A study of the Claisen—Eschenmoser reaction for hydroxymethylbenzofurans and -indoles

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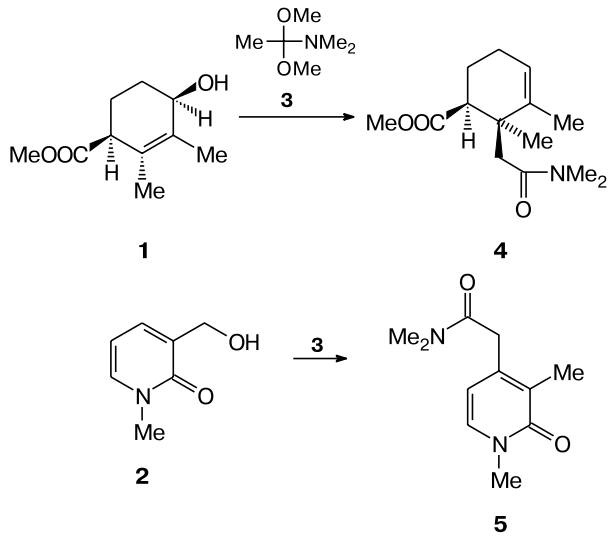
N,*N*-Dimethylacetamide dimethyl acetal reacted with 5(7)-substituted 2-(hydroxymethyl)benzofurans to give *N*,*N*-dimethyl-2-(2-methylbenzofuran-3-yl)acetamides. Analogous reactions with 3-(hydroxymethyl)indole and 1-hydroxy-6-methyl-1,2,3,4-tetrahydrocarbazole afforded *N*,*N*-dimethyl-3-(3-indolyl)propionamide and *N*,*N*-dimethyl-2-(6-methyl-1,2,3,4-tetrahydrocarbazol-1-yl)acetamide, respectively.

Key words: the Claisen—Eschenmoser reaction, *N*,*N*-dimethylacetamide dimethyl acetal, benzofurans, indoles, [3,3]-sigmatropic rearrangement, acetamides.

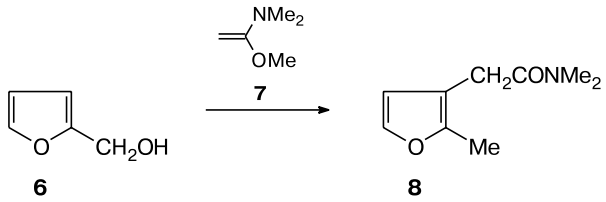
One of the most important approaches to a search for new biologically active compounds involves functionalization of basic substrates that already exhibit desired useful properties. The Claisen—Eschenmoser reaction of allylic alcohols with carboxamide acetals, the key step of which is [3,3]-sigmatropic rearrangement leading to more complex amides, has been widely described in the literature.[1—7] The representative examples of this transformation are the reactions of allylic alcohol **1** [2] or 3-hydroxymethyl-1-methyl-2-pyridone (**2**)[8] with *N*,*N*-dimethylacetamide dimethyl acetal (**3**), which yield *N*,*N*-dimethylamides **4** and **5**, respectively (Scheme 1).

Scheme 1



Despite considerable interest in the Claisen—Eschenmoser reaction, the use of hydroxymethyl derivatives of heteroarenes in it remains poorly studied. A rare related example is a reaction of furfuryl alcohol (**6**) with 1-dimethylamino-1-methoxyethene (**7**),[3] giving *N*,*N*-dimethyl-(2-methylfuran-3-yl)acetamide (**8**) (Scheme 2).

Scheme 2



The Claisen—Eschenmoser rearrangement has been most often used to obtain benzodioxin derivatives from heterocyclic compounds.[9]

Here we studied reactions of 2-(hydroxymethyl)benzofurans **9a—e**, 3-(hydroxymethyl)indole (**10**), and 1-hydroxy-6-methyl-1,2,3,4-tetrahydrocarbazole (**11**) with acetal **3**.

The starting 2-formylbenzofurans **12**, which are precursors of alcohols **9**, were prepared according to a known method[10,11] from appropriate salicylaldehydes and bromoacetaldehyde diethyl acetal (Scheme 3). Heating of a solution of 2-(hydroxymethyl)benzofurans **9a—e** and acetal **3** in DMF gave the expected amides **13a—e** as the result of the Claisen—Eschenmoser rearrangement (see Scheme 3). The structures of the compounds obtained

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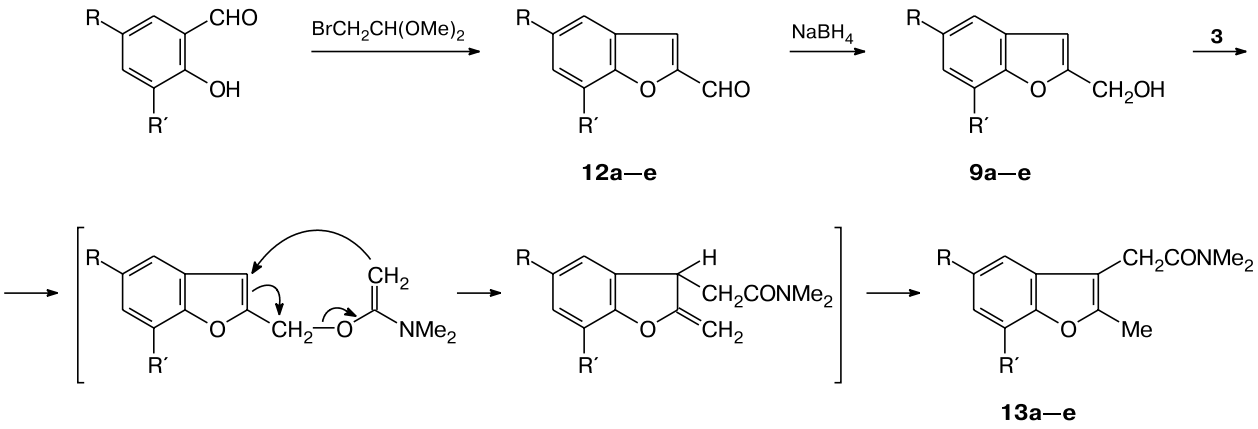
Scheme 3

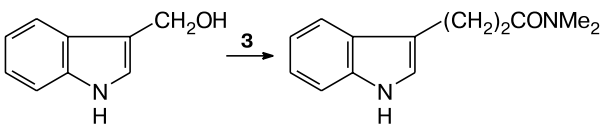


R = R′ = H (**a**); R = OMe, R′ = H (**b**); R = H, R′ = OMe (**c**); R = Br, R′ = H (**d**); R = R′ = Cl (**e**)

were proven by ^{1}H NMR and IR spectroscopy and mass spectrometry.

In the case of 3-(hydroxymethyl)indole (**10**), the sole reaction product *N*,*N*-dimethyl-3-indolylpropionamide (**14**) was obtained in 46% yield (Scheme 4). In this compound, the acetamide fragment is attached to the C atom that bears the hydroxy group in the starting alcohol **10** rather than to the allylic position, as this takes place in the rearrangement of furans[3] or benzodioxins[9] (see Scheme 2) and in the above transformation **9** → **13**.

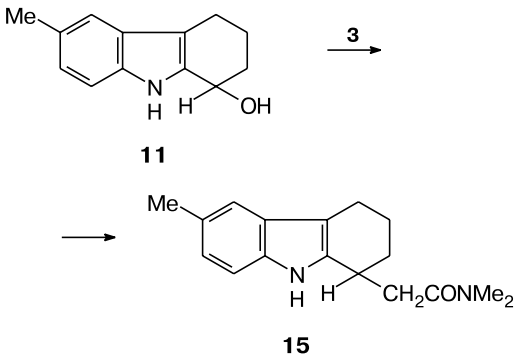
Scheme 4



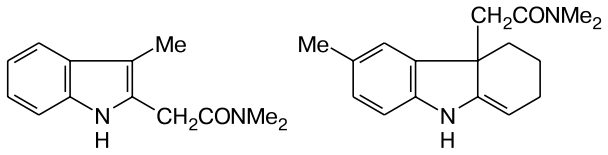
10 **14**

A reaction of another representative of the indole series, namely, tetrahydrocarbazole **11**, occurred analogously (Scheme 5).

Scheme 5



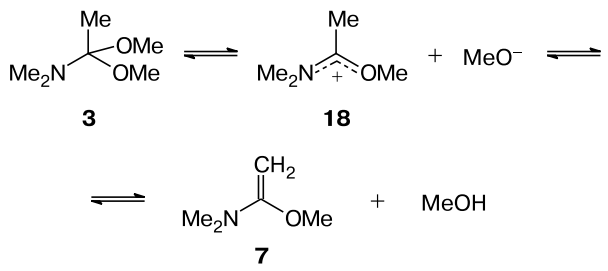
It should be noted that the conditions for the transformations of benzofurans **9a**—**e** and indoles **10** and **11** into amides **13a**—**e**, **14**, and **15**, respectively, differ substantially. As noted above, the transformation **9** → **13** requires heating in DMF, while reactions of indole derivatives occur at room temperature. The reactions of indoles **10** and **11** did not give compounds **16** and **17**, which could be expected to form if the reaction proceeded as with benzofurans **9a**—**e**.



16 **17**

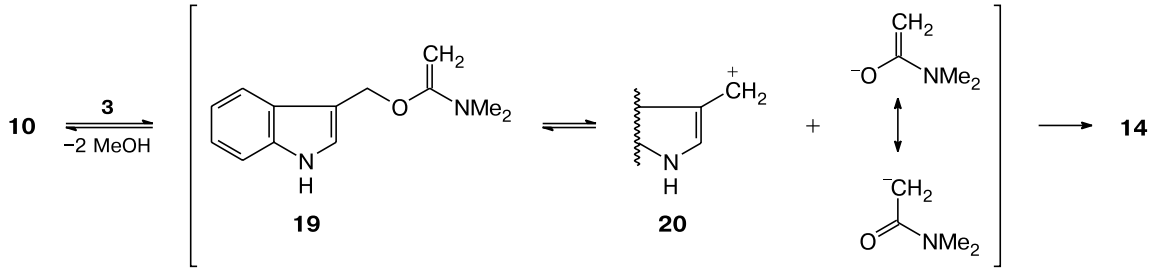
The role of *N*,*N*-dimethylacetamide dimethyl acetal (**3**) in the Claisen—Eschenmoser reaction is determined by the presence of the ternary equilibrium between the main acetal form, the ambident cation **18** + the alkoxy anion, and α-alkoxy enamine **7** + MeOH [12] (Scheme 6).

Scheme 6



Note that enamine **7** can be obtained from acetal **3** (*e.g.*, by heating with metallic calcium[13]) and used in the

Scheme 7



rearrangement under consideration instead of acetal **3** as described earlier.[3] It is a considerable partial negative charge in the β-position of enamine[14] that makes the rearrangement possible. Although the mechanism of the Claisen—Eschenmoser reaction for various carbinols has not been discussed in detail in the literature, one can assume that a concerted [3,3]-sigmatropic rearrangement takes place in standard cases like that observed for 2-(hydroxymethyl)benzofurans **9a—e**.

Apparently, for indole derivatives **10** and **11**, the reaction mechanism is different. Let us consider it with 3-(hydroxymethyl)indole (**10**) as an example (Scheme 7). Since indole is appreciably more electron-abundant than benzofuran, it is quite probable that the formation of a cationic or cation-like center in indole derivatives stabilizes the resulting species better than in the case of benzofurans. As for benzofurans (see Scheme 3), the reaction of carbinol **10** with acetal **3** starts with the transetherification[15,16] (known for amide acetals) leading to compound **19**, which seems to dissociate into stabilized cation **20** and the corresponding anion; recombination of cation **20** with the mesomeric anion gives amide **14**.

In conclusion, we studied two types of the Claisen—Eschenmoser transformations: with attachment of the dimethylacetamide residue to the allylic position (in the case of substituted 2-(hydroxymethyl)benzofurans) or to the C atom bearing the hydroxy group (in the case of 3-(hydroxymethyl)indole and 1-hydroxy-6-methyl-1,2,3,4-tetrahydrocarbazole).

Experimental

IR spectra were recorded on an FSM-1201 instrument (Nujol). Mass spectra were recorded on Waters ZQ2000 (ESI, direct inlet probe) and Finnigan SSQ-710 spectrometers (EI, 70 eV, direct inlet probe). ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer in DMSO-d_6. The yields, melting points, and elemental analysis data for the compounds obtained are given in Table 1.

The course of the reactions was monitored and the purity of the products was checked by TLC on Merk 60 F_{254} plates with benzene—methanol (20 : 1) as an eluent.

N,*N*-Dimethylacetamide dimethyl acetal (**3**) and 3-hydroxymethylindole (**10**) were purchased from Lancaster Co. 2-Formylbenzofurans **12a—e** were prepared according to known procedures.[10,11]

Table 1. Yields, melting points, and elemental analyses of compounds **9b—e**, **13a—e**, **14**, and **15**

Compound	Yield (%)	M.p./°C (solvent)	Found / Calculated (%)			Molecular formula
			C	H	N	
9b	90	70—71 (heptane)	67.48 / 67.41	5.52 / 5.66	—	$C_{10}H_{10}O_3$
9c	95	46—47 (heptane)	67.19 / 67.41	5.43 / 5.66	—	$C_{10}H_{10}O_3$
9d	98	109—110 (water)	47.60 / 47.61	3.14 / 3.11	—	$C_9H_7BrO_2$
9e	94	116—118 (water)	49.76 / 49.80	2.96 / 2.79	—	$C_9H_6Cl_2O_2$
13a	22	41—46 (heptane)	71.87 / 71.87	6.90 / 6.96	6.48 / 6.45	$C_{13}H_{15}NO_2$
13b	81	70—71 (heptane)	68.41 / 68.00	6.77 / 6.93	5.64 / 5.66	$C_{14}H_{17}NO_3$
13c	80	111—112 (heptane)	67.92 / 68.00	6.70 / 6.93	5.69 / 5.66	$C_{14}H_{17}NO_3$
13d	66	121—122 (AcOEt)	52.25 / 52.72	4.71 / 4.76	4.75 / 4.73	$C_{13}H_{14}BrNO_2$
13e	46	105—106 (heptane)	54.74 / 54.56	4.66 / 4.58	4.88 / 4.90	$C_{13}H_{13}Cl_2NO_2$
14	46 (***A***), 25 (***B***)	44 (AcOEt)	71.79 / 72.19	7.18 / 7.46	13.01 / 12.95	$C_{13}H_{16}N_2O$
15	37	142—143 (MeCN)	75.67 / 75.52	7.81 / 8.20	10.27 / 10.30	$C_{17}H_{22}N_2O$

2-Hydroxymethylbenzofuran (9a). Sodium borohydride (1.51 g, 40 mmol) was added in portions at 40—50 °C to a solution of 2-formylbenzofuran (**12a**) (1.46 g, 10 mmol) in a mixture of methanol (20 mL) and chloroform (10 mL). After the reduction was completed (4 h), the solvents were removed and the residue was diluted with water (30 mL). The product was extracted with chloroform, and the extract was concentrated. The resulting oil (1.3 g, 88%) was used in a reaction with acetal **3** without additional purification. IR, ν/cm^{-1}: 3370, 3310 (OH). ^{1}H NMR, δ: 4.58 (d, 2 H, C$\underline{H}_2$OH, J = 5.4 Hz); 5.50 (t, 1 H, CH$_2$O$\underline{H}$, J = 5.4 Hz); 6.75 (s, 1 H, H(3)); 7.24, 7.51 (both m, 2 H each, H(4)—H(7)).

2-Hydroxymethyl-5-methoxybenzofuran (9b). Sodium borohydride (0.42 g, 11 mmol) was added in portions at 30—40 °C to

a solution of 2-formyl-5-methoxybenzofuran (**12b**) (1.76 g, 10 mmol) in a mixture of methanol (20 mL) and chloroform (10 mL). After the reduction was completed (1 h), the solvents were removed and the residue was diluted with water. The precipitate that formed was filtered off, washed with water and light petroleum, and dried. The yield of compound **9b** was 1.6 g. IR, ν/cm^{-1}: 3318, 3260 (OH). ^{1}H NMR, δ: 3.76 (s, 3 H, OMe); 4.51 (d, 2 H, C$\underline{H}_2$OH, J = 5.4 Hz); 5.45 (t, 1 H, CH$_2$O$\underline{H}$, J = 5.4 Hz); 6.67 (s, 1 H, H(3)); 6.84 (dd, 1 H, H(6), ^3J = 8.8 Hz, ^4J = 2.4 Hz); 7.10 (d, 1 H, H(4), ^4J = 2.4 Hz); 7.41 (d, 1 H, H(7), ^3J = 8.8 Hz).

2-Hydroxymethyl-7-methoxybenzofuran (9c) was obtained analogously from 2-formyl-7-methoxybenzofuran (**12c**) (1.76 g, 10 mmol). The yield of compound **9c** was 1.7 g. IR, ν/cm^{-1}: 3410, 3350 (OH). ^{1}H NMR, δ: 3.93 (s, 3 H, OMe); 4.54 (d, 2 H, C$\underline{H}_2$OH, J = 5.4 Hz); 5.37 (t, 1 H, CH$_2$O$\underline{H}$, J = 5.4 Hz); 6.66 (s, 1 H, H(3)); 6.71, 7.11 (both m, 1 H + 2 H, H(4)—H(6)).

5-Bromo-2-hydroxymethylbenzofuran (9d) was obtained analogously from 5-bromo-2-formylbenzofuran (**12d**) (2.25 g, 10 mmol). The yield of compound **9d** was 1.7 g. IR, ν/cm^{-1}: 3368, 3281 (OH). ^{1}H NMR, δ: 4.57 (d, 2 H, C$\underline{H}_2$OH, J = 6.0 Hz); 5.53 (t, 1 H, CH$_2$O$\underline{H}$, J = 5.4 Hz); 6.75 (s, 1 H, H(3)); 7.40 (dd, 1 H, H(6), ^3J = 8.4 Hz, ^4J = 2.1 Hz); 7.52 (d, 1 H, H(7), ^3J = 8.8 Hz); 7.80 (d, 1 H, H(4), ^4J = 2.1 Hz).

5,7-Dichloro-2-hydroxymethylbenzofuran (9e) was obtained analogously from 5,7-dichloro-2-formylbenzofuran (**12e**) (0.80 g, 3.7 mmol). The yield of compound **9e** was 0.76 g. IR, ν/cm^{-1}: 3188 (OH). ^{1}H NMR, δ: 4.61 (d, 2 H, C$\underline{H}_2$OH, J = 6.0 Hz); 5.64 (t, 1 H, CH$_2$O$\underline{H}$, J = 5.4 Hz); 6.86 (s, 1 H, H(3)); 7.40 (dd, 1 H, H(6), ^3J = 8.4 Hz, ^4J = 2.1 Hz); 7.52 (d, 1 H, H(7)); 7.52, 7.70 (both d, 1 H each, H(4), H(6), ^4J = 1.8 Hz).

***N*,*N*-Dimethyl-(2-methylbenzofuran-3-yl)acetamide (13a).** A mixture of 2-hydroxymethylbenzofuran (**9a**) (1.04 g, 7 mmol) and *N*,*N*-dimethylacetamide dimethyl acetal (**3**) (2.3 mL, 14 mmol) was refluxed in DMF (8 mL) for 15 h. Volatile substances were removed *in vacuo*. Column chromatography of the residue on silica gel eluted with benzene gave the starting alcohol **9a** (0.38 g) and amide **13a** (0.33 g). IR, ν/cm^{-1}: 1640 (C=O). MS, *m*/*z*: 240 [M + Na]$^{\bullet+}$, 218 [M + H]$^{\bullet+}$, 145 [M – C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR, δ: 2.38 (s, 3 H, Me); 2.85, 3.06 (both s, 3 H each, NMe$_2$); 3.69 (s, 2 H, CH$_2$); 7.17, 7.44 (both m, 2 H each, H(4)—H(7)).

***N*,*N*-Dimethyl-(5-methoxy-2-methylbenzofuran-3-yl)acetamide (13b).** A mixture of 2-hydroxymethyl-5-methoxybenzofuran (**9b**) (0.89 g, 5 mmol) and *N*,*N*-dimethylacetamide dimethyl acetal (**3**) (1.6 mL, 10 mmol) was refluxed in DMF (8 mL) until the starting reagent **9b** was completely consumed. Volatile substances were removed *in vacuo*. The residue was diluted with ether (10 mL) and allowed to crystallize at 0 °C. The precipitate that formed was filtered off and dried. The yield of amide **13b** was 1 g. IR, ν/cm^{-1}: 1647 (C=O). MS, *m*/*z*: 270 [M + Na]$^{\bullet+}$, 248 [M + H]$^{\bullet+}$, 175 [M – C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR, δ: 2.34 (s, 3 H, Me); 2.83, 3.04 (both s, 3 H each, NMe$_2$); 3.66 (s, 2 H, CH$_2$); 3.74 (s, 3 H, OMe); 6.77 (dd, 1 H, H(6), ^3J = 8.8 Hz, ^4J = 2.4 Hz); 6.99 (d, 1 H, H(4), ^4J = 2.4 Hz); 7.32 (d, 1 H, H(7), ^3J = 8.8 Hz).

***N*,*N*-Dimethyl-(7-methoxy-2-methylbenzofuran-3-yl)acetamide (13c)** was obtained analogously from alcohol **9c** (1.2 g, 6.7 mmol) and acetal **3** (2.3 mL, 14 mmol) in DMF (10 mL). The yield was 1.34 g. IR, ν/cm^{-1}: 1638 (C=O). MS (EI), *m*/*z* (I_{rel} (%)): 247 [M]$^{\bullet+}$ (65), 175 [M – C(O)NMe$_2$]$^{\bullet+}$ (100). ^{1}H NMR, δ: 2.39 (s, 3 H, Me); 2.86, 3.04 (both s, 3 H each, NMe$_2$); 3.62 (s, 2 H, CH$_2$); 3.92 (s, 3 H, OMe); 6.76, 7.02 (both m, 1 H + 2 H, H(4)—H(6)).

***N*,*N*-Dimethyl-(5-bromo-2-methylbenzofuran-3-yl)acetamide (13d)** was obtained analogously from alcohol **9d** (1.8 g, 8 mmol) and acetal **3** (2.6 mL, 16 mmol) in DMF (12 mL). The yield was 1.56 g. IR, ν/cm^{-1}: 1638 (C=O). MS, *m*/*z*: 318 [M + Na]$^{\bullet+}$, 296 [M + H]$^{\bullet+}$, 223 [M – C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR, δ: 2.38 (s, 3 H, Me); 2.84, 3.06 (both s, 3 H each, NMe$_2$); 3.70 (s, 2 H, CH$_2$); 7.33 (dd, 1 H, H(6), ^3J = 8.4 Hz, ^4J = 2.1 Hz); 7.43 (d, 1 H, H(7), ^3J = 8.4 Hz); 7.66 (d, 1 H, H(4), ^4J = 2.1 Hz).

***N*,*N*-Dimethyl-(5,7-dichloro-2-methylbenzofuran-3-yl)acetamide (13e)** was obtained analogously from alcohol **9e** (0.5 g, 2.3 mmol) and acetal **3** (0.75 mL, 4.6 mmol) in DMF (4 mL). The yield was 0.3 g. IR, ν/cm^{-1}: 1638 (C=O). MS, *m*/*z*: 308 [M + Na]$^{\bullet+}$, 286 [M + H]$^{\bullet+}$, 213 [M – C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR, δ: 2.42 (s, 3 H, Me); 2.84, 3.07 (both s, 3 H each, NMe$_2$); 3.73 (s, 2 H, CH$_2$); 7.44, 7.54 (both d, 1 H each, H(4), H(6), ^4J = 1.8 Hz).

N*,*N*-Dimethyl-3-(indol-3-yl)propanamide (14).** ***A. The synthesis was carried out as described for compound **13b**. Amide **14** was obtained from 3-(hydroxymethyl)indole (**10**) (1.47 g, 10 mmol) and acetal **3** (3.2 mL, 20 mmol) in DMF (15 mL). The yield was 1 g. IR, ν/cm^{-1}: 3210 (NH), 1634 (C=O). MS, *m*/*z*: 455 [2 M + Na]$^{\bullet+}$, 239 [M + Na]$^{\bullet+}$, 130 [M – CH$_2$C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR, δ: 2.63, 2.90 (both t, 2 H each, (C$\underline{H}_2$)$_2$CONMe$_2$, J_1 = J_2 = 7.2 Hz); 2.81, 2.92 (both s, 3 H each, NMe$_2$); 6.96, 7.05, 7.32, 7.50 (all m, 1 H each, H(4)—H(7)); 7.12 (d, 1 H, H(2), $^4J_{NH,H(2)}$ = 2.1 Hz); 10.76 (br.s, 1 H, NH).

B. A mixture of alcohol **10** (0.37 g, 2.5 mmol) and acetal **3** (0.5 mL, 3.1 mmol) was stirred in benzene (5 mL) at 20 °C for 5 h. The solvent and the excess of acetal **3** were removed *in vacuo*. The residue was diluted with ether (5 mL) and allowed to crystallize at 0 °C. The precipitate was filtered off, washed with light petroleum, and dried. The yield was 0.135 g; the sample was identical with that obtained according to procedure ***A***.

***N*,*N*-Dimethyl-2-(6-methyl-1,2,3,4-tetrahydrocarbazol-1-yl)acetamide (15).** Acetal **3** (4 mL, 25 mmol) was added to a suspension of 1-hydroxy-6-methyl-1,2,3,4-tetrahydrocarbazole (**11**)[17] (4 g, 20 mmol) in benzene (30 mL). The precipitate dissolved rapidly and the resulting solution spontaneously heated from 20 to 30 °C. The mixture was stirred for 30 min, the solvent was removed, and the residue was dissolved in ether (20 mL) and allowed to crystallize at 4 °C. The precipitate that formed was filtered off and washed with ether (4 mL). Recrystallization from MeCN (6 mL) gave amide **15** (2 g). MS, *m*/*z*: 309 [M + K]$^{\bullet+}$, 293 [M + Na]$^{\bullet+}$, 271 [M + H]$^{\bullet+}$, 226 [M – NMe$_2$]$^{\bullet+}$, 184 [M – CH$_2$C(O)NMe$_2$]$^{\bullet+}$. ^{1}H NMR (CDCl$_3$), δ: 1.66, 2.08 (both m, 1 H each, C(2)H$_2$); 1.83 (m, 2 H, C(3)H$_2$); 2.45 (s, 3 H, Me); 2.62 (d, 2 H, CH$_2$CO, J = 6.7 Hz); 2.70 (m, 2 H, C(4)H$_2$); 2.99, 3.04 (both s, 3 H each, NMe$_2$); 3.46 (m, 1 H, H(1)); 6.94 (dd, 1 H, H(7), ^3J = 8.2 Hz, ^4J = 1.6 Hz); 7.20 (d, 1 H, H(8), ^3J = 8.2 Hz); 7.26 (m, 1 H, H(5)); 9.18 (br.s, 1 H, NH).

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