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Mass Spectral Behavior of Some Indole Schiff-Base Derivatives

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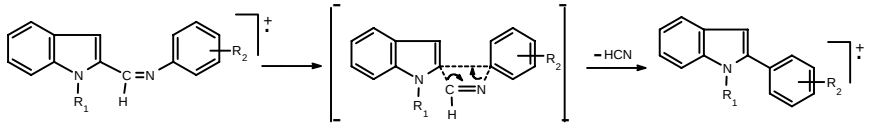
Abstract: Twenty-two indole Schiff-base derivatives were synthesized. Two special ways of cleavage were discussed in the formation of the specific fragment ions in the mass spectra(MS).

Key words: Schiff-base, cleavage, specific fragment ions, EI high resolution MS .

The analysis of MS data of twenty two indole Schiff-base derivatives indicates a class of specific fragment ions (**Table1**). These specific fragment ions are X, Y and Z. Here we put forward the possible MS cleavage mechanism of forming these specific fragment ions. The structures of the twenty-two derivatives are confirmed by ^{1}H-NMR data[1].

As seen from **Table 1**, X is a kind of specific fragment ions, *i.e.* $[M-27]^+$ or $[(M-H_2O)-27]^+$. The development of M^+-27 fragment ion may go through four membered transition state[2] and M^+ loses HCN by inner extrusion (**Figure1**).

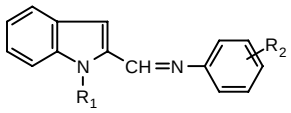
Figure 1 The special MS fragmentation pattern of compounds **1~22**



M^+ **(X) $[M-27]^+$**

The analysis of MS data of compounds **9~22** indicates another class of specific fragment ions (Y) and their complementary ions (Z) (**Table 1**). Y is *m/z* 144 and Z is M^+-144 fragment ions. Among them *m/z* 144 is considerably stable fragment ion. The development of these fragment ions probably goes through an intermediate states with shift of hydrogen[4]. The MS fragmentation pattern of compound **13** illustrates the possible mechanism as follows:

Table 1. Structures of compounds **1~22** and specific fragment ions and relative abundance by EIMS



Compd. (No.)	R^1	R_2	M^+	X	Y	Z
				(relative abundance)		
1	H	4'-OCH_3	250 (100)	223 (2)		
2	H	4'-SO_2NH_2	299 (100)	272 (1)		
3	H	4'-OH	236 (20)	209 (2)		
4	H	4'-$NHCOCH_3$	277 (100)	249 (1)		
5	H	2'-OH	236 (88)	208 (3)		
6	H	3'-COOH	264 (100)	237 (4)		
7	H	3'-COOH, 4'-OH	280 (100)*	235 (25)		
8	H	4'-$COOC_2H_5$	292 (100)	264 (20)		
9	CH_3	4'-OCH_3	264 (75)	236 (8)	143 (3)◆	121 (100)
10	CH_3	4'-$COOC_2H_5$	306 (100)	279 (4)	144 (6)	163 (10)
11	CH_2Ph	4'-OCH_3	340 (50)	313 (1)	143 (1)◆	197 (100)
12	CH_3	4'-OH	250 (100)	222 (10)	144 (85)	107 (35)
13	CH_2Ph	4'-OH	326 (60)	298 (1)	144 (72)	183 (50)
14	CH_3	2'-OH	250 (100)	222 (4)	144 (70)	107 (5)
15	CH_3	4'-$NHCOCH_3$	291(100)	263 (4)	144 (38)	148 (38)
16	CH_2Ph	4'-$NHCOCH_3$	367 (85)	339 (1)	144 (4)	224 (100)
17	CH_3	4'-SO_2NH_2	313 (100)	285 (6)	143 (1)◆	170 (3)
18	CH_2Ph	4'-SO_2NH_2	389 (48)	361 (1)	144 (2)	246 (30)
19	CH_3	3'-COOH, 4'-OH	294 (100)*	248 (18)	144 (40)	151 (10)
20	CH_3	3'-COOH	278 (100)	250 (12)	143 (4)	135 (10)
21	CH_2Ph	3'-COOH	354 (100)	326 (2)	∽	211 (66)
22	CH_2Ph	3'-COOH, 4'-OH	370 (98)*	324 (15)	144 (100)	227 (30)

*Molecular ions lose water before its specific cleavage[3].
◆Y of a small number of compounds are 143 but abundance is very small.

As **Figure 2** shows, the intermediate state with H-shift in compound **13** leads to the formation of *m/z*144 and its complementary ion *m/z* 183 with the abundance of 72% and 50% respectively.

The specific cleavage of compounds **9~22** was further confirmed by the result of EI high resolution MS of compound **13.** As seen from **Table 2**, *m/z* 183 ($C_{13}H_{11}O$), and *m/z* 144 ($C_9H_8N_2$), have unequivocal elemental compositions.

Figure 2. The major MS fragmentation pattern of compound **13**

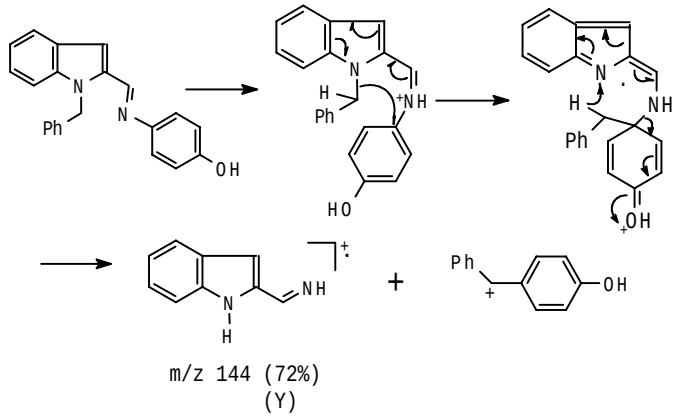


Table2. High resolution mass spectrum analysis of compound **13**

Ion	Mass(obs.)	Mass(calc.)	C	H	O	N
M^+	326.1414	326.1419	22	18	1	2
m/z 183	183.0804	183.0810	13	11	1	0
m/z 144	144.0682	144.0687	9	8	0	2

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Referance and notes

1. notes: H-NMR (δ ppm , DMSO) of parts of compounds (**1, 5, 6, 7, 8, 10, 11, 13, 14, 16, 19, 22)**
   1 3.77 (s, CH_3), 6.97 (d, 3',5'-H), 6.99 (s, 3-H), 7.01 (t, 5-H), 7.18 (t, 6-H), 7.31 (d, 2',6'-H), 7.42 (d,7-H) 7.60, (d, 4-H), 8.60 (s, CH=N);
   5 6.82~6.92 (m, 3',4'-H), 7.02 (s, 3-H), 7.04~7.13 (m, 5,5'-H), 7.23 (t, 6-H), 7.45 (s, 6',7-H),7.64 (d, 4-H), 8.83 (s, CH=N);
   6 7.05 (t, 5-H), 7.10 (s, 3-H), 7.22 (t, 6-H), 7.45 (d, 7-H), 7.54~7.56 (m, 5',6'-H), 7.64 (d, 4- H), 7.80~7.83 (m, 2',4'-H), 8.67 (s, CH=N);
   7 7.00~7.05 (m, 3,5,5'-H), 7.20 (t, 6-H), 7.43 (d, 7-H),7.57 (dd, 6'-H), 7.62 (d, 4-H), 7.74 (sd, 2'-H), 8.65 (s, H=N);

8 1.32 (t, CH_3), 4.31 (q, CH_2), 7.04 (t, 5-H), 7.12 (s, 3-H), 7.23 (t, 6-H), 7.37 (d, 2', 6'-H), 7.44 (d,7-H), 7.65 (d, 4-H), 8.00 (d, 3',5'-H), 8.63 (s, CH=N);

10 1.32 (t,CH_3), 4.17 (s,1-CH_3), 4.31(q,CH_3), 7.11 (t,5-H), 7.22 (s,3-H), 7.33 (t,6-H) 7.39 (d,2',6'-H),
7.57 (d, 7-H), 7.68 (d, 4-H), 8.00 (d, 3',5'-H), 8.74 (s, CH=N);

11 3.75 (s, CH_3), 6.08 (s, CH_2), 3.75 (s, CH_3), 6.08 (s,CH_2,), 6.95 (d, 2H, 2-3',5'-H), 7.06~7.27 (m,3,5,6-H,2-2,6-H, and 1-Ar-H), 7.53 (d, 7-H), 7.67 (d, 4-H), 8.75 (s, CH=N);

13 6.08 (s, CH_2), 6.77 (d, 2-3',5'-H), 7.05~7.27 (m, 3,5,6-H, 2-2',6'-Hand 1-Ar-H), 7.51 (d, 7-H), 7.66 (d, 4-H), 8.82 (s, CH=N) ;

14 4.17 (s, CH_3), 6.81~ 6.91(m, 3', 4'-H), 7.04 ~7.12 (m, 5', 6'-H), 7.17 (s, 3-H), 7.17~7.32 (m, 5, 6-H), 7.55 (d, 7-H), 7.65(d, 4-H), 8.75 (s, CH=N);

16 2.03 (s, CH_3), 6.08 (s, CH_2), 7.10 (d, 2-2',6'-H), 7.14 ~7.27 (m, 3,5,6-H and 1-Ar-H),7.52 (d, 7-H),
7.59 (d, 2-3',5'-H), 7.68 (d,4-H), 8.75 (s, CH=N), 9.99 (s, NH);

19 4.16 (s,CH_3), 7.02 (d, 5'-H), 7.09 (t,5-H), 7.13 (s,3-H), 7.29 (t,6-H), 7.54 (d, 7-H), 7.59 (dd,6'-H),
7.65 (d, 4-H), 7.748 (d, 2-5'-H), 7.07~7.27 (m, 3,5,6-Hand 1-Ar-H), 7.49 (dd, 2-6'-H), 7.51 (d,H),
7.68 (d,4-H), 8.79 (s, CH=N).

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