Mass Spectrometric Studies of Sulfonyl Esters of Diazonaphthalenones: Relationship Between Fragmentation Patterns and Photolithographic Mechanisms

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Synopsis

Esters of 2-diazonaphthalenone sulfonic acid were examined by mass spectrometry using electron impact and chemical ionization techniques. Characteristic differences in the fragmentation patterns of positional isomers have been observed. In a manner analogous to photo-induced decompositions, the diazoketo functional groups fragment by elimination of N_2 to form an indenoketene ion. An alternative process involves the apparent loss of 26 mass units from the molecular ion. The latter process is explained by evoking the abstraction of two hydrogen atoms following the loss of N_2. With deuterium isotope labeling, it has been shown that the hydrogens are abstracted from the surface of the probe tip used for introduction of the samples into the mass spectrometer. It is concluded that an environment rich in hydrogen or proton-donating properties promotes and enhances the incorporation of the hydrogen atoms and formation of the [M-26] species at the expense of the ketene moiety, which is an important intermediate in the photoresist process. By extrapolation it may be inferred that the efficiency of the photolithographic process could be influenced by the availability of protons in the photoresist matrix.

INTRODUCTION

Orthoquinone diazides have continued to attract considerable interest in the photoresist industry because of their use as sensitizers to produce high-contrast resist images.[1,2] Their effectiveness in various lithographic applications is associated with their propensity to undergo a Wolff rearrangement upon exposure to light[3] or electron beams.[4]

The accepted mechanism for the photolytically initiated polymerization process of naphthoquinone diazides is shown in Scheme 1. It has been proposed that upon exposure to radiation, the molecule undergoes fragmentation to release molecular nitrogen and form a ketene intermediate. The latter, a highly reactive species, undergoes a series of reactions including cross-linking with undecomposed light-sensitive elements to improve its solubility. Functional group substitution at R, typically in the form of a sulfonyl ester or diester of benzophenone at the 4- or 5-positions, influences the reactivity of the quinone diazide groups and, presumably, the quantum yield of the reaction.

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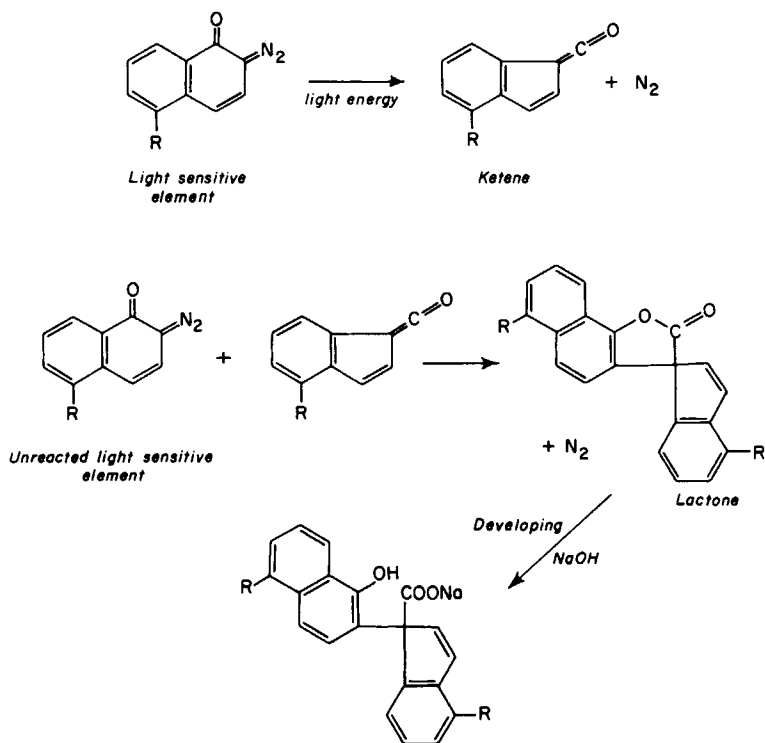
Scheme 1.   Mechanism for photoinduced decomposition of naphthoquinonediazides.

Our interest in the mass spectrometry of these compounds was prompted, in part, by the general paucity of data on the mass spectrometric behavior of sulfonate esters of 2-diazonaphthalenones. The study was further motivated by frequently encountered analogies between photochemically induced processes and electron-impact-initiated ionic fragmentation reactions in the mass spectrometer. We were thus hopeful that the mass spectrometric data might reveal some fundamental information related to the behavior of these materials upon exposure to various types of radiation such as light or ion beams and the associated uses in general lithographic processes. As shown in the following, many of the mass spectrometric fragmentations can indeed be rationalized using intermediates proposed to be generated in photo-induced decompositions.

EXPERIMENTAL

Apparatus

Electron-impact mass spectra were obtained with a Nuclide 12-90-G magnetic mass spectrometer at an ionization energy of 70 eV. The ionizing current was 50 μA, and the ion source temperature 200°C. The fragmentation patterns of the compounds did not change significantly in experiments where the ion source temperature was decreased to less than 100°C. Samples were introduced into the mass spectrometer via the direct insertion probe.
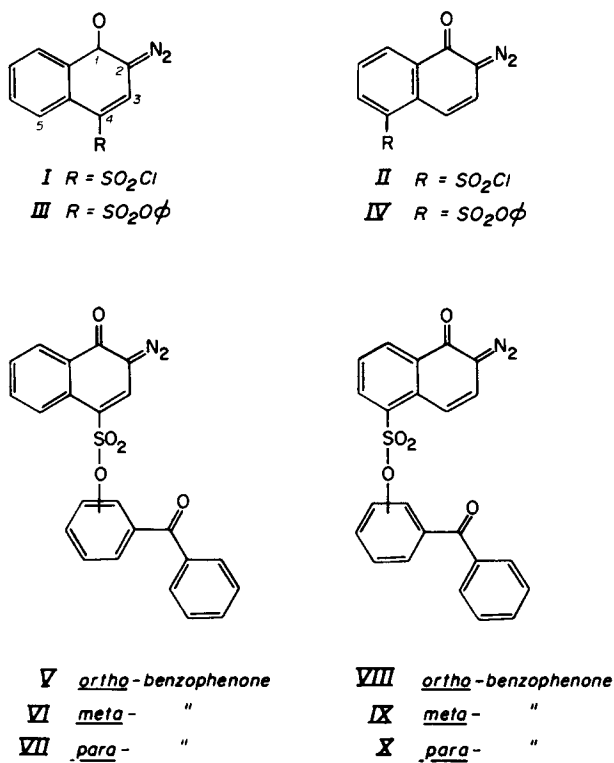
Fig. 1. Structures of 2-naphthalenone diazide derivatives.

Chemical ionization spectra (positive or negative) were obtained with a Finnigan 4021B mass spectrometer interfaced to an Incos data system. The indicated reagent gas (CH_4) pressure was 0.4 torr.

Synthesis of Aryl Sulfonyl Esters of 2-Naphthalenone Diazides

The sulfonyl chlorides I and II (Fairmount Chemical) were used as starting materials for the preparation of compounds III–X by reaction with the appropriate aryl alcohol (see Fig. 1 for structures). The general synthetic procedure was based on the use of a phase transfer catalysis method to effect the formation of a sulfonate ester. The aryl alcohol and potassium hydroxide were dissolved in water to form a potassium salt. Methylene chloride, containing a crown ether and the sulfonyl chloride, was brought in contact with the aqueous mixture and the aryl oxide-potassium ion-pair extracted into the organic layer with the crown ether to react with the sulfonyl chloride. All of the arylsulfonyl ester remained in the organic layer while the KCl was back-extracted into the water. This procedure greatly simplifies the final cleanup and isolation of the desired product. The exact details of the procedure are as follows:

18-Crown-6 (1 mg) was added to a solution of the sulfonyl chloride (1 mmol) in methylene chloride (20 mL). Phenol (1 mmol) in methylene chloride (10 mL) was slowly added to this mixture. After 5 min, KOH solution (50% 5 mL) was added dropwise with vigorous stirring. The reaction mixture was stirred at

room temperature for 1 h and monitored by TLC using a solvent of hexane: ethyl acetate (2 : 1 V/V) in order to assess the completeness of the reaction. The mixture was then poured onto water, the organic layer washed with brine, dried over MgSO$_4$, and concentrated to yield a mixture which was separated on silica gel column using ethyl acetate-hexane solvent system. A yield of 80% was obtained.

The samples were refrigerated immediately upon isolation and stored under nitrogen in the dark. In addition to mass spectra, infrared (IR) and nuclear magnetic resonance (NMR) spectra were obtained to confirm the structures of the products.

RESULTS

Ten different compounds substituted at the 4- or 5-positions were investigated. These included the sulfonyl chlorides I and II, the 4- and 5-sulfonylphenol esters (III and IV) and a total of six isomeric 2-diazonaphthalenone sulfonyl esters of hydroxybenxophenone (V–X). The structures of the compounds are shown in Figure 1. Electron impact as well as positive and negative ion chemical ionization spectra of the compounds were examined. Samples were introduced into the MS ion source via the direct insertion probe. The ion-source temperature was maintained at 200°C although the fragmentation patterns of the compounds did not change significantly even at source temperatures under 100°C. The control of the probe tip temperature appeared to introduce quantitative differences in the spectral patterns, consistent with some of the surface-catalyzed phenomena discussed below. In these studies, the spectra of the sulfonyl chloride and the phenol ester derivatives were obtained at probe temperatures of 60–80°C, while the benzophenone esters were vaporized at 100–120°C.

Electron Impact (70 eV) Mass Spectra

Spectra of Sulfonyl Chlorides (I and II)

The electron impact (70 eV) spectra of the isomeric compounds I and II are compared in Figure 2. The spectra of both compounds exhibit well-defined molecular ion peaks at m/z 268. The 3 : 1 chlorine isotope ratio provides group labeling information which aids in the interpretation of the mass spectrum by identifying the halogen content of the various fragment ions.

For example, it is quite clear that the ions at m/z 240, 176 and 148 contain the chlorine atom. In comparing the spectra of the two isomers it may be noted that the ion peaks at m/z 157 and 129 provide the basis for differentiation between the 4- and 5-sulfonylchlorides. These ions are of significant abundance in the spectrum of I but at much lower levels in that of II.

Of particular significance in both spectra is the observed loss of 28 mass units from the molecular ion to give the peak of m/z 240. A similar process has also been reported previously in the spectra of related 2-diazonaphthalenones by DeJongh et al.[5] High resolution mass measurements confirmed that the loss of 28 U involves elimination of N$_2$. Analogous to the photolytic
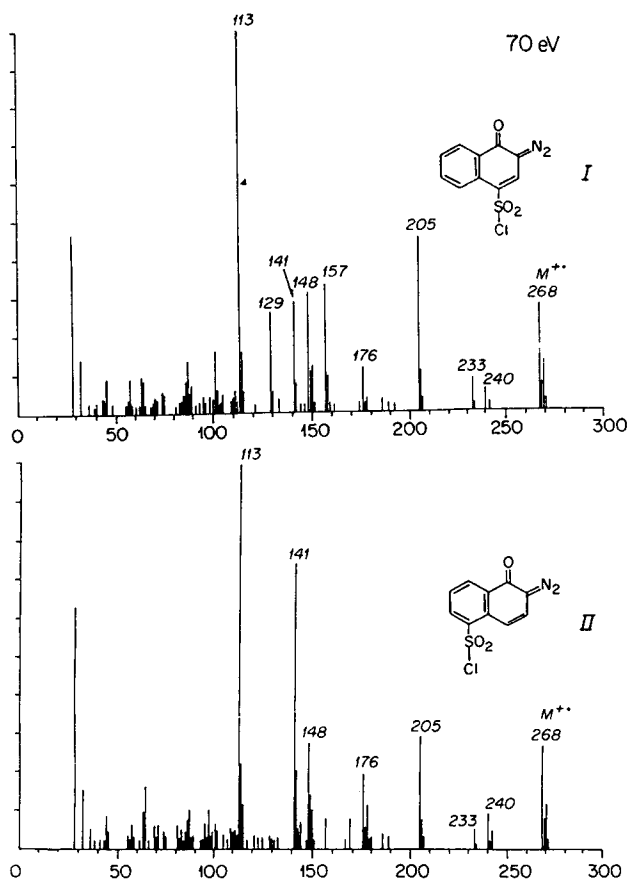
Fig. 2.   Mass spectra (EI, 70 eV) of compounds I and II.

decomposition process, it can be explained by the formation of an indenoketene ion. Competing with the elimination of N_2 from the molecular ion is a loss of Cl· to yield the peak at m/z 233. This initiates the production of a series of related fragment ions as outlined in Scheme 2 for the 4-positional isomer, I. A similar scheme, not shown here, can be written for the fragmentation of II. The indicated structural assignments are consistent with elemental compositions obtained from high resolution mass measurements. Fragmentations for which metastable transitions were observed, are indicated by an asterisk on this and all subsequent schemes.

On the basis of the structures proposed for the various ion fragments in Scheme 2, it is possible to speculate on some of the key differences between the spectra of I and II. We refer particularly to the significant variation in the relative intensities of m/z 157 and 129 in the two spectra. It may be reasoned that these fragments are formed more favorably in the 4-isomer since in this case it is possible to depict these ions in terms of ion structures which retain an intact aromatic ring (Scheme 2). This is not possible in the case of the 5-isomer.
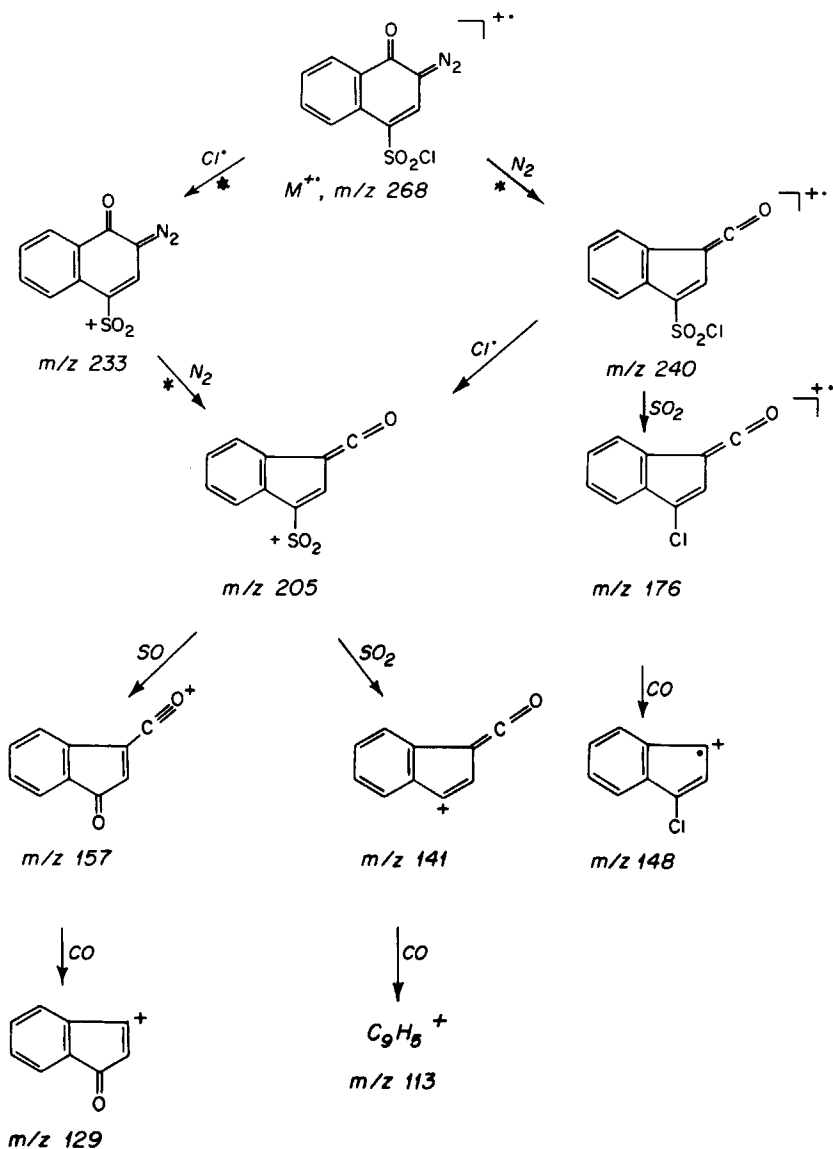
Scheme 2. Fragmentation pattern of sulfonylchloride derivative I.

Mass Spectra of Sulfonyl Phenol Esters (III and IV)

The 70 eV mass spectra of the two isomeric phenol esters (III and IV) are shown in Figure 3. It is interesting to note the presence of many of the same peaks (e.g., m/z 205, 141, 113) observed previously in the spectra of the sulfonyl chlorides. Moreover, as before, the peaks at m/z 157 and 129 are distinctly more prominent in the spectrum of 4- as opposed to the 5-substituted isomer. Again this provides a means of differentiating between these two compounds. In addition, the spectrum of the 4-isomer (II) exhibits a major peak at m/z 94 corresponding to a phenol ion. This peak is much
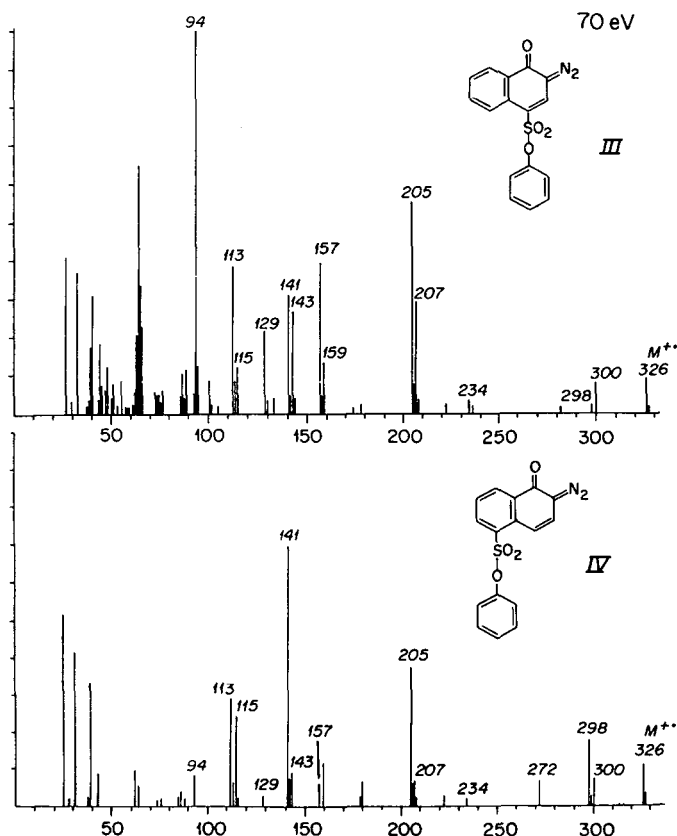
Fig. 3. Electron-impact mass spectra of phenyl sulfonate esters, III and IV.

weaker in the spectrum of IV. Formation of a phenol ion can be explained in terms of a six-membered ring rearrangement process and retention of the charge with the phenol moiety (Scheme 3). The reason for the more favorable occurrence of this process in the 4-isomer is not clear.

The fragmentations associated with the diazoketo function are more readily apparent in the high mass region of the spectrum. Loss of N_2 (28 U) gives rise to the peak at m/z 298. Consistent with the spectra of the sulfonyl chlorides, loss of N_2 from the molecular ion occurs more favorably in the 5- than in the 4-isomer. A second surprising fragmentation was observed to yield an ion corresponding to [M-26]$^{+\cdot}$ at m/z 300. This ion further loses 28 U to give a peak at m/z 272. It is also interesting to point out that in the spectrum of III, where [M-26]$^{+\cdot}$ is more prominent than [M-28]$^{+\cdot}$, some of the lower order
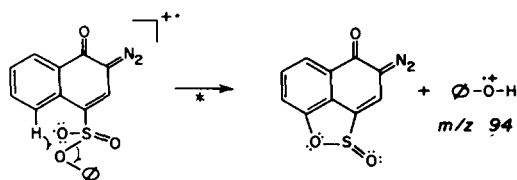
Scheme 3. Formation of phenol ion in the spectrum of phenyl sulfonate ester III.

fragment ions such as m/z 205 and 141 are accompanied by intense satellite peaks 2 U higher at m/z 207 and 143. It thus appears that the initial loss of 26 U from $M^{+ \cdot}$ initiates an alternative fragmentation sequence which competes with the fragmentation process that originates from $[M-28]^{+ \cdot}$.

In order to clarify the nature of the $[M-26]^{+ \cdot}$ ion, compounds III and IV were further analyzed by high resolution mass spectrometry. An exact mass of 300.0436 was found for this ion which, within 0.003 mass units, corresponds to an elemental composition of $C_{16}H_{12}O_4S$. According to this formulation, the $[M-26]^{+ \cdot}$ ion contains two more hydrogen atoms than the molecular ion. An alternative fragmentation pathway in addition to that initiated by elimination of N_2 from $M^{+ \cdot}$ is thus proposed, whereby loss of N_2 is accompanied by incorporation of two hydrogens to produce a naphthol derivative (Scheme 4). The compositions of all ions have been verified by high resolution MS, and many of the transitions have been confirmed by metastable ion data. The origin of the hydrogens and the potential implications of this phenomenon to the lithographic process are discussed in the Discussion section.
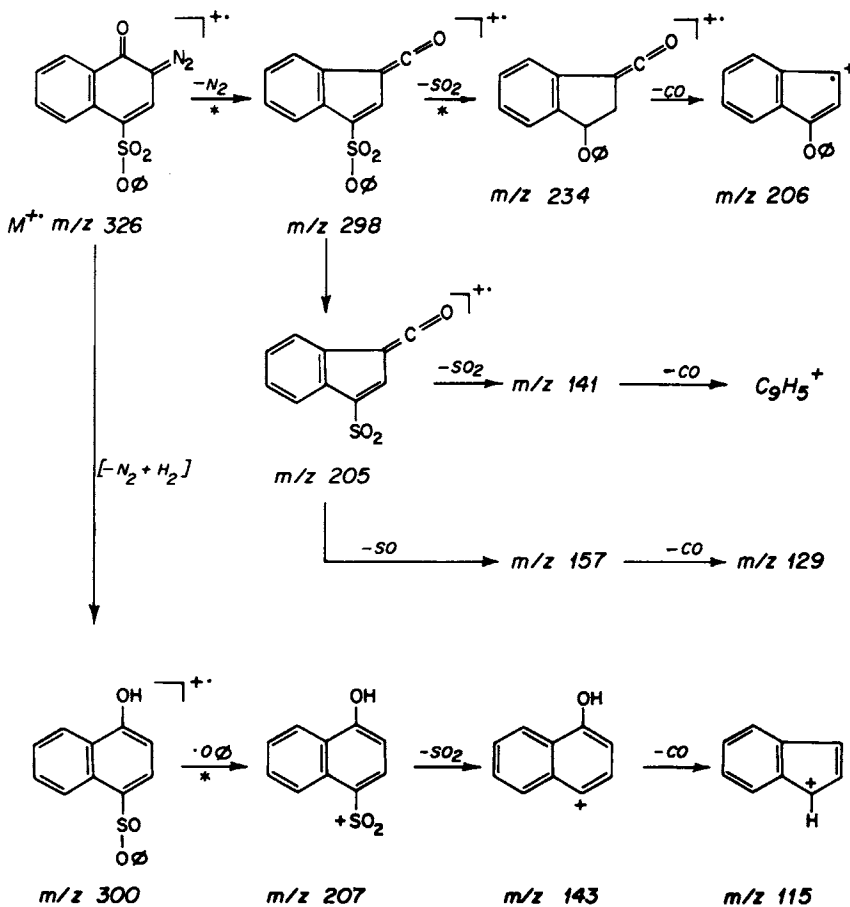
Scheme 4. Fragmentation of 2-naphthalenonediazide-4-phenylsulfonate.

Mass Spectra of Hydroxybenzophenone Esters (V–X)

Six isomeric benzophenone sulfonate esters of 2-diazonaphthalenone (V–X) were prepared according to the procedure described in the Experimental section. For purposes of this presentation they will be discussed in two sets: those of the 4-substituted naphthoquinone-diazides (V–VII) and their corresponding 5-substituted counterparts (VIII–X). Three isomers (*o-*, *m-*, and *p*-benzophenones) are included in each of the two categories. This classification provides a means of comparing the effect of 4- vs. 5-ring substitution on the ionization and fragmentation of the quinonediazide function. In addition, it permits an evaluation of the influence of the *ortho*- vs. *para*-benzophenone isomerism on the same process.
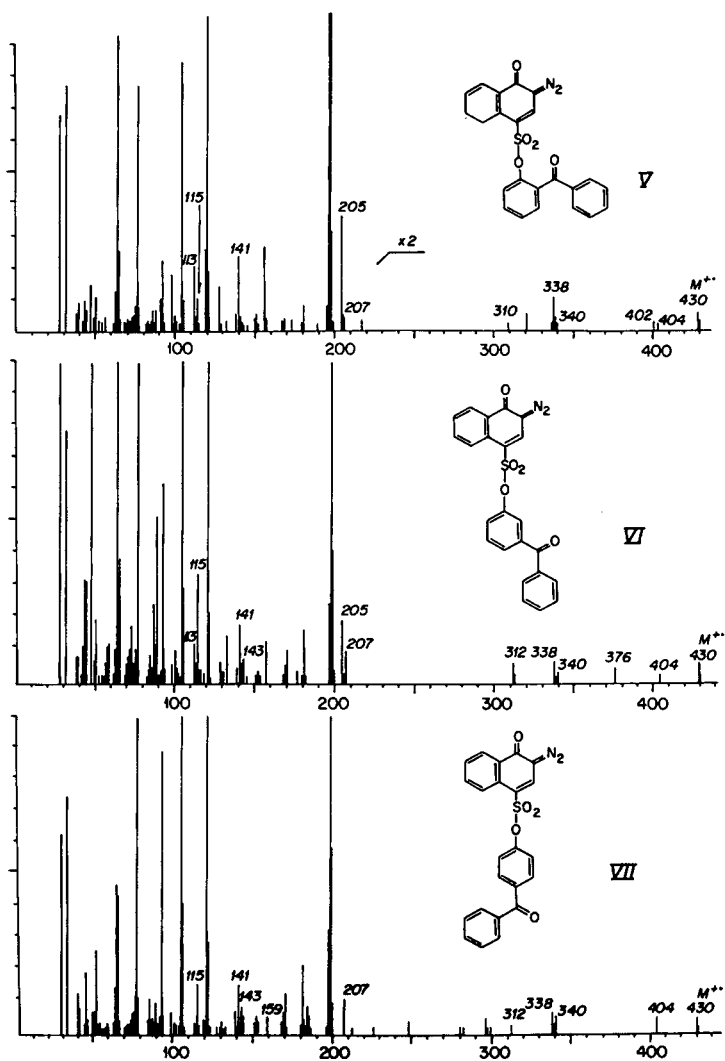

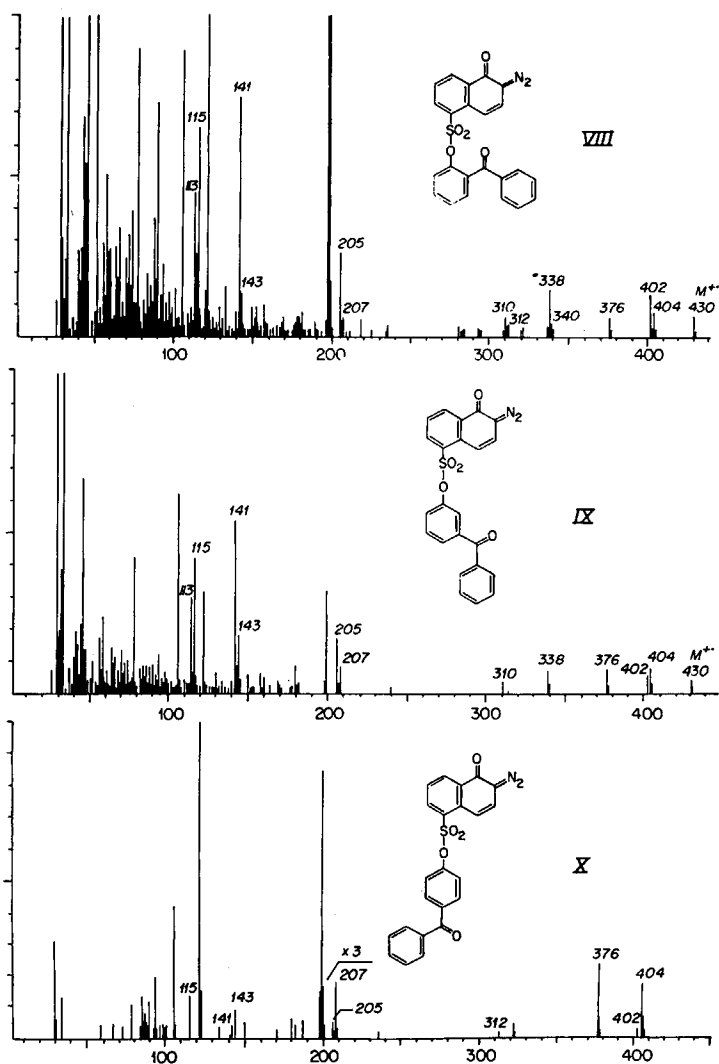Fig. 4.   Electron-impact mass spectra of compounds V–VII.

Fig. 5. Electron-impact mass spectra of compounds VIII–X.

The EI mass spectra of the 4-positional isomers are presented in Figure 4 and those of the 5-positional isomers in Figure 5. As expected, in all six spectra fragments arising from retention of the charge with the benzophenone moiety predominate, and this is reflected in the peaks at m/z 198, 121, 105, 93, and 77. A metastable peak, corresponding to the transition 430 (M$^{+\cdot}$) → 198 in several of the spectra, suggests that the formation of hydroxybenzophenone and the subsequent fragments is, at least in part, ionically rather than thermally induced. Moreover it is interesting to note that generally, on a relative basis, the benzophenone fragments are significantly more prominent in the spectra of the 4- as opposed to the 5-positional isomers. The same trend

m/z 198   m/z 121   m/z 105   m/z 93   m/z 77
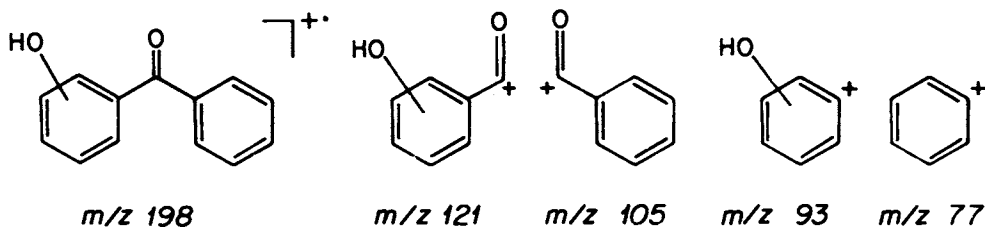
was also apparent in the spectra of the phenol esters (See, the higher relative intensity of m/z 94 in the spectrum of the 4-phenol ester by comparison to the 5-phenol ester in Figure 3). It is assumed that the mechanism of this fragmentation involves a six-membered ring hydrogen transfer as shown previously in Scheme 3, and that this trend probably reflects a higher lability of the 5- as opposed to the 4-hydrogen.

A further interesting variation exists among the *ortho*, *meta*, and *para* isomers of benzophenone. This is best illustrated in the comparison of the isomeric 5-sulfonates in Figure 5. It is noted that the driving force for transfer of a hydrogen to form the corresponding hydroxybenzophenone ion is highest in the *ortho* and *para* isomers. Since the benzophenone group is electron withdrawing, it may be reasoned that in the *ortho* and *para* isomers the resulting resonance produces a positive charge adjacent to the ester oxygen and facilitates the subsequent hydrogen radical abstraction and $S=O$ bond cleavage.

Of particular interest for this study is the behavior of the diazoketo function upon electron impact ionization. Ions associated with the fragmentation of this group are generally masked by the high abundance of the benzophenone-related ions. Nevertheless, the high sensitivity and dynamic range of the mass spectrometer provide signals of sufficient intensity to permit a reasonably detailed evaluation of the behavior of this group.

The mass spectra of the three isomeric 4-benzophenone esters, V–VII (Fig. 4) exhibit well defined molecular ion peaks at m/z 430. The competition between loss of N_2 and "loss" of 26 U from $M^{+\cdot}$ is apparent from the peaks at m/z 402 and 404, respectively. In fact, the m/z 404, $[M-26]^{+\cdot}$ ion, is considerably more prominent in the *meta* and *para* as opposed to the *ortho* isomer. Consistent with the behavior of the phenol esters, it is interesting to note the various fragments derived from each pathway. For example, loss of N_2 initiates a pathway leading to the series of m/z 338, m/z 310, m/z 205, m/z 141, and m/z 113 (Scheme 5). The alternative pathway initiated by the loss of 26 U gives rise to the series of m/z 340, m/z 312, m/z 207, m/z 143, and m/z 115 (Scheme 6). Plausible ion structures for all these fragments are indicated in the schemes. The increased preference for the second pathway in the *para* and *meta* benzophenones indicates a strong influence of the ester group on the fragmentation of the diazoketo function. It appears that this may be due to progressively decreasing steric effects in the sequence from *ortho*- to *meta*- to *para*-benzophenone isomerism. Such patterns can, of course, be utilized for the structural characterization of related unknown compounds.

The competition between loss of 28 amu (N_2) and 26 amu ($-N_2 + H_2$) from $M^{+\cdot}$ which characterized the 4-positional isomers is also apparent in the
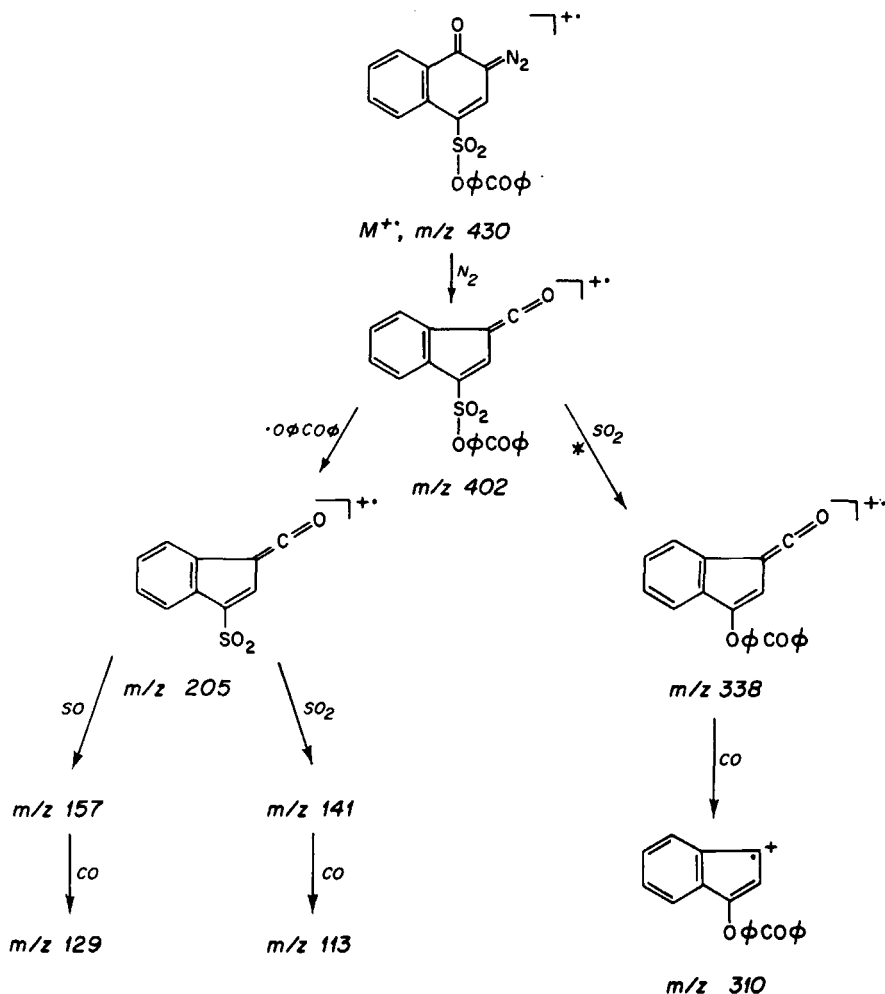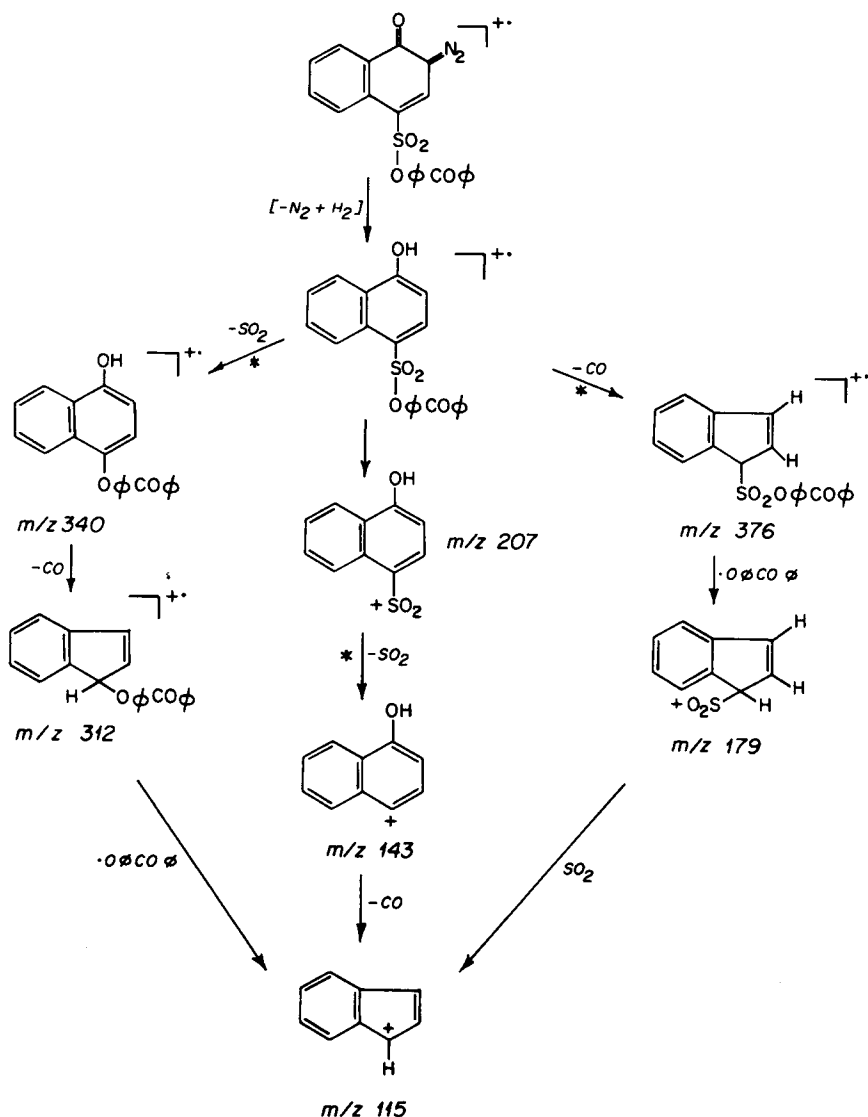
Scheme 5.   Fragmentation sequence of benzophenone esters initiated by loss of N_2.

5-benzophenone esters (VIII–X). The preference for loss of 26 U rather than 28 U and the related series of ions increases again in the sequence from *ortho-*, *meta-*, *para*-benzophenone. Plausible ion structures and the pathways associated with the respective fragmentations in the esters of hydroxybenzophenone are given in Scheme 5 for the $[M\text{-}N_2]^{+\cdot}$ series and Scheme 6 for the $[M\text{-}N_2 + H_2]^{+\cdot}$ series.

Chemical Ionization Mass Spectrometry

Chemical ionization mass spectra of the target compounds were obtained using methane as reagent gas. As representative examples, the positive ion CI spectra of the phenol ester IV and the hydroxybenzophenone ester VIII are shown in Figure 6. As expected, in each case the base peak in the spectrum arises from retention of the charge with the aromatic ester functions to yield a protonated phenol ion (m/z 95) and a protonated hydroxybenzophenone (m/z

Scheme 6. Fragmentation sequence of benzophenone esters initiated from the [M-26]$^{+\cdot}$ ion.

199), respectively. Adduct ions at m/z 227 $[M + C_2H_5]^+$, and m/z 239 $[M + 41]^+$, are also present.

Protonated molecular ion peaks of relatively low intensity were observed in the spectra of both compounds (m/z 327 in IV and m/z 431 in VII). In neither case, however, was there any significant loss of N_2 observed from $[M + H]^+$. Instead the loss of 26 U appeared to be the preferred fragmentation route of the protonated molecular ions. This is evident from the peaks at m/z 301 and m/z 405 in the spectra of IV and VII, respectively. This was followed by a further elimination of CO to give, in each case, the corresponding peaks at m/z 273 and 377. It thus appears that under the conditions
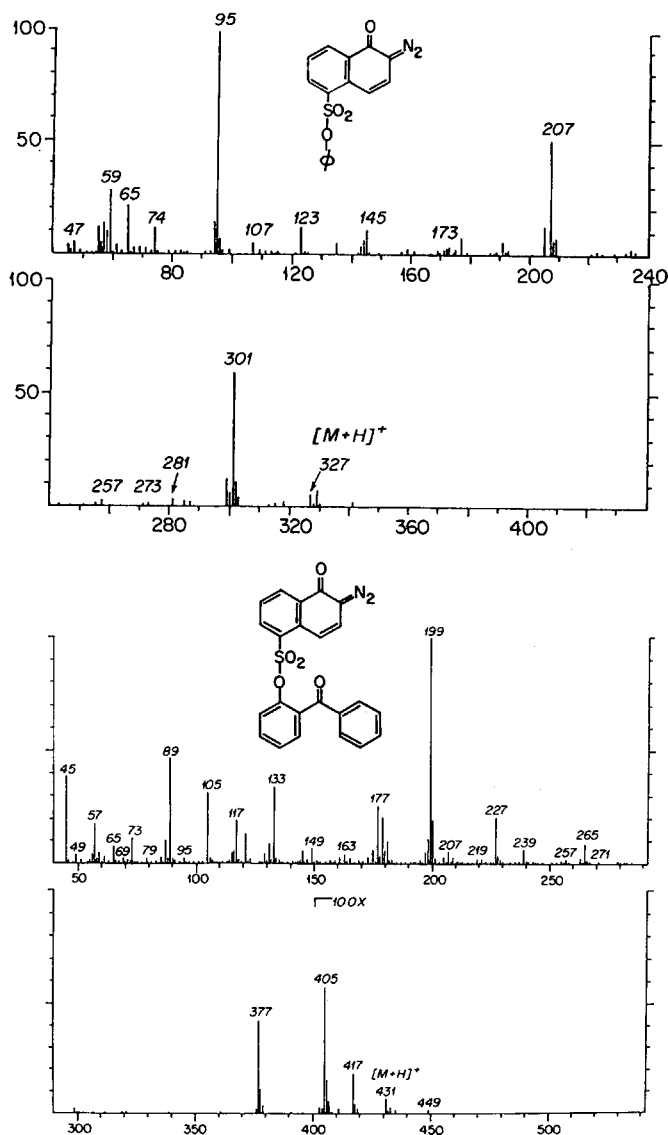
Fig. 6. Chemical ionization (CH$_4$) mass spectra of compound IV (top) and compound VIII (bottom).

prevailing in chemical ionization MS, i.e., a proton-rich environment, the *a priori* unexpected loss of 26 U effectively suppresses the elimination of N$_2$.

In the context of the discussion of the chemical ionization spectra of the compounds, it is interesting to comment on the differences between the positive and negative ion CI spectra of compound IV. The negative ion CI spectrum of IV contains the following major peaks:

$$m/z\ 298\ (40\%);\ [M\text{-}N_2]^-$$

$$m/z\ 207\ (100\%);\ [M\text{-}N_2 + H_2\text{-}\varnothing O^{\bullet}]^-$$

$$m/z\ 206\ (75\%);\ [M\text{-}N_2\text{-}SO_2\text{-}CO]^-$$
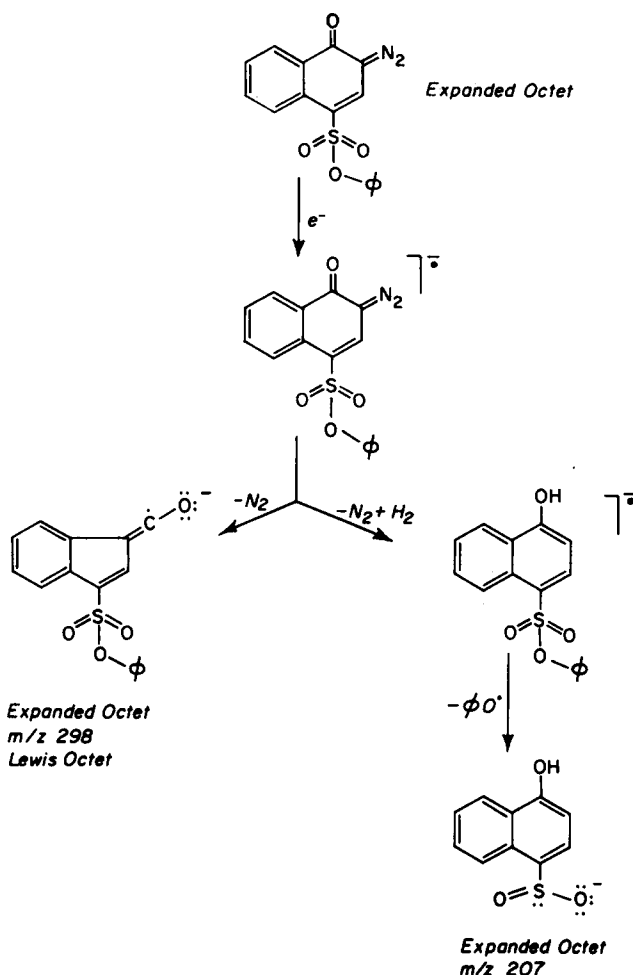
Scheme 7.   Fragmentation of compound IV under negative ion CI conditions.

Clearly, the molecular anion is not sufficiently stable and prefers to decompose by loss of N_2 rather than give an [M-26]$^-$ ion. However, the competing process generated from the [M-N_2 + H_2]$^-$ anion is obviously still functioning judging from the intense anion of m/z 207, typical of the [M-26] series (see, e.g., Scheme 4). It can be rationalized that, both the molecular anion, M$^-$, and the [M-26]$^-$ ion are electronically unstable. Consequently, as shown in Scheme 7, they both prefer to decompose to anions with a stable electronic structure possessing either a Lewis octet or an expanded octet for the sulfur atom.

DISCUSSION

In reviewing the mass spectrometric behavior of the diazoketo function in 2-diazonaphthalenones, two major processes are apparent. First, the observed elimination of N_2 from the molecular ion follows a pattern similar to that observed under photoirradiation. Formation of an indenoketene is thus a logical explanation and this is followed by a series of related fragment ions as indicated in Schemes 2–7. The second major process, formation of [M-26]$^{+\cdot}$,

which appears to occur in competition with the loss of N_2, is rather unusual and *a priori* surprising. As indicated above, the $[M-26]^{+\bullet}$ ion corresponds to loss of N_2 and addition of two H's according to high resolution mass measurements. Clearly then this ion and the subsequent series of fragments is also initiated by the loss of N_2. Therefore, the question which needs to be addressed is the origin of the hydrogen atoms which would also provide some clues regarding the mechanism of the process.

Since the electron impact ionization process is conducted at low ion source pressure, it is unlikely that incorporation of the hydrogen atoms into the $[M-N_2]$ species occurs as a result of a vapor phase bimolecular collision. Instead, a possible alternative is the surface of the glass tip of the MS direct insertion probe. In order to confirm this hypothesis, a series of experiments was conducted with several representative compounds in which the probe tip surfaces were saturated with deuterium atoms. In the initial experiments, ^2H_2O was used to saturate the hydrogen active sites of the tip surface. Indeed, a shift of the $[M-26]^{+\bullet}$ ion to $[M-25]^{+\bullet}$ and $[M-24]^{+\bullet}$ was observed corresponding to ions of $[M-N_2 + H^2H]^{+\bullet}$ and $[M-N^2 + H_2]^{+\bullet}$, respectively.

Significantly, in all cases examined, no deuterium incorporation was found in the molecular ion or the $[M-N_2]^{+\bullet}$ ion. This indicates that the latter ions
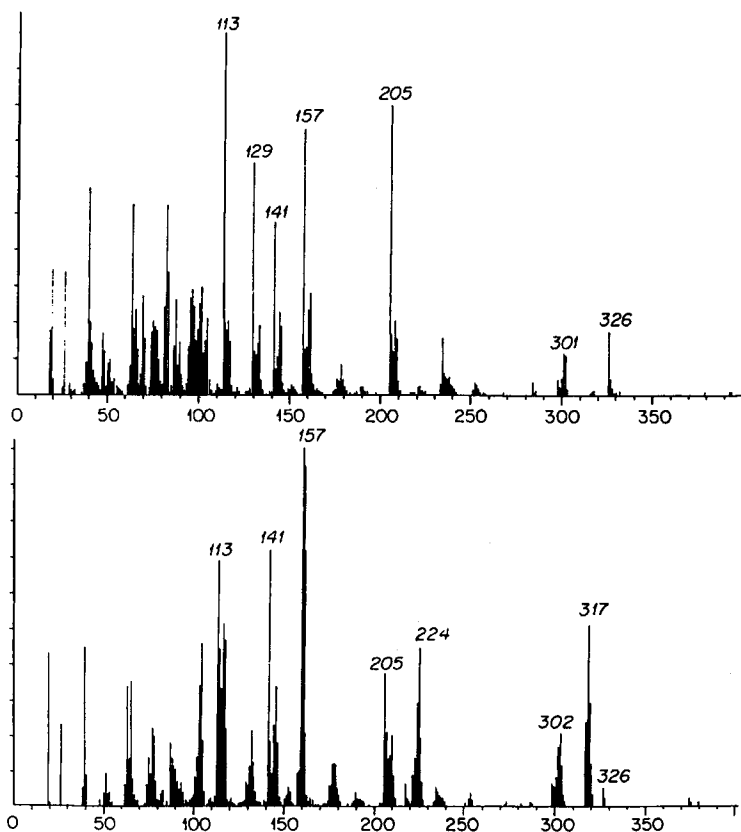

Fig. 7.   Electron-impact mass spcetra of compounds III and IV following isotope exchange on a ^2H_2O (top) and a ^2H_2O, $^2H_2PO_4$-treated surface (bottom).

were formed either after they were vaporized and before they could undergo any surface reaction, or upon fragmentation of the respective molecular ions. Because of the low yield in deuterium isotope incorporation, the experiments were repeated using a mixture of ^2H_2O and $^2H_2PO_4^-$ to coat the surface. While the presence of an acidic medium appeared to induce some additional reactions associated with the ketene intermediate, the deuterium incorporation was significant and, despite poor reproducibility in isotope yield, provided unequivocal evidence for the occurrence of a surface-related process.

Figure 7 shows the mass spectra of the 4-sulfonylphenol ester of 2-diazonaphthalenone III obtained from a probe tip whose surface had been treated with a mixture of ^2H_2O (top) and a ^2H_2O solution of $^2H_2PO_4^-$. The top spectrum shows a well defined molecular ion peak at m/z 326. Loss of N_2 is responsible for the peak at m/z 298 while the m/z 300 ion has been shifted from m/z 300 to m/z 301 and 302. The latter peaks correspond to [M-N_2 + H^{2}H]$^{+\cdot}$ and [M-N_2 + $^2H_2$]$^{+\cdot}$, respectively. It is interesting to point out that the series of fragment ions related to the [M-N_2]$^{+\cdot}$ process (m/z 205, m/z 157, m/z 141, m/z 113) retain the original mass values. Deuterium isotope incorporation is evident, however, for the ions associated with the [M-26]$^{+\cdot}$ process. Note, for example, the partial shifts of m/z 207, 159, 143, and 115. This is consistent with the structural assignment for the various ions in Scheme 4. Similar results were generally obtained when the same isotope exchange experiment was conducted with a solution of $^2H_2PO_4^-$ in ^2H_2O. A notable exception as shown in the bottom spectrum of Figure 7 is the presence of the clusters of peaks around m/z 317, 224, and 159. The ion cluster at m/z 317 corresponds to a mixture of unlabeled and mono- and di-deuterated acid derivatives of indenoketene with structure *a*. Sequential loss of phenoxide and sulfur dioxide radicals from ion *a* is responsible for the clusters about m/z 224 and 160. The presence of the 3-indene carboxylic acid is consistent with the previously proposed formation of a methyl ether derivative of the acid when 2-diazonaphthalenones were irradiated in the presence of methanol.[6]
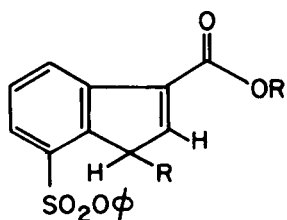
where R = H and/or ^{2}H
[R = H ; m/z 316]

(*a*)

Three of the benzophenone sulfonate esters were also analyzed by electron impact mass spectrometry using probe tips whose surfaces had been treated with a $^2H_2O/^2H_2PO_4^-$ solution. In general, the results were very similar to those observed with the phenol esters.

As a final example we also examined the mass spectrum of 2-diazonaphthalenone-5-sulfonyl chloride (II). In this experiment, the probe-tip surface was only treated with ^2H_2O without the acid in order to minimize the
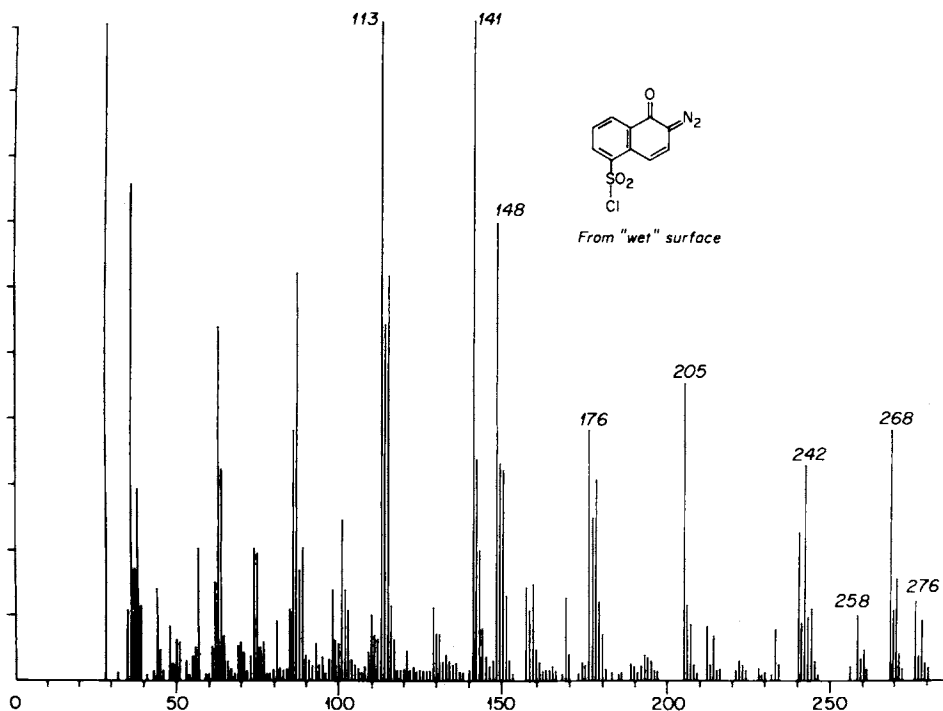
Fig. 8. Electron-impact mass spectrum of compound IV vaporized from a probe tip surface treated with ^2H_2O.

likelihood of hydrolysis of the sulfonyl chloride. In examining the spectrum obtained (Fig. 8) it should be recalled that, under "normal" spectral acquisition conditions, this compound showed no propensity for loss of 26 U from $M^{+\cdot}$. Instead, loss of N_2 was the prevailing process. Distinct features of the spectrum of Figure 8 are the intense molecular ion peak at m/z 268 and the peaks at 276, 258, and 242 whereas, in general, the rest of the spectral pattern is similar to that of Figure 2. The ion of m/z 276 contains two chlorine atoms and, on the basis of the previous examples, it can be assigned the structure of an indene acid chloride, b. The ion of m/z 258 corresponds to the indenoic acid, c, while that of m/z 242 may be assigned the phenol structure d. The origin of the latter is not certain, but it is possible that if reflects the incorporation of two hydrogen atoms into the $[M\text{-}28]^{+\cdot}$ species of m/z 240. If that is the case, the inference may be made again that in the presence of moisture—or a hydrogen-donating medium—formation of the ketene system can be suppressed in favor of an aromatic system of structure, d. It may seem surprising that no deuterium incorporation is evident here to shift the $[M\text{-}26]^{+\cdot}$ (m/z 242) ion to higher values as shown in Figure 7 for the phenol esters. It should be pointed out, however, that the isotope yield in experiments which relied on the use of pure ^2H_2O has been relatively poor due to facile back exchange. Moreover, it should be noted that none of the other ions in the spectrum of Figure 8 show any appreciable deuterium incorporation.

Further supporting evidence to the effect that the $[M\text{-}N_2 + H_2]^{+\cdot}$ ion was formed as a result of a surface reaction was provided by linked scan experiments using a VG70-250SE double focussing mass spectrometer. Linked scans

in the E/B mode confirmed that the ions of $[M-N_2]^{+\cdot}$ series, indeed, related to $M^{+\cdot}$ via ionically induced decompositions. No such relationship was found between $M^{+\cdot}$ and the $[M-N_2 + H_2]^{+\cdot}$ ions under the latter experimental conditions.

(b) [276]   (c) [258]   (d) [242]
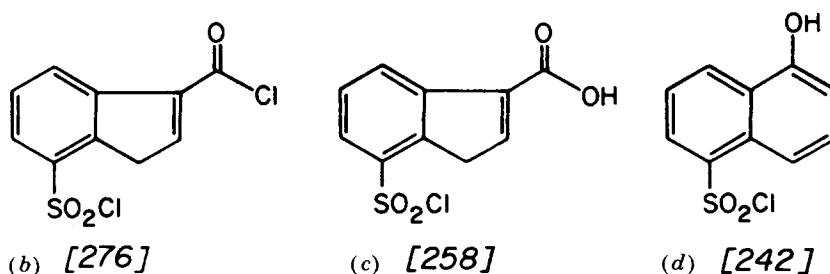
The results from the surface labeling and the linked scan experiments provide convincing evidence that the formation of the $[M-26]^{+\cdot}$ ion observed during EI ionization does, indeed, originate from hydrogen incorporation following release of N_2. There are two basic courses for the elimination of molecular nitrogen from the parent molecule during electron-impact mass spectrometry. First, $[M-N_2]^{+\cdot}$ fragment ions may be formed from the EI ionization and fragmentation of vaporized 2-diazoketonaphthalenone esters. An indenoketene ion structure may be assigned to these ions. Alternatively, loss of N_2 may also be induced during the thermal vaporization process which will bring a neutral indoketene into the MS ion source for ionization by electron impact. It is probably during this thermal degradation step that the $[M-N_2]$ species becomes hydrogenated by interaction with hydrogens from the probe tip surface. We speculate that the thermal decomposition may proceed via a carbene intermediate, similar to the photoinduced decomposition of 2-diazonaphthalenones.[6] Hydrogenation of the carbene would lead to the naphthol structure by rearrangement of the β-ene-ketone as shown in Scheme 8. The process is obviously further enhanced under chemical ionization conditions where there is an environment rich in protons.
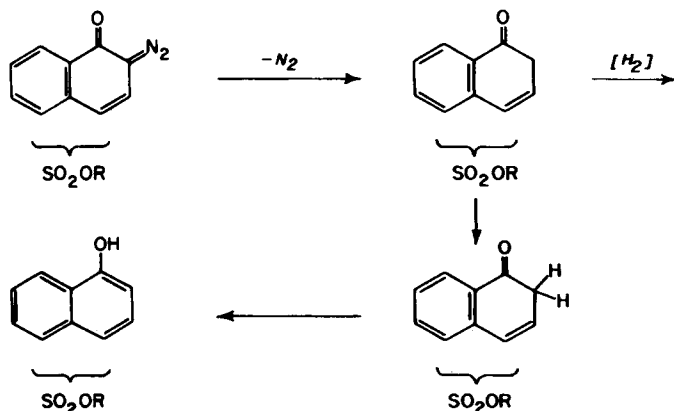
Scheme 8. Proposed mechanism for the formation of the [M-26] species in the mass spectrometric analysis of 2-diazonaphthalenones.

Further indication of the strong propensity of the [M-N$_2$] species to incorporate hydrogen atoms was demonstrated in a preliminary examination of the spectra produced by fast atom bombardment (FAB) ionization. When benzophenone esters of the type V–X were dispersed in a glycerol medium, ions corresponding to the loss of N$_2$ plus incorporation of two H's dominated the spectra instead of the Wolff rearrangement species. There results clearly indicate that the use of a hydrogen-rich matrix promotes the formation of a phenol and suppresses the formation of a ketene. Further work under varying FAB conditions is currently in progress.

In the context of these observations it would be interesting to speculate on the potential implications of the results to the use of the diazonaphthalenones as photoresist sensitizers. As indicated above, their use in polymer thin films, relies on the production of a ketene intermediate. The efficiency of the process will increase with an improved yield of this reactive species, but the cross-linking and further reaction will be effectively halted if this hydrogen-deficient intermediate can be hydrogenated to yield a naphthol product. In a recent report, Pacansky and Waltman,[7] have shown that the electron beam sensitivity of a photoresist component is dependent on its concentration in a mixture. Our results suggest that it may also be dependent on the hydrogen donating capabilities of the medium.

CONCLUSIONS

In summary, the following conclusions may be drawn from the mass spectrometric data discussed above:

1. There is a close analogy between the electron impact-induced and the photoinduced decomposition of the naphthoquinone diazides in terms of their tendency to eliminate N$_2$ and produce a ketene species.
2. The position of substitution on the naphthalene ring strongly influences the fragmentation of the system resulting in well-defined quantitative differences in the mass spectra of positional isomers. Steric and/or electronic effects transmitted through the ring system probably play a role to that effect.
3. Sulfonic acid esters (phenyl or hydroxybenzophenone) exhibit a competing loss of 26 U from the molecular ion resulting from incorporation of two hydrogen atoms into the [M-N$_2$] species. This process is initiated on the surface of the direct insertion probe and competes effectively with the loss of N$_2$, each cleavage yielding a specific sequence of fragment ions.
4. A hydrogen-rich environment (e.g., CI conditions) appears to suppress the formation of a ketene [M-N$_2$] species in favor of the competing [M-N$_2$ + H$_2$] moiety.
5. It could be inferred from these results that the efficiency of the photoresist process may be affected by the hydrogen-donating ability of the medium in which it is formulated.

Given these considerations; it is our intent to examine further the possibility of using mass spectrometry as a screening method to predict the value of and effectiveness of 2-naphthalenone diazides for electron-beam or photoex-

posure processes. Current studies are focussing on further examination of surface-related phenomena and exploration of surface ionization methods (e.g., fast atom bombardment) using matrices typical of those employed in lithographic processes. Thus it might be possible to establish more direct evidence regarding the types of intermediates which are formed by particle bombardment and the role of the resin matrix toward enhancing (or quenching) the generation of species which promote the desired photoresist performance.

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