Thermochimica Acta, 137 (1989) 391–395
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THE EFFECT OF TEMPERATURE ON THE MASS FRAGMENTATION OF SOME 3,1-BENZOXAZINES

ALI. A.H. SAEED * and SALAM J. TITINCHI

Department of Chemistry, College of Science, Basrah University, Basrah (Iraq)

(Received 25 February 1988)

ABSTRACT

The effect of temperature on the mass fragmentation of some 3,1-benzoxazines was investigated. The data indicate that 1,2-dihydro-4*H*-2-(α-furyl)-3,1-benzoxazine undergoes significant thermal rearrangement to anilide, and to a much lesser extent the α-pyrryl analogue before fragmentation, whereas the mass spectrum of the α-thienyl derivative was unchanged with temperature.

INTRODUCTION

3,1-benzoxazines have become an important class of compounds since some of their derivatives were selected as potential antileukemia agents [1]. Earlier studies have included preparation and reactions [2–4], electronic spectra and the effect of solvents on the tautomerism of 3,1-benzoxazine—Schiff base [3,4], mass fragmentation [3,4], and recently IR studies [5]. The present work deals with the effect of temperature on the mass fragmentation of 3,1-benzoxazines derived from *o*-aminobenzyl alcohol and five-membered heterocyclic aldehydes.

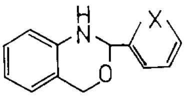
EXPERIMENTAL

The mass spectra were performed by Alfred Berhardt, Mikroanalytisches Laboratorium, F.R.G., at different sample temperatures. They were obtained on an SM 1B (Varian MAT) mass spectrometer with data system SS 100 at 70 EV; the direct inlet system was used. All the five-membered heterocyclic 3,1-benzoxazines Ia–c (Scheme 1) used throughout this work were prepared and purified using procedures described in the literature [4].

---

* To whom correspondence should be addressed. Present address: Department of Chemistry, College of Science, Al-Mustansiriyha University, Baghdad, Iraq.

0040-6031/89/$03.50



X = O , Ia
X = NH , Ib
X = S , Ic

Schema 1

RESULTS AND DISCUSSION

The breakdown of compounds Ia–c follows the general mass fragmentation pathways of 1,2-dihydro-4*H*-2-substituted-3,1-benzoxazines [3,4]. Tables 1 and 2 represent the major fragment ions (Schemes 2 and 3) which were observed in the mass spectra of Ia–c at different temperatures. These fragment ions were identified on the basis of previous findings [3,4] unless otherwise indicated. Our thermal data show that significant thermal rearrangement of compound Ia to anilide (Scheme 4), and to a much less extent to compound Ib, may occur before fragmentation, whereas Ic does not undergo such thermal rearrangement. This suggestion is confirmed by the following findings.

TABLE 1

Major fragment ions and their relative intensities observed in the mass spectra of compound Ia at different temperatures

Fragment ion [a]	Relative intensity (%)			
	160 °C	195 °C	235 °C	300 °C
$M^{\cdot+}+1$ (202)	35	7	4	–
$M^{\cdot+}$ (201)	90	35	15	2
$M^{\cdot+}-H$ (200)	13	6	12	–
$M^{\cdot+}-OH$ (184), IIa	30	21	20	5
$M^{\cdot+}-CHO$ (172), IIb	17	15	6	6
IIIa (134)	36	17	12	4
IIIb (132)	19	12	14	5
IIIc (120)	25	18	19	2
IVa + H (107)	5	5	13	70
IVa (106)	45	44	69	100
IVa – H (105)	97	100	100	23
IVb (104)	100	84	95	21
Va (96)	18	12	10	2
Va – H (95)	11	8	10	6
Vb (81)	89	51	31	17

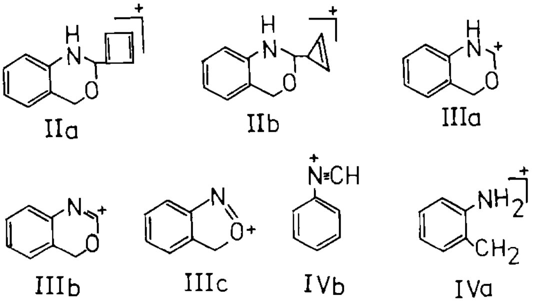
[a] *m/z* in parentheses.

TABLE 2

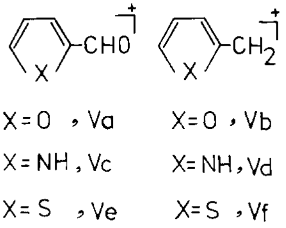
Major fragment ions and their relative intensities observed in the mass spectra of compound Ib at 70 and 80 °C and of compound Ic at 60 °C

Compound Ib			Compound Ic	
Fragment ion	Relative intensity		Fragment ion [a]	Relative intensity at 60 °C (%)
	70 °C	80 °C		
$M^{\cdot +}+1$ (201)	7	23	$M^{\cdot +}+1$ (218)	9
$M^{\cdot +}$ (200)	50	92	$M^{\cdot +}$ (271)	70
$M^{\cdot +}-H$ (199)	16	39	$M^{\cdot +}-H$ (216)	7
$M^{\cdot +}-NH_2$ (184), IIa	2	4	$M^{\cdot +}-SH$ (184), IIa	10
$M^{\cdot +}-CH_2N$ (172), IIb	2	5	IIb (172)	–
IIIa (134)	–	2	IIIa (134)	2
IIIb (132)	10	29	IIIb (132)	11
IIIc (120)	9	23	IIIc (120)	20
IVa+H (107)	2	5	IVa+H (107)	–
IVa (106)	15	10	IVa (106)	15
IVa−H (105)	13	13	IVa−H (105)	100
IVb (104)	19	2	IVb (104)	62
Vc (95)	9	20	Ve (112)	10
Vc−H (94)	5	14	Ve−H (111)	13
Vd (80)	100	100	Vf (97)	69

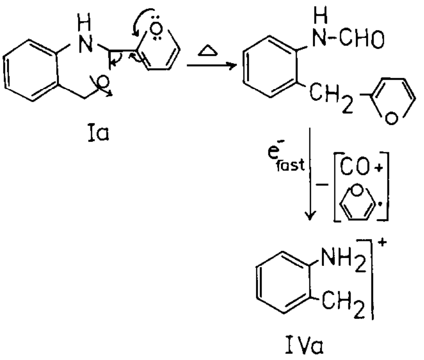
[a] *m/z* in parentheses.



Schema 2



Schema 3



Schema 4

(i) the mass spectrum of Ic was unchanged with sample temperature. On the other hand, the intensity of the $M^{\cdot+}$ peak of Ib increases with temperature, whereas the intensity of the $M^{\cdot+}$ peak of Ia decreases sharply with increasing temperature, indicating that the molecular ion in this case is less stable at high temperatures. In other words, the compound may rearrange with increasing temperature to a compound which has a less stable molecular ion.

(ii) the intensities of the fragment ions of Ia—$M^{\cdot+} - OH$ (m/z 184, suggested structure IIa), $M^{\cdot+} - CHO$ (m/z 172, suggested structure IIb), and IIIa–c—decrease with increasing temperature, whereas the intensities of the corresponding fragment ions of Ib—$M^{\cdot+} - NH_2$ (m/z 184), $M^{\cdot+} - CH_2N$ (m/z 172), and IIIa–c—increase with temperature.

(iii) the intensities of the fragment ions of Ia:—IVa, IVa + H, IVa − H, and to a less extent IVb—increase sharply with increasing temperature. These fragment ions represent the base peak in the mass spectra of Ia at different temperatures (Table 1). While these fragment ions are of much smaller intensities in the mass spectra of Ib and Ic (Table 2), they may originate from a one-step transition following electron impact after the thermal rearrangement of Ia, as shown in Scheme 4.

(iv) the low intensity of the fragment ion (of Ia) Vb, at high temperatures compared with the corresponding fragment ion of Ib, i.e. Vd, confirm that the fragmentation of Ia occurs mainly by the mechanism shown in Scheme 4. The less important fragment ions which were observed in the mass spectra of Ia–c at m/z values 79, 78, 77, 68–65, 53–51, 44, 40, and 39 may originate from further fragmentation of the ions IIIa–c [3,4], IVb [6–11], and IVa.

Accordingly, it can be concluded that Ia may undergo significant thermal rearrangement, at temperatures >235 °C (and especially at 300 °C) to give a mixture of anilide and 3,1-benzoxazine, where the former appears to be predominant. The mechanism of this thermal rearrangement is probably similar to the Chapman rearrangement of *N*-alkyl formimidate to *N*-alkyl formanilide at elevated temperatures [12–14].

REFERENCES

1 Private communication, National Cancer Institute (NCI), Bethesda, MD, U.S.A., 1985.
2 J.K. Landquist, Comprehensive Organic Chemistry Heterocyclic Compounds, Pergamon, Oxford, Vol. 4, 1979, p. 1056.
3 A.A.H. Saeed, J. Heterocycl. Chem., 19 (1982) 113.
4 A.A.H. Saeed and E.K. Ebraheem, Can. J. Spectrosc., 28 (1983) 169.
5 A.A.H. Saeed, Can. J. Spectrosc., (1988), in press.
6 J.H. Bowie, R.G. Cooks, J.W. Fisher and T.M. Spotswood, Aust. J. Chem., 21 (1968) 2021.
7 C.S. Barnes, E.J. Halbert, R.J. Goldsack and G. Wilson, Aust. J. Chem., 26 (1973) 1031.
8 R.A. Abramovitch, E.P. Kyba and E.F.V. Scriven, J. Org. Chem., 36 (1971) 3796.
9 A.A.H. Saeed, A.W.A. Sultan, S.A. Selman and N.A. Abood, Can. J. Spectrosc., 28 (1983) 104.
10 A.A.H. Saeed, E.K. Ebraheem and A.A. Tossonian, Thermochim. Acta, 97 (1986) 337.
11 A.W. Chapman, J. Chem. Soc., (1927) 1743.
12 R.M. Roberts and P.J. Vogt, J. Am. Chem. Soc., 78 (1956) 4779.
13 A.A.H. Saeed, S.A. Selman, A.W.A. Sultan and N.A. Abood, Can. J. Spectrosc., 28 (1983) 63.
14 A.A.H. Saeed and A.W.A. Sultan, Iraqi J. Sci., 24 (1983) 29.