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MOLECULAR ORBITAL APPROACHES TO THE INTERPRETATION OF ORGANIC MASS SPECTRA

THE MASS SPECTRA OF MESOIONIC COMPOUNDS

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Abstract—High and low resolution mass spectral data are presented for a series of seven ψ-1,3,4-thiadiazole-2-thiones; seven other mesoionic heterocycles and two nonmesoionic analogs of the ψ-1,3,4-thiadiazole-2-thione ring system. The fragmentation pathways for the mesoionic systems and the marked differences with the non-mesoionic analogs can be easily rationalized by application of MO theory. In its present form, this MO interpretation is an extension of the usual resonance approach to the explanation of mass spectral reactions, which has been successfully applied to other heterocycles.

THE electron impact-induced fragmentation of 5-membered heterocycles is usually dominated by cleavage into 2 and 3 (ring) atom fragments.[1] The specific fragmentation patterns can generally be rationalized by examining the location of the double bonds in the lowest energy resonance form of the ring, and qualitatively considering the enthalpies of formation for possible ions and neutrals. The characteristic feature of mesoionic compounds[2–6] is that they contain a 5-membered aromatic heterocyclic ring which cannot be represented by a single unchanged covalent structure. The interpretation of the mass spectra of these compounds is thus considerably complicated. The reported studies of the mass spectra of sydnones[7] and 1,3,4-oxadiazole-thiones[8] did not employ the usual ground state "bond order" arguments[9] for interpretation of the spectra simply because qualitative ground state π-bond orders are not available by inspection of the canonical forms of mesoionic structures.

We have calculated the π-electron bond orders of representative mesoionic systems using ω-iterated Hückel MO theory[10] with the parameters that were developed by Kier and Roche.[11] At the outset these bond orders can be used as a qualitative guide to possible fragmentation patterns in direct analogy to the usual resonance procedure.[9] Bond order data can also be used in sophisticated MO analysis of mass spectral fragmentation. If the reactive electronic states can be determined either by reference to metastable ions[12] or some other criterion, ground state bond order (π and σ) can be applied directly to the prediction of relative rates for simple cleavage reactions. The result of this approach would be a MO simplification of the formalism of quasi-equilibrium theory,[13] if one were willing to assume that differences in activation energy would dominate the relative rates. This general approach did not give a satisfying rationalization for the mass spectral fragmentation of the tolunitriles.[14] In this case, no attempt was made to analyze the reactive electronic states. Furthermore,

rearrangement prior to cleavage, which is probably important in the tolunitriles, was not considered.

In order to apply bond order arguments with semi-quantitative confidence to the prediction of mass spectral fragmentation, the quantitative relevance of bond orders to activation energies and frequency factors must be established. In the present instance, the frequency factors for ring cleavage should be similar, since roughly the same amount of transition state organization would be required in each case. Within the usual σ-π approximation the π bond orders should be the determining factor in the differences in enthalpies of bond cleavage. The enthalpies of bond cleavage should be linearly related to the "activation energies," ε, for the mass spectral reactions if the effects of reverse activation energies can be neglected. In the present case, the reverse activation energies are quite small ($\leqslant$0·1 ev) as shown by the widths of the metastable probes for the processes in question. The total energy, E, oscillator frequency factors, ν, and effective number of oscillators, n-1 in the classical rate expression,[13] should be virtually constant for a series of ring cleavage reactions. It should be possible to "calculate" fragmentation patterns for a series of similar compounds using the classical rate expression with suitable

$$\log k = (n\text{-}1) \log \frac{E\text{-}\varepsilon}{E} + \log \nu$$

approximations for E and n-1, and relative values of ε obtained from bond order calculations.

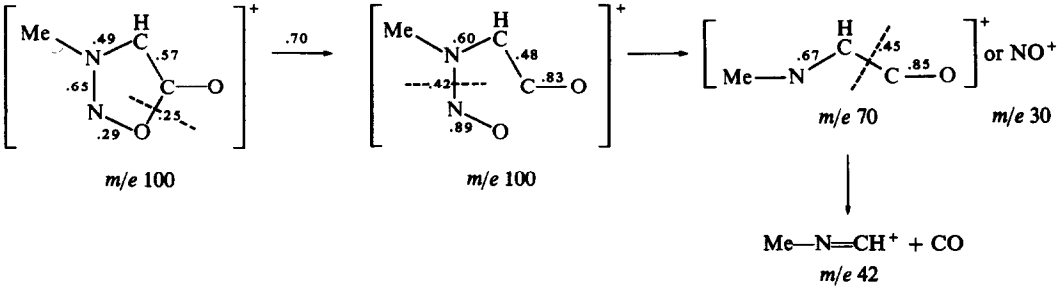


FIG. 1 Bond order based interpretation of the fragmentation of methyl sydnone (1)

This level of sophistication is, however, not required for a general organic chemical approach to the interpretation of mass spectra. Bond orders can be used in place of valence bond diagrams for reactants, and product stabilities estimated by the usual arguments from bond energy and intuition. Figs 1 and 2 indicate calculated bond orders and anticipated fragmentation pathways for a representative sydnone and isosydnone. The 70 ev mass spectra of these molecules are indicated in Figs 3 and 5.

The 70 ev mass spectrum of methyl sydnone had intense ions that corresponded to M^+, $(M—No)^+$ and $(M—NO—CO)^+$. The only significant fragmentation at 10 ev was $(M—NO)^+NO)^+$, furthermore, this fragmentation is the only one for which an intense normal metastable ion was observed. These facts suggest that the M—NO cleavage was a ground state process[12] in the molecule ion, and it should be explicable by the bond order arguments we have given above, (Fig. 1). The structure of the *m/e* 70 ion is, however, indeterminant. If an open chain or relaxed cyclic structure is selected for the

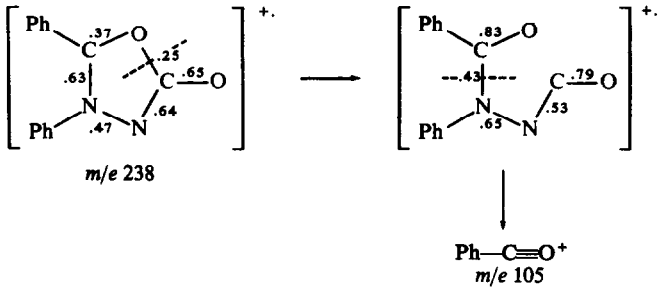


FIG. 2 Bond order based interpretation of the fragmentation of diphenyl isosydnone (3).

m/e 70 ion, the ground state bond orders correlate well with the postulated fragmentation. The fact that ring substituents perturb activation energies and the product stabilities sufficiently to alter the apparent ring fragmentation is clear from the spectrum of 3-phenyl sydnone (2, Fig. 4) and other substituted sydnones.[7] The ion, whose elemental composition corresponds to that of a protonated benzoisonitrile

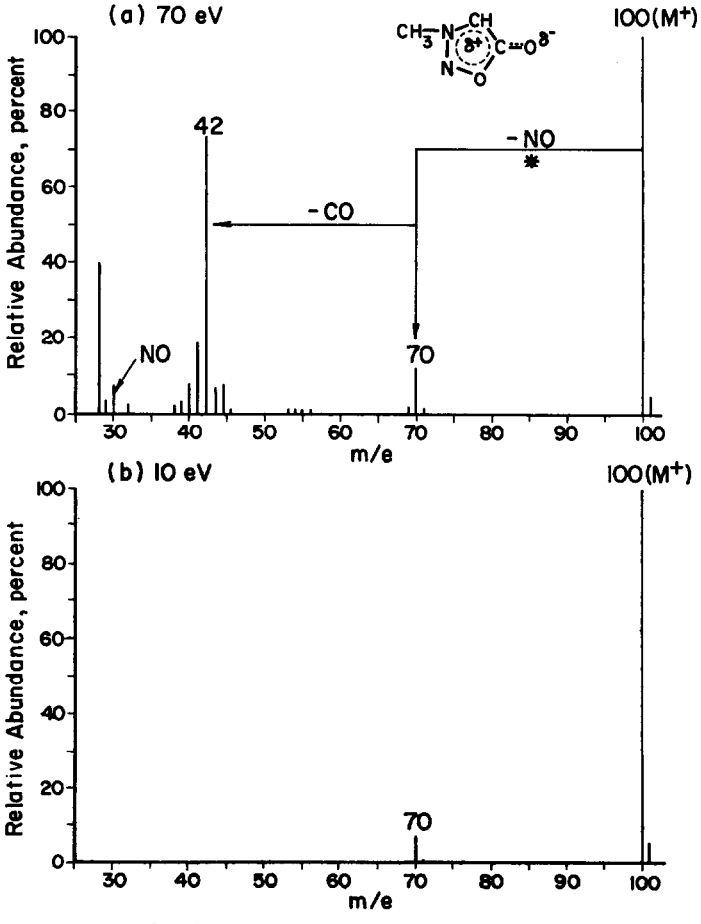


FIG. 3 Mass spectra of methyl sydnone (1).

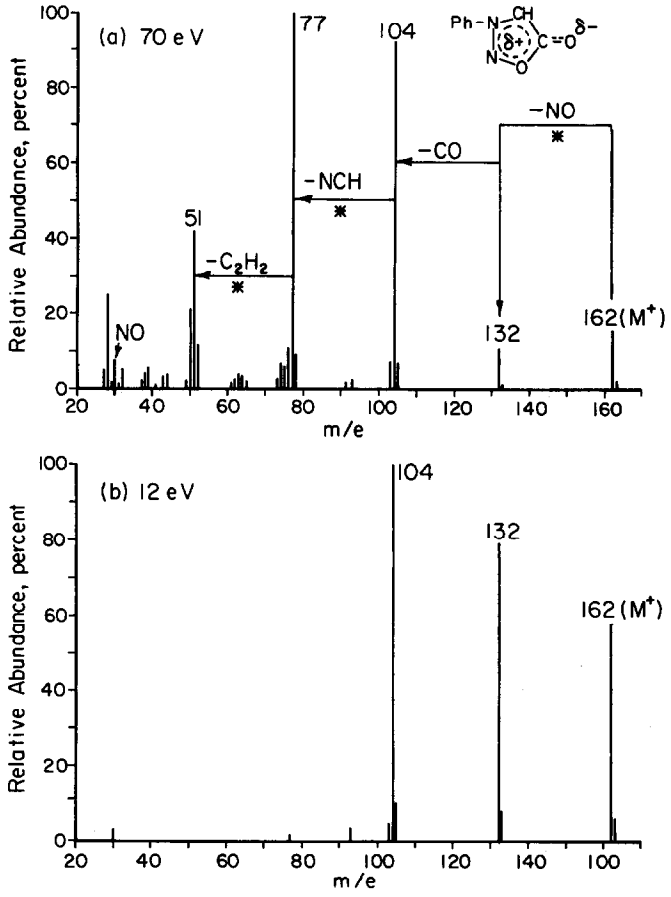


FIG. 4 Mass spectra of phenyl sydnone (2).

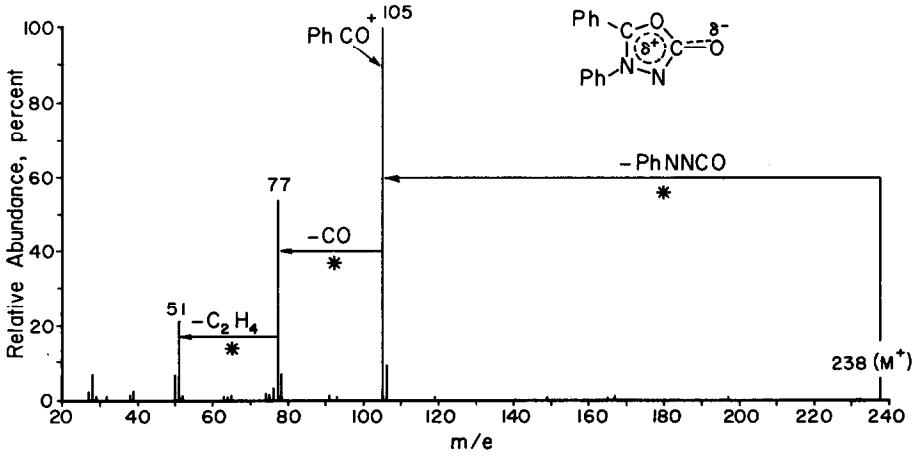
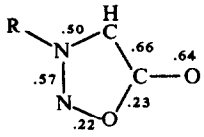


FIG. 5 Mass spectrum of 4,5-diphenyl isosydnone (3).

(*m/e* 104), should be considerably more stable and charge delocalized than its Me analogue. It is not surprising that this ion dominated the fragmentation pattern of **2** even at relatively low voltages (Fig. 4 [B]). It is possible that *m/e* 104 is formed from two (distinct) states of the molecule ion, one of which decomposes directly to *m/e* 104 in a one step process and one which decomposes through the intermediate *m/e* 132. This scheme would be consistent with the observed voltage dependence of the spectrum if the sum of the activation energies for the stepwise pathway was higher than that for the concerted path. A detailed study of the kinetic energy distribution of the fragmentations could resolve this question.

The availability of qualitative data on the products of pyrolysis of **2** at low pressure ($200°/10^{-6}$torr)[7] provides an interesting test for the viability of this general approach[12] when applied to mass spectral and thermal reactivity of the same compound. The high mol. wt. products of low pressure pyrolysis appeared to be M—CO; M—CO_2 and Ph—N=C. These results are substantially different from those of the "ground state" mass spectral cleavages. Examination of the bond orders in the neutral sydnone, and



the relative product stabilities for successive cleavages provides an easy and reasonable explanation for the observed differences. In the thermal reaction the rate differences for cleavage of the 1,5 or the 1,2 bond should be smaller than in the ionic reactions. Once either bond is cleaved, the subsequent cleavages will give the most stable neutrals, respectively CO, M—CO or CO_2, M—CO_2. In the mass spectral reaction cleavage of the 1,5 bond is expected to be followed by loss of NO both from analysis of bond orders (Fig. 1) and the observation that loss of NO leaves an even electron, resonance stabilized ion.

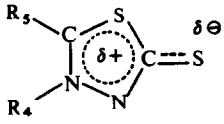
The obvious differences between the mass spectra of the sydnones and that of diphenyl isosydnone (**3**, Fig. 5) are easily rationalized by these elementary MO arguments. The dominant ring cleavage in **3** shows a strong metastable ion and thus, should be a ground state process in the doublet molecule ion.[12] The ground state bond orders in the ion (Fig. 2) suggest that the 1,5 bond should again be the first to cleave. The subsequent formation of Ph—CO^+ is suggested by bond order arguments and the fact that the benzoyl cation is a highly delocalized even electron ion.

It should be clear at this point that the mass spectral rationalizations, based on bond order arguments, are entirely analogous to the usual resonance descriptions.[9] In the preceding example, it is possible that both bonds are broken simultaneously, or that a very loose complex is involved in a virtually simultaneous bond breaking. The theory will not decide these questions; however, it does provide a reasonable guide to the experimentally available data, namely, the art fragmentation patterns.

The general fragmentation scheme for derivatives of thiophene, pyrrole and furan are reasonably similar[9] as one would expect if the general resonance approach to the interpretation of fragmentation were valid. In mass spectral fragmentation, as in general organic reactions, the perturbation introduced by changing the electronegativity, etc. of the heteroatom is small when compared to the total energy of the

π-electronic structure.[15] This means that the bond order calculations and the arguments developed for the sydnones and isosydnones should be valid (to the present levels of approximation) for the sulfur analogs of these compounds.

TABLE 1. STRUCTURES OF ψ-1,3,4-THIADIAZOLES



No	R_4	R_5	No	R_4	R_5
4	C_6H_5—	—C_6H_5	**8**	C_6H_5—	C_2H_5—
5	C_6H_5—	—*P*Cl—C_6H_4—	**9**	CH_3—	CH_3—
6	C_6H_5—	—H	**10**	CH_3—	C_2H_5—
7	C_6H_5—	—CH_3—			

Table 1 indicates the structures of the ψ-1,3,4-thiadiazoles for which mass spectral data have been obtained. The reasonably wide variety of substituents and substitution patterns on the ring presents the possibility of critically examining the fragmentation of these molecules. The effects of substituents on the relative abundance of ions, which arise by the path suggested above as well as the rearrangement processes which occur in the mass spectra of these molecules, are of particular interest. Unit-resolution plots along with pertinent high resolution and metastable ion data for most of these compounds appear in Figs 6–11. For all cases in which the daughter $R_5C = S^+$ ion was more than one third the mass of the molecule ion (**4, 5, 9, 10**) there was a normal metastable ion which corresponded to the transition.

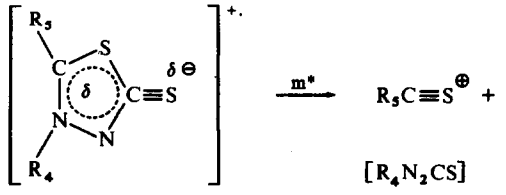


FIG. 2. RELATIVE ION INTENSITIES AS A FUNCTION OF STRUCTURE

Compound No.	$R_5CS^+/m+$	$R_4CS^+/m+$	$R_5S^+/m+$	$R_4S^+/m+$
4	2·6[a]	2·6[a]	0·32[a]	0·32[a]
5	3·6	0·003	0·047	0·31
6	0·33	0·032	0·084	0·39
7	1·3	0·003	0·019	0·28
8	1·3	0·0039	0·0043	0·14
9	0·52[a]	0·52[a]	0·025[a]	0·025[a]
10	1·1	0·019	0·0068	0·032

[a] R_4 and R_5 are identical in compounds **4** and **10**. The values in these cases represent the sum of R_4 and R_5 substituted ions.

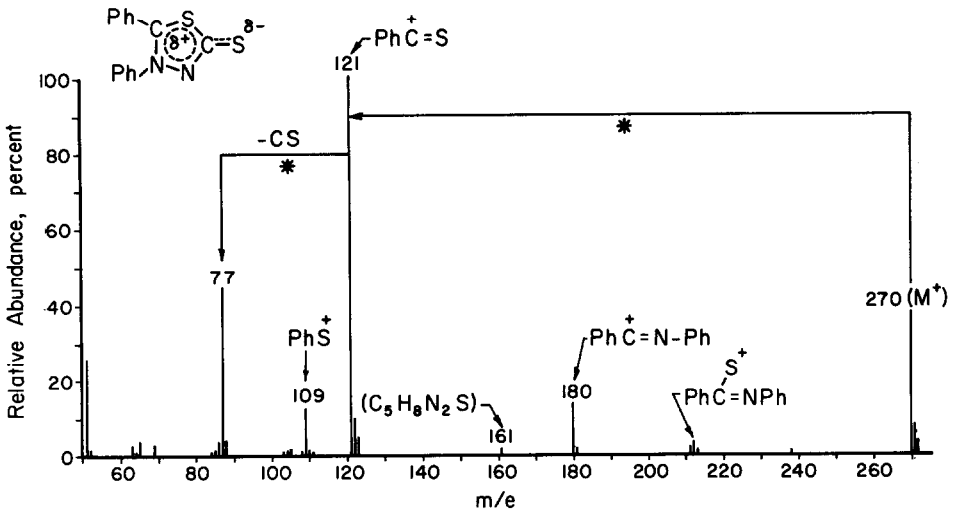


FIG. 6 Mass spectrum of 4,5-diphenyl-ψ-1,3,4-thiadiazole (4).

The substantial discrimination against metastable ions in which the daughter is a low mass fragment compared to the parent, no doubt accounts for the fact that normal metastable ions were not observed for **6**, **7**, and **8**. The effect of substituents on two groups of important cleavage and rearrangement lons in these compounds is indicated in Table 2.

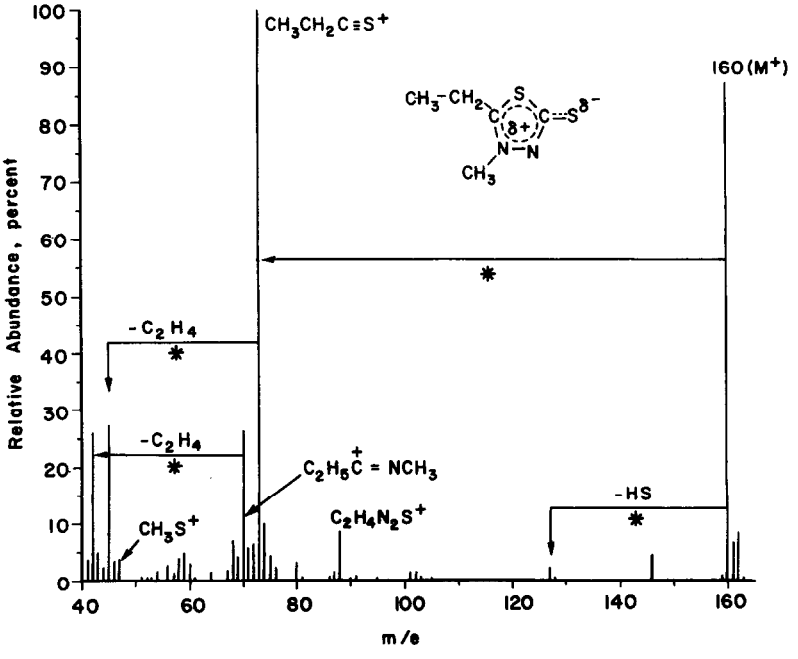


FIG. 7 Mass spectrum of 4-phenyl-ψ-1,3,4-thiadiazole (6).

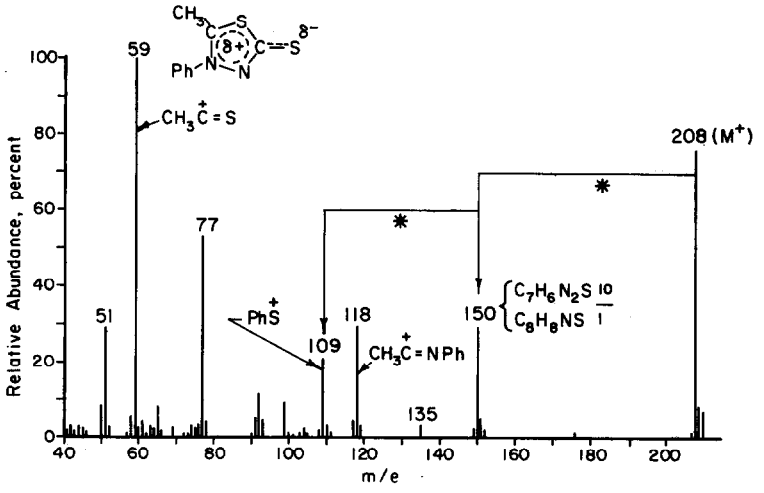


FIG. 8 Mass spectrum of 4-phenyl-5-methyl-ψ-1,3,4-thiadiazole (7).

The cleavage suggested by the ground state bond order analysis is one of the major processes in all of the compounds studied. In most cases, $R_5C{\equiv}S^{\oplus}$ is the most intense fragment ion in the 70 ev mass spectrum.

The rearrangement ion, whose mass corresponded to $R_4C{\equiv}S^{\oplus}$, appeared in all of the data-reduced high resolution spectra. In the absence of labeling or apparent metastable ions (either normal metastables or metastables that decomposed between the source and electric sector) there is some uncertainty about the origin of the CS

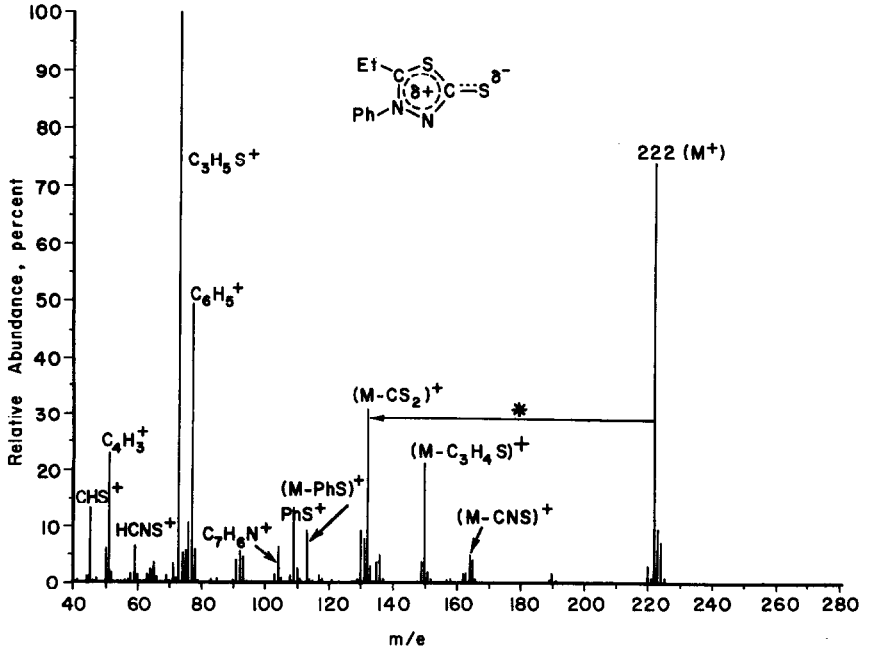


FIG. 9 Mass spectrum of 4-phenyl-ψ-1,3,4-thiadiazole (8).

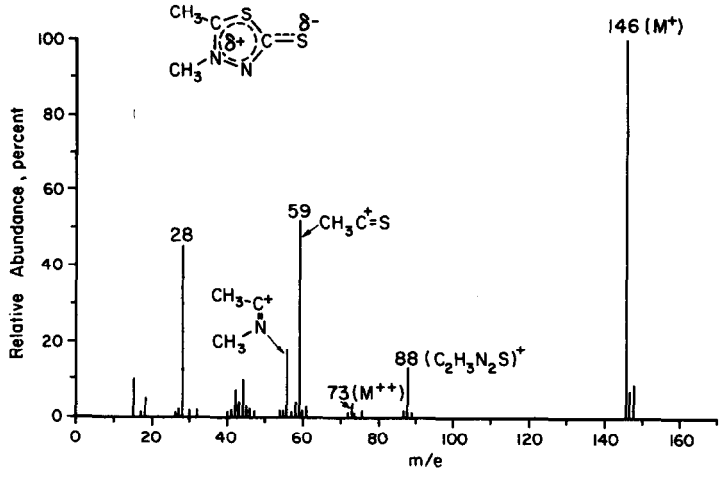


FIG. 10 Mass spectrum of 4,5-dimethyl-ψ-1,3,4-thiadiazole (9).

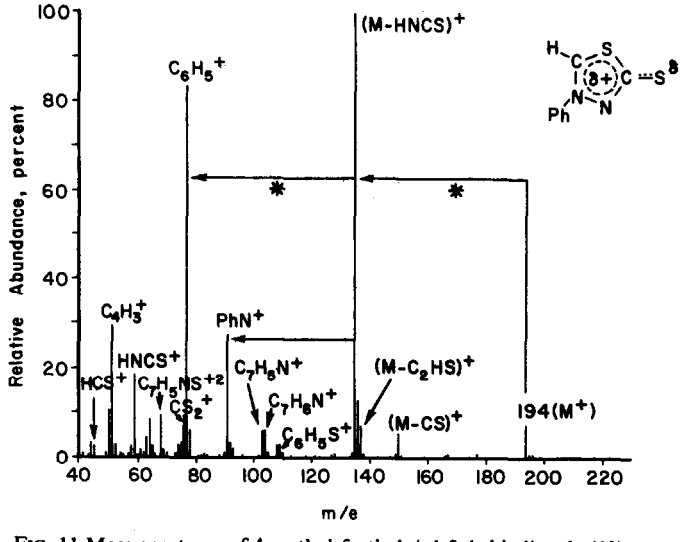
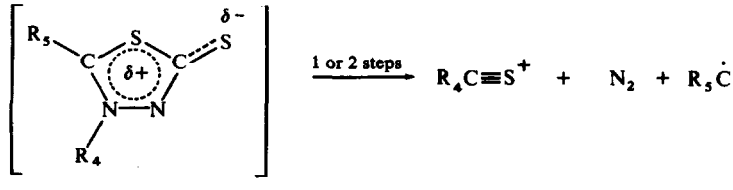


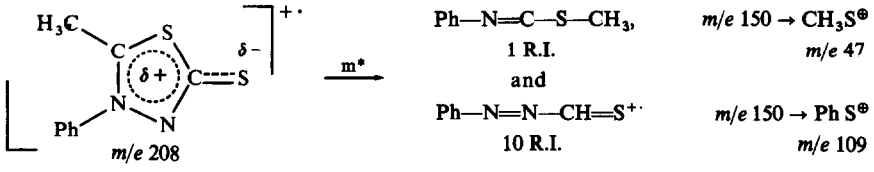
FIG. 11 Mass spectrum of 4-methyl-5-ethyl-ψ-1,3,4-thiadiazole (10).

portion of these fragments. It seems most likely on chemical grounds that the fragment arose by a 1-3 or 1-4 migration of R_4 to the thiocarbonyl in either the open chain molecule ion or a fragment.

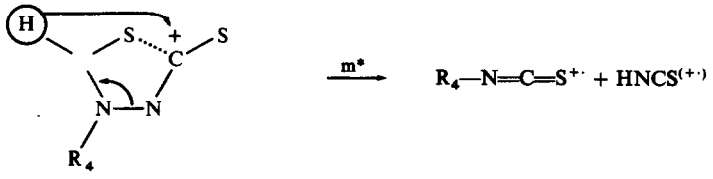


The definitive and consistent intensity pattern for the $R_5C{\equiv}S^{\oplus}$ and $R_4C{\equiv}S^{\oplus}$ ion throughout this series will allow for rapid structural assignments of isomeric compounds of this type. The absence of metastable ions for the formation of $R_4C{\equiv}S^{\oplus}$ indicates that this process either requires a large amount of energy[13] or an electronically excited state.[12]

Rearrangements in which $RS^{\oplus}$ are formed from molecules which do not contain an R—S bond are reasonably common.[16] In the present series, rearrangement ions for both $R_4S^{\oplus}$ and $R_5S^{\oplus}$ are prominent in all of the spectra (Table 2). Metastable ions for formation of $R_4S^{\oplus}$ appear in most of the spectra. The $R_4S^{\oplus}$ ions are almost an order of magnitude more abundant than the $R_5S^{\oplus}$ ions, and there are generally no prominent metastable ions which can be related to the formation of $R_5S^{\oplus}$. Both of these observations reflect the relative abundance of the precursor ions to these rearrangement species. The rearrangement and cleavage processes which form $R_4S^{\oplus}$ and $R_5D^{\oplus}$ result in the formation of stable neutrals. Both processes probably occur in the ground states of the precursor ions. The lack of an obvious metastable ion for the formation of $R_5S^{\oplus}$ is probably due to relative intensity and not metastable kinetic considerations.



The mass spectra of the ψ-1,3,4-thiadiazole in which R_5 is a hydrogen atom, 6, was substantially different in qualitative appearance from the patterns of other substituted derivatives. The major reason for this difference is the prominence of the ion R_4 NCS^+ which arises from the molecule ion by prototropic rearrangement and cleavage.



The relative intensities of the R_4NCS and HNCS ions are no doubt related to their heats of formation. The fact that corresponding ions are virtually absent in the spectra of other ψ-1,3,4-thiadiazoles in which R_5 is an alkyl (or aryl residue) may reflect a high degree of stereoelectronic control of the rearrangement or a large substituent effect on the stability of the molecule ion. The fact that CS_2 ions are prominent (>1% R.I.) only in the spectra of these two ψ-1,3,4-thiadiazoles suggests that the latter explanation may be the more reasonable.

The mass spectra of aliphatic and aromatic hydrocarbon isomers are often so similar as to be virtually indistinguishable. This is particularly true for simple Me position isomers. The mass spectra of the methyl position isomers of the hetero-

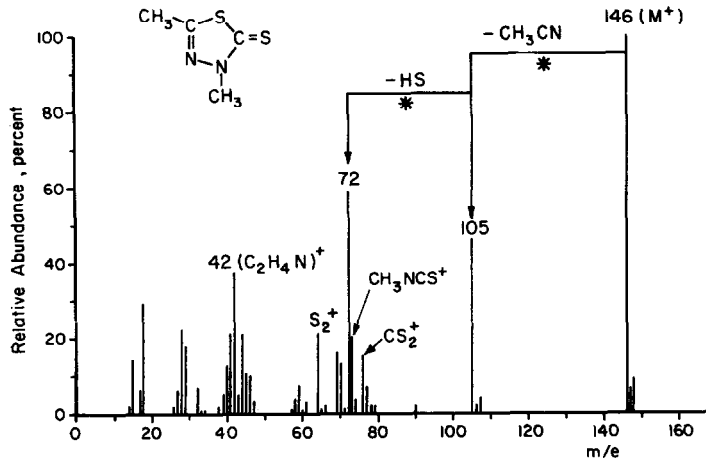


FIG. 12 Mass spectrum of 3,5-dimethyl-1,3,4-thiadiazole-2-thione (**11**).

cycles discussed above are both qualitatively and quantitatively distinguishable from those of their mesoionic analogs. The mass spectra of the Me position isomer of 9 is shown in Figure 12. The spectrum of the related nonmesoionic 3-methyl-1,3,5-thiadiazolethione (**12**) is shown in Fig. 13. These two 1,3,5-thiadiazoles are not mesoionic. For the purposes of the present discussion, a qualitative assessment of π-bond order based on low energy resonance forms will be sufficient. The π-bonds in both **11** and **12** should be essentially localized in the ground state (the same is true of the ground state of the ion). On this basis, we should expect to observe fragments that correspond to the rupture of any two of the single bonds in the ring. The expectation is realized in the spectra, and both the expectation and mass spectrum are substantially different from those for the corresponding mesoionic heterocycles with the same ring skeleton. The sulfur ion spectra to **11** and **12** are very similar below *m/e* 105 which suggest that either most of the sulfur-containing fragment ions originate

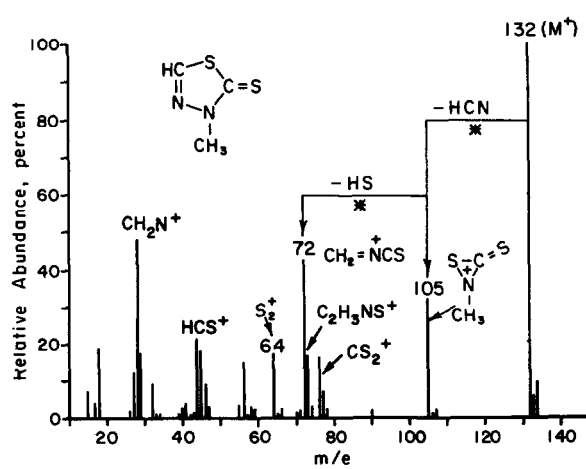
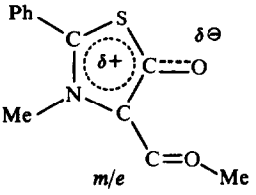


FIG. 13 Mass spectrum of 3-methyl-1,3,4-thiadiazole-2-thione (**12**).

from *m/e* 105 or the substituent R_5 only slightly perturbs the fragmentation of the ring. The nitrogen ion spectrum shows a methylene shift between **11** and **12**. The *m/e* 72 ion must arise from a β-hydrogen shift in the *m/e* 105 ion. The driving force for this rearrangement is the high stability of the CH_2NCS^+ ion. The immediate precursor of the S_2^+ ion in both of the spectra is not clear. This same ion appears in the mass spectrum of CS_2;[17] however, the relative intensities of S_2^+ with reference to M^+ is almost two orders of magnitude lower in the spectra of CS_2 than in the present case.

The mass spectra of the four following mesoionic systems indicates the general utility of qualitative bond order arguments and the limits on the reasoning we have developed thus far.



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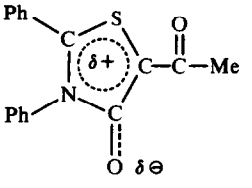

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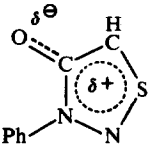

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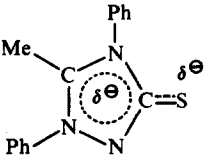

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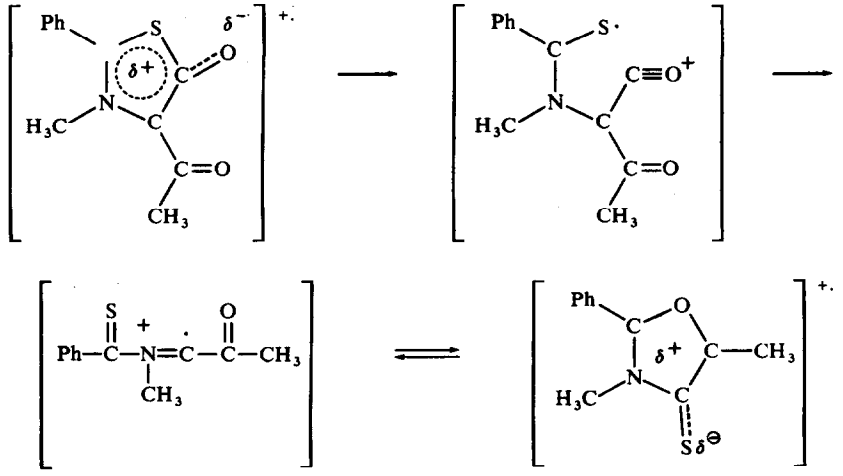
With the exception of the fact that the relative intensities of the $R—C{\equiv}S^+$ and $RC{\equiv}NR'^+$ are inverted when compared to the mesoionic thiadiazole thiones above, the major fragment ions in **13** follow the pattern established for the previous series. The M—CO ion may be explained on the same basis. Cleavage of the ring's weakest bond would labilize the ring carbonyl for expulsion. Alternate cleavage of the 1,2 bond,



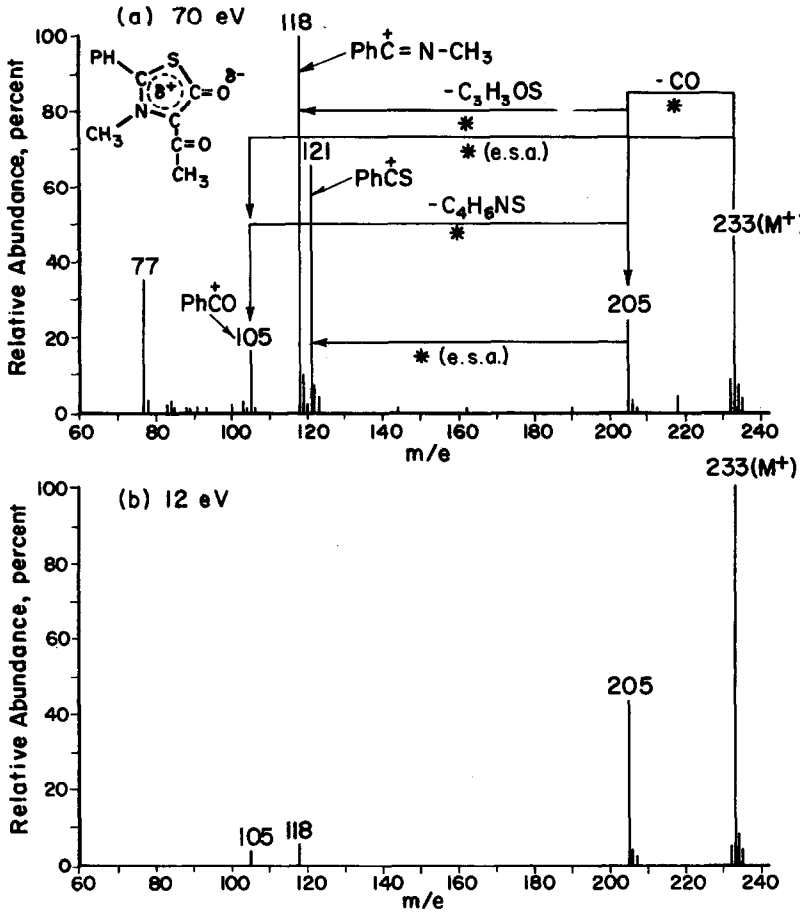


FIG. 14 Mass spectrum of 2-phenyl-3-methyl-4-acetyl-ψ1,3-thiazol-5-one (13).

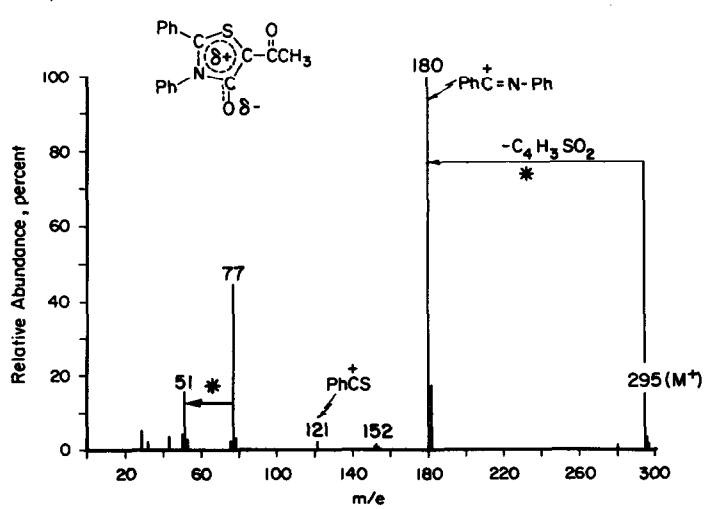
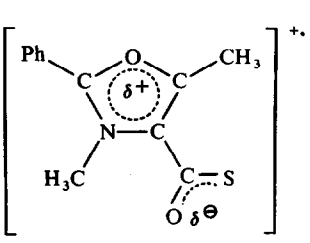
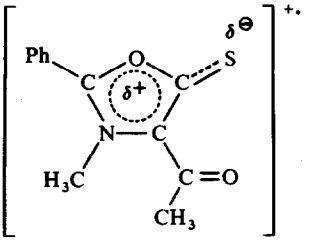


FIG. 15 Mass spectrum of 2,3-diphenyl-5-acetyl-ψ-1,3-thiazol-4-one (14).

which occurs in the formation of the Ph—C=N—CH_3 ions, would allow formation of either of the structures below, both of which would be expected to yield benzoyl ions. The fact that metastable ions were observed for formation of benzoyl ions both from the molecule ion and $(M—CO)^+$ suggests either of the O atoms can participate in formation of Ph—C≡O^+. Attempts to decide this question by^{18} exchange have been unsuccessful, as the exchange conditions destroyed the substrate. If the equilib-



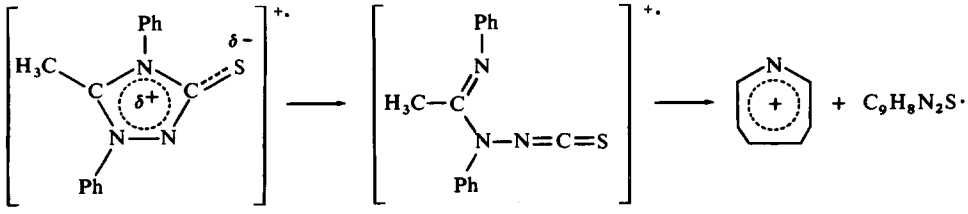


rium suggested above for the molecular ion occurred in solution, it would explain the "non-exchangeability" of the carbonyl oxygen, and also the fact that stable carbonyl derivatives have not been isolated for this compound.

The structure of **14** is very similar to that of **13** with the exception uf the fact that the ring-chain-ring tautomerism mentioned above is no longer possible. This change in structure is certainly responsible for the very substantial change in the mass spectrum (Fig 15). In this case there are no peaks that suggest complex rearrangements. The peaks at *m/e* 152, 77 and 51 are anticipated for a Ph—z—z—Ph structure. The relative intensities of the two major ring fragment ions can easily be explained on the basis of bond orders.

The ψ-thiadiazole **15** is a considerably permuted version of the series we examined above. If we follow the previous procedures, and assume that the carbonyl–heteroatom bond will be the weakest bond in the ring, the mass spectral fragmentation of this molecule is easily understood. Cleavage of the 3,4 bond and subsequent (or simultaneous) cleavage of the 1,2 bond would yield the relatively stable phenyl diazonium ion. Loss of a nitrogen molecule from this ion gives the base peak in the spectrum $C_6H_5^{\oplus}$.

The mesoionic triazole, **16**, is the last of our series of iso-electronic heterocycles. By analogy, with all of the other systems in this series, the major fragment ion in the mass spectum of **17** (Fig. 17), CH_3C^+=N—Ph, must arise by cleavage of the 3,4 and 1,5 bonds in the heterocycle. The minor fragment at *m/e* 91, Ph—$N^{\oplus}$, suggests that the ring opening which gives *m/e* 118 is stepwise as required by our initial bond order arguments. The *m/e* 91 ion, which is most likely an azatropillium ion, could be easily



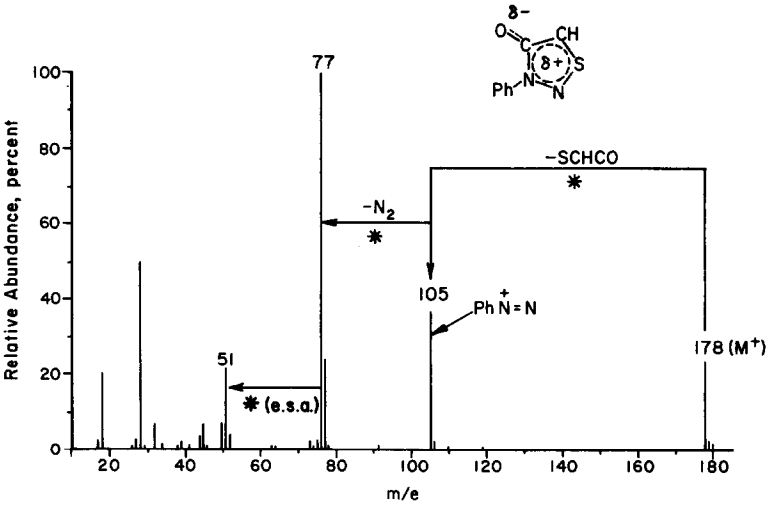


FIG. 16 Mass spectrum of 3-phenyl-ψ-1,2,3-thiadiazol-4-one (**15**).

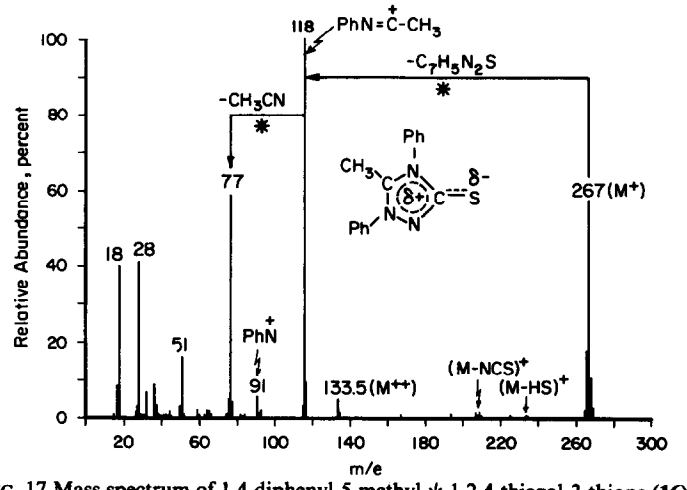


FIG. 17 Mass spectrum of 1,4-diphenyl-5-methyl-ψ-1,2,4-thiazol-3-thione (**16**).

formed from the ring opened form of the molecular ion that resulted from the bond with the lowest bond order being cleaved first.

CONCLUSIONS

It is clear that electron impact mass spectra can be reliably used to unravel the multitude of structural isomers of mesoionic formulae. Isomeric mesoionic compounds in which side chains are exchanged give distinct spectra. Isomerization by permutation of the ring atoms leads to a larger change in the spectra. The spectra of nonmesoionic heterocycles are radically different from those of their mesoionic isomers.

It appears that ground state bond orders in the molecule ions can be used as a reliable guide to the low energy (ground state[12]) fragmentation paths of heterocycles.

This approach to the interpretation of complex heterocycles should substantially augment the well developed conventional approaches to the interpretation of organic mass spectra.

EXPERIMENTAL

The mass spectral data were obtained using AEI MS-9 and MS-902* mass spectrometers. Unless otherwise stated, the mass spectra were obtained at 70 ev and an accelerating voltage of 8 KV. The samples were introduced into the mass spectrometer by means of a direct insertion probe. Mass measurements were obtained by means of automated data reduction and the peak-matching technique using perfluorotributylamine as the reference compound. The elemental compositions of major ions which are recorded in the figures agreed to within 10 ppm of the measured masses.

Previously published procedures were used for the preparation of methyl sydnone (**1**, R = Me);[19] phenyl sydnone (**1**, R = Ph);[20] 4,5-diphenyl isosydnone (**3**);[21] 4-phenyl-5-methyl-ψ-1,3,4-thiadiazole[7, 22] (**7**); 4,5-diphenyl-ψ-1,3,4-thiadiazole /**4**/,[22] 4-methyl-ψ-1,3,4-thiadiazole (**10**);[23] 4,5-dimethyl-ψ-1,3,4-thiadiazole (**9**);[23] 3,5-dimethyl-1,3,4-thiadiazole-2-thione (**11**);[23] 3-methyl-1,3,4-thiadiazole-2-thione (**12**);[23] 2,3-diphenyl-5-acetyl-ψ-1,3-thiazol-4-one (**15**);[24] 2-phenyl-3-methyl-4-acetyl-ψ-1,3-thiazol-5-one (**14**);[25] and 3-phenyl-ψ-1,2,3-thiadiazole-4-one (**16**).[26]

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