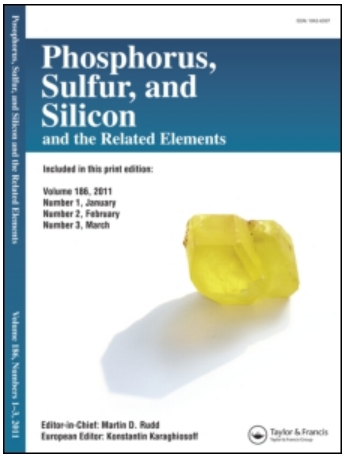

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MASS SPECTRA OF 1-SUBSTITUTED-3-FORMYL-2(1*H*)-PYRIDONES, -THIONES AND -SELONES

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MASS SPECTRA OF 1-SUBSTITUTED-3-FORMYL-2(1*H*)-PYRIDONES, -THIONES AND -SELONES

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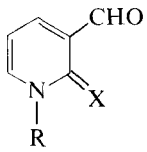
The mass spectra of a series of 1-substituted 3-formyl-2(1*H*)-pyridinethiones have been recorded and compared with those of the corresponding pyridones and pyridineselones. Interpretation of the mass spectra have been performed with high resolution mass measurements and by application of the metastable defocusing technique as well as the daughter ion technique. The observed electron impact induced fragmentations are compared with those of the corresponding monofunctional compounds.

INTRODUCTION

The electron impact induced decomposition of heterocyclic compounds has been widely described.[1,2] The title compounds represent a new class of pyridine derivatives. In the course of their study in this Institute,[3–5] we found it necessary to study the mass spectrometric fragmentation pattern of these polyfunctional compounds to see if there were any differences from that of the isolated functions. Among the many compounds in this series, a few were selected to represent the similarities and differences of their characteristic fragmentations.



R	$x = O$	$x = S$	$x = Se$
hydrogen		**1b**	
deuterium		**2b**	
methyl	**3a**	**3b**	**3c**
ethyl		**4b**	
n-propyl		**5b**	
isopropyl	**6a**	**6b**	**6c**
cyclohexyl		**7b**	**7c**
phenyl	**8a**	**8b**	**8c**
2,6-xylyl		**9b**	
2,6-dichlorphenyl		**10b**	
1-naphthyl	**11a**	**11b**	
2-naphthyl	**12a**	**12b**	**12c**

SCHEME I

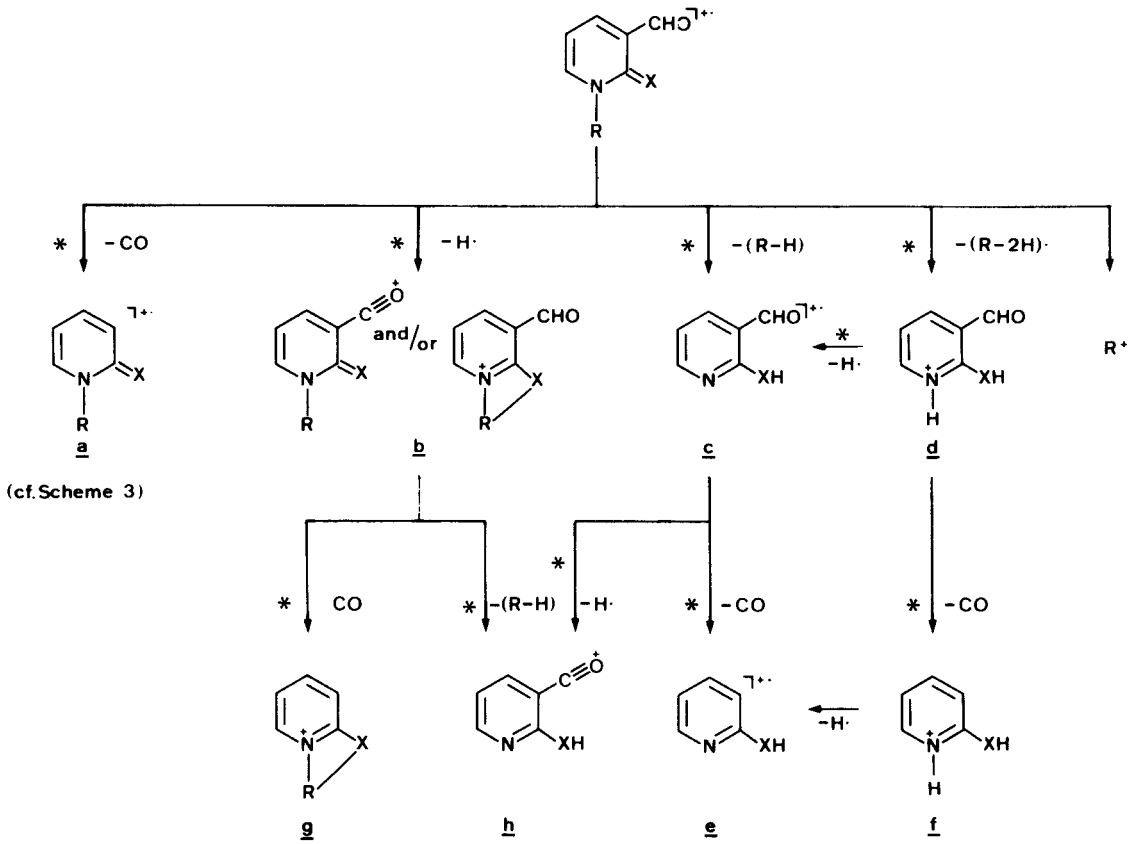
RESULTS

3-*Formyl*-2(1*H*)-*pyridinethiones* (**1b**–**12b**)

Fragmentation of the molecular ion is shown in Scheme 2. The $(M—CO)^{+\cdot}$ ion is frequently the base peak. In the compound **9b** and **10b**, the loss of CO was not observed from the molecular ion. In these compounds, loss of $CH_3^{\cdot}$ or $Cl^{\cdot}$ was observed prior to the loss of CO. Apart from this, the $(M—CH_3)^+$ and the $(M—Cl)^+$ ions behave in the way described for $M^{+\cdot}$ in the other compounds of this series.

Besides loss of CO four other routes are observed (Scheme 2) for fragmentation of the molecular ion. Loss of $H^{\cdot}$, as seen in simple aldehydes, is seen here too. This is followed by a loss of CO with formation of the ion *g*. This ion also arises from *a* by loss of $H^{\cdot}$. The $(M—H)^+$ peak is always small, whereas *g* sometimes is found as the base peak.

Rearrangement of one or two hydrogen atoms with subsequent loss of (R—H) or (R—2H) is very prone to happen in the molecular ion leading to formation of *c* or *d* respectively. Subsequent loss of $H^{\cdot}$ and CO, in arbitrary order, lead to formation of *e* and *f*. The direct loss of the radical without rearrangement of hydrogen is not observed for R = aryl and methyl. It is seen to a smaller extent for R=H, as demonstrated in **2b**, where $(M—D)^+$ amounts to 3% of the base peak. However, loss of a charged radical R^+ is very abundant for R = aryl.



SCHEME 2

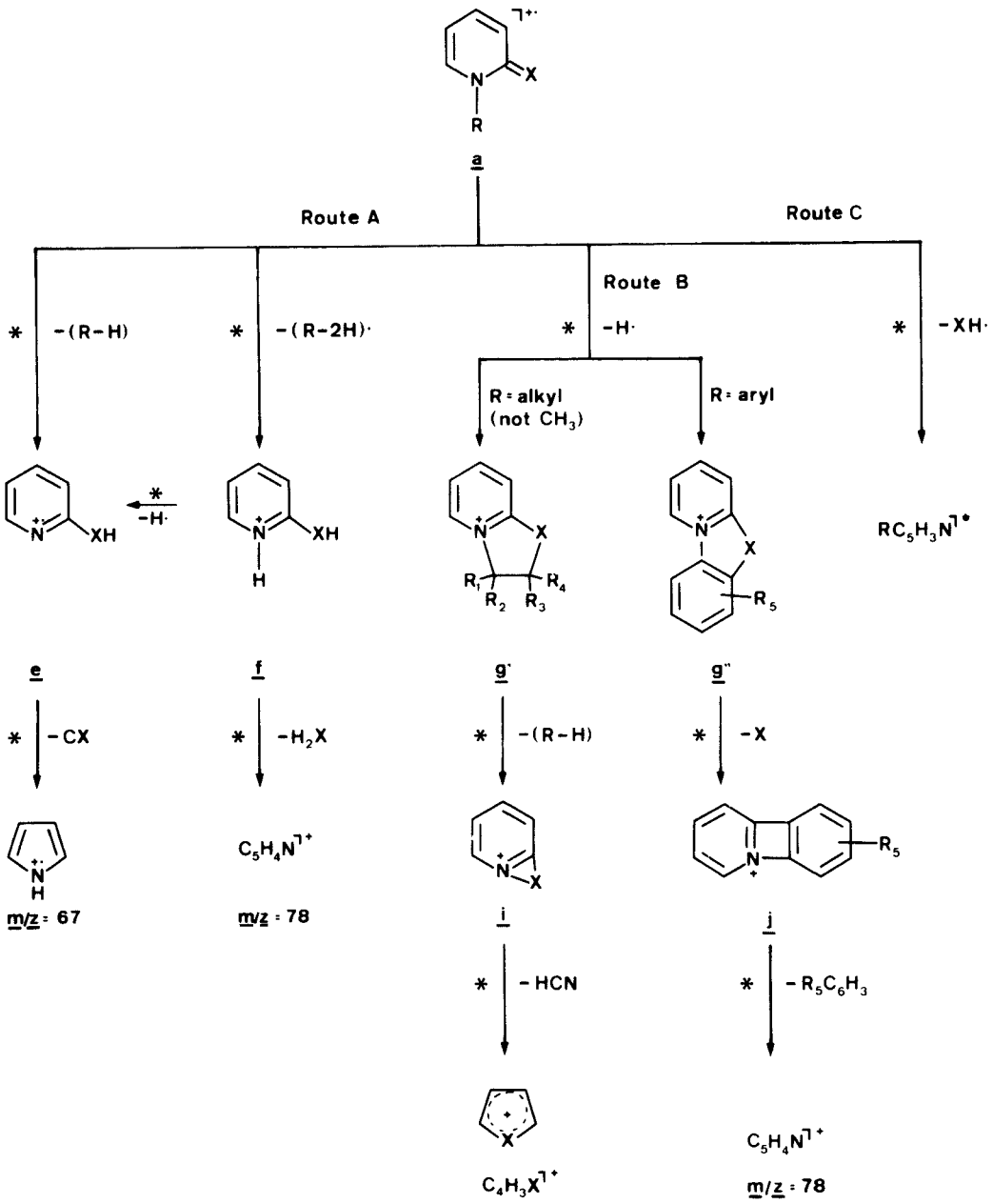
The fate of the odd-electron ion *a* is shown in Scheme 3. The fragmentation of *a* should correspond well with that of 2-pyridinethiones. The loss of CS from *a* is only seen for R = CH_3 (Scheme 4) or H, *cf.* the ion-radical *e* in Scheme 3.

When R = alkyl but not methyl (**4b–7b**) we see a McLafferty rearrangement with loss of (R—H) and formation of *e* (Scheme 3, route A). This is in accordance with the fragmentation in carbostyrils described by Møller and Buchardt.[6] Further, we again find a loss of (R—2H)· resulting in the conversion of *f* to *e*, and first at this stage the pyridine ring is broken down; initiated by loss of CS and formation of pyrrole (*m/z* = 67). Route A is not followed for R = aryl.

For R = aryl (**8b–12b**) or alkyl except methyl (**4b–7b**) we observed a loss of H· leading to formation of *g″* and *g′*, respectively (Scheme 3, route B). *g′* decomposes by ejection of (R—H) to the ion depicted as *i*, which in turn loses HCN. *g″* eliminates elemental sulfur with formation of the ion depicted as *j*. The loss of aryne from *j* forms the ion at *m/z* = 78, which is seen for all compounds. Route C (Scheme 3) is found independent of R; but see below for the dependence on X.

3-*Formyl*-2(1*H*)-*pyridineselones* (**3c**, **6c**, **7c**, **8c**, **11c** *and* **12c**)

The mass spectra of the selones in most respects resemble those of the thiones, however with the following differences. The loss of (R—H) and (R—2H)· from the molecular ion is never found in this series. Besides the elimination of R· the main fragmentation of the selones takes place via *a*, *g* and *h* (Scheme 2), but only for R = alkyl other than methyl, as for the thiones. The further fragmentation of these ions is similar to that of the pyridinethiones. As a consequence, loss of (R—H) and (R—2H)· is prone to happen in the selenium



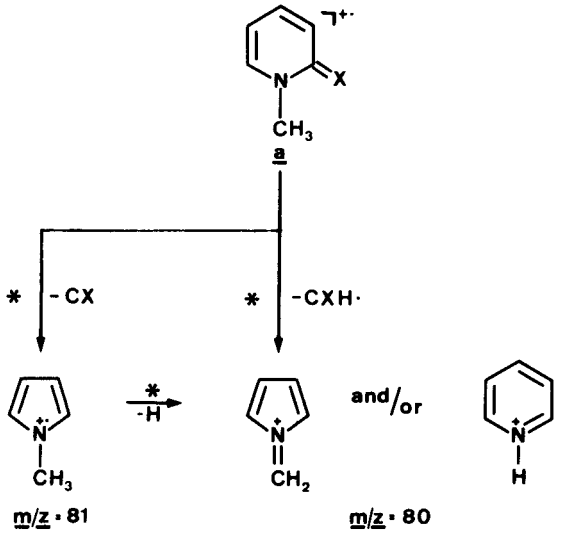
SCHEME 3

series, but will only occur after the ejection of CO or both CO and H·.

3-*Formyl*-2-(*1H*)-*pyridones* (**3a**, **6a**, **8a**, **11a** *and* **12a**)

The fragmentations described in Scheme 2 are identical in all respects for the oxygen and the sulfur analogues with no exceptions. The charged radical formed from the molecular ion by direct loss (R = aryl, only) is always doubly intense compared to that in the spectra of the sulfur series, with the intensity of the same ion (R^+) in the selenium series lying in between.

In Scheme 3, route A is followed under the same conditions as described for the sulfur and



SCHEME 4

selenium series. Route B is never seen in the oxygen series. Instead, for R = aryl, the R is lost with or without the charge from the ion *a*. This might explain why R^+ is always most intense in the oxygen series.

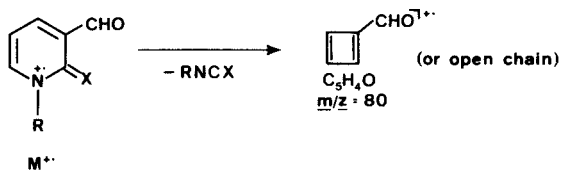
The loss of OH· from the radical ion *a* in the oxygen series is not found for R = alkyl in contrast to the sulfur and the selenium analogues. In the oxygen series, route C (Scheme 3) is highly dependent upon R, in that the loss of OH· is only observed for R = aryl.

DISCUSSION

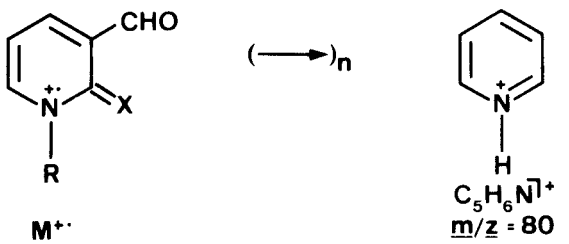
In benzaldehyde as well as in pyridine-3-carboxaldehyde, the main fragmentation of the molecular ion is loss of H· followed by loss of CO.[1-2] Loss of CO from the molecular ion is unimportant. By contrast, loss of CO from the molecular ion of the title compounds is generally prevailing, forming *a* (Scheme 2). In the oxygen series, this could in the theory be due to loss of the ring atom C(2) instead of that in the aldehyde function. In simple 2-pyridiones and carbostyrils,[6] this is in fact the most important fragmentation. Although we did not perform an ^{18}O labelling, we consider the loss of CO in the oxygen series to be due to the aldehyde function. The reason is that we neither see a corresponding loss of CS nor of CSe from the molecular ion in the other series. Both of these series show a primary loss of CO, due to the aldehyde function.

The obvious differences in the mass spectra of benzaldehyde or pyridine-3-carboxaldehyde on the one hand and the title compounds on the other is explained by an ortho effect. In the latter compounds, the aldehyde hydrogen can be donated to or rest on the chalcogen in the 2-position while CO is lost from the 3-position. This possibility is not given in simple aromatic aldehydes; consequently these compounds eject H· before losing CO.

The loss of CO from the aldehyde group does not affect the stable six-membered aromatic ring (*a*), whereas loss of CX from the 2-position in the ring would result in a five-membered ring. Although still aromatic, this is not as stable as the six-membered ring. The fact that the ion $(M—CO)^{+\cdot}$ very often is the most abundant in the mass spectra therefore indicates that CO is lost from the aldehyde group. As the three classes of compounds were prepared[3-5] by condensation of the corresponding isothio-, isoseleno- and isocyanates with the glutaconaldehyde anion, it is possible that the reverse process occurs in the mass spectrometer. Cleavage of the ring with loss of isothio-, isoseleno- or isocyanate would lead to formation of a radical ion at $m/z = 80$ with the elemental composition C_5H_4O:



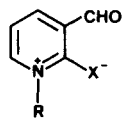
In each spectrum this peak is observed, but peak matching showed the elemental composition C_5H_6N for this ion:



This was further confirmed by the daughter ion technique, which showed that the molecular ion never broke down to this fragment ion in one step. Moreover, in some of the spectra there were metastable ions, that showed $m/z = 80$ to have a different origin.

CONCLUSION

The progressive importance of charge separated forms of the type in going from the pyridones via thiones to selones as reflected in the UV spectra[7] could not be justified in the mass spectrometric fragmentation. Here there is no regular trend in abstracting R^+ from the molecular ion or the



radical ion *a* on descending the periodic table. The lower hydrogen bonding ability for selenium[7] might be the reason why no loss of (R—H) or $(R - 2H)^{\cdot}$ from the molecular ion is observed in the selenium series.

Substitution of sulfur or selenium for oxygen in the 2-position in 3-formyl-2(1H)-pyridones results in identical pathways for the electron impact induced fragmentation. The routes which are preferred in the fragmentation are highly affected by the chalcogen.

EXPERIMENTAL

Instrumentation. The mass spectra were recorded on a VARIAN MAT 311A and on a VARIAN MAT CH7A spectrometer. Below are given *m/z* and relative intensities more than 10% of base peak in parentheses.

3-Formyl-1-methyl-2(1H)-pyridine (**3a**) 137(26.2), 109(100.0), 108(30.1), 81(13.6), 80(15.5), 53(11.7), 42(17.0), 39(17.5).

3-Formyl-1-isopropyl-2(1H)-pyridone (**6a**) 165(11.0), 137(75.2), 122(18.3), 95(100.0), 94(22.0), 67(20.2), 43(13.8), 41(16.5), 39(20.2).

3-Formyl-1-phenyl-2(1H)-pyridone (**8a**) 172(13.2), 171(100.0), 170(50.0), 154(14.7), 115(25.0), 94(20.6), 93(19.1), 77(41.9), 51(26.4), 39(13.2).

3: 3-Formyl-1-(1-naphthyl)-2(1H)-pyridone **11a**) 249(12.0), 222(17.2), 221(100.0), 220(56.9), 204(19.0), 192(15.5), 191(13.8), 165(10.3), 128(54.3), 127(27.6), 126(11.2), 77(12.9).

3 - Formyl - 1 - (2 - naphthyl) - 2(1H) - pyridone (**12a**) 250(10.0), 249(46.4), 222(17.3), 221(100.0), 220(22.5), 193(11.3), 165(13.6), 128(57.8), 127(24.0).

3 - Formyl - 2(1H) - pyridinethione (**1b**) 139(43.5), 111(100.0), 110(23.0), 83(18.0), 78(22.0), 77(18.0), 67(99.0), 51(22.0), 50(15.0), 39(33.0).

1 - Deuterio - 3 - formyl - 2(1H) - pyridinethione (**2b**) 140(48.0), 139(12.0), 112(95.0), 111(40.0), 110(12.0), 84(15.0), 83(14.0), 82(11.0), 78(22.0), 77(24.0), 69(10.5), 68(100.0), 52(12.0), 51(27.0), 50(22.0).

3 - Formyl - 1 - methyl - 2(1H) - pyridinethione (**3b**) 154(15.0), 153(100.0), 125(69.0), 124(31.0), 81(60.0), 80(47.0), 79(13.0), 78(12.0), 65(12.0), 42(14.0), 39(17.0).

1 - Ethyl - 3 - formyl - 2(1H) - pyridinethione (**4b**) 168(12.0), 167(100.0), 139(29.0), 138(43.0), 111(61.0), 110(13.0), 80(10.0), 78(22.0), 67(82.0), 51(13.0), 39(22.0).

3 - Formyl - 1 - propyl - 2(1H) - pyridinethione (**5b**) 181(76.0), 153(18.0), 152(22.0), 138(16.0), 112(13.0), 111(100.0), 110(11.0), 78(21.0), 67(63.0), 41(20.0), 39(25.0).

3 - Formyl - 1 - isopropyl - 2(1H) - pyridinethione (**6b**) 182(11.0), 181(90.0), 153(19.0), 152(33.0), 138(15.0), 112(13.0), 111(100.0), 110(16.0), 78(17.0), 67(77.0), 41(15.0), 39(19.0).

1-Cyclohexyl-3-formyl-2(1H)-pyridinethione (**7b**) 222(12.0), 221(74.0), 195(14.0), 181(24.0), 167(13.0), 140(53.0), 138(21.0), 113(12.0), 112(100.0), 111(96.0), 110(12.0), 78(19.0), 69(14.0), 67(77.0), 55(27.0), 54(12.0), 41(35.0), 39(23.0).

3 - Formyl - 1 - phenyl - 2(1H) - pyridinethione (**8b**) 215(38.5), 187(29.4), 186(100.0), 77(12.8), 51(12.3).

3 - Formyl - 1 - (2,6 - xylyl) - 2(1H) - pyridinethione (**9b**) 243 (48.0), 228(20.0), 215(25.0), 201(17.0), 200(100.0), 183(10.0), 182(68.0), 181(10.0), 167(30.0), 79(10.5), 78(11.0), 77(27.0), 51(15.0).

1 - (2,6 - Dichlorophenyl) - 3 - formyl - 2(1H) - pyridinethione (**10b**) 250(30.0), 249(10.0), 248(70.0), 222(45.0), 221(20.0), 220(100.0), 219(10.0), 185(18.0), 109(15.0), 82(11.0), 75(12.0), 74(12.0), 69(22.0), 51(13.0).

3 - Formyl - 1 - (1 - naphthyl) - 2(1H) - pyridinethione (**11b**) 265 (36.0), 237(29.0), 236(100.0), 204(34.0), 127(13.0), 92(11.0), 91(13.0).

3 - Formyl - 1 - (2 - naphthyl) - 2(1H) - pyridinethione (**12b**) 265 (26.0), 238(26.0), 237(100.0), 41(11.0).

3 - Formyl - 1 - methyl - 2(1H) - pyridineselone (**3c**) 203(12.0), 201(59.0), 199(31.0), 198(11.0), 197(12.0), 173(25.0), 172(18.0), 171(13.0), 170(13.0), 93(21.0), 92(20.0), 81(15.0), 80(100.0), 79(16.0), 78(24.0), 66(13.0), 65(29.0), 52(11.0), 51(18.0), 50(10.0), 42(20.0), 39(29.0).

3 - Formyl - 1 - isopropyl - 2(1H) - pyridineselone (**6c**) 231(12.0), 229(53.0), 227(28.0), 226(11.0), 225(12.0), 200(15.0), 186(10.0), 161(19.0), 160(10.0), 159(87.0), 158(15.0), 157(48.0), 156(22.0), 155(22.0), 131(10.0), 80(12.0), 79(29.0), 78(100.0), 67(24.0), 52(20.0), 51(35.0), 50(14.0), 43(40.0), 42(11.0), 41(50.0), 39(52.0).

1-Cyclohexyl-3-formyl-2(1H)-pyridineselone (**7c**) 269(43.0), 267(21.0), 186(12.0), 161(19.0), 160(23.0), 159(100.0), 158(17.0), 157(51.0), 156(23.0), 155(20.0), 98(10.0), 83(17.0), 81(14.0), 79(18.0), 78(64.0), 67(29.0), 55(77.0), 54(12.0), 53(13.0), 51(14.0), 43(16.0), 41(58.0), 39(26.0).

3 - Formyl - 1 - phenyl - 2(1H) - pyridineselone (**8c**) 263(32.0), 261(17.0), 236(20.0), 235(22.0), 234(100.0), 233(13.0), 232(49.0), 231(21.0), 230(20.0), 154(27.0), 127(13.0), 78(29.0), 77(31.0), 51(37.0), 50(11.0), 39(11.0).

3 - Formyl - 1 - (2 - naphthyl) - 2 - (1H) - pyridineselone (**12c**) 313(33.0), 311(18.0), 286(21.0), 285(27.0), 284(100.0), 283(15.0), 282(52.0), 281(21.0), 280(20.0), 205(12.0), 204(35.0), 203(10.0), 127(17.0), 126(14.0), 115(12.0), 78(15.0), 77(11.0), 51(11.0).

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