Mass Spectral Fragmentation Patterns of Heterocycles. IX [1]. Investigation of Fundamental Processes in 5*H*-Dibenz[*b*,*f*]azepines and Dihydro-5*H*-dibenz[*b*,*f*]azepines

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Electron impact induced fragmentation patterns of 5*H*-dibenz[*b*,*f*]azepine (**1a**), 10,11-dihydro-5*H*-dibenz-[*b*,*f*]azepine (**2a**) and some 5-substituted derivatives were investigated using metastable ion studies, exact mass measurements and deuterated analogues. Studies employing 4,6-dideuterio derivatives indicate that the formations of ions of m/e 191, 180, 167, 166 and 152 are associated with a variety of skeletal reorganization processes accompanied by hydrogen (or deuterium) transfers involving peri (4- or 6-) hydrogen (or deuterium) atoms. The methyl radical expelled in the formation of the M-15 ion in the spectrum of **2a** is derived from the benzylic carbon(s). A similar process is, in part, responsible for the expulsion of a methyl radical from the molecular ion of 5-methyl-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (**2c**) based on the fragmentation of the trideuteriomethyl derivative (**2d**). Side chain α-cleavage processes dominate the spectra of (5*H*-dibenz[*b*,*f*]azepine-5-yl)acetaldehyde diethylacetal and its 10,11-dihydro analogue. Hydrogen atom transfer processes involving benzylic hydrogen atoms occur in the fragmentation of the 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepines **2a**, **2c** and **2e**.

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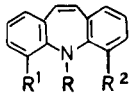
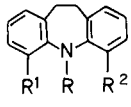
The mass spectra of 5*H*-dibenz[*b*,*f*]azepine (iminostilbene, **1a**) and 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (iminodibenzyl, **2a**) and their derivatives have been investigated to a relatively limited extent [3-6]. Our interest in the electron impact fragmentation of tetracyclic derivatives (*i.e.*, the indolobenzazepines [7]) led us to reexamine the behavior of the simpler tricyclic systems in order to clarify some of the fragmentation patterns. Thus, 5*H*-dibenz[*b*,*f*]azepines **1a** and **1c**, 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepines **2a**, **2c** and **2e**, and the corresponding deuterated derivatives **1b**, **2b** and **2d** were examined. Metastable ion studies were carried out to elucidate fragmentation pathways and exact mass meaurements (see Table 1) were performed to determine ion compositions.



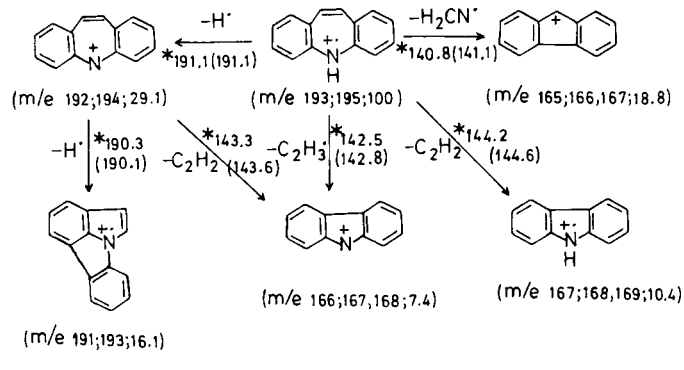
1 **a** R = R_1 = R_2 = H
b R = H, R_1 = R_2 = D
c R = $CH_2CH(OC_2H_5)_2$, R_1 = R_2 = H
d R = $CH_2CH(OC_2H_5)_2$, R_1 = R_2 = D



2 **a** R = R_1 = R_2 = H
b R = H, R_1 = R_2 = D
c R = CH_3, R_1 = R_2 = H
d R = CD_3, R_1 = R_2 = H
e R = $CH_2CH(OC_2H_5)_2$, R_1 = R_2 = H
f R = $CH_2CH(OC_2H_5)_2$, R_1 = R_2 = D

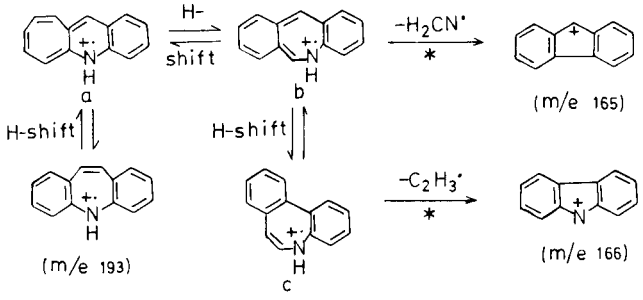
Principal fragment ions for **1a**, **2a** and several of their derivatives have been described by Jovanovic [3]. Brief mention of the mass spectra of **1a** and its *N*-ethyl derivative has also been made in a review [4]. A detailed analysis of the electron impact mass spectrum of the 5-carbamoyl derivative of **1a** (carbamazepine) has been made [5]. Many of the principal ions have been identified and their elemental compositions determined by exact mass measurements. Except for the latter study [5], however, metastable ion studies were not performed and consequently little is known concerning fragmentation pathways.

Scheme 1



The mass spectrum of **1a** (Scheme 1) is characterized by an intense molecular ion (base peak), a moderately intense M-1 ion, and a less intense doubly charged molecular ion (m/e 96.5, relative intensity 6%). Fragment ions at m/e 167, 166 and 165 result from expulsions of C_2H_2, C_2H_3· and H_2CN· from the molecular ion as shown by metastable ion studies and exact mass measurements. In the case of the 4,6-dideuterio derivative these processes appear to involve the loss of more than the statistically predicted amount of deuterium, indicating that skeletal rearrangements of the kind suggested by Baker and Frigerio [5] and involving deuterium (or hydrogen) shifts (*i.e.*, *via* ions **a** → **c**, see Scheme 2) prior to the expulsions of C_2H_2,

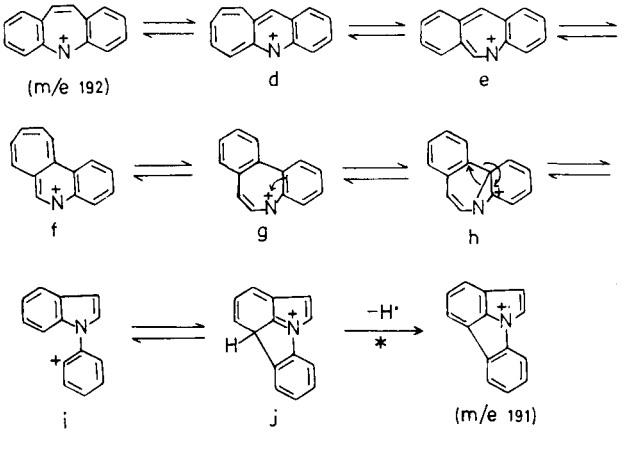
Scheme 2



C_2H_3· and H_2CN· from **1a** must indeed occur. The peri (4-and 6-) hydrogen (or deuterium) atoms are more likely to undergo shifts associated with the skeletal rearrangements (**a** ⇌ **b** ⇌ **c**) to positions where they are lost as part of a small neutral fragment. Thus, **1b** expells DHCN·, C_2H_2D· and C_2HD to form ions of m/e 166, 167 and 168 respectively.

The m/e 191 ion, which is also relatively abundant in the spectrum of **1a**, is derived exclusively from the M-1 ion (intense metastable ion at m/e 190.3). A relatively intense doubly charged ion at m/e 95.5 (7% relative abundance) suggests that the m/e 191 ion has the very stable aromatic pyrrolocarbazolium structure shown (see Scheme 1). The observation that ions of m/e 190, 164 and 163 generated in the electron impact induced fragmentation of pyrrolocarbazole, itself [1], also appear in comparable relative abundance and appropriate elemental composition in the spectrum of **1a** support this structure. The pyrrolocarbazolium ion has also been observed in the mass spectra of pyrrolophenothiazine [8] and the indolobenzazepines [7]. In the spectrum of **1b** consecutive losses of protons occur to form ions of m/e 194 and 193 with no apparent loss of deuterium. This result suggests that the pyrrolocarbazolium ion can not form *via* scission of the 10,11-bond and subsequent ring closure of the M-1 ion, since loss of a deuterium atom (194→192) after ring closure would be the most probable result. To explain the retention of deuterium in the m/e 191 ion the series of skeletal reorganizations involving ions **d-j** and deuterium (or hydrogen) transfers shown in Scheme 3 is invoked.

Scheme 3



Two processes dominate the fragmentation of **2a**, namely the expulsions of hydrogen and methyl radicals from the molecular ion to form the M-1 (m/e 194) and M-15 (m/e 180) ions, respectively (see Scheme 4). A significant amount of m/e 193 ion (relative intensity 16.3%), is formed from the M-1 ion. This process presumably involves hydrogen transfer from the benzylic positions. The mass spectrum of **2a**, therefore, resembles that of **1a** in large part. The M-15 ion is believed to be initiated by cleavage of the 10,11-bond to form ion **k**, followed by ring closure to ion **l**. The latter then experiences hydrogen atom transfer with subsequent expulsion of a methyl radical to give m/e 180 as shown in Scheme 5. The m/e 180 ion then expells H_2CN radical *via* a series of skeletal rearrangements to ions **m** and **n** [5] giving m/e 152. The formation of this ion from the 4,6-dideuterio derivative **2b** is associated with considerable deuterium loss as is evidenced by the relative abundance of the ion of m/e 153 formed. The molecular ion of **2a** also forms the carbazole ion (m/e 167) by expelling ethylene (Scheme 4).

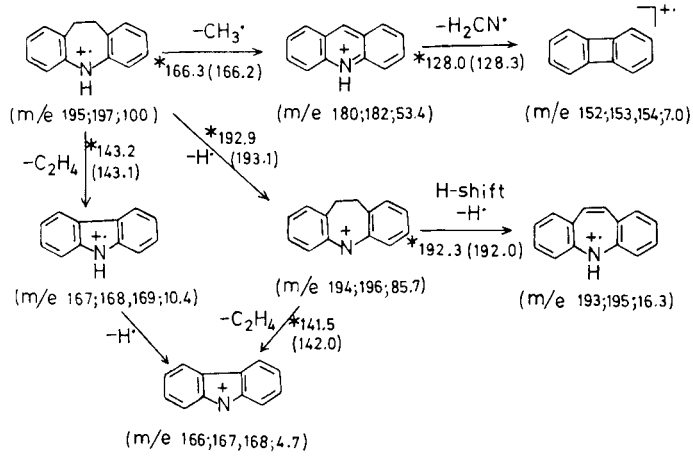
Table 1

Exact Mass Measurements

Ion (m/e)	Empirical Formula	Calcd.	Observed	Present in cpd(s) [a]
311	$C_{20}H_{25}NO_2$	311.1885	311.1896	**2e** [M⁺]
309	$C_{20}H_{23}NO_2$	309.1697	309.1713	**1c** [M⁺]
266	$C_{18}H_{20}NO$	266.1545	266.1545	**2e**
264	$C_{18}H_{18}NO$	264.1389	264.1388	**1c**
220	$C_{16}H_{13}N$	220.1126	220.1108	**2e**
218	$C_{16}H_{11}N$	218.0970	218.0967	**(1c)**
209	$C_{15}H_{15}N$	209.1205	209.1193	**2c** [M⁺], **2e**
208	$C_{15}H_{14}N$	208.1126	208.1123	**(1c)**, **2c**, **2e**
207	$C_{15}H_{13}N$	207.0998	207.1009	**1c**, **(2c)**
206	$C_{15}H_{12}N$	206.0970	206.0963	**1c**, **(2e)**
205	$C_{15}H_{11}N$	205.0891	205.0893	**1c**, **(2e)**
204	$C_{15}H_{10}N$	204.0814	204.0811	**1c**, **(2e)**
195	$C_{14}H_{13}N$	195.1049	195.1053	**2a** [M⁺], **2c**, **2e**
194	$C_{14}H_{12}N$	194.0970	194.0970	**2a**, **2c**, **2e**
193	$C_{14}H_{11}N$	193.0891	193.0889	**1a** [M⁺], **1c**, **2a**, **2c**, **2e**
192	$C_{14}H_{10}N$	192.0813	192.0809	**1a**, **1c**, **2a**, **2c**, **2e**
191	$C_{14}H_9N$	191.0735	191.0730	**1a**, **1c**, **2a**, **(2c)**, **(2e)**
190	$C_{14}H_8N$	190.0656	190.0664	**1a**, **1c**, **(2a)**, **(2c)**
180	$C_{13}H_{10}N$	180.0814	180.0813	**2a**, **2c**, **2e**
179	$C_{14}H_{10}$	179.0861	179.0840	**1c**, **2c**, **(2a)**
179	$C_{13}H_9N$	179.0736	179.0743	**2a**, **2c**
178	$C_{14}H_9$	178.0783	178.0772	**1c**, **2a**, **2c**
167	$C_{12}H_9N$	167.0735	167.0737	**1a**, **2a**, **2c**, **(2e)**
166	$C_{12}H_8N$	166.0657	166.0657	**1a**, **2a**, **2c**, **(2e)**
165	$C_{13}H_9$	165.0704	165.0698	**1a**, **1c**, **2a**, **2c**, **(2e)**
164	$C_{12}H_7N$, or $C_{13}H_8$	164.0501 164.626	164.0556 [b]	**1a**, **(1c)**
163	$C_{13}H_7$	163.0548	163.0517	**1a**, **(1c)**
152	$C_{12}H_8$	152.0626	152.0617	**(1a)**, **(1c)**, **2a**, **(2c)**, **(2e)**

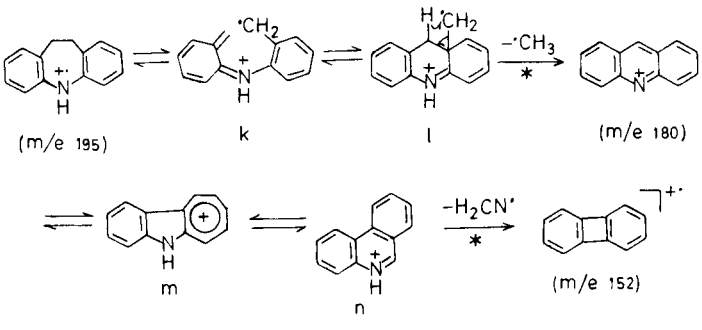
[a] Parenthesis indicates that ion is present in less than 3% relative abundance. [b] Probably doublet [1].

Scheme 4

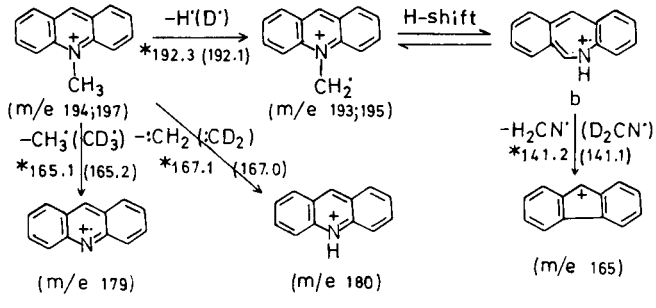


As expected, the primary fragmentation path for **2c** involves the loss of a methyl radical to form the M-15 (m/e 194) ion, which is the base peak in the spectrum (see Scheme 6). The spectrum of the dideuterio derivative **2d** indicates that, although the anticipated cleavage of the carbon-nitrogen bond (and consequent loss of the trideuteriomethyl radical to give m/e 194) is the dominant pathway, a significant amount of the 10,11-bond cleavage process (and subsequent loss of a methyl radical to give m/e 197, see Scheme 5) also occurs. The M-1 ion (m/e 208) is also relatively abundant in the spectrum of **2c**. The spectrum of **2d** gives ions of m/e 210 and 211 indicating losses of deuterium and hydrogen radicals from the molecular ion, respectively. Thus, hydrogen atoms may be lost from both the benzylic and methyl carbons of **2c**. The M-1 peak may then expell a methyl (or trideuteriomethyl radical) to give the m/e 193 ion or a hydrogen (or deuterium atom) to give the m/e 207 (or 209) ion. It will be noted that the m/e 194 ion formed by the expulsion of a methyl radical derived from either the 10- or 11-carbon atom is expected to have the very stable *N*-methylacridinium structure (Scheme 6). Fragmentation of this ion is shown in Scheme 7. Ions of m/e 180, 179 and 165 resulting from losses of CH_2 (carbene!), a methyl radical and H_2CN radical are shown to occur based on metastable ion studies. It is noteworthy that little or no deuterium is retained in these fragmentations.

Scheme 5

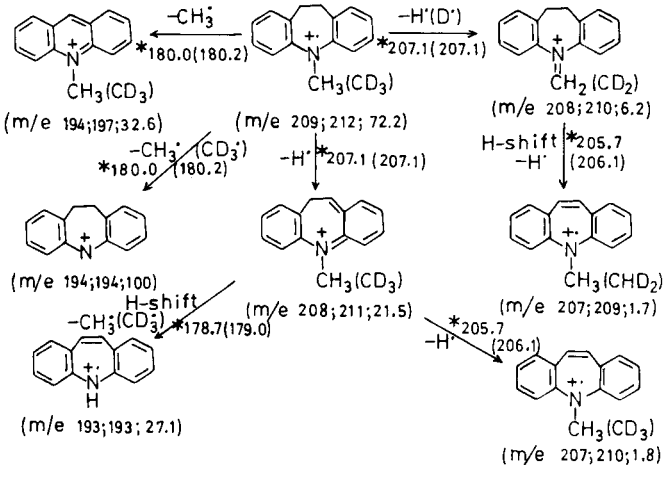


Scheme 7



The spectra of **1c** and **2e** are similar. α-Cleavage processes dominate the spectra of both compounds. Thus, the base peak for **1c** (see Scheme 8) occurs at m/e 103 and corresponds to the diethoxymethyl carbonium ion [$^+CH(OEt)_2$] formed by the expulsion of radical **o**. Of nearly equal probability is the formation of the corresponding m/e 206 ion with the liberation of the diethoxymethyl radical. The m/e 206 ion expells both hydrogen cyanide (HCN) and H_2CN radical to give ions of m/e 179 and 178, having the compositions $C_{14}H_{10}$ and $C_{14}H_9$ (see Table 1 for exact masses), respectively. The spectrum of the 4,6-dideuterio-derivative **1d** indicates that some deuterium is lost in these fragmentations. Metastable ion studies indicate that ions of m/e 205 and 204 are formed by successive losses of hydrogen radicals. Considerable deuterium is lost in the corresponding m/e 208 ion of **1d** suggesting that a rearrangement process involving a ring opened ion **p** (see Scheme 9), which recloses to a dihydronaphthoindolinium

Scheme 6



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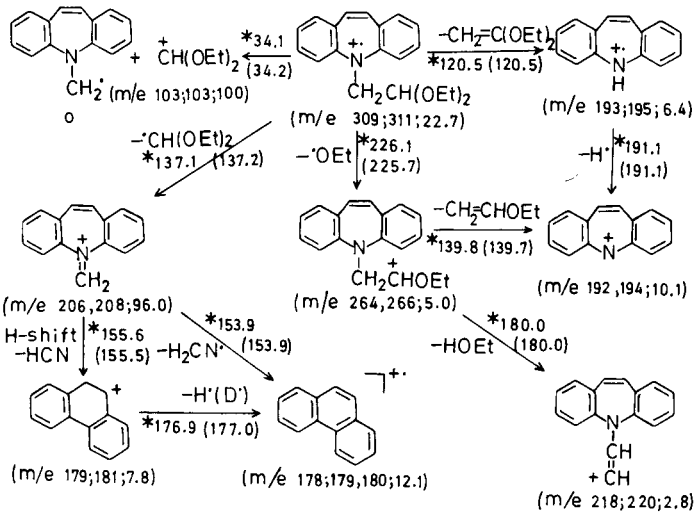
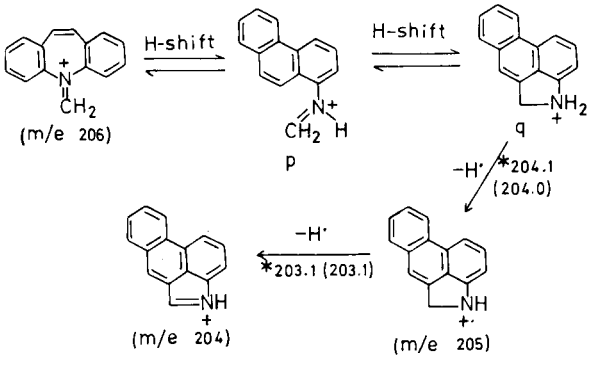
ion **q**, may occur. Successive losses of hydrogen radicals then give m/e 205 and m/e 204.

Scheme 8

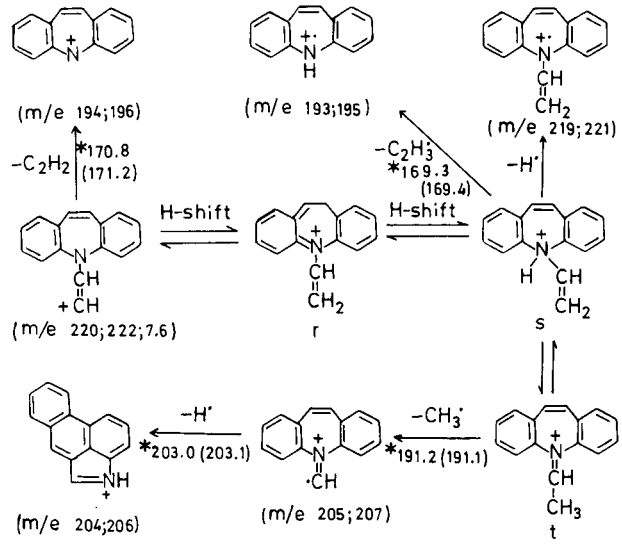


Scheme 9



Hydrogen atom transfer processes involving the benzylic hydrogens in secondary fragmentation reactions of **2e** contribute to differences in its spectrum as compared to that of **1c**. Thus, in contrast to the behavior of the corresponding m/e 206 ion from **1c**, the m/e 208 ion from **2e** [9] expells a methyl radical to give m/e 193 (metastable ion at m/e 178.9) following transfer of a benzylic hydrogen atom (see Scheme 6). The loss of a hydrogen radical to form m/e 207 (metastable ion at m/e 206.1) is a relatively minor pathway. Hydrogen atom transfers are similarly involved in the fragmentation of the m/e 220 ion (formed from **2e** by successive expulsions of ethoxy radical and ethanol from the molecular ion). Thus, the m/e 220 ion can directly lose acetylene to form m/e 194, or experience a series of hydrogen transfers to form ions **r**, **s** and **t** (see Scheme 10). Expulsion of a hydrogen atom or a C_2H_3 radical from **s** gives m/e 219 or m/e 193, respectively. Ion **t** can lose a methyl group to give m/e 205, which most probably rearranges before releasing a hydrogen atom to give m/e 204.

Scheme 10



EXPERIMENTAL

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 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.

5*H*-Dibenz[*b,f*]azepine (**1a**).

5*H*-Dibenz[*b,f*]azepine (Aldrich Chemical Co.) was purified by recrystallization from ethanol, mp 196-197° (lit [10] mp 196.5-198°); ms: m/e 195 (M+2, 2.1), 194 (M+1, 18.9), 193 (M, 100.0), 192 (29.1), 191 (16.1), 190 (7.4), 189 (1.2), 178 (1.5), 177 (1.4), 168 (1.4), 167 (10.4), 166 (7.5), 165 (18.8), 164 (4.3), 163 (3.7), 152 (1.6), 140 (2.6), 139 (3.5), 128 (1.0), 115 (1.8), 101 (1.0), 96.5 (6.1), 96 (1.8), 95.5 (6.8), 90 (2.0), 89 (3.6), 88 (1.1), 87 (1.5), 86 (1.0), 84 (1.2), 83.5 (7.8), 82.5 (3.1), 82 (3.0), 81.5 (2.2), 77 (2.0), 76 (1.7), 75 (2.3), 74 (2.0), 70.5 (1.7), 69.5 (2.1), 65 (1.2), 63 (5.2), 62 (2.1), 52 (1.2), 51 (4.1), 50 (3.0).

4-6-Dideuterio-5*H*-dibenz[*b,f*]azepine (**1b**).

This compound was reported previously by us [11]. It has a mp 195-197°; ms: (high resolution) m/e calcd. for $C_{14}H_9D_2N$ 195.1017, found: 195.1020; ms: (low resolution) m/e (%) 195 (M+1, 2.1), 194 (M+1, 18.9), 193 (M, 100), 192 (29.1), 191 (61.1), 190 (7.4), 189 (1.2), 178 (1.5), 177 (1.4), 168 (1.4), 167 (10.4), 166 (7.5), 165 (18.8), 164 (4.3), 163 (3.7), 152 (1.6), 140 (2.6), 139 (3.5), 128 (1.0), 115 (1.8), 101 (1.0), 96.5 (6.1), 96 (1.8), 95.5 (6.8), 90 (2.0), 89 (3.6), 88 (1.1), 87 (1.5), 86 (1.0), 84 (1.1), 83.5 (7.8), 82.5 (3.1), 82 (3.0), 81.5 (2.2), 77 (2.0), 76 (1.4), 75 (2.3), 74 (2.0), 70.5 (1.7), 69.5 (2.1), 65 (1.2), 63 (5.2), 62 (2.1), 52 (1.2), 51 (4.1), 50 (3.0).

Anal. Calcd. for $C_{14}H_9D_2N$: C, 86.11; H+D, 6.71; N, 7.17; Found: C, 85.89; H+D, 6.83; N, 6.92.

5*H*-Dibenz[*b*,*f*]azepine-5-acetaldehyde Diethylacetal (**1c**).

We have reported the synthesis of this compound in earlier publications [12,13]; ms: m/e (%): 310 (M + 1, 5.1), 309 (M, 22.7), 265 (1.1), 264 (5.0), 234 (1.3), 220 (1.3), 218 (2.8), 217 (2.0), 208 (2.9), 207 (17.5), 206 (96.0), 205 (6.1), 204 (11.6), 203 (1.0), 193 (4.4), 192 (10.1), 191 (6.4), 190 (3.8), 189 (1.1), 180 (1.9), 179 (7.8), 178 (12.1), 177 (2.7), 176 (2.7), 166 (1.2), 165 (4.4), 164 (1.6), 163 (1.4), 12 (2.7), 139 (1.1), 128 (3.5), 108.5 (1.0), 104 (6.3), 103 (100.0), 102.5 (2.5), 102 (3.0), 101 (1.4), 95.5 (1.3), 89 (2.9), 88 (2.0), 85 (2.0), 77 (3.5), 76 (4.6), 75 (64.2), 74 (1.0), 63 (2.7).

4,6-Dideuterio-5*H*-dibenz[*b*,*f*]azepine Diethylacetal (**1d**).

Compound **1a** (6.84 g, 0.035 mole) was added at room temperature to a solution of 1.26 g (0.053 mole) of sodium hydride in 120 ml of dioxane. After refluxing had been maintained for four hours, 10.4 g (0.053 mole) of bromoacetaldehyde diethylacetal was added dropwise to the vigorously stirred mixture during a period of one hour under reflux. The mixture was refluxed for an additionl 17 hours under argon atmosphere and then cooled to 25°. The excess sodium hydride was then destroyed by methanol and the reaction mixture was then poured into toluene and water. The aqueous phase was extracted several times with toluene, and the combined organic phases were washed with water, dried over magnesium sulfate and evaporated to give the crude acetal as a yellow oil. Chromatography (silica, toluene) gave 5.0 g (74%) as a pale yellow oil; ms: (high resolution) m/e calcd. for $C_{20}H_{21}D_2NO_2$: 311.1855, found: 311.1859; ms: (low resolution) m/e 312 (M + 1, 5.5), 311 (M, 22.5), 267 (1.1), 266 (4.7), 222 (1.8), 220 (2.2), 219 (2.0), 211 (1.3), 210 (7.3), 209 (20.1), 208 (99.6), 207 (8.9), 206 (12.8), 205 (4.4), 196 (1.3), 195 (6.4), 194 (12.2), 193 (6.7), 192 (5.7), 191 (2.5), 182 (2.5), 181 (8.2), 180 (13.5), 179 (5.9), 178 (3.9), 177 (1.7), 168 (1.5), 167 (5.0), 166 (2.7), 165 (1.9), 164 (1.1), 154 (2.2), 153 (2.4), 152 (1.7), 141 (1.3), 140 (1.0), 130 (1.1), 129 (3.2), 128 (1.1), 104 (6.8), 103.5 (1.3), 103 (100.0), 102 (1.5), 90 (2.1), 89 (1.5), 85 (3.1), 78 (2.6), 77 (2.4), 76 (3.2), 75 (59.4), 64 (1.6), 63 (1.4), 61 (2.4), 57 (1.3), 52 (1.3), 51 (1.6), 47 (60.3).

Anal. Calcd. for $C_{20}H_{21}D_2NO_2$: C, 77.13; H + D, 8.09; N, 4.50. Found: C, 77.02; H + D, 7.92; N, 4.38.

10,11-Dihydro-5*H*-dibenz[*b*,*f*]azepine (**2a**).

"Iminodibenzyl" (Aldrich Chemical Co.) was sublimed to give pale yellow crystals, mp 106-107° (lit 110° [14]), ms: m/e 197 (M + 2, 1.1), 196 (M + 1, 14.5), 195 (M, 100), 194 (85.7), 193 (16.3), 192 (10.0), 191 (6.1), 190 (1.9), 181 (7.5), 180 (53.4), 179 (9.9), 178 (7.7), 177 (2.8), 176 (1.5), 168 (3.0), 167 (10.4), 166 (4.6), 165 (7.8), 164 (2.2), 163 (1.5), 154 (1.4), 153 (2.2), 152 (7.0), 151 (2.9), 140 (2.6), 139 (3.3), 129 (1.1), 128 (2.9), 127 (1.8), 126 (1.1), 119 (1.1), 118 (10.8), 117 (5.1), 116 (4.8), 115 (3.1), 113 (1.2), 102 (1.5), 101 (1.4), 97.5 (2.5), 97 (5.4), 96.5 (20.5), 96 (1.2), 95.5 (4.4), 91 (6.1), 90 (7.8), 89.5 (1.1), 89 (9.3), 88 (1.2), 87 (1.5), 84 (2.7), 83.5 (17.4), 82.5 (2.4), 82 (2.0), 81.5 (1.3)), 78 (2.7), 77 (8.2), 76 (3.7), 75 (2.9), 74 (2.1), 70.5 (2.6), 70 (1.2), 69.5 (1.7), 69 (1.3), 65 (5.2), 64 (2.5), 63 (8.2), 62 (3.5), 61 (17.1), 60 (2.0), 57 (1.4), 56 (1.1), 55 (1.4), 52 (3.1), 51 (8.4), 50 (3.8).

4,6-Dideuterio-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (**2b**).

We have reported this compound previously [11]. It gave mp 105-107°; ms: (high resolution) m/e calcd. for $C_{14}H_{11}D_2N$: 197.1173, found: 197.1164; ms: (low resolution) 199 (M + 2, 1.1), 198 (M + 1, 14.8), 197 (M, 100.0), 196 (91), 195 (26.7), 194 (10.8), 193 (6.5), 192 (3.4), 191 (1.1), 183 (5.9), 182 (39.4), 181 (12.8), 180 (7.3), 179 (4.0), 178 (2.2), 170 (1.7), 169 (6.1), 168 (5.2), 167 (5.3), 166 (3.3), 165 (1.5), 155 (1.4), 154 (3.3), 153 (3.4), 152 (1.7), 141 (1.8), 140 (1.5), 130 (1.3), 129 (1.9), 128 (1.2), 120 (1.7), 119 (7.8), 118 (4.2), 117 (3.3), 116 (2.1), 98.5 (3.1), 98 (6.4), 97.5 (22.4), 97 (8.7), 96.5 (4.0), 96 (2.7), 95 (1.1), 92 (4.1), 91 (7.1), 90.5 (2.3), 90 (5.9), 89 (1.8), 85 (2.7), 84.5 (12.3), 84 (10.3), 83.5 (2.6), 83 (3.0), 82.5 (1.8), 82 (1.3), 81 (1.2), 79 (2.3), 78 (4.6), 77.5 (1.1), 77 (3.2), 76 (1.8), 75 (1.4), 71.5 (1.1), 71 (3.7), 70.5 (1.5), 70 (1.6), 69 (2.6), 67 (1.1), 66 (2.4), 65 (2.3), 64 (3.6), 63 (3.1), 62 (1.3), 61 (6.5), 57 (2.8), 55 (2.0), 53 (1.4), 52 (3.7), 51 (4.5), 50 (1.6).

Anal. Calcd. for $C_{14}H_{11}D_2N$: C, 85.23; H + D, 7.66; N, 7.10. Found: C, 85.26; H + D, 7.60; N, 7.03.

10,11-Dihydro-5-methyl-5*H*-dibenz[*b*,*f*]azepine (**2c**).

This compound, prepared by the alkylation of **2a** with methyl iodide in the presence of *n*-butyllithium according to a literature procedure [15] gave mp 107-109° (lit [15] mp 106-107°); ms: m/e 210 (M + 1, 11.7), 209 (M, 72.2), 208 (M-1, 19.9), 207 (1.8), 206 (2.0), 204 (1.0), 196 (1.1), 195 (15.4), 194 (10.0), 193 (27.1), 192 (8.8), 191 (4.8), 190 (1.6), 181 (2.0), 180 (4.4), 179 (10.0), 178 (7.3), 177 (1.9), 176 (1.2), 168 (1.7), 167 (6.2), 166 (3.5), 165 (6.7), 164 (1.2), 153 (1.5), 152 (3.7), 151 (1.4), 140 (1.3), 139 (1.5), 132 (1.8), 131 (1.1), 130 (1.7), 128 (1.8), 118 (2.5), 117 (2.3), 116 (2.5), 115 (2.4), 104.5 (M^{2+}, 1.8), 104 (2.9), 103.5 (8.4), 103 (1.7), 102.5 (1.6), 102 (1.9), 97 (2.0), 96.5 (4.0), 95.5 (2.3), 91 (6.8), 90.5 (4.2), 90 (3.0), 89.5 (1.0), 89 (6.3), 88 (1.1), 83.5 (4.3), 82.5 (1.3), 82 (1.0), 78 (1.6), 77 (5.0), 76 (2.8), 75 (1.9), 74 (1.3), 65 (4.8), 64 (1.6), 63 (5.5), 62 (2.0), 61 (7.9), 52 (2.0), 51 (6.2), 50 (2.9).

10,11-Dihydro-5-(trideuteriomethyl)-5*H*-dibenz[*b*,*f*]azepine (**2d**).

In a dry 5 ml flask 50 mg (0.26 mmole) of 10,11-dihydro-5*H*-dibenz[*b*,*f*]-azepine was added in dry ether and 234 ml (0.39 mmole) of 0.6 *N* *n*-butyllithium was added and the solution stirred for 2 hours under a nitrogen atmosphere. Then 24.7 μl (0.39 mmole) of trideuteriomethyl iodide was added through a microsyringe, and the mixture stirred overnight. The mixture was then extracted with ether and the solvent evaporated *in vacuo* (aspirator) to give a pale yellow solid after chromatography on silica (toluene); mp 106-109°; ms: (high resolution) m/e calcd. for $C_{15}H_{12}D_3N$: 212.1394, found: 212.1401; ms: (low resolution) m/e 213 (M + 1, 14.1), 212 (M, 86.9), 211 (21.5), 210 (6.2), 209 (1.7), 208 (1.1), 198 (4.6), 197 (32.6), 196 (12.6), 195 (21.5), 194 (100.0), 193 (29.5), 192 (11.1), 191 (6.0), 190 (2.3), 185 (1.2), 184 (2.9), 183 (1.1), 182 (3.1), 181 (2.5), 180 (6.1), 179 (15.9), 178 (9.5), 177 (3.0), 176 (1.3), 169 (1.7), 168 (3.2), 167 (9.9), 166 (6.9), 165 (9.4), 164 (2.1), 163 (1.6), 154 (2.1), 153 (3.7), 152 (6.2), 151 (2.5), 141 (1.3), 140 (3.1), 139 (3.0), 135 (4.0), 134 (2.3), 132 (2.3), 129 (1.3), 128 (3.5), 127 (1.9), 126 (1.4), 121 (1.4), 120 (2.9), 119 (2.0), 118 (2.0), 117 (4.2), 116 (4.9), 115 (4.3), 114 (1.2), 113 (1.4), 106 (4.0), 105.5 (3.7), 105 (15.2), 104.5 (1.5), 104 (2.8), 103.5 (1.5), 103 (2.5), 102 (2.2), 101 (1.6), 98.5 (2.6), 98 (3.2), 97.5 (2.0), 97 (3.3), 96.5 (3.1), 96 (1.2), 95.5 (2.9), 93 (4.0), 92.5 (1.0), 92 (11.7), 91.5 (1.1), 91 (7.7), 90 (5.6), 89.5 (1.5), 89 (11.4), 88 (1.8), 87 (2.0), 86 (1.5), 85 (1.4), 84.5 (1.7), 84 (1.8), 83.5 (4.6), 83 (1.6), 82.5 (2.1), 82 (1.9), 81.5 (1.1), 80 (1.4), 79 (2.3), 78 (5.5), 77 (10.5), 76.5 (1.1), 75 (4.9), 74 (3.6), 70.5 (1.1), 69.5 (1.3), 69 (1.4), 67 (1.7), 66 (4.3), 65 (7.0), 64 (5.2), 63 (14.0), 62 (5.0), 60 (1.3), 53 (2.0), 52 (5.6), 51 (15.3), 50 (7.7).

Anal. Calcd. for $C_{15}H_{12}D_3N$: C, 84.86; H + D, 8.55; N, 6.60. Found: C, 85.11; H + D, 8.24; N, 6.48.

10,11-Dihydro-5*H*-dibenz[*b*,*f*]azepine-5-acetaldehyde Diethylacetal (**2e**).

This compound had been previously prepared by us [12]; ms: m/e 312 (M + 1, 3.6), 311 (M, 16.1), 266 (3.7), 221 (1.5), 220 (7.6), 219 (1.6), 218 (1.9), 210 (1.2), 209 (14.3), 208 (83.4), 207 (1.2), 206 (2.0), 205 (1.5), 204 (2.3), 195 (3.3), 194 (9.9), 193 (32.0), 192 (6.5), 191 (2.8), 180 (2.6), 179 (2.4), 178 (3.1), 167 (2.7), 166 (1.7), 165 (3.8), 152 (1.8), 117 (1.1), 116 (1.3), 115 (1.5), 104 (6.5), 103 (100.0), 102.5 (1.2), 102 (1.4), 96.5 (1.9), 95.5 (1.6), 91 (4.6), 90 (2.1), 89 (3.6), 83.5 (2.3), 83 (1.3), 78 (1.1), 77 (4.2), 76 (3.3), 75 (56.4), 65 (3.4), 63 (2.5), 52 (1.3).

4,6-Dideuterio-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-acetaldehyde Diethylacetal (**2f**).

Five g (0.025 mole) of 4,6-dideuterio-10,11-dihydro-5*H*-dibenz[*b*,*f*]-azepine (**2b**) was added at room temperature to a solution of 0.91 g (0.038 mole) of sodium hydride in 120 ml of dioxane. After the mixture had been refluxed for four hours, 7.5 g (0.038 mole) of bromoacetaldehydediethyl acetal was added dropwise to the vigorously stirred mixture during a period of one hour and under maintained reflux. After the mixture had been refluxed overnight under argon atmosphere the excess sodium hydride was destroyed by methanol and the reaction mixture was then poured into toluene and water. The aqueous phase was extracted several times with toluene and the combined organic phases were washed with water, dried over magnesium sulfate and evaporated to give the crude acetal as a yellow oil, yield 3.35 g (67%) after chromatography on silica (toluene); ms: (high resolution) m/e calcd. for $C_{20}H_{23}D_2NO_2$: 313.2012,

found: 313.2004; ms: (low resolution) m/e 314 (M + 1, 5.4), 313 (M, 22.6), 312 (2.3), 269 (1.1), 268 (5.1), 223 (1.6), 222 (7.2), 221 (5.1), 220 (2.5), 219 (2.0), 212 (1.8), 211 (18.9), 210 (100.0), 209 (11.6), 208 (2.8), 207 (2.1), 206 (2.6), 205 (1.7), 197 (1.9), 196 (11.0), 195 (41.3), 194 (13.0), 193 (5.0), 192 (2.3), 182 (2.3), 181 (3.3), 180 (4.5), 179 (2.2), 178 (1.2), 169 (2.6), 168 (2.9), 167 (4.5), 166 (2.6), 154 (1.7), 153 (1.8), 129 (1.2), 118 (1.4), 117 (1.9), 116 (1.9), 105 (1.2), 104 (6.6), 103 (98.6), 92.1 (5.8), 91 (2.7), 90 (3.7), 89 (1.3), 79 (1.5), 78, (3.5), 77 (2.2), 76 (2.6), 75 (54.5), 66 (3.4), 65 (2.2), 64 (1.9), 63 (1.7), 52 (2.1), 51 (2.4), 47 (60.3).

Anal. Calcd. for $C_{20}H_{23}D_2NO_2$: C, 76.64; H + D, 8.68; N, 4.47. Found: C, 76.22; H + D, 8.47; N, 4.19.

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