Competing Oxygen Migrations in *ortho* Nitro Aromatic Thioamides on Electron Impact

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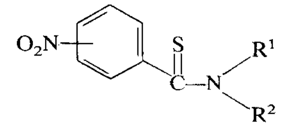
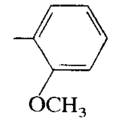
Interesting competitive oxygen migrations from the nitro group to the nitrogen and to the sulfur have been noticed during the mass spectral decomposition of *ortho* nitro aromatic thioamides on electron impact. The migration of the oxygen to the nitrogen of the thioamide function results in the formation of stable *o*-nitrosothiobenzoyl cation. The other novel *ortho* effect noticed in the *ortho* isomers is the transfer of an oxygen from the nitro group to the sulfur followed by the ejection of SO from the molecular ions. A mechanism involving the initial oxygen migration to the sulfur through a favourable 6-membered transition state followed by cyclization with the concomitant expulsion of SO is proposed for this process. Other interesting decomposition processes occurring as a consequence of this *ortho* effect have also been noticed. The proposed mechanisms for these processes are supported by mass analysed ion kinetic energy spectra and high voltage scans.

INTRODUCTION

The nitro group is a powerful interacting function in the mass spectral decompositions of *ortho* nitro aromatic compounds. Its ability to interact with the neighbouring groups may be due to its bulk, its readiness to form stable cyclic transition states through the electron-rich oxygens and its stable existence as the nitroso group after the transfer of an oxygen atom. The most interesting aspect of the *ortho* interaction of the nitro group is the transfer of an oxygen atom either to a double bond[1–12] or to a hetero-atom[13–20] present in the side chain leading to unexpected fragments. An oxygen transfer to the sulfur atom has been observed[17] in *N*,*N*-dimethyl-*o*-nitrothiobenzamide on electron impact leading to the expulsion of SO from the molecular ion. The transfer of an oxygen from the nitro group to the nitrogen atom of the aromatic amides is also known.[18] With a view to studying the competitive oxygen transfers to the sulfur and to the nitrogen atoms, the mass spectral study of *ortho*-nitro aromatic thioamides of cyclic amines has been undertaken in the present work.

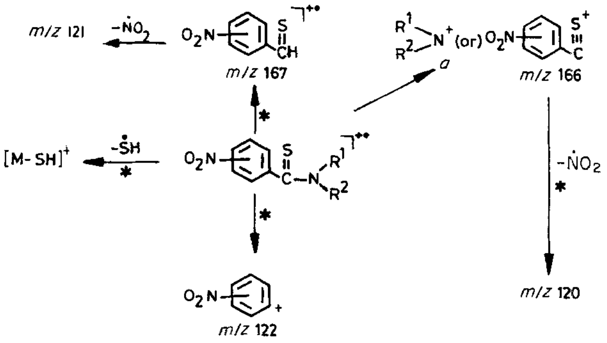


	Position of nitro group	R^1	R^2		Position of nitro group	R^1	R^2
1	ortho	$(\mathrm{CH_2})_5$		**9**	ortho	H	*n*-Butyl
2	meta	$(\mathrm{CH_2})_5$		**10**	ortho	H	Ph
3	para	$(\mathrm{CH_2})_5$		**11**	meta	H	Ph
4	ortho	$(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2$		**12**	ortho	CH_3	CH_3
5	meta	$(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2$		**13**	ortho	H	$-CH_2Ph$
6	para	$(\mathrm{CH_2})_2\mathrm{O}(\mathrm{CH_2})_2$		**14**	meta	H	$-CH_2Ph$
7	ortho	$(\mathrm{CH_2})_4$		**15**	ortho	CH_3	Ph
8	meta	$(\mathrm{CH_2})_4$		**16**	ortho	Ph	Ph
				17	ortho	H	

Structure 1

RESULTS AND DISCUSSION

Intense molecular ions (Table 1) have been noticed in most of the nitro substituted tertiary thioamides studied (see below). The expected simple α-cleavage in the thioamide group leads to the common fragment at *m/z* 166, which in turn expels the nitro group to afford the ion at *m/z* 120 (Scheme 1). The same α-fission can also place the charge on the nitrogen of the amine moiety leading to another common fragment ion *a* in these spectra. But the α-cleavage preceded by a hydrogen migration gives rise to another general fragment at *m/z* 167 corresponding to nitrothiobenzaldehyde molecular ion, which loses the NO_2



Scheme 1

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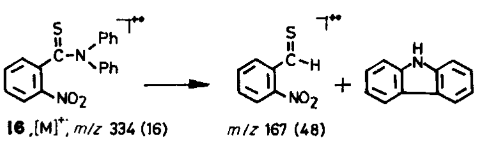
Table 1. Partial mass spectra of the compounds 1–17

Relative abundance[a] of	Compound No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$[M]^{+\cdot}$	65 (250)	100 (250)	100 (250)	49 (252)	81 (252)	49 (252)	65 (236)	81 (236)	5 (238)	4 (258)	65 (258)	98 (210)	2 (272)	39 (272)	42 (272)	16 (334)	6 (288)
$[M-H]^+$	— (249)	78 (249)	80 (249)	— (251)	19 (251)	12 (251)	— (235)	21 (235)	— (237)	2 (257)	60 (257)	— (209)	— (271)	4 (271)	7 (271)	— (333)	— (287)
$[M-SH]^+$	3 (217)	17 (217)	16 (217)	— (219)	8 (219)	6 (219)	2 (203)	19 (203)	— (205)	6 (225)	21 (225)	— (177)	1 (239)	7 (239)	— (239)	— (301)	— (255)
$[M-SH-C_2H_2]^+$	4 (189)	8 (189)	6 (189)	— (191)	3 (191)	— (191)	2 (175)	100 (175)	— (177)	—	—	—	—	—	—	—	—
$[M-SO]^{+\cdot}$ *d*	10 (202)	— (202)	— (202)	20 (204)	— (204)	— (204)	77 (188)	1 (188)	100 (190)	100 (210)	6 (210)	94 (162)	10 (224)	— (224)	100 (224)	80 (286)	100 (240)
m/z 167	3	9	8	3	14	10	3	10	—	4	6	—	2	3	6	48	5
m/z 166	10	43	32	16	17	34	11	21	7	11	65	3	10	7	5	11	7
m/z 151	14	5	2	14	2	2	11	2	7	3	2	4	6	1	5	5	3
m/z 150 *c*	47	12	9	27	8	5	30	7	30	3	3	12	29	3	3	—	1
m/z 149 *b*	5	62	54	3	10	8	5	21	8	—	3	21	3	4	1	—	1
m/z 134 *e*	26	—	3	32	3	—	47	3	53	4	—	26	15	—	—	—	7
m/z 122	11	7	4	12	5	3	15	4	8	—	4	17	7	2	4	—	7
m/z 121	30	23	13	26	17	9	37	16	14	—	7	42	17	6	8	—	7
m/z 120	23	78	59	25	66	49	34	46	16	12	100	31	8	13	16	7	20
m/z 119 *f*	20	7	7	30	6	6	32	6	13	4	4	26	4	—	5	—	3
m/z 104	30	3	3	39	3	2	52	2	17	16	2	38	20	5	25	7	20
g	3 (100)	— (100)	— (100)	8 (102)	2 (102)	3 (102)	4 (86)	2 (86)	— (88)	8 (108)	9 (108)	— (60)	7 (122)	2 (122)	4 (122)	3 (184)	1 (138)
a	100 (84)	68 (84)	62 (84)	100 (86)	48 (86)	31 (86)	100 (70)	83 (70)	6 (72)	10 (92)	2 (92)	20 (44)	22 (106)	22 (106)	24 (106)	30 (168)	7 (122)

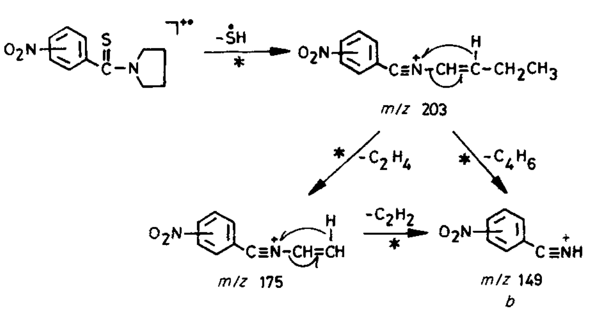
[a] Intensities as % of the base peak.
The figures in parentheses indicate the *m/z* value of the ion.



Scheme 2

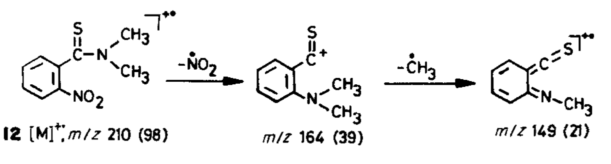
radical affording the fragment at *m/z* 121. In compound **16**, the fragment at *m/z* 167 is more intense (48%), due perhaps to the stability of the neutral species ejected (Scheme 2). The ion at *m/z* 122 is obtained directly from the molecular ion by a simple cleavage.

Another expected fragmentation pathway is the loss of sulfhydryl radical from the molecular ions. The mechanism of this process is discussed in detail elsewhere.[21] The $[M-SH]^+$ ion in turn decomposes through two parallel pathways giving rise to another general fragment ion *b* at *m/z* 149 (Scheme 3). This mode of fragmentation appears to be less important in the *ortho*-nitro compounds, due perhaps to the interaction of the nitro group which does not favour the formation of an $[M-SH]^+$ ion. In the case of compound **12**,[17] where no $\dot{S}H$ loss from the molecular ion is observed, the origin of the fragment at *m/z* 149 could be $[(M-NO_2)-CH_3]^{+\cdot}$ (Scheme 4).



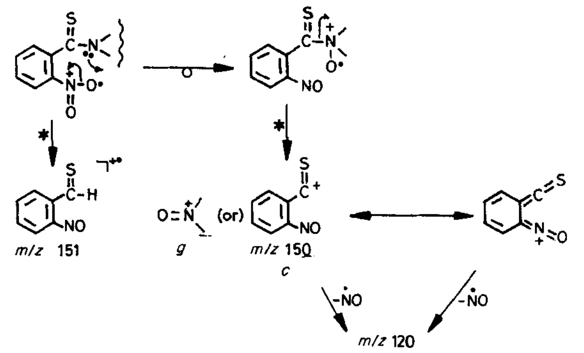
Scheme 3

The anticipated oxygen migrations from the nitro group to the sulfur and to the nitrogen in the side chain have been noticed in all the *ortho* isomers. The evidence for the oxygen transfer to the nitrogen of the amine function is adduced from the presence of a fragment at *m/z* 150 (*c*), where the charge is located on



Scheme 4

the sulfur-containing moiety after the initial oxygen migration from the nitro group to the nitrogen of the amine function through a 6-membered transition state followed by an α-fission (Scheme 5). Further, the mass analysed kinetic energy (MIKE) spectrum of the molecular ion at *m/z* 236 of compound **7** (Fig. 1(a)) has revealed the formation of the ion at *m/z* 150 directly from the molecular ion. The MIKE spectrum also contains the peak due to the daughter ion at *m/z* 86 corresponding to the 1-pyrrolidinyloxy radical, although this general fragment g, is not seen regularly in the mass spectra of all the *ortho* isomers (Table 1). The fragment at *m/z* 150 is of smaller abundance in those *ortho* nitro compounds, where other competing processes such as the 4-centered phenyl migration, intramolecular cyclization, etc., are potentially more favourable. Another fragmentation in the same direction with a β-hydrogen migration is the formation of the ion at *m/z* 151 (Scheme 5) and its direct formation from the molecular ion is also supported by the MIKE spectrum (Fig. 1(a)) of the molecular ion of compound **7**. The ion at *m/z* 150 in the case of **13** could also be due to $[\mathrm{Ph{\cdot}CH_2NH{\cdot}C{\equiv}S}]^+$, formed as a result of simple cleavage. However, its contribution to the fragment at *m/z* 150 may be small as it is found to be present only to the extent of 3% in the spectrum of the *meta* isomer **14**.



Scheme 5

Another novel competitive oxygen migration noticed in the mass spectra of the *ortho* isomers is the transfer of an oxygen from the nitro group to the sulfur of the thioamide function through a 6-membered transition state followed by the ejection of SO from the molecular ions. A mechanism, involving the initial migration of the oxygen atom from the nitro group to the sulfur followed by the attack of the oxygen of the nitroso function on the carbon, with the concomitant expulsion of SO from the molecular ion leading to a cyclized fragment *d*, is being proposed for this process (Scheme 6). The elemental composition of this ion at *m/z* 188 in the case of compound **7** is found

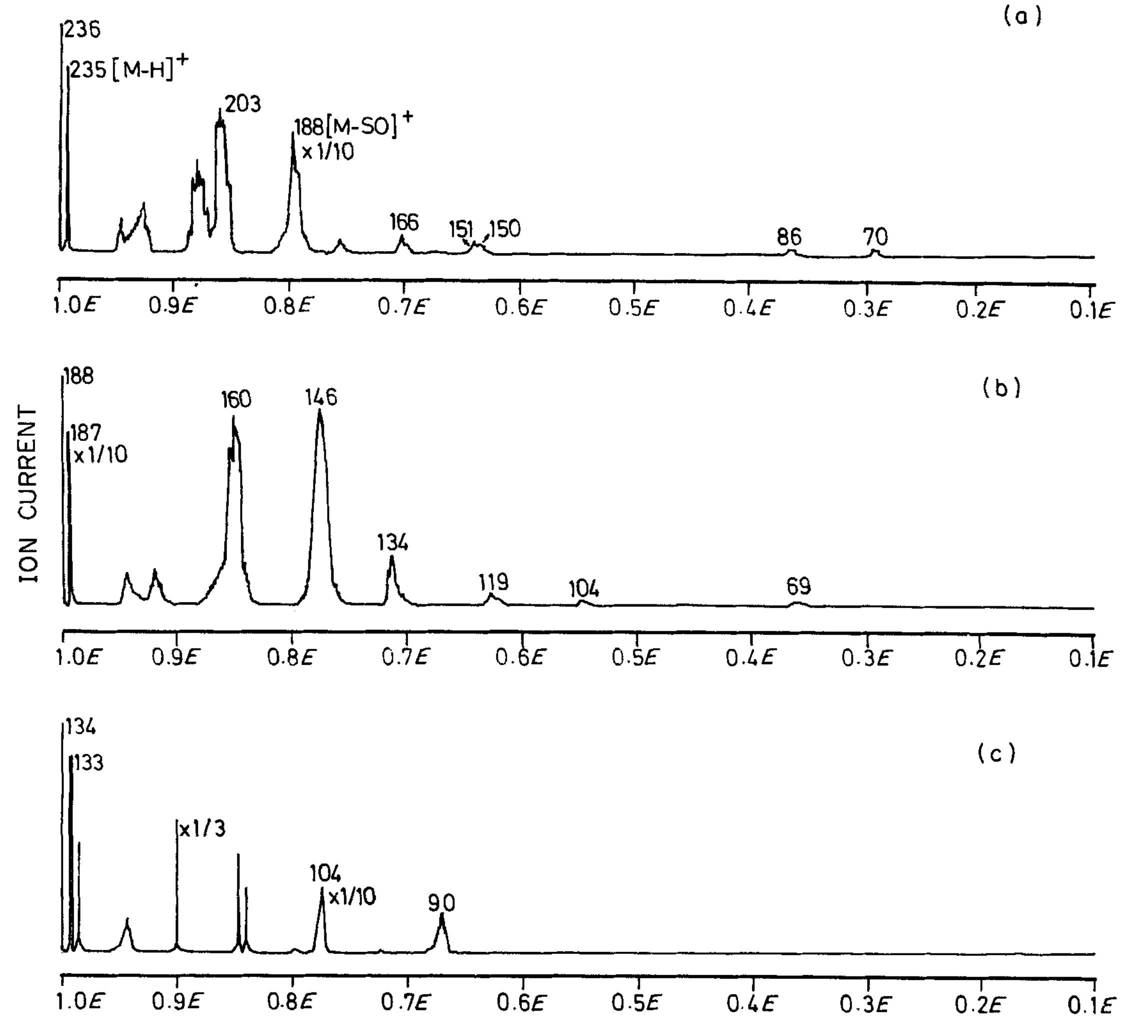
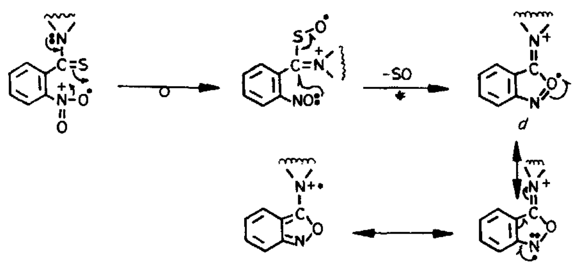


Figure 1. MIKE spectra of compound **7**: (a) $[\mathrm{M}]^{+\cdot}$ at *m/z* 236; (b) $[\mathrm{M-SO}]^{+\cdot}$ at *m/z* 188; (c) *m/z* 134.



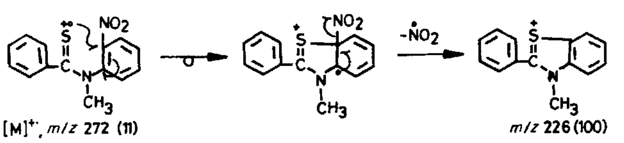
Scheme 6

to be $C_{11}H_{12}N_2O$ (188.0949), confirming the origin of this ion to be due to the loss of SO from the molecular ion.

An interesting piece of indirect evidence for the initiation of the oxygen transfer from the nitro group to the sulfur through the lone pair of electrons of the nitrogen of the amine function leading to the formation of the cyclized ion *d*, $[M-SO]^{+\cdot}$, is adduced from the fact that the $[M-H]^+$ ion is totally absent (Table 1) in compounds **1**, **4** and **7**. The $[M-H]^+$ ion in these compounds requires stability[21] through the nitrogen of the amine moiety. Such stability may not be available in the *ortho* isomers since the loss of SO from the molecular ion, which is also envisaged to require the same pair of electrons of the nitrogen, appears to be energetically more favourable.

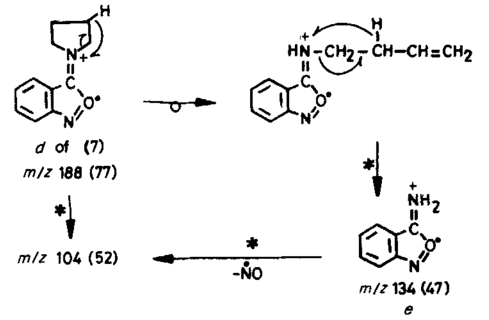
This interesting oxygen migration to the sulfur from the nitro group seems to be an important process considering the high abundance of the fragment ion *d* in many of the *ortho* compounds (Table 1) and even appears as the base peak in a few of them. However, the $[M-SO]^{+\cdot}$ ion is of smaller abundance (10%) in compound **13**, where the formation of the tropylium ion appears to be a more favourable process energetically.

In addition, no oxygen migration either to the sulfur or to the nitrogen was observed[22] in the mass spectrum of *N*-(2-nitrophenyl)-*N*-methylbenzenecarbothioamide, where the nitro group is present in the *ortho* position of the amine part. This may be due perhaps to the unfavourable transition states for the oxygen migration from the nitro group to the nitrogen of the amine (5-membered) and to the sulfur (7-membered). In contrast, loss of the nitro group from the molecular ion of this compound, leading to a cyclized fragment involving aromatic substitution at the *ortho* carbon atom, happens to be an important fragmentation process in this compound (Scheme 7). Such a cyclization is hardly seen in compounds **10**, **15** and **16**, where the interaction of the nitro group leading to the $[M-SO]^{+\cdot}$ fragment is a facile process.



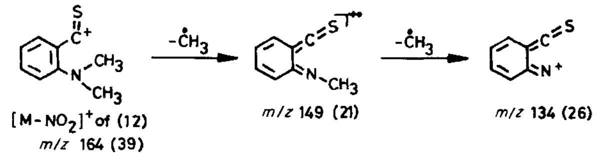
Scheme 7

One of the consequences of the oxygen migration to the sulfur in the *ortho* isomers is the formation of the ion *e* at *m*/*z* 134 from $[M-SO]^{+\cdot}$ (Fig. 1(b)). The formation of the ion *e* is rationalized to be the result of a hydrogen transfer from the amine moiety to the nitrogen with either a ring-contraction or a ring-opening followed by another β-hydrogen migration with simple α-fission as shown in Scheme 8 in the case of compound **7**. In compounds **9** and **13**, fragment *e* arises from $[M-SO]^{+\cdot}$ by a single hydrogen transfer. This ion is hardly seen in the mass spectra of compounds **10**, **16** and **17** because of the non-availability of the hydrogens for the transfer to the nitrogen atom for its formation. But the ion at *m*/*z* 134 in compound **12** can arise by the successive eliminations of NO_2 and two methyl radicals from its molecular ion (Scheme 9).



Scheme 8

Another common fragment noticed in the case of the ortho isomers is due to the ejection of NO radical from *e* leading to a fragment ion at *m*/*z* 104, which is also observed to originate from *d* as has been shown



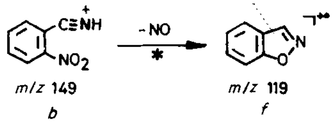
Scheme 9

Table 2. Physical data for the unknown compounds discussed

Compound No.	Method of preparation	Yield (%)	M.p. (°C) (C_6H_6)	Micro-analytical data Required C	Required H	Observed C	Observed H
1	A	69	116.5	57.60	5.60	57.60	5.50
8	B	78	115.5	55.94	5.09	55.60	5.30
9	A	46	42	55.46	5.88	55.30	6.10
10	A	29	114	60.46	3.87	60.10	3.70
11	A	86	122.5	60.46	3.87	60.20	3.80
13	A	52	65.5	61.76	4.41	61.80	4.70
14	A	72	100	61.76	4.41	61.30	4.50
16	A	47	188	68.26	4.19	67.90	4.40
17	A	33	126	58.33	4.17	57.90	4.20

by the MIKE spectra (Fig. 1(b and c)) of the ions *d* and *e* respectively in compound **7** (Scheme 8).

Another interesting *ortho* interaction during the secondary fragmentation process in the *ortho* isomers is the expulsion of a NO radical from *b* at *m*/*z* 149 (Scheme 10). Ion *f* is also produced from *d* as shown by the MIKE spectrum of $[M-SO]^{+\cdot}$ of compound **7** (Fig. 1(b)). Furthermore, the high voltage scan spectrum of the ion *f* at *m*/*z* 119 (Fig. 2) of **7** also supports its formation both from *b* and *d*. All the fragment ions afforded due to oxygen migrations are less important in the case of *meta* and *para* isomers.



Scheme 10

It can be seen from the abundances of the fragments due to the competitive oxygen migrations that the transfer of the oxygen to sulfur appears to be more facile, due perhaps to the larger size of the sulfur atom and also owing to the availability of the vacant *d* orbitals in sulfur, which can readily form a bond with the electron-rich oxygen of the nitro group. The oxygen migrations from the nitro group to the nitrogen of the amine function have been reported only in the case of amides,[18] but no report is available in the literature regarding such interaction in thioamides. The oxygen migration to sulfur in *N*,*N*-dialkyl-*o*-nitrothiobenzamides leading to the $[M-SO]^{+\cdot}$ ion has also been observed independently and reported by Clausen and co-workers.[23] In the present investigation, apart from independently[24] noticing that the oxygen transfer from the nitro group to the sulfur in aromatic thioamides leads in general to the $[M-SO]^{+\cdot}$ ion, a detailed examination of this process has been carried out from the point of view of mechanism, supported by high resolution data, MIKE spectra and the high voltage scan spectra.

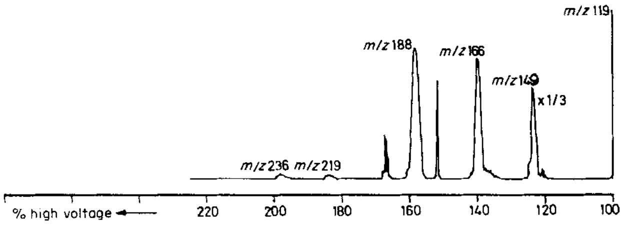


Figure 2. High voltage scan of the ion at *m*/*z* 119 of compound **7**.

EXPERIMENTAL

All the compounds discussed in this work were prepared either by treating[25] their corresponding amides with phosphorus pentasulfide in dry benzene or in dry pyridine (method A) or by Willgerodt-Kindler reaction[26] from their corresponding aldehydes (method B). The purity of the compounds was checked by thin-layer chromatography and the structures were confirmed by infrared and nuclear magnetic resonance spectral data. Table 2 gives the method used for the preparation, yield, melting points and the micro-analytical data for the unknown compounds discussed in the present work.

The mass spectra were taken on a Varian MAT CH-7 mass spectrometer. The spectra were run at 70 eV with an emission current of 100 μA. All the compounds were introduced into the mass spectrometer through the direct probe insertion at a probe temperature varying between 38 °C and 110 °C.

The MIKE spectra and high voltage scan spectra were taken on a Varian MAT 311A mass spectrometer. The MIKE spectra were run at 70 eV and at an accelerating potential of 8 kV. The high voltage scan spectra were run at 70 eV and at an accelerating potential of 3–8 kV.

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REFERENCES

1. J. Seibl and J. Vollmin, *Org. Mass. Spectrom.* **1**, 713 (1968).
2. R. J. C. Kleipool and J. I. Heins, *Nature (London)* **203**, 1280 (1964).
3. C. Djerassi and J. Sample, *Nature (London)* **208**, 1314 (1965).
4. D. Goldsmith and C. Djerassi, *J. Org. Chem.* **31**, 3661 (1966).
5. J. Seibl, *Org. Mass Spectrom.* **3**, 417 (1970).
6. J. Cable, S. A. Kagel and J. K. MacLeod, *Org. Mass. Spectrom.* **6**, 301 (1972).
7. D. Johnstone and D. M. Smith, *Org. Mass Spectrom.* **9**, 789 (1974).
8. S. Middleton, M. Butcher and R. J. Mathews, *Aust. J. Chem.* **27**, 2583 (1974).
9. D. V. Ramana and M. Vairamani, *Indian J. Chem.* **17B**, 369 (1979).
10. R. K. M. R. Kallury and J. Hemalatha, *Org. Mass. Spectrom.* **15**, 659 (1980).
11. M. Mintas, K. Jakopcic, L. Klasink and H. Gusten, *Org. Mass. Spectrom.* **12**, 544 (1977).
12. D. V. Ramana and M. Vairamani, *Org. Mass. Spectrom.* **9**, 1158 (1974).
13. J. Martens, K. Praefcke and H. Schwarz, *Org. Mass Spectrom.* **8**, 317 (1974).
14. J. Martens, K. Praefcke, U. Schulze, H. Schwarz and H. Simon, *Tetrahedron* **32**, 2467 (1976).
15. D. N. B. Mallen and J. M. Smith, *Org. Mass Spectrom.* **14**, 171 (1979).
16. J. Martens, K. Praefcke and H. Schwarz, *Leibigs Ann. Chem.* 62 (1975).
17. H.-F. Grützmacher and D. V. Ramana, *Org. Mass Spectrom.* **16**, 227 (1981).

18. H. Schwarz and F. Bohlmann, *Org. Mass Spectrom.* **9,** 283 (1974).
19. J. Martens, K. Praefcke, H. Schwarz and H. Simon, *Phosphorus* **6,** 247 (1976).
20. R. L. Carney, *Org. Mass Spectrom.* **6,** 1239 (1972).
21. D. V. Ramana and S. K. Viswanadham, *Org. Mass Spectrom.* **17,** 409 (1982).
22. T. J. Broxton and J. E. Rowe, *Org. Mass Spectrom.* **12,** 185 (1977).
23. K. Clausen, S. Scheibye, S. O. Lawesson, J. H. Bowie and T. Blumenthal, *Org. Mass Spectrom.* **15,** 640 (1980).
24. The results obtained in the present study have already been presented at the "All India Chemists Convention", held at Indian Institute of Technology, Bombay, in December 1980. Abstract No. 124.
25. N. Pravdic and V. Hahn, *Croat. Chem. Acta.* **34,** 85 (1962).
26. K. A. Jensen and C. Pedersen, *Acta. Chem. Scand.* **15,** 1087 (1961).

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