First Reactions of Dialkoxycarbenium Tetrafluoroborates with Pyrroles, 5*H*-Dibenz[*b*,*f*]azepines, and Electron-Rich Arenes

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Pyrrole (**2a**) and 2,5-dimethylpyrrole (**2b**) react with the dialkoxycarbenium tetrafluoroborates **1a-1c** under kinetic control to yield the corresponding acylpyrrole derivatives. 5*H*-Dibenz[*b*,*f*]azepine (**9a**) and the 10,11-dihydro derivative **9b** react only with the most electrophilic of the series of electrophiles tested, namely, diethoxycarbenium tetrafluoroborate (**1a**), to furnish the corresponding formyl derivatives. Similarly, in arene chemistry, the highly electron-rich *N*,*N*-dimethylaniline (**13a**) and 1,3,5-trimethoxybenzene (**13b**) are formylated by reaction with **1a**.

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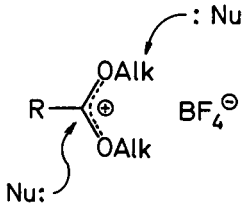
Introduction.

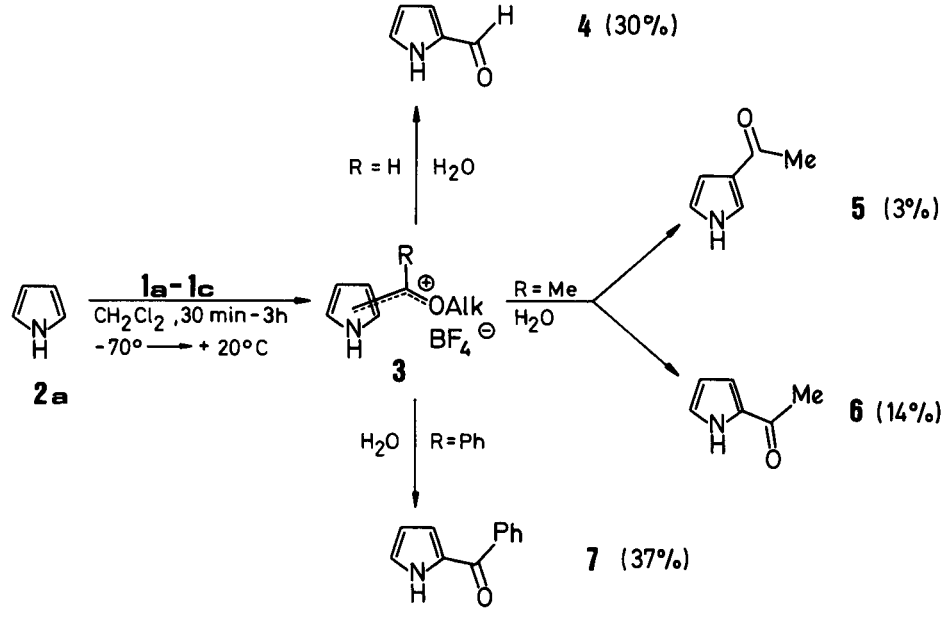
The dialkoxycarbenium tetrafluoroborates **1** were synthesized for the first time by Meerwein and co-workers [1,2] and represent an extremely interesting class of oxo-stabilized carbenium ions. These cations possess ambident electrophilic reactivity as acylium and alkylium synthons and have been employed by others [2] and by ourselves as acylation or alkylation reagents for the highly regioselective functionalization of electron rich π-systems [2-6]. In continuation of our investigations on the reactions of electron-rich heterocyclic compounds with orthocarboxylic acid derivatives, we now report on the first reactions of the dialkoxycarbenium tetrafluoroborates **1a-1c** with pyrroles **2**, 5*H*-dibenz[*b*,*f*]azepines **9a** and **9b**, and the electron-rich arenes **13a** and **13b**. The reactions proceed under kinetic and, in some cases, under thermodynamic control.



1	R	Alk
a	H	Et
b	Me	Et
c	Ph	Me

Results and Discussion.

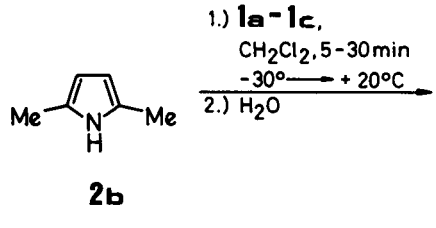
Pyrroles constitute one of the most nucleophilic classes of π-excessive hetarenes available for use in electrophilic substitution reactions [7,8]. The parent pyrrole (**2a**) reacts, aside from yield-diminishing polymerization processes, with the dialkoxycarbenium tetrafluoroborates **1a-1c**, acting exclusively as acylium synthetic equivalents, under strictly anhydrous conditions and an argon atmosphere to



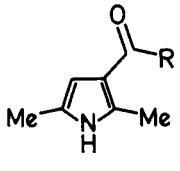
form the pyrrolyl-stabilized carbenium tetrafluoroborates **3**. On account of their high instability even under inert gas atmospheres at low temperatures and in contrast to the analogous indolyl-stabilized systems [3-5], the products **3** could not be purified sufficiently for structural analytical investigations. Thus, the salts **3** were hydrolyzed under mild conditions (20°) directly subsequent to their formation to produce the acylated pyrroles **4-7**. In accord with our further investigations in the indole and carbazole series [3-5], in these reactions also **1a** possesses the highest electrophilicity of the series of salts **1** (for example, the highly resonance-stabilized $(CH_3O)_3C^+$ BF_4^- gave no products at all on reaction with the substrates tested in this work as a result of a significant ground state effect [2]).

The observed product spectrum of the acylated pyrroles **4-7** reflects very well the already known positional reactivity patterns of pyrroles while the 2-position of **2a** is the most nucleophilic site under kinetically controlled conditions. The relatively low yields of **4-7** found here are all a consequence of the, in general, extreme polymerization reactivity of pyrroles.

In the same way, 2,5-dimethylpyrrole (**2b**), which is somewhat more nucleophilic than **2a**, reacts with **1a-1c** to give exclusively the 3-acylated pyrroles **8a-8c** in satisfactory yields.



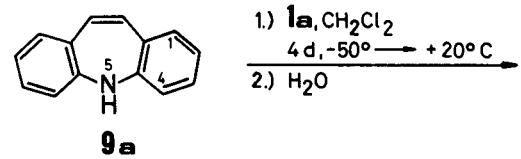
2b



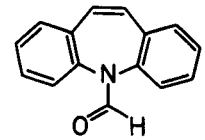
8	R	yield [%]
a	H	55
b	Me	54
c	Ph	45

The physical data of the products **4-8** are in complete agreement with those reported to date in the literature [8,9]. For compounds **4-7**, in addition, 400 MHz ^{1}H, ^{1}H-nOe measurements were also carried out. No alkylated products could be detected in any of the reaction mixtures by the analytical methods used up to now (^{1}H-nmr, tlc).

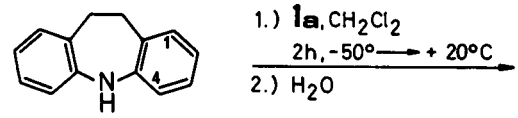
In a further study, we have investigated the reactivities of 5*H*-dibenz[*b*,*f*]azepine (**9a**) and 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (**9b**), both of which formally represent a conformationally restricted *N*,*N*-diphenylamine, towards the compounds **1**. Of the tested electrophiles **1a-1c**, only the reactions with the sufficiently reactive diethoxycarbenium tetrafluoroborate (**1a**) [2] were successful. The tricyclic compound **9a** was regioselectively formylated at the nitrogen atom by **1a** to furnish exclusively the product **10** in low yield. In contrast to this result, the 10,11-dihydro derivative **9b** was formylated nonselectively at both the *N*- and 2-positions to furnish the products **11** and **12**. Furthermore, in the latter reactions, the primarily formed analogs of the salts **3** can be isolated, however, they decompose immediately *via* dealkylation [2] at room temperature. The compounds **9** are less nucleophilic than the pyrroles **2** tested and this is reflected in the relatively low yields obtained. MO calculations for **9a** and **9b** do indeed predict lower nucleophilicities than those of the pyrroles **2** as well as the preferred positional attack of the electrophile at **9** *via* a charge-controlled orientation of the reactants [10].



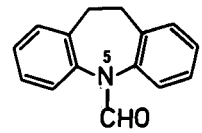
9a



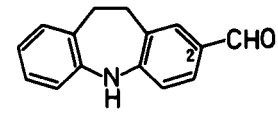
10 (9%)



9b



11 (6%)



12 (6%)

The constitutions of the products obtained from the reactions of **9a,b** were clarified principally by 400 MHz ^{1}H-nmr measurements (homo-decoupling, nOe spectra). The thus established, diagnostically relevant aromatic protons of compound **12** are shown exemplarily in Figure 1. The structural formula **I** in Figure 1 illustrates the respective, diagnostically important nOe's.

In the case of compound **11**, the temperature dependent 400 MHz ^{1}H-nmr spectra reveal dynamic processes associated with the restricted conformational mobility of the central seven-membered ring (*e.g.*, amide rotation and inversion of the seven-member ring [11]). On going from a measurement temperature of $-60°$ to $+50°$, the H_2C-

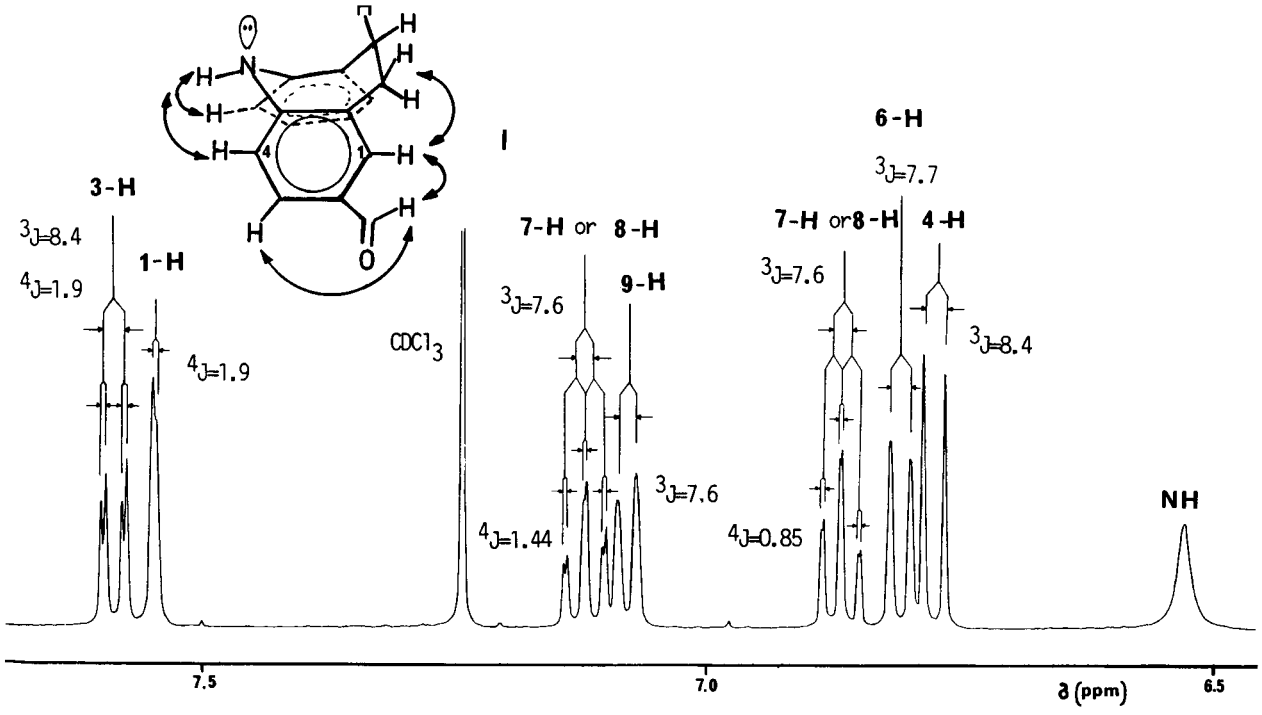
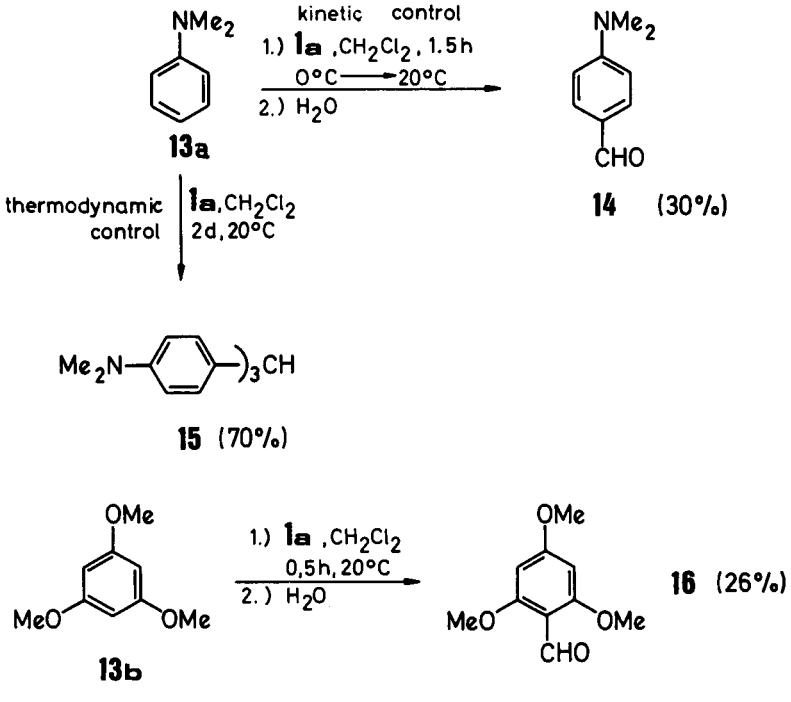


Figure 1. 400 MHz ^{1}H-nmr spectrum of the aromatic region of compound **12** in deuteriochloroform (coupling constants J in Hz). Structural formula **I** illustrates the diagnostically important ^{1}H, ^{1}H-nOe's of **12**.



H_2C spin system changes from an ABCD type *via* an AA'BB' to an A_4 spin system (coalescence, rapid exchange). According to the Eyring equation [12], the change from an AA'BB' to an A_4 spin system is characterized by an energy barrier given by the equation: $\Delta G^{\neq}_{323\,K}$ = 67.21 kJ/mol.

Our investigations of the reactivity of compounds **1** as electrophiles in arene chemistry demonstrate that only the use of highly electron-rich arenes gives rise to definable results on account of their high π-electron densities and

their high-lying HOMO energies [10]. Thus, simple mono- and diphenols and their methyl ethers do not even react with **1a** (the most electrophilic member of the series). However, *N,N*-dimethylaniline (**13a**) and 1,3,5-trimethoxybenzene (**13b**) do react with **1a** in analogy to the Vilsmeier formylation [13] to furnish the known aromatic aldehydes **14** and **16**. Under more strictly thermodynamically controlled conditions (2 days at 20°), **13a** reacts with **1a** *via* tandem electrophilic substitution to yield the triarylmethane **15** as the major product. We have found [14] that compound **15** is the sole reaction product obtainable from the electrophilic substitution sequence of **13a** with triethyl orthoformate under strictly anhydrous conditions with zinc chloride diethyl etherate as catalyst.

EXPERIMENTAL

Materials and Techniques.

The proton magnetic resonance spectra were recorded on Bruker WH-90 and WM-400 spectrometers using tetramethylsilane as internal standard (δ scale). The infrared spectra were recorded on a Beckman IR 4200 spectrophotometer. The ei mass spectra were measured on a Varian CH 7A instrument at 70 eV. Elemental analyses were performed using a Carlo Erba Strumentazione apparatus. Melting points were determined on a Büchi SMP-20 apparatus and are not corrected. Merck silica gel (grain size: 0.063-0.200 mm) was used for column chromatography and Merck silica gel (grain size: 0.040-0.063 mm) for "flash" chromatography. Centrifugal thin layer chromatography was performed with a Harrison Research Chromatotron Type 7924T apparatus on Merck silica gel $60PF_{254}$ (detection: uv absorption at 254 nm).

All reactions with the dialkoxycarbenium salts **1** must be performed in absolutely pure, anhydrous solvents under an argon atmosphere. The dialkoxycarbenium tetrafluoroborates **1** were prepared from ortho esters in a special apparatus described by us previously [5,15]. All contract of compounds **1** with air and/or moisture must be strictly avoided.

General Procedure for the Synthesis of the Acylated Compounds **4-8**, **10-12**, **14**, **16**, and Product **15**.

To an excess of the dialkoxycarbenium tetrafluoroborate **1a-1c** (prepared according to ref [5]) was slowly added dropwise using a syringe a solution of the *N*-hetarene or arene (10-15 mmoles) in 75 ml of dichloromethane at −70°. The reaction mixture was then stirred under an argon atmosphere at −70 to +20° for several minutes to several days (for details, see under the individual compounds). When not otherwise stated, the reaction mixture or the precipitated crystals were hydrolyzed for about 1 hour in a two phase system consisting of dichloromethane/water at 20° and then neutralized with 3% aqueous sodium hydroxide solution. The organic phase was separated, dried with sodium sulfate, and the solvent removed under mild conditions using a rotary evaporator. Separation and purification of the residue was achieved by various chromatogrphic methods and/or by crystallization.

Pyrrole-2-carboxaldehyde (**4**).

The reaction was performed following the general procedure using 1.0 g (15 mmoles) of pyrrole (**2a**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.26 g (30 mmoles) of boron trifluoride diethyl etherate ($Et_2O{\cdot}BF_3$)]. The reaction time was 0.5 hour, the reaction temperature −40 to 0°. The residue was purified using centrifugal thin layer chromatography [eluent: petroleum ether (40-60°)/ethyl acetate, 2/1]. The product **4** was obtained as light brown crystals in 30% yield (410 mg), mp 44-46° (petroleum ether/ethyl acetate), ref [9], mp 44-45°; ir (potassium bromide): ν 3280 (NH), 2880, 2860, 1650 (CO), 1540, 1440, 1400, 1350, 1310, 1250, 1215, 1170, 1135, 1085, 1040, 960, 930, 880, 860, 760, 600, 500 cm^{-1}; ms: m/e (%) 95 ($M^{+\cdot}$, 100), 94 (99), 67 (15), 66 (99), 52 (8), 50 (9), 41 (39); ^{1}H-nmr (90 MHz, trideuterionitromethane): δ 6.35 (mc, 1H, C4-H), 7.00 (mc, 1H, C3-H), 7.17 (mc, 1H, C5-H), 9.54 (d, $^5J_{CHO,C2\text{-}H}$ = 2.82 Hz, 1H, CHO), 10.05 (br s, 1H, NH).

Anal. Calcd. for C_5H_5NO (95.10): C, 63.15; H, 5.30; N, 14.73. Found: C, 63.15; H, 5.31; N, 14.88.

3-Acetylpyrrole (**5**) and 2-Acetylpyrrole (**6**).

The reaction was performed with 1.00 g (15 mmoles) of pyrrole (**2a**) and diethoxy(methyl)carbenium tetrafluoroborate (**1b**) [prepared from 3.24 g (20 mmoles) of triethyl orthoacetate and 4.24 g (30 mmoles) of boron trifluoride diethyl etherate]. The reaction time was 3 hours, the temperature −50 to −20°. The residue was separated by "flash" chromatography (eluent: petroleum ether/ethyl acetate, 2/1) and low temperature crystallization from petroleum ether. Compound **5** was obtained as colorless crystals in 3% yield (43 mg), mp 114°, ref [9], mp 115-116°; ir (potassium bromide): ν 3220 (NH), 3180, 3100, 2965, 2680, 2600, 1630 (CO), 1540, 1505, 1435, 1400, 1360, 1335, 1260, 1170, 1130, 1090, 1040, 1020, 975, 930, 885, 790, 740, 660 cm^{-1}; ms: m/e (%) 109 ($M^{+\cdot}$, 55), 95 (5), 94 (100), 67 (3), 66 (17), 53 (3), 43 (3); ^{1}H-nmr (90 MHz, deuteriochloroform): δ 2.44 (s, 3H, CH_3), 6.66 (mc, 1H, C4-H), 6.77 (mc, 1H, C5-H), 7.44 (mc, 1H, C2-H), 8.80 (br s, 1H, NH).

Anal. Calcd. for C_6H_7NO (109.13): C, 66.04; H, 6.46; N, 12.80. Found: C, 66.13; H, 6.39; N, 12.63.

Compound **6** was obtained as light yellow crystals in 14% yield (222 mg), mp 89°, ref [9], mp 91°; ir (potassium bromide): ν 3270 (NH), 1635 (CO), 1540, 1430, 1400, 1365, 1325, 1260, 1220, 1140, 1130, 1090, 1070, 1045, 1020, 970, 930, 885, 845, 770, 750, 630, 610 cm^{-1}; ms: m/e (%) 109 ($M^{+\cdot}$, 70), 95 (5), 94 (100), 66 (51), 53 (9), 43 (16); ^{1}H-nmr (90 MHz, deuteriochloroform): δ 2.44 (s, 3H, CH_3), 6.29 (mc, 1H, C4-H), 6.92 (mc, 1H, C3-H), 7.04 (mc, 1H, C5-H), 9.70 (br s, 1H, NH).

Anal. Calcd. for C_6H_7NO (109.13): C, 66.04; H, 6.46; N, 12.80. Found: C, 66.10; H, 6.49; N, 12.67.

2-Benzoylpyrrole (**7**).

The reaction was performed with 1.00 g (15 mmoles) of pyrrole (**1a**) and dimethoxy(phenyl)carbenium tetrafluoroborate (**1c**) [prepared from 3.64 g (20 mmoles) of triethyl orthobenzoate and 4.25 g (30 mmoles) of boron trifluoride diethyl etherate]. The reaction time was 1.5 hours, the reaction temperature −40 to −20°. The residue was recrystallized directly from petroleum ether. Compound **7** was obtained as colorless crystals in 37% yield (0.95 g), mp 77° (petroleum ether, ref [9], mp 77-78°; ir (potassium bromide): ν 3270 (NH), 3210, 3140, 1620 (CO), 1565, 1530, 1440, 1420, 1400, 1330, 1310, 1280, 1250, 1200, 1135, 1085, 1040, 1025, 1000, 980, 920, 890, 870, 845, 830, 780, 750, 730, 690, 670, 600 cm^{-1}; ms: m/e (%) 171 ($M^{+\cdot}$, 100), 170 (27), 143 (8), 115 (8), 105 (12), 94 (88), 77 (24), 66 (18), 51 (13); ^{1}H-nmr (90 MHz, deuteriochloroform): δ 6.34 (mc, 1H, C4-H), 6.90 (mc, 1H, C3-H), 7.15 (mc, 1H, C5-H), 7.47 (mc, 3H, phenyl-H), 7.90 (mc, 2H, phenyl-H), 9.70

(br s, 1H, NH).

Anal. Calcd. for $C_{11}H_9NO$ (171.20): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.14; H, 5.15; N, 8.00.

2,5-Dimethylpyrrole-2-carboxaldehyde (**8a**).

The reaction was performed with 1.43 g (15 mmoles) of 2,5-dimethylpyrrole (**2b**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.26 g (30 mmoles) of boron trifluoride diethyl etherate). The reaction time was 5 minutes, the reaction temperature −70°. The residue was purified by "flash" chromatography (eluent: petroleum ether/ethyl acetate, 7/3). Compound **8a** was obtained as colorless crystals in 55% yield (1.0 g), mp 141° (petroleum ether/ethyl acetate), ref [9], mp 144-145°; ir (potassium bromide): ν 3400 (NH), 2970, 2940, 2870, 2840, 2790, 1665 (CO), 1600, 1575, 1470, 1460, 1430, 1410, 1330, 1230, 1215, 1200, 1190, 1160, 1130, 1060, 1025, 955, 920, 810, 785, 720, 685, 640, 585, 500 cm^{-1}; ms: m/e (%) 123 ($M^{+\cdot}$, 96), 122 (100), 95 (5), 94 (46), 93 (9), 67 (21), 53 (11); ^{1}H-nmr (90 MHz, dideuteriochloromethane): δ 2.19 (s, 3H, C5-CH_3), 2.47 (s, 3H, C2-CH_3), 6.13 (mc, 1H, C4-H), 8.60 (bs, 1H, NH), 9.76 (br s, 1H, CHO).

Anal. Calcd. for C_7H_9NO (123.10): C, 68.28; H, 7.37; N, 11.38. Found: C, 68.26; H, 7.39; N, 11.31.

3-Acetyl-2,5-dimethylpyrrole (**8b**).

The reaction was performed with 1.43 g (15 mmoles) of 2,5-dimethylpyrrole (**2b**) and diethoxy(methyl)carbenium tetrafluoroborate (**1b**) [prepared from 3.25 g (20 mmoles) of triethyl orthoacetate and 4.26 g (30 mmoles) of boron trifluoride diethyl etherate). The reaction time was 20 minutes, the reaction temperature −50°. The residue was purified by "flash" chromatography (eluent: petroleum ether/ethyl acetate, 7/3). Compound **8b** was obtained as pale pink-colored crystals in 54% yield (1.13 g), mp 92° (petroleum ether/ethyl acetate), ref [9], mp 89°; ir (potassium bromide): ν 3200 (NH), 3160, 3110, 3020, 1640 (CO), 1620 (CO), 1595, 1520, 1450, 1360, 1275, 1230, 1140, 1040, 1020, 1000, 950, 835, 810, 775, 760, 680, 635, 600 cm^{-1}; ms: m/e (%) 137 ($M^{+\cdot}$, 66), 136 (4), 123 (9), 122 (100), 94 (21), 93 (7), 67 (15), 61 (8), 54 (6); ^{1}H-nmr (90 MHz, dideuteriodichloromethane): δ 2.19 (d, ^4J = 0.55 Hz, 3H, C5-CH_3), 2.31 (s, 3H, $COCH_3$), 2.46 (s, 3H, C2-CH_3), 6.14 (mc, 1H, C4-H), 8.45 (br s, 1H, NH).

Anal. Calcd. for $C_8H_{11}NO$ (137.10): C, 70.08; H, 8.02; N, 10.21. Found: C, 70.21; H, 7.95; N, 10.16.

3-Benzoyl-2,5-dimethylpyrrole (**8c**).

The reaction was performed with 1.43 g (15 mmoles) of 2,5-dimethylpyrrole (**2b**) and dimethoxy(phenyl)carbenium tetrafluoroborate (**1c**) [prepared from 3.64 g (20 mmoles) of trimethyl orthobenzoate and 4.25 g (30 mmoles) of boron trifluoride diethyl etherate]. The reaction time was 15 minutes, the reaction temperature −50°. The residue was separated by "flash" chromatography (eluent: petroleum ether/ethyl acetate, 7/3). Compound **8c** was obtained as yellow crystals in 45% yield (1.34 g), mp 129° (petroleum ether/ethyl acetate), ref [9], mp 129-130°; ir (potassium bromide): ν 3240 (NH), 1620 (CO), 1595, 1585, 1570, 1510, 1450, 1425, 1390, 1360, 1265, 1245, 1170, 1130, 1070, 1040, 1030, 1000, 970, 930, 910, 810, 800, 760, 730, 700, 675, 640, 600 cm^{-1}; ms: m/e (%) 199 ($M^{+\cdot}$, 51), 198 (55), 182 (12), 123 (54), 122 (100), 94 (41), 77 (17), 67 (24), 53 (14); ^{1}H-nmr (90 MHz, dideuteriodichloromethane): δ 2.19 (d, ^4J = 0.67 Hz, 3H, C5-CH_3), 2.46 (s, 3H, C2-CH_3), 6.03 (mc, 1H, C4-H), 7.46 (mc, 3H, phenyl-H), 7.75 (mc, 2H, phenyl-H), 8.40 (br s, 1H, NH).

Anal. Calcd. for $C_{13}H_{13}NO$ (199.21): C, 78.30; H, 6.56; N, 7.03. Found: C, 77.99; H, 6.48; N, 7.10.

5*H*-Dibenz[*b*,*f*]azepine-5-carboxaldehyde (**10**).

The reaction was performed with 1.93 g (10 mmoles) of 5*H*-dibenz[*b*,*f*]azepine (**9a**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.07 g (20 mmoles) of tetrafluoroboric acid diethyl etherate (HBF_4.Et_2O)]. The reaction time was 4 days, the reaction temperature 20°. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 5/2). Compound **10** was obtained as colorless crystals in 9% yield (200 mg), mp 137° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3060, 3020, 2860, 1700 (CO), 1625, 1600, 1570, 1495, 1465, 1440, 1400, 1340, 1300, 1225, 1205, 1155, 1120, 1090, 1040, 960, 885, 870, 820, 795, 770, 745, 670, 600 cm^{-1}; ms: m/e (%) 221 ($M^{+\cdot}$, 79), 194 (10), 193 (74), 192 (100), 191 (35), 190 (22), 165 (24); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): δ 6.90 (pseudo-q, ^3J = 11.73 Hz, 2H, C10-H and C11-H), 7.30 (d, ^3J = 7.80 Hz, 1H, aromatic H), 7.38 (mc, 5H, aromatic H), 7.45 (mc, 2H, aromatic H), 8.27 (s, 1H, CHO).

Anal. Calcd. for $C_{15}H_{11}NO$ (221.26): C, 81.43; H, 5.01; N, 6.33. Found: C, 81.46; H, 5.18; N, 6.22.

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

The reaction was performed with 1.95 g (10 mmoles) of 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (**9b**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.07 g (25 mmoles) of tetrafluoroboric acid diethyl etherate]. The reaction time was 2 hours, the reaction temperature −50 to +20°. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 4/1). Compound **11** was obtained as colorless crystals in 6% yield (140 mg), mp 137° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3060, 2920, 2870, 1690 (CO), 1600, 1580, 1490, 1450, 1400, 1340, 1300, 1270, 1260, 1220, 1180, 1150, 1110, 1085, 1050, 1035, 970, 940, 910, 880, 810, 780, 760, 750, 725, 710, 665 cm^{-1}; ms: m/e (%) 223 ($M^{+\cdot}$, 99), 196 (12), 195 (92), 194 (100), 193 (32), 192 (22), 180 (35), 179 (28), 167 (18), 165 (14), 91 (16), 77 (15); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): δ 2.87 (br mc, 2H, C10-H_2 or C11-H_2), 3.39 (br mc, 2H, C11-H_2 or C10-H_2), 7.27 (mc, 8H, aromatic H), 8.35 (s, 1H, CHO).

Anal. Calcd. for $C_{15}H_{13}NO$ (223.27): C, 80.69; H, 5.87; N, 6.27. Found: C, 80.89; H, 5.85; N, 6.05.

10,11-Dihydro-5*H*-dibenz[*b*,*f*]azepine-2-carboxaldehyde (**12**).

The reaction was performed as described above for compound **11** and the product isolation was achieved using column chromatography. Compound **12** was obtained as pale brown crystals in 6% yield (135 mg), mp 120° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3320 (NH), 3210, 3140, 2940, 2810, 2730, 1665 (CO), 1630, 1580, 1535, 1490, 1440, 1400, 1350, 1320, 1295, 1260, 1230, 1215, 1180, 1125, 1050, 990, 940, 900, 850, 835, 820, 760, 720, 690, 650 cm^{-1}; ms: m/e (%) 223 ($M^{+\cdot}$, 100), 222 (33), 208 (12), 194 (25), 193 (13), 192 (11), 165 (6); ^{1}H-nmr (400 MHz, deuteriochloroform): δ 3.09 (pseudor-q, AA'BB' spin system, ^3J = 8.60 Hz, 4H, C10-H_2 and C11-H_2), 6.53 (s, 1H, NH, exchangeable with deuterium oxide), 6.77 (d, ^3J = 8.40 Hz, 1H, C4-H), 6.80 (d, ^3J = 7.70 Hz, 1H, C6-H), 6.86 (dt, ^3J = 7.60 Hz, ^4J = 0.85 Hz, 1H, C7-H or C8-H), 7.07 (d, ^3J = 7.60 Hz, 1H, C9-H), 7.11 (dt, ^3J = 7.60 Hz, ^4J = 1.44 Hz, 1H, C8-H or C7-H), 7.54 (d, ^4J = 1.9 Hz, 1H, C1-H), 7.58 (dd, ^3J = 8.40 Hz, ^4J = 1.9 Hz, 1H, C3-H),

9.76 (s, 1H, CHO).

Anal. Calcd. for $C_{15}H_{13}NO$ (223.27): C, 80.69; H, 5.87; N, 6.27. Found: C, 80.42; H, 5.80; N, 6.10.

4-(*N,N*-Dimethylamino)benzaldehyde (**14**).

The reaction was performed with 1.22 g (10 mmoles) of *N,N*-dimethylaniline (**13a**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.26 g (30 mmoles) of boron trifluoride diethyl etherate]. The reaction time was 1.5 hours, the reaction temperature 0 to 20°. The residue was purified by column chromatography (eluent: dichloromethane). Compound **14** was obtained as light blue crystals in 30% yield (450 mg), mp 74° (dichloromethane/petroleum ether), ref [16], mp 73°; ir (potassium bromide): ν 2880, 2810, 2740, 2700, 1660 (CO), 1600, 1555, 1530, 1485, 1465, 1450, 1435, 1370, 1355, 1315, 1230, 1165, 1120, 1065, 1000, 940, 830, 815, 730, 600 cm^{-1}; ms: m/e (%) 149 ($M^{+\cdot}$, 75), 148 (100), 132 (8), 120 (7), 77 (11); ^{1}H-nmr (90 MHz, deuteriochloroform): δ 3.09 (s, 6H, $N(CH_3)_2$), 6.78 (d, 2H, AA', aromatic H), 7.60 (d, 2H, BB', aromatic H), 9.76 (s, 1H, CHO).

Anal. Calcd. for $C_9H_{11}NO$ (149.19): C, 72.45; H, 7.43; N, 9.39. Found: C, 72.52; H, 7.66; N, 9.37.

Tris[4-(*N,N*-dimethylamino)phenyl]methane (**15**).

The reaction was performed as described above for **14** but with 30 mmoles of **13a**. The reaction time was 2 days, the reaction temperature +20°. The residue was worked-up using centrifugal thin layer chromatography (mobile phase: petroleum ether/ethyl acetate, 7/3). Compound **15** was obtained as blue-colored (oxidation by air) crystals that are sensitive to oxidation in 70% yield (2.1 g), mp 175-176° (methanol). Further physical data were in complete agreement with those reported by us in ref [14].

2,4,6-Trimethoxybenzaldehyde (**16**).

The reaction was performed with 2.52 g (15 mmoles) of 1,3,5-trimethoxybenzene (**13b**) and diethoxycarbenium tetrafluoroborate (**1a**) [prepared from 2.96 g (20 mmoles) of triethyl orthoformate and 4.26 g (30 mmoles) of boron trifluoride diethyl etherate]. The reaction time was 0.5 hours, the reaction temperature 0°. The residue was purified by "flash" chromatography (eluent: chloroform/2-propanol, 14/1). Compound **16** was obtained as pink-colored crystals in 26% yield (0.77 g), mp 119° (chloroform/2-propanol), ref [13], mp 118°; ir (potassium bromide): ν 2960, 2870, 2840, 2790, 1665 (CO), 1600, 1580, 1475, 1460, 1430, 1410, 1335, 1230, 1215, 1200, 1190, 1150, 1130, 1060, 1030, 955, 925, 815, 790, 580 cm^{-1}; ms: m/e (%) 196 ($M^{+\cdot}$, 58), 195 (34), 179 (23), 168 (82), 150 (100), 140 (55), 128 (25), 86 (27), 72 (56); ^{1}H-nmr (90 MHz, dideuteriodichloromethane): δ 3.81 (s, 3H, OCH_3), 3.85 (s, 6H, OCH_3), 6.10 (s, 2H, aromatic H), 10.29 (s, 1H, CHO).

Anal. Calcd. for $C_{10}H_{12}O_4$ (196.17): C, 61.23; H, 6.17. Found: C, 61.24; H, 6.15.

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