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THERMAL DECOMPOSITION AND MASS FRAGMENTATION OF SOME NEW HYDROXY SCHIFF BASES

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ABSTRACT

New hydroxy Schiff bases have been synthesized from salicylaldehyde, *o*-hydroxyacetophenone, *β*-hydroxynaphthaldehyde, and 4,5-dimethyl-*o*-phenylenediamine. Their thermal decomposition and mass fragmentation at different temperatures were studied and compared. *β*-Hydroxynaphthaldehyde Schiff bases decompose to give naphthoisoxazole, whereas salicylaldehyde and *o*-hydroxyacetophenone Schiff bases decompose through benzimidazole derivative intermediates.

INTRODUCTION

Several salicylidene Schiff bases have been synthesized previously. The earlier studies have included electronic spectra [1,2], effect of solvent on the keto-enol equilibria [3–5], luminescence properties [6,7], mass fragmentation [8,9], kinetics of hydrolysis [10,11], and complexation with various metal ions [12–19]. The present work deals with new hydroxy Schiff bases derived from hydroxy carbonyls and diamines, namely salicylidene (**Ia**) *o*-hydroxyacetophenonylidene (**Ib**) *β*-hydroxynaphthylidene-4,5-dimethyl-*o*-phenylenediamine (**Ic**) bis(salicylidene) (**Id**), and bis(*β*-hydroxynaphthylidene)-4,5-dimethyl-*o*-phenylenediamine (**Ie**) (Scheme 1); their thermal decompositions were studied and compared with their mass fragmentation, a study which has not been attempted previously on any kind of Schiff bases.

EXPERIMENTAL

Details of the elemental analyses, IR, UV, mass spectra and thermogravimetric (TG and DTG) analyses were discussed elsewhere [20,21].

Compounds **Ia** and **Ib** were prepared by refluxing equimolar amounts of

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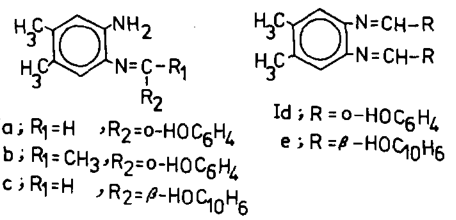


Scheme 1

4,5-dimethyl-*o*-phenylenediamine and the corresponding hydroxy carbonyl compound in an oil bath for 1 h. Upon cooling, ethanol was added, a yellow crystalline product separated, which was collected, and then recrystallized from ethanol.

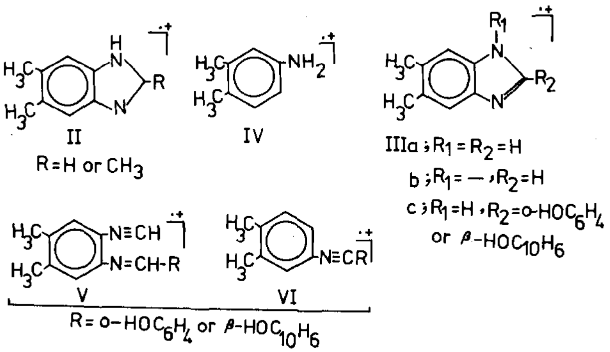
Compounds **Ic** and **Id** were prepared by boiling equimolar amounts of the diamine and the corresponding hydroxy aldehyde in ethanol solution for a few minutes. Upon cooling, a reddish-orange or yellow crystalline product separated, which was collected, and then recrystallized from ethanol.

Compound **Ie** was prepared by refluxing **Ic** for 2 h in glacial acetic acid. Upon cooling, an orange powder separated, which was collected, and then washed repeatedly with hot ethanol.

Naphthoisoxazole (**VII**) was prepared by heating **Ic** at 205–215°C for 1 h. Upon cooling, a brownish-yellow crystalline product separated, which was collected, and then washed repeatedly with hot ethanol. The elemental analyses, melting points, IR and UV spectra of compounds **Ia–e** and **VII** are shown in Table 1.

RESULTS AND DISCUSSION

The IR and UV–visible absorption bands represented in Table 1 are characteristic of hydroxy Schiff bases [3–5, 20, 22]. Tables 2 and 3 and



Scheme 2

TABLE 1

The melting points, elemental analyses, IR and UV spectral data of compounds **I** and **VII**

Compound No.	mp (°C)	% Calc. (found)			IR bands in nujol mull (cm^{-1})	UV bands in cyclohexane λ_{max}(nm)(ϵ, $m^2 mol^{-1}$)
		C	H	N		
Ia	89–90	75.00 (75.03)	6.67 (6.75)	11.67 (11.61)	3420–3340(O–H) and (N–H), 1605 (C=N), 1560 (N–H bend)	392(950), 348(720), 326(620) [a], 312(540) [a], 279(1400), 246(1680), 222(2830)
Ib	105–106	75.59 (75.51)	7.09 (7.14)	11.02 (11.02)	3470(O–H), 3370 (N–H), 1625(C=N) 1575(N–H bend).	370(460) [a], 330(690), 315(600) [a], 225(680) [a], 217(2730)
Ic	196–197	78.62 (78.45)	6.21 (6.27)	9.66 (9.53)	3380(O–H), 3320–3220(N–H), 1640 (C=N), 1610 (N–H bend)	412(1000), 370(670) [a], 318(730), 254(1630) [a], 223(3440), 205(3410)
Id	149–150	76.72 (76.63)	5.81 (5.76)	8.14 (8.10)	3440–3360(O–H) 1620(C=N)	365(200) [a], 340(2480), 271(3210), 234(3330), 213(4390)
Ie	256–257	81.08 (80.95)	5.41 (5.43)	6.31 (6.27)	3460–3440(O–H) 1620(C=N)	396(300) [a], 372(380), 319(360), 230(1310), 220(1260)
VII	282–283	78.11 (77.74)	4.14 (4.24)	8.29 (8.53)	1610(C=N) 1100(C–O)	–

[a] Shoulder.

Scheme 2 represent the major fragment ions which were observed in the mass spectra of **Ia–e**. The thermogravimetric curves for compounds **Ia** and **Ib** (Figs. 1 and 2) show that they decompose at 219 and 227°C, respectively, forming **II** and **IV** – H (Schemes 2 and 3). These ions may decompose further above 500°C. The mass spectra of **Ia** and **Ib** at 80 and 75°C, respectively, show that **II** is the most abundant ion (Table 2) which sometimes represents the base peak. Our suggested mechanism for the thermal decomposition and mass fragmentation of **Ia** and **Ib** is reasonable since it is well known that the reaction of *o*-phenylenediamine with diaryl ketones yields benzimidazole derivatives (**II** or **III**) through the formation of benzylidene-*o*-aminoaniline Schiff base intermediates [23], a structure similar to **Ia–c**. On the other hand, the thermogravimetric curves for compounds **Ic** and **Ie** show that they form **VII** at 264 and 148°C, respectively (Fig. 1 and Scheme 3), which decomposes further or evaporates above 500°C. In a separate experiment, **VII** has been prepared from **Ic** and identified (see Experimental section, Table 1 and Scheme 3). It can be concluded that **Ia** and **Ib** decompose directly since they are more stable at high temperatures

TABLE 2

Major fragment ions and their relative abundances observed in the mass spectra of compounds **Ia–c**

Ia (80°C)		**Ib** (75°C)		**Ic** (135°C)		Fragment ion
m/z	Relative intensity (%)	*m/z*	Relative intensity (%)	*m/z*	Relative intensity (%)	
241	8	255	2	291	8	$M^{\cdot+}+1$
240	48	254	16	290	35	$M^{\cdot+}$
239	51	253	3	289	25	$M^{\cdot+}-H$
–	–	239	100	–	–	$M^{\cdot+}-CH_3$
147	100	161	22	147	100	**II**
–	–	–	–	146	4	**IIIa**
–	–	–	–	145	10	**IIIb**
–	–	–	–	144	7	$C_{10}H_8O^{\cdot+}$ (β-Naphthol)
136	71	–	–	136	6	$C_8H_{12}N_2^{\cdot+}$ 4,5-Dimethyl-*o*-phenylenediamine
135	33	–	–	–	–	$C_8H_{11}N_2^+$
121	22	121	1	–	–	**IV**
120	13	120	13	–	–	**IV** – H
119	6	119	6	–	–	**IV** – H_2
93	10	93	7	–	–	$C_6H_5O^{\cdot+}$ (phenoxide)
77	11	77	7	128	7	$C_6H_5^+$ and $C_{10}H_8^{\cdot+}$

than their corresponding di-Schiff bases, namely **Id** (see Experimental section). Whereas **Ic** decomposes only after it converts thermally to the di-Schiff base **Ie**, through formation of the intermediate **VIII** (Scheme 3). This is confirmed by: (i) conversion of **Ic** in glacial acetic acid to **Ie** through

TABLE 3

Major fragment ions and their relative abundances observed in the mass spectra of compounds **Id** and **Ie**

Id (140°C)		**Ie** (220°C)		Fragment ion
m/z	Relative intensity (%)	*m/z*	Relative intensity (%)	
345	27	445	12	$M^{\cdot+}+1$
344	100	444	43	$M^{\cdot+}$
343	13	443	13	$M^{\cdot+}-H$
322	14	–	–	?
251	35	301	4	**V**
238	53	288	100	**IIIc**
224	31	274	19	**VI**
208	11	258	14	Cyclised ion **VI** – 16(O)

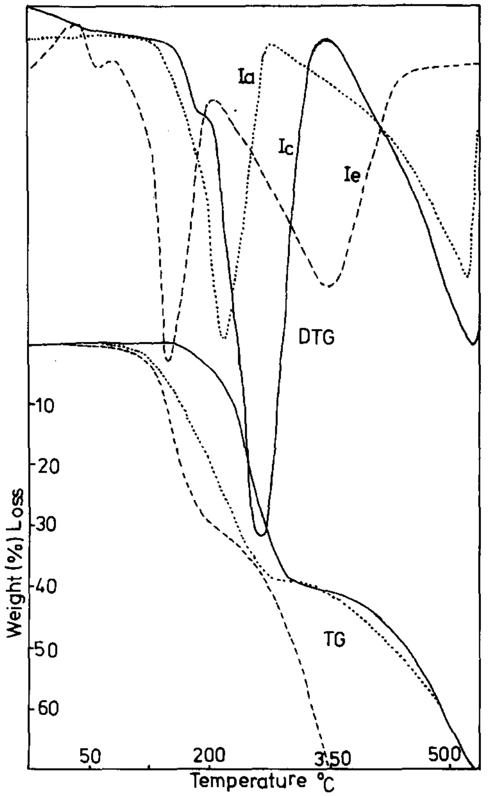
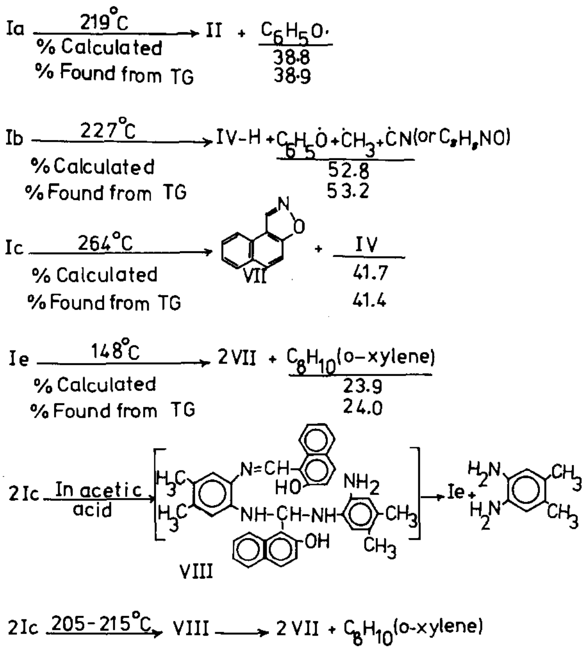


Fig. 1. Thermogravimetric curves (DTG and TG) for compounds **Ia** (······), **Ic** (———) and **Ie** (- - - - - -).



Scheme 3

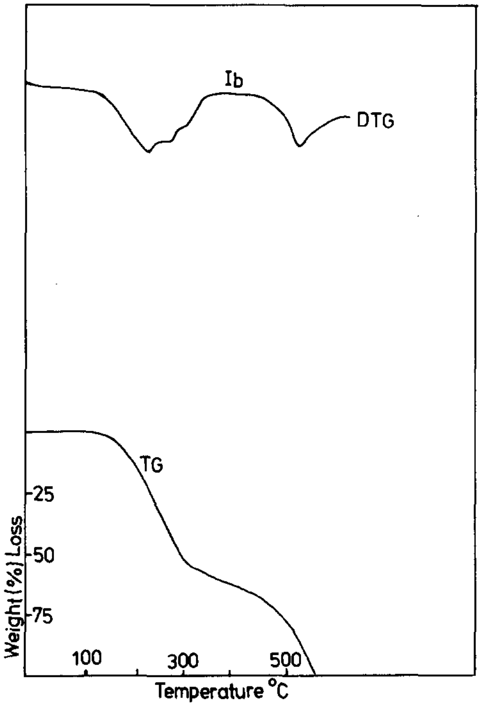


Fig. 2. Thermogravimetric curves (DTG and TG) for compound **Ib**.

formation of the intermediate **VIII** (Scheme 3), (ii) thermal conversion of **Ic** to **VII** via **VIII** (Scheme 3), and (iii) the thermal decomposition of both **Ic** and **Ie** leading to **VII** (Scheme 3). The preparation of naphthoisoxazole from Schiff bases has never been reported previously. The mass fragmentation of **Ie** at 220°C behaves almost identically to that of **Ia–d**, this is because **Ie** yields **VII** only at low temperature, namely at 148°C (Scheme 3).

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