectrometry demonstrates the power of this method and its usefulness for organic chemists.

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