

MASS SPECTRAL FRAGMENTATION OF β -KETOSULFOXIDES AND β -KETOSULFONES.

NEUTRAL PRODUCT STABILITY AS A DRIVING FORCE

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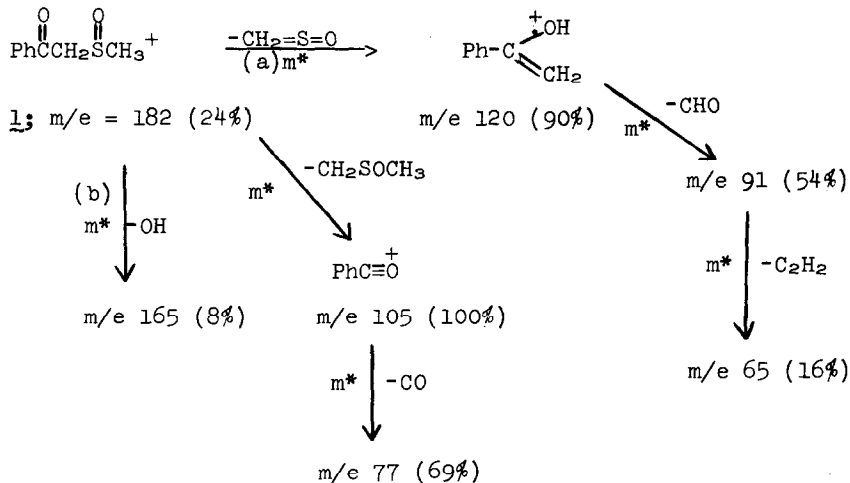
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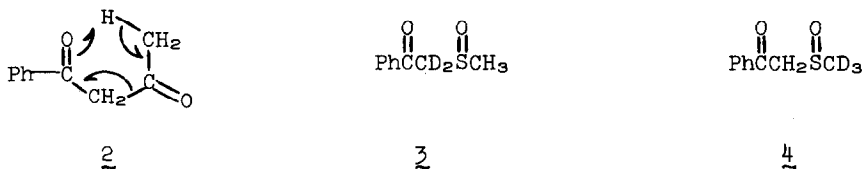
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Although a wide variety of sulfur containing organic molecules have been subjected to mass spectral analysis (2), the synthetically important β -ketosulfoxides (3) and β -ketosulfones (4) have apparently been overlooked.

The major fragmentation routes of ω -(methylsulfinyl) acetophenone (1) are outlined in the scheme. Simple single bond cleavage leads to the base peak at m/e 105. Particularly interesting is pathway (a), an apparent McLafferty



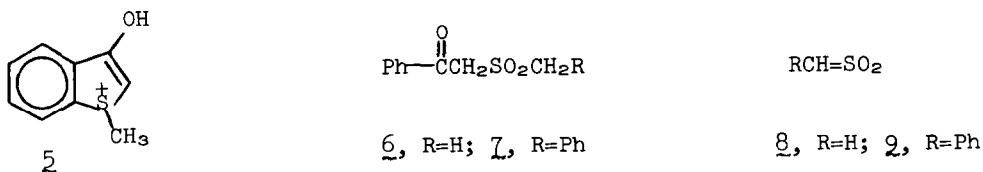
rearrangement to produce the enol of acetophenone with elimination of the simple sulfine, thioformaldehyde S-oxide, a compound which has not been isolated in pure form. Many more highly substituted sulfines are known, however (5). That this rearrangement is indeed of the McLafferty type (2) is



demonstrated by the clean shift of the m/e 120 ion of 1 to m/e 122 in the spectrum of 3 and to m/e 121 in the spectrum of 4. This specific rearrangement persists to very low electron energies and is analogous to the loss of ketene from β -diketones (6). This is the first report of the electron impact induced formation of sulfine from an ion of (presumably) unrearranged structure (7).

The formation of the m/e 91 ion (8) by a metastable loss of CHO from the m/e 120 ion is a particularly curious fragmentation and will be discussed more fully in the complete paper. Clean shifts to m/e 93 and m/e 92 occur in the spectra of 3 and 4, respectively.

The metastable loss of OH from the molecular ion, pathway (b), must involve one of the aromatic hydrogens (9) since no deuterium is lost from 3 or 4 in this process. The formation of a benzothiophene ion, 5, explains nicely the subsequent metastable loss of $-CH_3$ from 1 and 3 and CD_3 from 4 to form a stable ion which fragments no further.



The spectrum of the corresponding sulfone 6 showed no evidence for an analogous McLafferty rearrangement accompanied by the loss of sulfene 8. Sulfenes are non-isolable reactive intermediates in several chemical reactions (5). Phenyl substitution would be expected to stabilize a sulfene and indeed

the β -ketonesulfone 7 does form an ion at m/e 120 accompanied by the metastable loss of sulfene 9. The loss of sulfene 8 from aryl methanesulfonates has been postulated previously (11) but no mechanistic documentation was reported (12).

The evidence for neutral product stability as a strong driving force in the McLafferty rearrangements described above led us to compare the complete series of compounds 10. A McLafferty rearrangement in the ether (10, X=O, R=H)



would produce a formaldehyde, a commonly formed neutral product of high stability. The instability of monomeric thioformaldehyde and thiocarbonyl compounds in general is well known (14), although ejection of such species are known to occur upon electron impact (2, 15, 16). Table I shows the results of this study. Typically, substitution of R=Ph for R=H results in an increase of

Table I

<u>10</u> : <u>X</u>	<u>Neutral Fragment Z</u>	<u>(M-Z)⁺/M⁺</u>
SO ₂	CH ₂ =SO ₂	0
S	CH ₂ =S	0.13
SO	CH ₂ =SO	3.74
O	CH ₂ =O	42.6

the McLafferty rearrangement ion, in accord with increased stability of the neutral fragment. This constitutes a most striking corroboration of the concept that neutral stability provides an important driving force for mass spectral rearrangement reactions (17).

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8. Undoubtedly this is the tropylium ion based on the extent of hydrogen scrambling observed prior to loss of acetylene from the analogous ions from 3 and 4. This ion was also observed in the spectrum of benzoylacetone (6a).
9. This -OH loss is therefore mechanistically different from the processes which lead to the M-17 ions in either aliphatic sulfoxides (7) or styryl sulfoxides (10).
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18. Spectra were generated using an Atlas CH-4 mass spectrometer with direct insertion probe. Inlet and source temperatures were maintained below 100°.