Mass Spectral Fragmentation Patterns of Heterocycles. VI [1]. Carbazole and 1,8-Dideuteriocarbazole

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The mass spectral fragmentation of carbazole was reinvestigated using metastable ion studies, exact mass measurements and 1,8-dideuteriocarbazole. 1,8-Dideuteriocarbazole was prepared by successive metalations and deuterations of carbazole. The ^{1}H- and ^{13}C-nmr spectra of 1,8-dideuteriocarbazole confirmed earlier assignments for carbazole.

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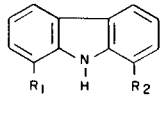
Very few reports describing the behavior of carbazole and its derivatives on electron impact appear in the literature. Riepe and Zander have described, in a short note, mass spectral fragmentation patterns of 27 carbazoles (including carbazole, itself, *N*-alkyl and *N*-arylcarbazoles and several annelated carbazoles) along with their ionization potentials [3]. Brief mention of the mass spectrum of carbazoles has been made by Das, *et al.* in an investigation of the fragmentation patterns of aromatic amides [4]. Our interest in carbazole mass spectral fragmentation behavior relates to the fact that the fragmentation of other dibenzo heterocyclic systems, such as phenothiazines [5-10] and 5*H*-dibenz[*b*,*f*]azepines [11] in which we have a special interest [1,12,13], proceed, in part, through carbazole ion intermediates. We, therefore, wished to more accurately characterize the carbazole contribution to the fragmentation of these systems. A reinvestigation of the mass spectral behavior of **1** is reported herein using metastable ion studies, exact mass measurements, and the 1,8-dideuterio derivative **2**. The synthesis of **2** and its ^{1}H- and ^{13}C-nmr spectral properties are also described.

The mass spectrum of **1** is exceedingly simple [3,4]. The stability of the carbazole ring system to electron impact is reflected in the intensity of the molecular ion (base peak) and a relatively intense doubly charged molecular ion at m/e 83.5 (10% relative intensity). The latter ion undergoes the expected shift to 84.5 in **2**. The only other ions of reasonable relative intensity (> 10%) appear at m/e 166 (M-1), m/e 140 and m/e 139. Exact mass measurements had previously shown [3] (no data) that the peak at m/e 140 results from the loss of ethylene radical ($C_2H_3\cdot$), and not loss of hydrogen cyanide, from **1**. Similarly, the peak at m/e 139 is due to the loss of dihydrogen cyanide radical ($H_2CN\cdot$) from **1** [3]. Our exact mass measurements (Table 1) and metastable ion studies confirm these conclusions and, in addition, show that the M-1 ion is also a source of m/e (loss of acetylene) and 139 (loss of hydrogen cyanide) as shown in Scheme 1.



1 $R_1 = R_2 = H$
2 $R_1 = R_2 = D$
3 $R_1 = H$, $R_2 = D$

Scheme I

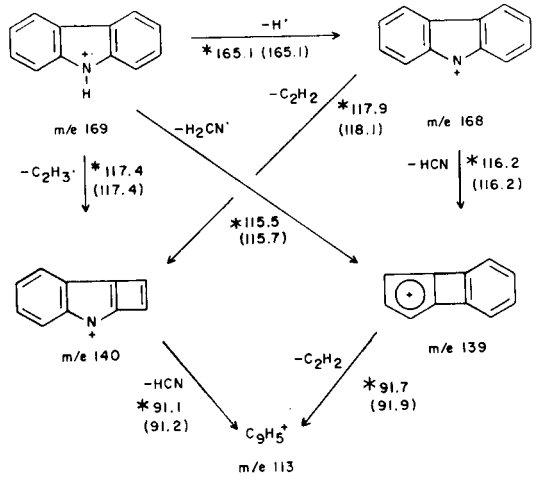


Table 1

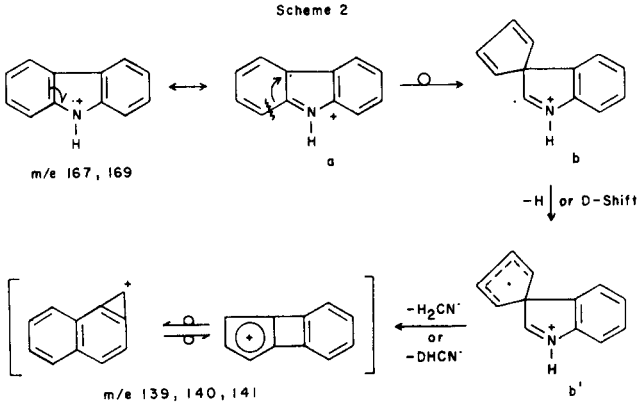
Exact Mass Measurements

Compound	Ion (m/e)	Emperical Formula	Calculated	Found
1	167 (M)	$C_{12}H_9N$	167.0735	167.0721
1	166 (M − 1)	$C_{12}H_8N$	166.0656	166.0642
1	140	$C_{10}H_6N$	140.0500	140.0512
1	139	$C_{11}H_7$	139.0547	139.0530
1	113	C_9H_5	113.0391	113.0390
2	169 (M)	$C_{12}H_7D_2N$	169.0861	169.0861
2	141	$C_{11}H_5D_2$	141.0673	141.0667

The mass spectrum of **2** reveals that both losses of hydrogen and deuterium radicals from the molecular ion occur to form M-1 (m/e 168, *r.i.* 21%) and M-2 (m/e 167, *r.i.* 4%) ions. No M-2 ion appears in the spectrum of carbazole. Significant retention of deuterium is evident in the loss of dihydrogen cyanide radical ($H_2CN\cdot$) from the molecular ion (or hydrogen cyanide from M-1), but not for the

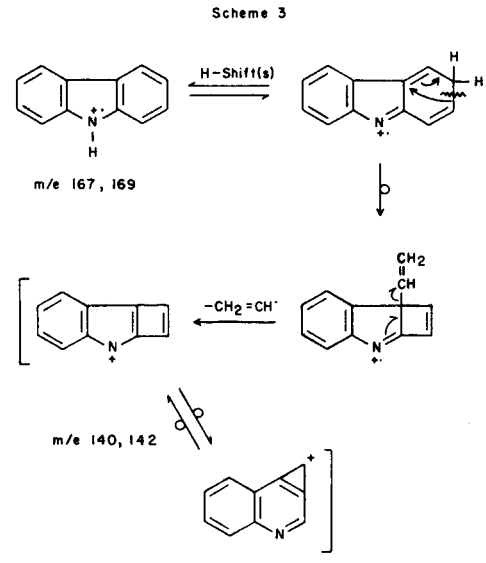
loss of ethylene radical (C_2H_3·) from $M^{+\cdot}$ (or acetylene from M-1). Thus, the expected peaks at m/e 142 (M-C_2H_3·, M-1-C_2H_2, *r.i.* 5.5%), m/e 141 (M-H_2CN·, M-1-HCN, *r.i.* 11%) and m/e 140 (M-DHCN·, M-1-DCN, *r.i.* 4%) are observed in the spectrum of **2**, but the peak at m/e 141 was a singlet calculated (high resolution) to have the composition $C_{11}H_5D_2$ with no contribution from $C_{10}H_5DN$. Deuterium scrambling thus apparently occurs in the expulsion of the carbon-nitrogen containing fragment, but not the carbon-carbon fragment. A plausible mechanism consistent with the approximately statistical distribution in the daughter ions (11% $C_{11}H_5D_2$, 4% $C_{11}H_6D$) is outlined in Scheme 2. Homolytic cleavage of the 1-1_a (9-9_a) bond in ion **a** is believed to occur with simultaneous formation of a 3-spiro cyclopentadienyl radical ion **b**. Hydrogen (four possibilities) or deuterium (one possibility) shift could then give **b'**, which would lose H_2CN· or HDCN· to give the observed distribution of m/e 140 and 141 ions. Scheme 3 provides a mechanism by which ethylene radical could be expelled from the molecular ion with retention of deuterium in the daughter ion, $C_{10}H_4D_2N$ (m/e 142). Metastable ion studies on **1** indicate that the same low intensity (2.8%) hydrocarbon ion, C_9H_5 (high resolution measurement), is derived from both m/e 140 (loss of HCN) and m/e 139 (loss of C_2H_2). Thus, it is not possible to determine with certainty which carbon atoms are involved in the expulsion of ethylene radicals from the molecular ion. It is interesting to note that neither the *N*-alkylated- or *N*-arylated carbazoles, or any of the annelated carbazoles expell ethylene radical on electron impact [3]. The reason why carbazole is unique in this regard is unknown. Specifically carbon-13 labelled compounds may be required to find the answer.

Scheme 2



1,8-Dideuteriocarbazole was prepared according to the general procedure that had previously been successfully employed for the synthesis of 1,9-dideuteriophenothiazine [14], 4,6-dideuterio-5*H*-dibenz[*b*,*f*]azepine [15], and 4,6-dideuterio-5*H*-dibenz[*b*,*f*]azepine [15], namely, successive metalation and deuteration sequences on the parent heterocycle. Thus, treatment of **1** with *n*-butyl lithium resulted,

Scheme 3



after trapping with deuterium oxide, in a 92% isolated yield of 1-deuteriocarbazole (**3**). No other sites of deuterium substitution could be detected from ^{1}H-nmr and ^{13}C-nmr analyses. Twice repeated metalations and subsequent deuterations of **3** gave a 91% yield fo pure 1,8-dideuteriocarbazole **2** uncontaminated with **1** or **3**, as indicated by ^{1}H-nmr and ms analysis.

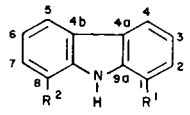
The above result is surprising in view of the fact that previous attempts to metalate carbazole reportedly gave low to moderate yields of 1-substituted derivatives. Thus, 1-carboxycarbazole was obtained in 1% yield after metalation of **1** with *n*-butyllithium in ether followed by quenching with carbon dioxide [16]. It was also found that lithiation of 9-ethylcarbazole led to a somewhat higher yield of the carboxylic acid when ether/tetrahydrofuran instead of ether was used as the metalating solvent [17]. It is interesting to note that 9-ethylcarbazole monometalates in the 1-position with excess *n*-butyllithium, although still in low yield, while 9-methylcarbazole is dimetalated using the same reagent under corresponding conditions [18]. This difference in behavior has been ascribed to a possible influence of steric factors, not only in the metalation, but also in the carbonation reaction [18].

Our results imply that no steric hindrance is involved in the metalation step and that lithiation of carbazole, in fact, occurs as efficiently as in the related tricyclic systems phenothiazine [14,19-22] and 5*H*-dibenz[*b*,*f*]azepine [15,23,24], which in turn, have been derivatized in good yields to a variety of compounds. Steric, and possibly also electronic, effects in the carbonation and subsequent steps must be responsible for the observed differences.

The assignment of the ^{13}C-nmr spectrum of **1** has been accomplished simply *via* comparison with **2** and agreed with reported data [24,25]. Table 2 shows that the resonance from the deuterated carbons in **2** appears as a shiel-

Table 2

^{13}C-NMR Chemical Shifts of Carbazole (**1**). 1,8-Dideuteriocarbazole (**2**) and 1-Deuteriocarbazole (**3**) in Hexadeuterioacetone at 27°



1 R^1, R^2 = H
2 R^1, R^2 = D
3 R^1 = D, R = H

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9a	C-4a	C-4b	C-8a
1	110.57	125.84	119.48	120.33	120.33	119.48	125.84	110.57	139.55	123.42	123.42	139.55
2	110.28 [a]	125.69	119.44	120.28	120.28	119.44	125.69	110.28 [a]	139.43	123.40	123.40	139.43
Difference	−0.29	−0.15	−0.04	−0.05	−0.05	−0.04	−0.15	−0.29	−0.12	−0.02	−0.02	−0.12
3	110.32 [b]	125.73	119.47	120.32	120.32	119.47	125.84	110.57	139.47	123.41	123.41	139.53

[a] $^1J^{13}C_1{}^2H_1$ = 26.4 Hz. [b] $^1J^{13}C_1{}^2H_1$ = 26.4 Hz.

ded triplet. The signals derived from carbons adjacent to a deuterated carbon are known to appear shifted upfield compared to the corresponding signals from the nondeuterated compound [26] and the signal at 125.84 ppm and the signal from the quaternary carbon at 139.55 ppm are therefore assigned to C-2(8) and C-9a(8a), respectively. The considerable broadening of the signal at 119.48 ppm in the spectrum of **2** compared to the corresponding signal in the spectrum of **1** is due to an unresolved $^3J_{CD}$ coupling, and this signal is consequently derived from C-3 (C-6). The assignment of the carbons in the monodeuterated compound **3** is also included in the Table.

EXPERIMENTAL

The mass spectra were recorded on a Varian MAT 311A double focusing mass spectrometer at 70 eV. The samples were introduced by a direct inlet probe and were heated at a rate of about 450° in 200 seconds. The metastable ion spectra were obtained by focusing on the parent ion and scanning the electrostatic sector and magnetic fields in the first field free region of the spectrum at a rate such that the ratio E/B remained constant at a constant accelerating voltage. The high resolution spectra were recorded at a resolution of 7000 and processed with a Varian SS-200 data system. The temperature was raised manually to obtain the optimum spectrum. Compound purity was checked by tlc and gc (Varian model 3700) with fid.

The ^{1}H-nmr and ^{13}C-nmr spectra were recorded on a Bruker WH-250 NMR Spectrometer at a frequency of 250.13 MHz (data point resolution 0.37 Hz) and 62.9 MHz (data point resolution 1.8 Hz) respectively. A 5 mm ^{1}H probe and a 10 mm broadband probe (32-105 MHz) were used. The samples were run as 0.5 *M* solutions and tetramethylsilane was used as internal standard.

Carbazole (**1**).

Carbazole (Aldrich Chemical Co.) was recrystallized from 95% ethanol and had mp 246-247° (lit [27] mp 246-247°); ms: m/e (%) 168 (M + 1, 13.7), 167 (M, 100), 166 (M − 1, 21.9), 140 (11.0), 139 (13.0), 113 (2.8), 83.5 (M/2, 9.9).

1-Deuteriocarbazole (**3**).

To a solution of 16.7 g (0.10 mole) of carbazole (**1**) in 500 ml of dry ether, 151.5 ml (0.25 mole) of 1.65 *N* *n*-butyl lithium in hexane was added dropwise at room temperature under an atmosphere of nitrogen. After stirring the reaction mixture for 28 hours, 9.0 g (0.50 mole) of deuterium oxide was added and the mixture was then poured into water. The organic phase was separated and the aqueous phase was extracted several times with ether. The combined organic phases were washed three times with 10% sodium carbonate solution, dried and evaporated to give 16.2 g of a mixture of carbazole **1** (8%) and 1-deuteriocarbazole **3** (92%), according to ^{1}H-nmr and ms analyses, mp 244-246°; ^{1}H-nmr (hexadeuterioacetone): (ppm) 10.35 (1H, bs, NH), 8.12 (2H, d, H-4, H-5), 7.52 (1H, bd, H-8), 7.39 (1H, bd, H-2), 7.39 (1H, bt, H-7), 7.18 (2H, bt, H-3, H-6), $J_{H\text{-}3,H\text{-}4}$ = $J_{H\text{-}5,H\text{-}6}$ = 7.8 Hz, $J_{H\text{-}7,H\text{-}8}$ = 8.1 Hz, $J_{H\text{-}2,H\text{-}3}$ = $J_{H\text{-}6,H\text{-}7}$ = 7.6 Hz; ms: m/e (%) 169 (M + 1, 12.1), 168 (M, 100), 167 (M − 1, 21.0), 166 (3.1), 141 (7.0), 140 (9.5), 139 (4.4), 84 (M/2, 15.6).

1,9-Dideuteriocarbazole (**1**).

The mixture of **1** (8%) and **3** (92%) obtained above was lithiated and deuterated analogously two more times and, after work up, 15.4 g (91%) of 1,8-dideuteriocarbazole was obtained, mp 244-246°; ^{1}H-nmr (hexadeuterioacetone): (ppm) 10.35 (1H, bs, NH), 8.12 (2H, dd, H-4, H-5), 7.39 (2H, dd, H-2, H-7), 7.18 (2H, bt, H-3, H-6), $J_{H\text{-}2,H\text{-}3}$ = 7.6 Hz, $J_{H\text{-}3,H\text{-}4}$ = 7.8 Hz, $J_{H\text{-}2,H\text{-}4}$ = 1.4 Hz; ms: m/e (%) 170 (M + 1, 12.2), 169 (M, 10), 168 (M − 1, 21.2), 167 (3.9), 142 (5.5), 141 (11.0), 140 (4.1), 139 (3.0), 84.5 (9.5). No traces of either undeuterated or monodeuterated carbazole could be detected in the ^{1}H-nmr of ^{13}C-nmr spectra of 250 MHz.

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