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STUDY OF MASS SPECTRAL MCLAFFERTY FRAGMENTATION OF β-KETOSULFIDES AND β-KETOSULFONES

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ABSTRACT

Mass Spectral approach and PM3 calculation method for McLaffert fragmentation determination are studied. In an increase of the McLafferty rearrangement ion, in accord with increased stability of the neutral fragment. Studies Mass spectral and PM3 calculation match. Distance O...H is determined with PM3 calculation for McLaffert rearrangement.

Keywords: mass spectroscopy, PM3 calculation, McLafferty rearrangement, b-ketosufide.

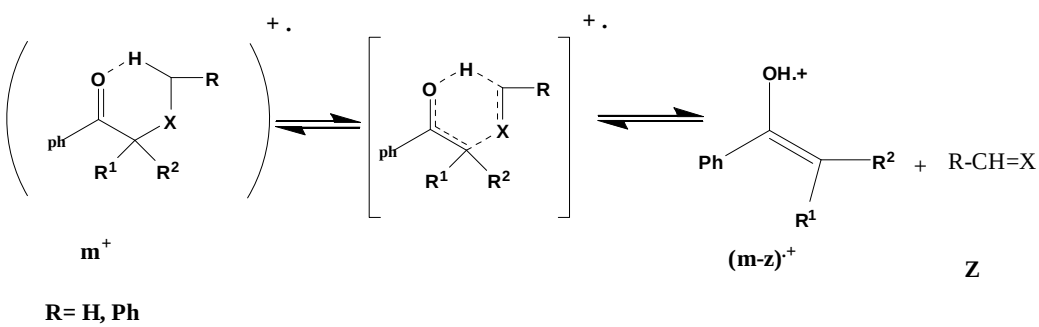
INTRODUCTION

Although a wide variety of sulphur containing organic molecules have been subjected to mass spectral analysis [1], the synthetically important β-keto-sulfoxides [2], and β- ketosulfones [3] have apparently been overlooked. The most important fragmentation of β-ketosulfoxides and β-ketoethers are McLafferty rearrangement fragmentation (see Scheme I).

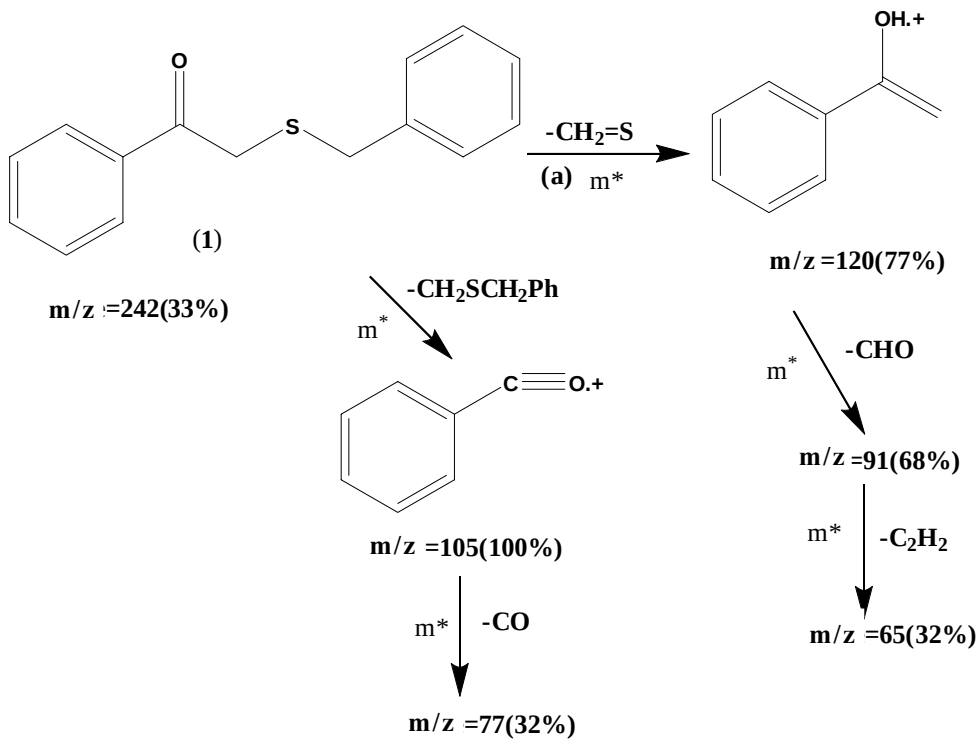
EXPERIMENTAL

β-ketosulfides, was synthesised according to reaction thioles with α-bromoacetophenone in absence of sodium carbonate, and then oxidation β-ketosulfides with *m*CPBA reagent we reached to β-ketosulfones, also, reaction α-bromoacetophenone with alcohols in presence of a base produced β-ketoetheres.

All of compounds are determined with spectroscopy methods. Melting point were determined using a Liukam HF591 heating stage, used in conjunction with a TC92 controller and are uncorrected, NMR spectra were recorded using Bruker DRX500 machine at room temperature; *J* values are given in Hertz and are quoted to the nearest 0.5 Hz, and δ values are quoted in ppm.; ^{1}H NMR spectra were measured using deuterochloroform as solvent using residual solvent as an internal standard. Mass spectra were obtained using a Micro mass LCT machine in ES or EI mode. Infra- red spectra were measured on a Perkin Elmer Paragon100 FT-IR spectro-



Scheme I. McLafferty rearrangement presentation.



Scheme II. MS fragmentation patterns of 1 (in parenthesis the relative intensity of the observed peaks s given).

photometer. All reaction solvents used were HPLC grade or distilled; petroleum ether refers to the fraction which boils in the range 40-60°C. TLC plates were visualized by UV light (254 nm). All organic extracts were dried over magnesium sulfate. All compounds were supplied by either the Lancaster chemical company or the Aldrich Chemical company and were used without further purification.

The major fragmentation routes of 2-(benzylthio)-1-phenylethanone (1) are outlined in the scheme II. Simple single bond cleavage leads to the best peak at m/z 105. Particularly interesting is pathway (a), an apparently McLafferty rearrangement to produce the enol of acetophenone with elimination of the simple sulfine, thioformaldehyde, a compound which has not been isolated in pure form. Many more highly substituted sulfines are known, however [4].

This rearrangement is indeed of the McLafferty type compound (1) (Scheme 2) is demonstrated by the clean shift of the m/z 120 ion. This specific rearrangement persists to very low electron energies and is analogous to the loss of ketene from β-diketone. [5] This is the first report of the electron impact induced formation of sulfine from an ion of (presumable) un rearranged structure [6].

The formation of the m/z 91 ion [7] by a metastable loss of CHO from the m/z 120 ion is a particularly curious fragmentation and will be discussed more fully in the complete paper. Also, the formation of the m/z 105 ion by a metastable loss of CH_2SCH_2Ph from the m/z 242 is carried out and then loss of CO gives m/z 77.

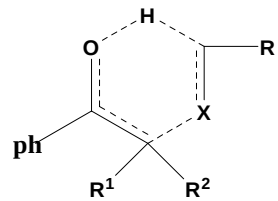


Table 1 shows the results of this study. Typically, substitution of R=Ph, R=H and R=Furyl results in an increase of the McLafferty rearrangement ion, in accord with increased stability of the neutral fragment. This constitutes a most striking corroboration of the concept that neutral stability provides an important driving force for mass spectral rearrangement reaction. Also, calculation PM3 shows that distance between O...H in six member cyclic transition state McLafferty rearrangement for same molecules with differences X =O, S, SO_2

Table 1. Effect distance O...H and Z on McLafferty rearrangement fragmentation

Entry	R	R^1	R^2	X	Neutral Fragment Z (R-CH=X)	$(m\text{-}z)^+/m^+$	Distance of O…H(A^o)[a]
1		H	H	O	Ph-CH=O	42.6	1.30131
2	H	H	H	O	CH2=O	41.7	1.31342
3		H	H	S	Ph-CH=S	0.13	3.71301
4	H	H	H	S	CH_2=S	0.11	3.79834
5		H	H	SO	Ph-CH=S=O	3.65	3.54871
6	H	H	H	SO	CH_2=S=O	3.74	1.34989
7		H	H	SO_2		0	1.61841
8	H	H	H	SO_2		0	
9		H	H	S	Fur-CH=S	1.1	2.37385
10		H	H	SO	Fur-CH=S=O	2.3	2.31345
11		H	H	SO_2		0	2.43203

increases and shows: $O...H_{X=O} < O...H_{X=SO} < O...H_{X=SO2}$ so, When we have $X=SO_2$ distance O...H is very value and formation Transition state don't occur, then fragment with m/z 105 don't observed, but for X=O distance O...H is small value and so formation transition state six member rearrangement McLafferty is much better and fragment m/z 105 produces easily. To clearing, we showed two molecule model optimized with PM3 calculation as below (Fig. 1).

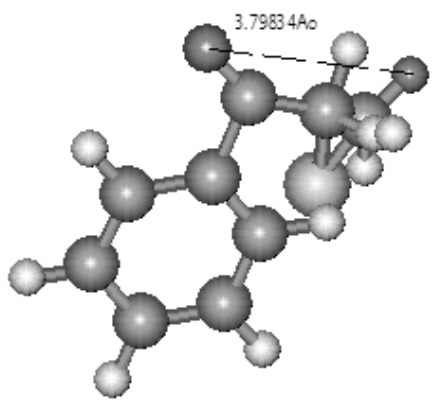
β-Ketosulfides are synthesized from reaction arylthiols with α-bromoacetophenone in absence of sodium bicarbonate as base and β-ketosulfones are prepared from oxidation β-ketosulfides with *m*CPBA in dichloromethane.

2-(benzylthio)-1-phenylethanone (Entry 5.): recrystallized yield from ethanol 100 %. ; m. p. 82°C. ; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.67 (s, 2H), 3.76 (s, 2H), 7.32 (m, 5H), 7.47 (t, J=7.6 Hz, 2H), 7.58 (t, J=7.4 Hz, 1H), 7.94 (d, J=8.1 Hz, 2H). ; ^{13}C NMR (101MHz, $CDCl_3$) δ ppm: 35.8, 36.0, 127.3, 128.5, 128.6, 128.7, 29.3, 133.3, 135.3, 137.3, 194.4(C=O). ; IR (neat, cm^{-1}): 3103, 3021, 2943, 2883, 1670(C=O), 1582, 1454, 1399, 1330, 1201, 1150, 1066, 752, 640, 582. ; HRMS (EI) Found: M^+, 242.0763; $C_{15}H_{14}OS$ requires M^+, 242.0765; LRMS m/z (EI): 242(35% M^+), 105(100%); ES+: MNa^+, 265, MH^+, 243; Elemental analysis: Found (%): C, 73.34; H, 5.82; S, 13.23; Calcd. for $C_{15}H_{14}OS$: C, 73.34; H, 5.82; S, 13.23.

2-((furan-2-yl)methylthio)-1-phenylethanone (Entry 9.): recrystallized yield from ethanol 97%.; m. p. 67–68°C(ethanol), ([8] m. p. 67.5°C(ethanol)) .; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.78 (s, 2H), 3.79 (s, 2H), 6.26 (d, J=2.8 Hz, 1H), 6.31 (dd, J=3.2, 1.9 Hz, 1H), 7.37 (m, 1H), 7.47 (t, J=7.6 Hz, 2H), 7.59 (ddd, J=8.4, 2.3, 1.1 Hz, 1H), 7.95 (dd, J=8.4, 1.1 Hz, 2H). ; ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 28.2, 36.3, 108.5, 110.4, 128.6, 128.6, 133.3, 135.4, 142.4, 150.4, 194.2. ; IR (neat, Cm^{-1}): 3103, 2942, 2884, 1671(C=O), 1598, 1582, 1506, 1454, 1399, 1330, 1302, 1258, 1200, 1148, 1065. ; HRMS (EI) Found: M^+, 232.0564; $C_{13}H_{12}O_2S$ requires M^+, 232.0558; LRMS m/z (EI): 232(62% M^+), 105(100%); ES+: MNa^+, 255, MH^+, 233; Elemental analysis: Found (%): C, 66.97; H, 4.98; S, 14.11; Calcd. for $C_{13}H_{12}O_2S$: C, 67.22; H, 5.21; S, 13.77.

2-(benzylsulfonyl)-1-phenylethanone (entry 7.): yield 62%. ; m. p. 111-113°C (ethanol), ([9] m. p. 112 – 113°C (ethanol)). ; ^{1}H NMR (400 MHz, CDCl3) δ ppm:

a)



b)

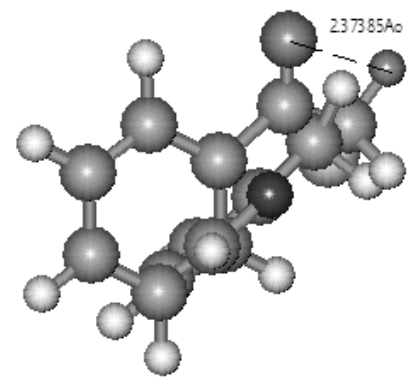


Fig. 1. Molecules model optimized energy with PM3 calculation: a) 2-(methylthio)-1-phenylethanone, b) 2-(furan-2-ylthio)-1-phenylethanone.

4.39 (s, 2H), 4.56 (s, 2H), 7.45-7.38 (m, 3H), 7.53 (td, J=12.1, 5.5 Hz, 4H), 7.66 (t, J=7.41 Hz, 1H), 7.97 (dd, J=8.35, 1.13 Hz, 2H). ; ^{13}C NMR (101 MHz, CDCl3) δ ppm: 56.6, 59.8, 129.1, 131.3, 133.1, 134.2, 135.6, 136.3, 148.4, 152.8, 201.5. ; IR (neat, Cm^{-1}): 3098, 2988, 1703(C=O), 1351, 1278, 1135, 904. ; HRMS (EI) Found: M^+, 274.07826; $C_{15}H_{14}O_3S$ requires M^+, 274.07553; LRMS m/z (EI): 274(33% M^+), 91(100%); ES+: MNa^+, 297, MH^+, 275; Elemental analysis: Found (%): C, 65.49; H, 5.44; S, 11.78; Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14; S, 11.69.

2-((furan-2-yl)methylsulfonyl)-1-phenylethanone (entry 11.): yield 56 %. ; m. p. 92°C. ; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.53 (s, 2H), 4.67 (s, 2H), 6.43 (dd, J=3.2, 1.9 Hz, 1H), 6.61 (d, J=3.4 Hz, 1H), 7.47 (dd, J=1.9, 0.9 Hz, 1H), 7.53 (t, J=7.7 Hz, 2H), 7.67 (t, J=7.4 Hz, 1H), 7.97 (dd, J=8.5, 1.2 Hz, 2H). ; ^{13}C NMR (101 MHz, $CDCl_3$) d ppm 53.2, 57.4, 111.7, 113.2, 129.0, 129.9, 134.7, 139.8, 145.5, 158.7, 198.2 9 (C=O). ; IR (neat, cm^{-1}): 3113, 2953, 2854, 1691(C=O), 1598, 1583, 1506, 1454, 1309, 1330, 1275, 1258, 1200, 1148, 1065, 750, 687, 544. ; HRMS (EI) Found: M^+, 264.3204; $C_{13}H_{12}O_4S$ requires M^+, 264.3201;m/z(CI+, NH_3), 282 (($M+NH_4$)$^+$, 100%), 201(($M-SO_2$)+1), 30%); Elemental analysis: Found(%): C, 59.28; H, 4.48; S, 12.11; Calcd. for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58; S, 12.13.

RESULTS AND DISCUSSION

The GC-Mass analysis of the studied products showed McLafferty fragmentation patterns for compounds of β-ketoetheres, β-ketosulfides and β-ketosulfoxides. When (X=O, S, SO), the mass spectrum exhibits intensive peak for molecular ion at m/z 120 ion, which is an agreement with the molecular mass and molecular formula of the product $[C_9H_8O]^{\cdot+}$ and when we have β-ketosufones ($X=SO_2$), McLafferty rearrangement fragmentation don't occurred. Calculations with PM3 showes a correlation between type of X and distance O...H in six member transition state McLafferty rearrangement fragmentation, which with increase distance of O...H, probability carry out of rearrangement decreases. We have $O...H_{(X=SO2)} < O...H_{(X=SO)} < O...H_{(X=S)}$ $O...H_{(X=O)}$ so $(m\text{-}z)^+/m^+_{(X=O)} > (m\text{-}z)^+/m^+_{(X=S)} > (m\text{-}z)^+/m^+_{(X=SO)}$ and for $(m\text{-}z)^+/m^+_{(X=SO2)}=0$. In conclusion, for X=S, we have the most probability of McLafferty rearrangement fragmentation and the lowest distance O...H.

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