240. Formation of the 5-Azoniafulvene Ion and its Benzo-annellated Analogue from N-*Mannich* Bases of Pyrrole and Indole

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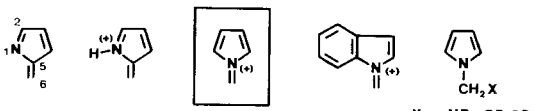
Dedicated to Prof. *Rolf Huisgen* on the occasion of his 65th birthday

(20.IX.85)

1-Dialkylaminomethylpyrroles are shown to behave in many respects like aminals. Acylation by an acid chloride, for instance, occurs normally at the amine-type N-atom rather than at the pyrrole ring. Spontaneous cleavage of the resulting quaternary acylammonium salts affords the 5-azoniafulvene ion (**3**). This higly reactive iminium ion, and its benzo-annellated analogue (**4**) can be trapped by electron rich aromatic compounds such as *N*-methylpyrrole or *N*,*N*-dimethylaniline. More elaborate N-*Mannich* bases are accessible by addition of indoles to enamines.

Derivatives of 1-azafulvene (**1**) and its conjugate acid, the 1-azoniafulvene ion (**2**) have attracted considerable attention in the past due to their prominent role in the chemistry of pyrromethenes and related pigments [1]. In contrast, little is known about the isomeric 5-azoniafulvene ion (**3**). This interesting cation is often invoked in the interpretation of mass spectra of *N*-alkylpyrroles and is believed to undergo ring expansion in the gas phase [2]. However, to the best of our knowledge, it has never been examined in solution. In this communication, we present methods which provide access to **3** as well as the analogues, indole-derived benzo[*a*]-5-azoniafulvene ion (**4**).



1 **2** **3** **4** **5**

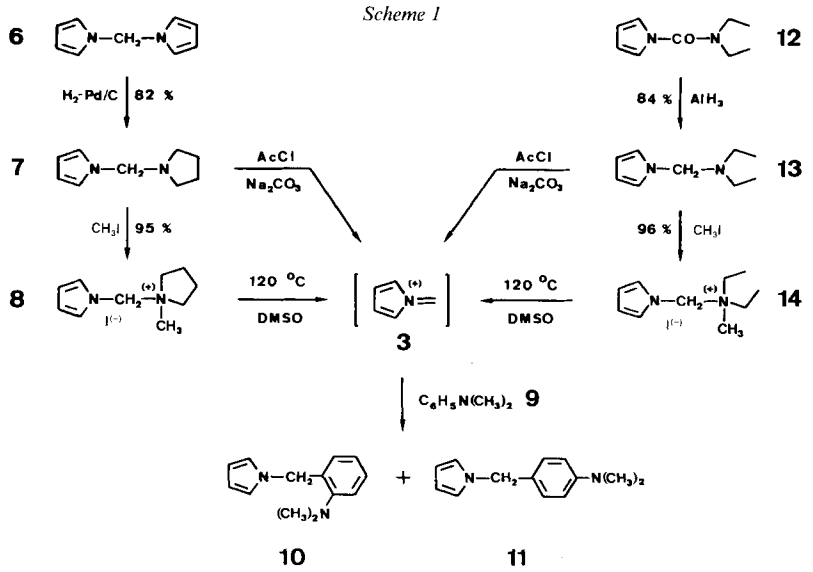
Viewing the ion **3** as a special case of an iminium ion suggests that its preparation could be effected from a N,N-, N,O- or N,S-acetal-type heterogeminal **5** by reaction with suitable electrophiles [3]. Preference is given here to *N*-aminoalkylpyrroles, which are accessible by several methods. The *Mannich* reaction normally results in *C*-aminoalkylation when applied to pyrroles with free C(α) or C(β) ring positions [4]. Indoles, in contrast, can undergo *N*-aminomethylation, when the *Mannich* reaction is conducted under acid-free conditions [5].

Results and Discussion. – The Pd-catalyzed hydrogenation of di(1-pyrrolyl)methane (**6**), readily available from pyrrole and CH_2Cl_2 [6], was found to occur selectively at one ring only, to give 1-(1-pyrrolidinylmethyl)pyrrole (**7**) in 82% yield. Treatment of **7** with

MeI gave the fairly stable quaternary salt **8**. When a DMSO solution of **8** was heated in presence of *N,N*-dimethylaniline (**9**), the *ortho*-and *para*-adducts **10** and **11** were formed in a total yield of 56%. Clearly, heterolysis of the quaternary salt had occurred in the desired fashion with concommitant formation of iminium ion **3**. However, the temperature necessary to achieve this transformation (*ca.* 120°), was quite high.

In an effort to generate ion **3** under milder conditions, we employed the aminal cleavage procedure developed by *Böhme* [7]. Treatment of the N-*Mannich* base **7** with AcCl and Na_2CO_3 at room temperature, again using **9** as trapping agent, afforded the adducts **10** and **11**, but unfortunately in only 25% total yield. Despite the poor yield, this experiment proves that acylation of **7** occurs at the pyrrolidine N-atom and is followed by spontaneous cleavage into the desired ion **3** and *N*-acetylpyrrolidine.

Scheme 1



The preparations of **3** from **6** described above involve the loss of one of the two initial pyrrole moieties as a leaving group (see left side of *Scheme 1*). An alternative and more flexible route to **3** which avoids this drawback starts from *N,N*-diethylpyrrole-1-carboxamide (**12**) [8]. AlH_3 reduction of **12** gave 1-[(diethylamino)methyl]pyrrole (**13**) [9]. Judging from the subsequent trapping experiments with **9**, this N-*Mannich* base also gave the 5-azoniafulvene ion (**3**) upon direct acylation or thermolysis of its methiodide **14**. In addition, ion **3** can also be obtained from the labile *N*-hydroxymethylpyrrole (**15**) [10] under non-acidic conditions. Tosylation of **15** in pyridine in the presence of *N*-methylpyrrole (**16**) gave the substitution products **17** and **18** in a total yield of 44% *(Scheme 2)*.

Scheme 2

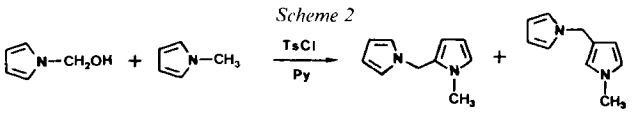


Table. *Comparison of Yields and Product Ratios*

Precursor of **3**	Method	Trapping agent[a]) *N,N*-dimethylaniline (**9**)		*N*-methylpyrrole (**16**)	
		Total yield [%] (**10** + **11**)	Ratio (**10**/**11**)	Total yield [%] (**17** + **18**)	Ratio (**17**/**18**)
7	Acylation[b])	25.2	0.671	48.1	1.23
8	Thermolysis[c])	56.1	0.677	78.4	1.24
13	Acylation[b])	28.0	0.671	44.2	1.28
14	Thermolysis[c])	58.3	0.658	85.2	1.24
15	Tosylation[d])	–	–	44.0	1.23

[a]) The trapping agent is used in all experiments in 10 fold excess.
[b]) AcCl, Na_2CO_3 in Et_2O at 25°.
[c]) DMSO at 120°.
[d]) Pyridine/Et_2O 1:1, at 25°.

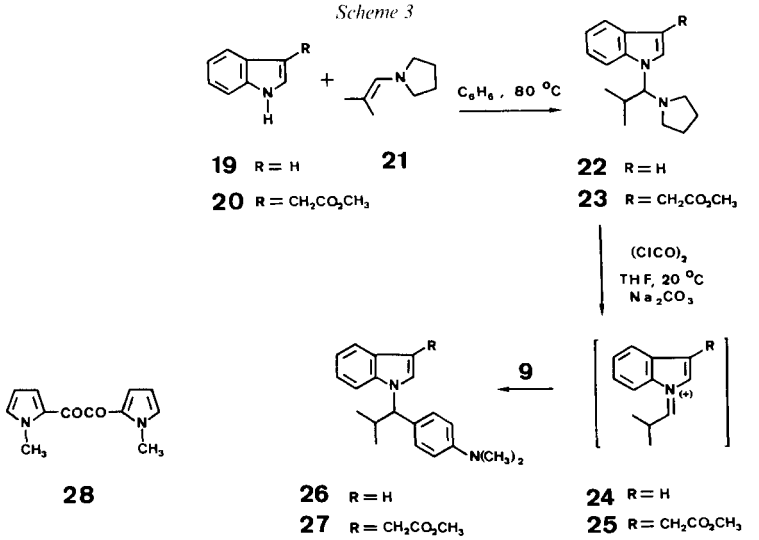
For comparison, the results described above, as well as the results of analogous experiments conducted with **16** as trapping agent, are compiled in the *Table*. The best yields are obtained from thermolysis of the quaternary salts **8** and **14**. The product ratios, *i.e. ortho- vs. para*-substitution in the case of **9** and α- *vs.* β-substitution in the case of **16** are seen to be nearly independent of the method chosen. This is in full agreement with the assumption that a common intermediate, *i.e.* the parent title ion **3**, is formed.

We next considered the possibility of preparing more elaborate 5-azoniafulvene ions, including those derived from indoles. In particular, we wanted to know what happens to an azoniafulvene ion possessing an H-atom prone to β-elimination. Can it still be intercepted by electron-rich, aromatic compounds, or will the formation of the *N*-vinylpyrroles or *N*-vinyl indoles prevail? N-*Mannich* bases other than those of the ordinary methylene type are, in favorable cases, accessible by addition of pyrroles or indoles to enamines [11]. In our hands, aldehyde-derived enamines gave better results than their ketone-derived counterparts. Thus, when the ester **20** was allowed to react with 1-(2-methyl-1-propenyl)pyrrolidine (**21**) [12] in refluxing benzene the aminal-type compound **23** was obtained in 94% yield. Free indole **19** behaves similarly to give **22** in 92% yield. Upon acylation with $(ClCO)_2$[1]) in presence of anhydrous Na_2CO_3 and *N,N*-dimethylaniline (**9**), both **22** and **23** gave only the products resulting from *para*-substitution, **26** and **27**, respectively *(Scheme 3)*. From these experiments, small amounts ($< 6\%$) of *N*-(α-hydroxyalkyl)indoles were isolated after non-acidic hydrolytic workup. Although the precise origin of these by-products is unknown at present, formation of the aniline derivatives, **26** and **27**, clearly reveals that proton elimination from the intermediate benzazoniafulvene ions **24** and **25** is slow in comparison to the substitution reaction[2]).

[1]) AcCl, due to its slow reaction with these sterically hindered N-*Mannich* bases, gave unsatisfactory results when used in combination with Na_2CO_3. Preliminary findings show that this difficulty can be overcome by using lutidine/AcCl 1:3.

[2]) It should be mentioned here that this substitution reaction could have a biological counterpart. *Hesse et al.* [13] have pointed out that the bis-indole alkaloid pleiomutine, isolated from *Pleiocarpa mutica* Benth., is likely to result from reaction of eburnamine with pleiocarpinine. The former has a *N*-(α-hydroxyalkyl)indole subunit and the latter an 'aniline' moiety. Both monoalkaloids are found in the same plant. Formation of pleiomutine is one of the few biochemical reactions in which azionafulvene ions are implicated.

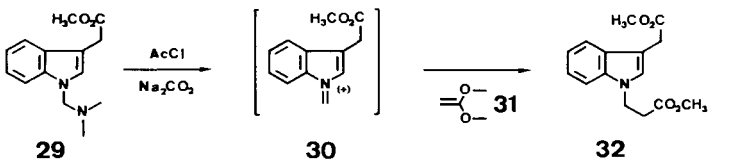
Scheme 3



Attempts to trap ions **24** and **25** with *N*-methylpyrrole (**16**) instead of *N*,*N*-dimethylaniline (**9**) were ineffective as $(ClCO)_2$ reacts faster with **16** than with the N-*Mannich* bases. The diketone **28** [14] was obtained as the principal product (65%) whereas **22** and **23** were recovered unchanged. This undesired reaction could possibly be avoided by the use of an AcCl/lutidine mixture[1].

In principle, 5-azoniafulvene ions should react readily with electron-rich olefins. In practice, however, we seldom isolated a characterizable 1:1 adduct. When the N-*Mannich* bases **7**, **13** or **29** were allowed to react with AcCl in presence of ordinary enol ethers, enamines, or dienamines, we obtained mainly polymeric materials. Reasonably clean reaction occurred only with the extremely electron-rich π-system of ketene acetal **31** [15]. When acylation of **29**, *e.g.*, was carried out in presence of **31** the diester **32** was obtained in 38% yield.

Scheme 4



It should finally be mentioned that we never observed ring expansion of an 5-azoniafulvene ion throughout this study. The latter process is clearly a privilege of the gas phase [2].

The authors wish to express their gratitude to Mr. *R. Etienne* (syntheses), Mr. *A. Pinto* (NMR) and Mrs. *D. Clément* (MS) for valuable technical assistance. Financial support was provided by the *Swiss National Science Foundation* (grant No. 2.033-0.83) and the *Stipendienfonds der Basler Chemischen Industrie*.

Experimental Part

General. See [16].

1-(1-Pyrrolidinylmethyl)pyrrole (**7**). A soln. of 5.11 g (35 mmol) of **6** [6] in 75 ml of AcOEt is placed in a *Parr* reactor and reduced in presence of 4.6 g (4.3 mg-atom) of Pd/C (10%) under H_2 pressure (5 atm., 55°, 6.5 h). Filtration and removal of the solvent leaves the mixture **7/6** 5:1. Compound **7** is purified by fractional crystallization (CCl_4) followed by distillation *i.v.*: yield 4.3 g (82%), colorless liquid, b.p. 97–99°/12 Torr. IR (CCl_4): 3100*w*; 2980–2800*s*; 1490*m*; 1290*s*; 1255*s*; 1085*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.78 (*m*, 4 H); 2.62 (*m*, 4 H); 4.76 (*s*, N–CH_2–N); 6.20, 6.76 (*AA'MM'*, 4 pyrrole H). ^{13}C-NMR ($CDCl_3$, 90.56 MHz): 23.5 (*t*); 50.3 (*t*); 67.3 (*t*, N–CH_2–N); 107.9 (*d*); 121.3 (*d*). MS ($C_9H_{14}N_2$, 150): 150 (9, M^+), 84 (100), 80 (25), 71 (20), 70 (30), 43 (50).

1-Methyl-1-(1-pyrrolylmethyl)pyrrolidinium Iodide (**8**). For 2 d, 4.0 g (27 mmol) of **7** is allowed to react at r.t. with 11.4 g (80 mmol) of MeI in 60 ml of Et_2O. The resulting crystalline precipitate (7.48 g, 95%) is washed with Et_2O and dried *i.v.*: colorless crystals, m.p. 110° (dec.). ^{1}H-NMR ((D_6) DMSO, 100 MHz): 2.12 (*m*, 4 H); 2.90 (*s*, 3 H); 3.44 (*m*, 4 H); 5.54 (*s*, N–CH_2–N); 6.26, 7.10 (*AA'MM'*, 4 pyrrole H). ^{13}C-NMR ((D_6) DMSO, 90.56 MHz): 21.0 (*t*); 46.7 (*q*); 61.3 (*t*); 71.7 (*t*, N–CH_2–N); 110.2 (*d*); 123.3 (*d*).

N,N-Dimethyl-o-(1-pyrrolylmethyl)aniline (**10**) *and N,N-Dimethyl-p-(1-pyrrolylmethyl)aniline* (**11**) *from* **8**. A soln. of **8** (1.46 g, 5 mmol) in 20 ml of DMSO is added to a hot soln. (120°) of **9** (6.1 g, 50 mmol) in 20 ml of DMSO, and kept at 120° for 2.5 h. The mixture is hydrolyzed with sat. Na_2CO_3 (100 ml) extracted with Et_2O (3 × 80 ml) washed with sat. brine and dried ($MgSO_4/Na_2CO_3$). Removal of the solvent and unreacted **9** (up to 78°/12 Torr) leaves an oil which is mainly a mixture **10/11** 0.677:1 (GC analysis on a 2-m column *QF-1* 5% on *Chromosorb G-HP 80–100*; temp. gradient 150–180°; rel. t_R 0.6 (**10**); 1.0 (**11**)). Separation by CC (*silica gel* 40–63 μm, hexane Et_2O 1:4): 225 mg (22.5%) of **10** and 336 mg (33.6%) of **11**.

10: colorless crystals, m.p. 67–68°. IR (CCl_4): 3080*w*; 2950–2800*m*; 1600*m*; 1495*s*; 1455*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 2.70 (*s*, 6 H); 5.20 (*s*, 2 H); 6.20, 6.74 (*AA'MM'*, 4 pyrrole H); 7.05 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 90.56 MHz): 45.1 (*q*); 49.1 (*t*); 108.2 (*d*, pyrrole); 119.6 (*d*); 121.4 (*d*, pyrrole C); 123.8 (*d*); 128.3 (*d*); 133.2 (*s*); 152.1 (*s*). MS ($C_{13}H_{16}N_2$, 200): 200 (45, M^+), 134 (100), 132 (28), 118 (20), 80 (< 3).

11: colorless crystals, m.p. 51–52°. IR (CCl_4): 3100*w*; 2980–2800*m*; 1620*s*; 1530*s*; 1500*m*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 2.96 (*s*, 6 H); 5.00 (*s*, 2 H); 6.20, 6.70 (*AA'MM'*, 4 pyrrole H); 6.71, 7.09 (*AA'MM'*, 4 arom. H). ^{13}C-NMR ($CDCl_3$, 90.56 MHz): 40.6 (*q*); 53.0 (*t*); 108.1 (*d*, pyrrole H); 112.7 (*d*); 120.8 (*d*, pyrrole H); 125.7 (*s*); 128.4 (*d*); 150.3 (*s*). MS ($C_{13}H_{16}N_2$, 200): 200 (38, M^+), 134 (100), 118 (18), 80 (< 5).

The preparation of **10** and **11** from **14** is carried out as described above for (**8**→**10** + **11**). Yields and ratio see the *Table*.

Compounds **10** *and* **11** *from* **7**. At 25°, 0.67 g (8 mmol) of AcCl in 10 ml of Et_2O is added to a mixture of **7** (1.0 g, 6.6 mmol), **9** (8.0 g, 66 mmol), and anh. Na_2CO_3 (1.55 g, 15 mmol) in 20 ml of Et_2O. The mixture is hydrolyzed after 5 h. Workup and isolation is carried out as described above for (**8**→**10** + **11**). Yields and ratio see the *Table*.

The preparation of **10** and **11** from **13** is carried out as described above for (**7**→**10** + **11**). Yields and ratio see the *Table*.

1-[(Diethylamino)methyl]pyrrole (**13**). *Cf.* [8] [9]. Drop by drop, 0.71 ml (13.3 mmol) of 98% H_2SO_4 is added to an ice-cold soln. of $LiAlH_4$ (1.01 g, 26.6 mmol) in 35 ml of THF. The mixture is stirred for 1 h at 0°. A soln. of *N,N-diethylpyrrole-1-carboxamide* (**12**) (3.32 g, 20 mmol) in 10 ml of anh. THF is added at 0°. The mixture then is allowed to reach r.t. (*ca.* 2 h). It is re-cooled to 0°, hydrolyzed (10 ml H_2O followed by 50 ml 1M NaOH) and extracted with Et_2O (3 × 50 ml). Distillation after drying ($MgSO_4/Na_2CO_3$) and removal of the solvent: 2.58 g (84%) of **13**; colorless liquid, b.p. 80–81°/12 Torr. IR (CCl_4): 2965*s*; 1550*m*; 1240*s*. ^{1}H-NMR ($CDCl_3$, 100 MHz): 1.14 (*t*, *J* = 7, 6 H); 2.60 (*q*, *J* = 7, 4 H); 4.78 (*s*, 2 H); 6.20, 6.74 (*AA'MM'*, pyrrole H). ^{13}C-NMR ($CDCl_3$, 90.56 MHz): 12.5 (*q*); 45.0 (*t*); 66.0 (*t*, N–CH_2–N); 107.7 (*d*); 121.1 (*d*). MS ($C_9H_{12}N_2$, 152): 152 (5, M^+); 86 (100); 80 (10); 58 (30).

Diethyl-methyl-(1-pyrrolylmethyl)ammonium Iodide (**14**). Preparation as described for **8**. Colorless crystals, m.p. 130° (dec.). ^{1}H-NMR ((D_6) DMSO, 100 MHz): 1.26 (*t*, 6 H); 2.86 (*s*, 3 H); 3.26 (*m*, 4 H); 5.52 (*s*, N–CH_2–N); 6.26, 7.08 (*AA'MM'*, 4 pyrrole H).

1-Methyl-2-(1-pyrrolylmethyl)pyrrole (**17**) *and 1-methyl-3-(1-pyrrolylmethyl)pyrrole* (**18**) *from* **15**. In small portions, 1.98 g (10.4 mmol) of TsCl is added to a stirred soln. of **15** (1.0 g, 10.4 mmol) [10] and **16** (8.4 g, 104 mmol) in 20 ml Py/Et_2O (1:1). After 3 h, the mixture is hydrolyzed (2N HCl), extracted with Et_2O, washed with sat. Na_2CO_3 and sat. brine. Drying ($MgSO_4$) and removal of the solvent gives an oil which is mainly a mixture **17/18** 1.23:1 (GLC analysis on a 2-m column *QF-1* 5% on *Chromosorb*, 150°). Separation by CC (silica gel, hexane:Et_2O, 4:1): 404 mg (24.3%) of **17** and 328 mg (19.7%) of **18**.

17: colorless crystals, m.p. 59–61° ([17]: 71–72°). IR (CCl_4): 3100*w*; 2940*m*; 1500*s*; 1270*s*; 1090*s*. ^{1}H-NMR ($CDCl_3$, *100 MHz*): *3.40* (*s*, 3 H); 5.02 (*s*, N–CH_2–N), 6.13 (*m*, 4 H); 6.62 (*M*, 3 H). ^{13}C-NMR ($CDCl_3$, 90.56

MHz): 33.5 (*q*); 45.1 (*t*); 106.9 (*d*); 108.3 (*d*); 110.2 (*d*); 120.2 (*d*); 123.5 (*d*); 127.4 (*s*). MS ($C_{10}H_{12}N_2$, 160): 160 (25, M^+), 94 (100), 80 (< 5).

18: colorless liquid ([17]: crystals, m.p. 60–61°). IR (CCl_4): 3100*m*; 2940*s*; 1500*s*; 1270*s*; 1170*s*; 1090*s*. ^{1}H-NMR ($CDCl_3$, 100 MHz): 3.60 (*s*, 3 H); 4.92 (*s*, N–CH_2–N); 6.04 (*m*, 1 H); 6.13 (*m*, 2 H); 6.52 (*m*, 2 H); 6.61 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 90.56 MHz): 35.9 (*q*); 46.4 (*t*); 106.5 (*s*); 107.7 (*d*); 108.0 (*d*); 120.1 (*d*); 120.4 (*d*); 122.1 (*d*). MS ($C_{10}H_{12}N_2$, 160): 160 (30, M^+); 94 (100); 80 (< 5).

1-[1-(1-Pyrrolidinyl)-2-methylpropyl]indole (**22**). *Cf.* [11]. For 5 h, 1.25 g (10.6 mmol) of **19** is allowed to react with 2.64 g (21.2 mmol) of *1-(2-methyl-1-propenyl)pyrrolidine* (**21**) [12] in 30 ml of refluxing benzene. The mixture is concentrated without hydrolysis, and unreacted **21** is removed *i.v.* (*ca.* 40°/12 Torr). The crude product is purified by medium-pressure chromatography [18] (silica gel 40–63 µm, hexane/AcOEt, 2:1): 2.36 g (92%) of **22**, colorless crystals, m.p. 42–43°. IR ($CDCl_3$): 3050*w*; 2980–2800*s*; 1510*m*; 1460*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 0.82 (*d*, *J* = 7, 3 H); 1.08 (*d*, *J* = 7, 3 H); 1.6–1.8 (*m*, 4 H); 2.4–2.6 (*m*, 3 H); 2.6–2.7 (*m*, 2 H); 4.80 (*d*, *J* = 7.6, N–CH–N, 1 H); 6.55, 7.25 (*AB*, *J* = 2.8, 2 indole H); 7.10, 7.20, 7.48, 7.65 (*ABCD*, 4 indole H). MS ($C_{16}H_{22}N_2$,242): 242 (< 2, M^+), 126 (100), 117 (61), 90 (28).

Methyl {1-[1-(1-Pyrrolidinyl)-2-methylpropyl]-3-indolyl}acetate (**23**) is prepared by the procedure described above (→**22**). Yield: 94%, colorless crystals, m.p. 30–32°. IR ($CDCl_3$): 3050*w*; 2980–2800*s*; 1740*s*; 1460*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 0.81 (*d*, *J* = 7, 3 H); 1.07 (*d*, *J* = 7, 3 H); 1.7 (*m*, 4 H); 2.45 (*m*, 1 H, couples with 2 CH_3 and N–CH–N); 2.5–2.7 (*m*, 4 H); 3.72 (*s*, 3 H); 3.80 (*s*, 2 H, CH_2CO); 4.78 (*d*, *J* = 7.8, N–CH–N); 7.25 (indolic *s*, 1 H); 7.15, 7.20, 7.45, 7.65 (*ABCD*, 4 indole H). MS ($C_{19}H_{26}N_2O_2$, 314): 314 (< 3, M^+), 189 (31), 130 (100), 126 (31), 125 (31), 124 (29), 110 (27).

1-[1-p-(Dimethylamino)phenyl-2-methylpropyl]indole (**26**). Under Ar, 180 mg (1.4 mmol) of $(ClCO)_2$ in 3 ml of anh. THF is added to a stirred soln. of **22** (244 mg, 1.0 mmol) and **9** (125 mg, 1.0 mmol) in 3 ml of THF in presence of 300 mg (2.8 mmol) of Na_2CO_3. The mixture is hydrolyzed after 1 h (5 ml H_2O), extracted with Et_2O (3 × 20 ml), washed with sat. brine and dried ($MgSO_4$). The crude product is mainly a mixture (6:1) of **26** and the more polar 2-methyl-1-(1-indolyl)propanol. The two components are separated by medium-pressure chromatography [18] (silica gel 40–63 µm, hexane/AcOEt 3:1): 105 mg (36%) of **26**: colorless crystals, m.p. 88–89°. IR ($CDCl_3$): 2980*w*; 1620*m*; 1525*s*; 1460*m*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 0.91 (*d*, *J* = 7, 3 H); 1.0 (*d*, *J* = 7, 3 H); 2.71 (*m*, 1 H); 2.90 (*s*, 6 H); 4.90 (*d*, *J* = 11, 1 H, couples with *m* at 2.71); 6.55, 7.35 (*AB*, *J* = 3.2, 2 indole H); 6.66, 7.25 (*AA'MM'*, 4 arom. H); 7.06, 7.18, 7.46, 7.60 (*ABCD*, 4 indole H). MS ($C_{20}H_{24}N_2$, 292): 292 (< 2, M^+), 149 (39), 81 (28), 69 (74), 57 (100).

Methyl {1-[1-[4-(Dimethylamino)phenyl]-2-methylpropyl]-3-indolyl}acetate (**27**) is prepared by the procedure described above (→**26**). Colorless crystals, m.p. 35–36°. Yield 39%. IR ($CDCl_3$): 2980–2800*m*; 1740*s*; 1620*s*; 1525*s*; 1460*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 0.90 (*d*, *J* = 7, 3 H); 0.98 (*d*, *J* = 7, 3 H); 2.70 (*m*, 1 H); 2.90 (*s*, 6 H); 3.71 (*s*, 3 H); 3.78 (*s*, 2 H); 4.86 (*d*, *J* = 11, 1 H, couples with *m* at 2.70); 6.65, 7.25 (*AA'MM'*, 4 arom. H); 7.1, 7.2, 7.45, 7.57 (*ABCD*, 4 indole H); 7.35 (*s*, indole H). MS ($C_{23}H_{28}N_2O_2$, 364): 364 (10, M^+), 321 (9), 176 (100), 161 (10).

Methyl 3-[3-(Methoxycarbonyl)methyl-1-indolyl]propionate (**32**). A soln. of **29** (370 mg, 1.5 mmol) [5] and dimethylketene acetal **31** (450 mg, 5.1 mmol) [15] in 5 ml of anh. Et_2O is put under Ar over 250 mg (2.4 mmol) of anh. Na_2CO_3. AcCl (120 mg, 1.5 mmol) in 3 ml of Et_2O is added slowly. After 3 h, the mixture is hydrolyzed (10 ml H_2O), extracted with Et_2O (3 × 20 ml) and dried ($MgSO_4$). CC (silica gel, hexane/AcOEt 1:1) of the concentrated crude product gives 157 mg (38%) of **32** (colorless liquid). IR (CCl_4): 3020*w*; 2980–2800*m*; 1740*s*; 1150*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 2.85 (*t*, *J* = 7, 2 H); 3.68 (*s*, 3 H); 3.71 (*s*, 3 H); 3.77 (*s*, 2 H); 4.43 (*t*, *J* = 7, 2 H); 7.12 (*s*, 1 indole H); 7.15, 7.24, 7.33, 7.61 (*ABCD*, 4 indole H). MS ($C_{15}H_{17}NO_4$, 275): 275 (27, M^+), 230 (16), 216 (100).

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