Indian Journal of Chemistry
Vol. 37B, November 1998, pp. 1194-1196

Note

2,6-Diaryl pyridinium cation—A precursor in the cleavage process of 5,7-diaryl-piperidino[3,4-*d*]-1,2,3-selenadiazoles/ thiadiazoles

D Bhaskar Reddy*, A Somasekhar Reddy & V Padmavathi

Department of Chemistry, S.V.University, Tirupati 517 502, India

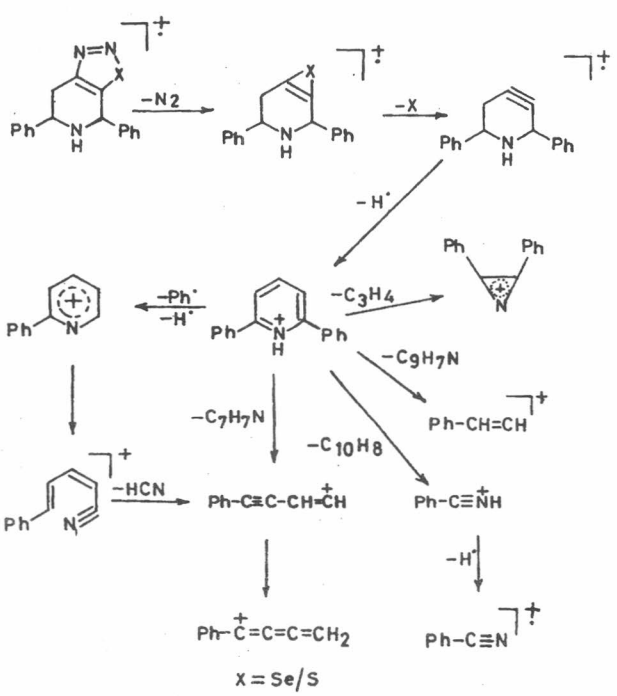
Received 9 December 1997; accepted (revised) 31 August 1998

The mass spectra of 5,7-diphenylpiperidino[3,4-*d*]-1,2,3-selenadiazole **1**, 5,7-di(4-methoxyphenyl)piperidino[3,4-*d*]-1,2,3-selenadiazole **2**, 5;7-di(4-chlorophenyl) piperidino [3,4-*d*]-1,2,3-selenadiazole **3**, 5,7-diphenylpiperidino [3,4-*d*]-1,2,3-thiadiazole **4**, 5,7-di(4-methoxy-phenyl) piperidino [3,4-*d*]-1,2,3-thiadiazole **5** and 5,7-di (4-chlorophenyl) piperidino [3,4-*d*]-1,2,3-thiadiazole **6**, have been studied under electron impact by low and high resolution mass spectrometry. It has been observed that 2,6-diaryl pyridinium cation is the predominant precursor ion in the cleavage process of the above molecules.

Heterocyclic compounds having nitrogen and sulfur possess potential pharmacological properties[1-4]. Since, sulfur and selenium being isosteric, the concept of isosteric exchange would modify the activity of biologically important molecules. Hence, it was thought of interest that the synthesis and comparative bio-assay of these compounds would add new dimensions to the existing knowledge. In this perspective, 5,7-diarylpiperidino-[3,4-*d*]selenadiazoles/thiadiazoles **1-6** were prepared. The synthesis and stereochemical aspects of these compounds have been discussed in our earlier communication[5]. The behaviour of some 5,7-diaryl-piperidino selenadiazoles **1-3** and thiadiazoles **4-6** under electron impact conditions were studied to characterize the compounds unambiguously.

In the mass spectrum of 5,7-diphenylpiperidino[3,4-*d*]-1,2,3-selenadiazole **1**- the M+2 appears with 100% intensity. The accurate mass of this is 342.3068 which corresponds to $C_{17}H_{15}N_3Se$ + 2H. The fragmentation process involves the expulsion of nitrogen followed by selenium resulting a radical cation at m/z 233. The appearance of an ion at m/z 312 confirms that the ejection of selenadiazole unit takes place in a stepwise manner. In fact, this type of fragmentation is analogous to compounds having selenadiazole ring[6]. The aromatization of an ion at m/z 233 by the elemination of H· followed by hydrogen rearrangement led to moderate intense pyridinium cation (m/z 232).

Cleavage of the bond α to the heteroatom seems to be the initiating step for the appearance of various daughter ions from the ion at m/z 232. The two peaks with substantial intensity at m/z 127 and 103 corresponds to 1-phenyl-3-buten-1-yne and styryl cations support such a type of fragmentation process. The former ion gets itself rearranged to a more stable allyl cation. On the other hand, the β-cleavage led to 2,3-diphenylaziridine cation with mass value 192 is another interesting decomposition process observed. In another mode of fragmentation, the phenyl hydrogen cyanide cation is formed, which by the ejection of H· gives phenyl cyanide radical cation (Scheme I). The occurrence



Scheme I

of 2-phenylpyridinium cation at m/z 154 could also arise from this ion by the expulsion of H· and Ph·. This cleavage process is further supported by the appearance of an ion at m/z 127 with the loss of HCN. Thus, different daughter ions observed indicates that 2,6-diphenyl pyridinium cation is the stable precursor ion formed in the cleavage process of **1**. The elemental composition of different daughter ions formed during the cleavage process have also been confirmed by the high resolution mass measurements. Chemical composition: $C_{17}H_{15}N_3Se$, Found: m/z 340.3022 (Calcd 340.2892); $C_{17}H_{15}N$; m/z 233.3045 (233.3158); $C_{17}H_{14}N$, m/z 232.2456 (232.3078); $C_{14}H_{11}N$, m/z 192.4002 (192.2425); $C_{10}H_7$, m/z 127.2394 (127.1672); C_8H_7, m/z 103.1564 (103.1449); C_7H_5N, m/z 103.1365 (103.1246).

In the mass spectrum of 5,7-diphenylpiperidino [3,4-*d*]-1, 2, 3-thiadiazole **4** also the M+2 ion appeared with 100% intensity which is confirmed by its chemical composition $C_{17}H_{15}N_3S$ + 2H (m/z 295.2162). The expulsion of N_2 and sulfur in a stepwise manner[7] as in **1** leads to the ions at m/z 265 and 233. The chemical composition of the daughter ions is similar to those observed in **1**. Thus, the cleavage process and the most abundant ions observed are similar to those as in **1** (see Table I). These formulations are in accord with the results of high resolution mass measurements. Chemical composition; $C_{17}H_{15}N_3S$, Found m/z 293.5246 (Calcd 293.3932); $C_{17}H_{15}N$, m/z 233.2642 (233.3158); $C_{17}H_{14}N$, m/z 232.3246 (232.3078); $C_{14}H_{11}N$, m/z 192.3452 (192.2425); $C_{10}H_7$, m/z 127.1864 (127.1672); C_8H_7, m/z 103.1389 (103.1449); C_7H_5N, m/z 103.1124 (103.1246).

The mass spectra of 5,7-di(4-methoxyphenyl) piperidino [3,4-*d*]-1,2,3-selenadiazole **2,** 5,7-di (4-chlorophenyl) piperidino [3,4-*d*]-1,2,3-selenadiazole **3**, 5, 7-di (4-methoxy-phenyl) piperidino [3,4-*d*]-1,2,3-thiadiazole **5** and 5,7-di (4-chlorophenyl) piperidino[3,4-*d*] 1,2,3-thiadiazole **6** showed identical fragmentation pattern thus confirming that the substituents have no influence on cleavage process. In all the cases M+2 ion appeared as the base peak of the spectrum. In **3** and **6** M+2, M+4, M+6 are observed which substantiate the presence of two chlorine atoms. In **2** and **5**, the anisyl cation ejects HCHO while forming phenyl cation which is a common process in such systems. All the fragmented ions encountered in **1-6** are corroborated by high resolution data.

Table I—Mass spectral data of compounds 1-6

Compd	Precursor ions (M^+)	Principal fragments m/z (relative intensity)
1	m/z 340	342 (100.0), 340 (28.4), 312 (35.4), 233 (26.0), 232 (36.0), 192 (30.0), 154 (76.2), 127 (48.2), 104 (17.8), 103 (28.9), 91 (50.1), 77 (50.4)
2	m/z 400	402 (100.0), 400 (15.8), 372 (39.8), 293 (46.0), 292 (34.1), 252 (25.9), 184 (34.8), 157 (61.2), 134 (38.4), 133 (54.1), 121 (31.8), 107 (40.3), 77 (41.2)
3	m/z 409	415 (25.5), 413 (45.9), 411 (100.0), 409 (18.8), 381 (36.3), 302 (54.8), 301 (69.2), 261 (68.2), 189 (40.6), 162 (60.1), 138 (34.9), 137 (46.5), 126 (21.7), 112 (55.1)
4	m/z 293	295 (100.0), 293 (14.5), 265 (29.8), 233 (15.1), 232 (26.6), 192 (46.5), 154 (50.3), 127 (40.2), 104 (21.3), 103 (34.5), 91 (56.3), 77 (41.8).
5	m/z 353	355 (100.0), 353 (24.6), 325 (63.5), 293 (72.9), 292 (38.4), 252 (56.8), 184 (29.0), 157 (46.9), 133 (46.3), 121 (23.7) , 107 (43.8), 77 (37.6)
6	m/z 362	368 (23.6), 366 (38.9), 364 (100.0), 362 (20.2), 334 (39.8), 302 (56.2), 301 (72.1), 261 (54.6), 189 (68.1), 162 (29.2), 138 (32.0), 137 (39.1), 126 (18.4), 112 (58.2)

It can be inferred from this study that in the fused ring systems where selenadiazole and thiadiazole are one of the rings fused to another ring the primary cleavage process is the expulsion of selenadiazole or thiadiazole rings. The high resolution mass spectra of all the compounds indicated the absence of sulfur and selenium in the chemical composition of different daughter ions formed during the splitting pattern thus lending support to the above observation.

Experimental Section

The compounds **1-6** were prepared according to literature procedures[5], **1** m.p. 112-113°C; **2**, m.p. 96-97°C; **3**, m.p. 102-103°C; **4**, m.p. 150-51°C; **5**

m.p.:114-115°C; **6,** m.p. 98°C dec. All the compounds were characterised by IR and ^{1}H NMR spectral data.

The EI mass spectra were measured on Jeol JMS-D 300 mass spectrometer at 70 eV with an emission current of 100 μA. Accurate mass measurements were carried out on Krates MS-80 double focussing mass spectrometer.

Acknowledgement

One of the authors (ASSR) is grateful to University Grants Commission (UGC), New Delhi for the award of Junior Research Fellowship.

References

1 Katritzky A R, *Advances in Heterocyclic Chemistry* (Academic Press, London), 38, **1985**, 135.

2 Prota G & Thomson R H, *Endevour*, 35, **1976**, 32.

3 Faria C, Priza M, Gamba A & Pifferi G, *Eur J Med Chem - Chim Ther*, 14, **1979**, 27.

4 Shafiee A, Lalezari I, Yazadany S, Shahbazian F M & Pontovi T, *J Pharm Sci*, 62, **1973**, 839.

5 Bhaskar Reddy D, Somasekhar Reddy A & Padmavathi V, *Phosphorus, Sulfur & Silicon*, 122, **1997**, 143.

6 Shafiee A, Lalezari I, Mirrashed M & Nercesian D, *J Heterocycl Chem*, 14, **1977**, 567.

7 Zeller K P, Meier H & Muller E, *Tetrahedron*, 28, **1972**, 1353.