176. Reaction of the 5-Azoniafulvene Ion with Enamines: A New Approach to Pyrrolizines

by **Daniel Schärer, Vladimir Jindra, Alain O. Bringhen**[1]), and **Ulrich Burger***

Department of Organic Chemistry, University of Geneva, CH–1211 Geneva 4

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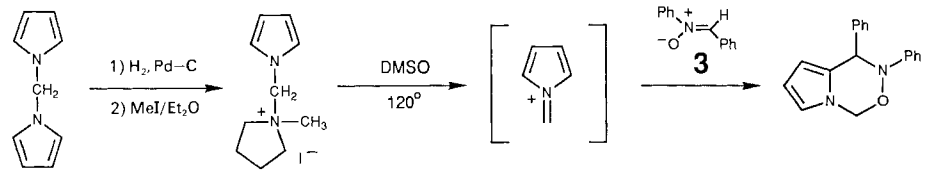
The synthesis of *N,N*-dimethyl-*N*-[(pyrrol-1-yl)methyl]anilinium chloride (**14**) and of the corresponding *p*-toluidinium salt **15** is described. These salts, when dissolved in polar solvents, are shown to be in equilibrium with 1-(chloromethyl)pyrrole (**17**) and thereby potentially with the 5-azoniafulvene ion (**2**). Consequently, they react under very mild conditions (MeCN, 60°) with enamines to give pyrrolizine derivatives in acceptable yield (40–50%). The process is rationalized in terms of an initial *Mannich*-type reaction which is immediately followed by a cyclization.

Introduction. – Some years ago, we demonstrated that a quaternary *N*-alkylammonium salt of pyrrole, *e.g.* **1**, could serve as a precursor of the 5-azoniafulvene ion **2** [1] [2] (*Scheme 1*). This iminium-type ion combines interesting structural and functional features which we intended to exploit. Attack by nucleophiles has been shown to occur at the exocyclic C-atom of **2**, both under orbital and charge control, with concomitant restoration of the pyrrolic π-system. This, in turn, provides a handle for further transformations including cyclizations. By heating **1** in the presence of a nitrone, for instance, novel pyrrolo-annellated structures have been obtained which result formally from [6π + 4π] cycloaddition of the ion **2** to the 1,3-dipolar reagent. This is shown in *Scheme 1* for the case of the *C,N*-diphenylnitrone **3** and the ensuing formation of the 1,4-dihydro-1,2-diphenyl-2*H*-pyrrolo[2,1-*d*][1,2,5]oxadiazine **4** [2].

Scheme 1

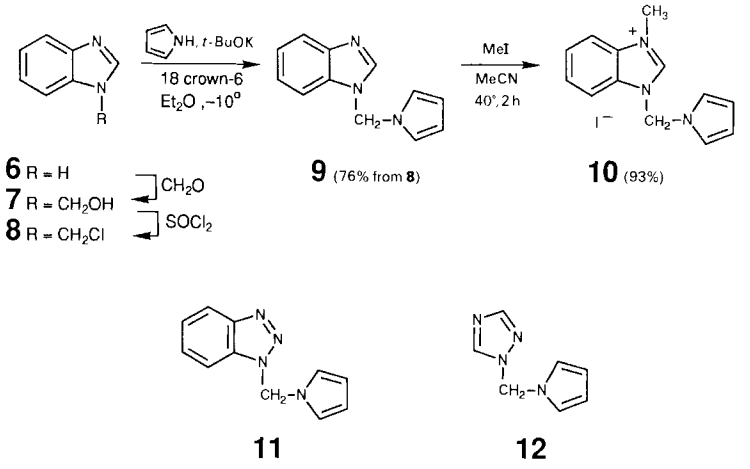


The quaternary precursor **1** used in our earlier work was obtained by selective reduction of 1-[(pyrrol-1-yl)methyl]pyrrole (**5**) followed by methylation. However, the conditions for the thermal cleavage into ion **2** (DMSO, 120°) are far to harsh for the extension of our studies to substrates more sensitive than nitrones. As we were particularly interested in studying the reaction of enamines with azoniafulvene ions, we had to generate the iminium ion **2** under much milder conditions. The present communication reports our findings.

[1]) Present address: *Givaudan SA*, CH–1214 Vernier.

Results and Discussion. – Initially we attempted to exploit the use of heteroaromatic compounds as leaving groups. Starting from benzimidazole **6**, we obtained in a straightforward procedure the 1-(chloromethyl)-1*H*-benzimidazole (**8**) [3]. The pyrrole moiety was introduced in a substitution step following the procedure of *Katritzky et al.* [4], to give *N*-[(pyrrol-1-yl)methyl]-1*H*-benzimidazole (**9**). This step enables in principle the flexible introduction of pyrrole derivatives. The aminal-type compound **9**, upon methylation with MeI in MeCN, gave the desired benzimidazolium salt **10** (*Scheme 2*). We have

Scheme 2

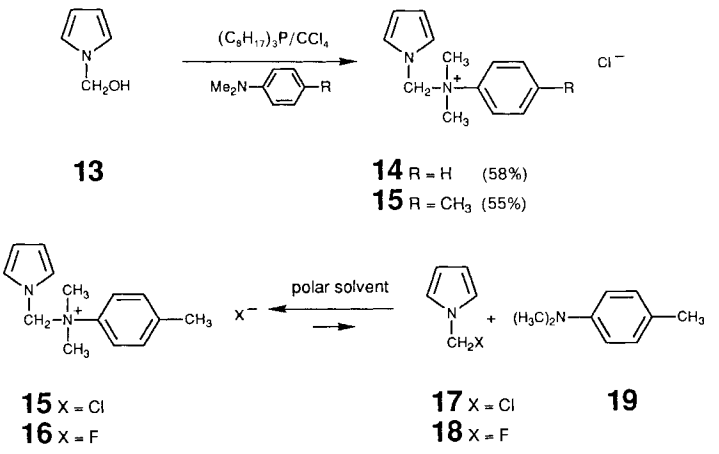


also synthesized the corresponding aminals **11** and **12** derived from benzotriazole and 1,2,4-triazole. However, difficulties were encountered on attempting methylation of these derivatives. Compound **11** did not react as expected with MeI under the above conditions; successful methylation required the use of *Meerwein*'s salt. The product resulting from methylation of compound **12** with MeI polymerized, when isolation was attempted.

The reactivity of the salt **10** towards the nitrone **3** was found, much to our disappointment, not to present an advantage over the quaternary salt **1** used in our earlier studies. Heating a mixture of compounds **10** and **3** in DMSO at 120° yielded the pyrrolo-oxadiazine **4** in modest 28% yield. Equally sluggish was the reaction of salt **10** with the nitrone in MeCN at 80° (sealed solution). It gave **4** in < 10% yield and was accompanied by considerable decomposition products.

For these reasons, an alternative route was investigated, and as it turned out, it was more successful. In this route, aromatic amines are used as leaving groups in the crucial azoniafulvene-ion formation step. The synthesis of the required quaternary anilinium salts **14** and **15** outlined in *Scheme 3*, resembles the formation of the aminal **9** from benzimidazole **8**. However, 1-(chloromethyl)pyrrole is not a stable compound under normal bench conditions. Therefore, we had to intercept it *in situ*. To this end, we reacted a solution of the readily available (pyrrol-1-yl)methanol **13** [5] and the appropriate aniline in CCl_4/Et_2O with trioctylphosphine (*cf.* [6]). This procedure yields the quaternary anilinium salts as greyish crystalline powders, that can be stored for several weeks in a refrigerator without decomposing.

Scheme 3



The ^{1}H-NMR analysis of the toluidinium salt **15** in CD_3CN revealed that this salt is in equilibrium at room temperature with free *N,N*-dimethyl-*p*-toluidine (**19**) and, what we believe to be, 1-(chloromethyl)pyrrole (**17**). The equilibrium constant at 20° in MeCN is $K_{20} \approx 2.7 \cdot 10^{-2}$ mol/l. Compound **17** shows, besides the aromatic *AA'MM'* splitting pattern, a *singlet* for the CH_2Cl group at 5.83 ppm. This value compares well with known *N*-(chloromethyl) compounds [7]. More importantly, exchange of Cl with F by treatment of the salt **15** with AgF (*cf.* [8]), produces a *doublet* for the ^{1}H resonance of the corresponding CH_2F group of 1-(fluoromethyl)pyrrole (**18**) at 5.85 ppm with $^2J(H,F) = 54.3$ Hz. By observing the sample in two different magnetic fields (4.7 Tesla and 9.4 Tesla), we ascertained that this was indeed a (heteronuclear) coupling constant. The $^2J(H,F)$ value is in good agreement with corresponding coupling constants of *N,F*-heterogeminal compounds whose reversible dissociation is slow on the NMR time scale [8].

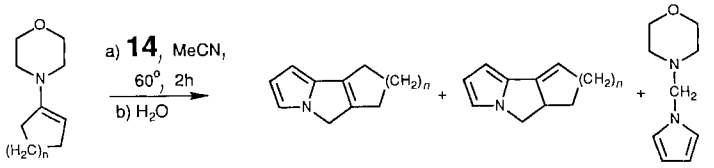
These findings clearly show that the relevant C–N bond of the quaternary salts **14** and **15** is very weak, and indeed both salts react at 60° in MeCN readily with the nitrone **3** to give the pyrrolo-oxadiazine **4** in 92 and 94% yield, respectively.

With these precursors at hand, we were able to examine their behavior towards enamines (*Scheme 4*). When the simple enamines **20a–c**, derived from morpholine and cyclic ketones [9] are warmed to 60° in an MeCN soln. with the salt **14** present, we obtained after hydrolytic workup a tautomeric mixture of the pyrrolizines **21a–c** and **22a–c** accompanied by 1-(morpholinomethyl)pyrrole **23**. The ratio between the tautomeric pyrrolizines of type **21** *vs.* **22** varies considerably with ring size.

From these observations, it can be clearly seen, that enamines do indeed react with the azoniafulvene ion (or with its chloride) in a *Mannich*-type reaction followed by cyclization. Unfortunately, under our reaction conditions, the primary cyclization products lose morpholine, to give the undesired aminal **23** with the concomitant consumption of a second equiv. of azoniafulvene ion.

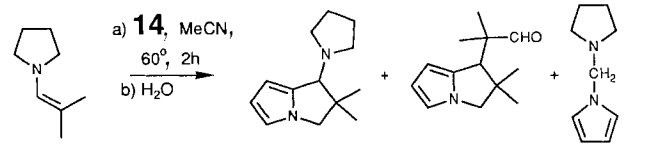
However, when we examined the branched enamine **24**, the primary cyclization product **25** was observed and isolated after hydrolysis in 31% yield. In this case, elimination to give a pyrrolizine is blocked by the geminal dimethyl grouping. Formation of the

Scheme 4



20a–c **21a–c** **22a–c** **23**

		Yields (mol-%)		
		21	**22**	**23**
a	$n = 2$	20	20	50
b	$n = 3$	14	31	15
c	$n = 4$	34	8.4	48



24 **25** (31%) **26** (20%) **27** (16%)

adduct **26**, however, indicates that compound **25** being an α-(aminoalkyl)pyrrole, can still eliminate pyrrolidine *via* a 1-azoniafulvene-type ion, and then react with a second equiv. of **24**.

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Experimental Part

General. GLC: *Carlo-Erba Fractovap-2150*; glass columns. MPLC: *Büchi/B-680* chromatograph. IR spectra [cm^{-1}]: *Polaris-Mattson FT-IR* spectrometer. NMR spectra: *Bruker AMX-400* (9.4 Tesla) or *Varian XL-200* (4.7 Tesla); chemical shifts in δ[ppm] relative to internal TMS; apparent scalar coupling constants *J* in Hz; multiplicities for ^{13}C according to DEPT editing or attached proton test (APT). MS: (*m/z*(% rel.)): *Finnigan-4024* with *INCOS* data system; electron impact, 70 eV.

*1-[(Pyrrol-1-yl)methyl]-1*H*-benzimidazole* (**9**). A soln. of freshly distilled pyrrole (386 mg, 5.76 mmol) in dry Et_2O (10 ml) was slowly added under N_2 and with stirring to a soln. of *t*-BuOK (647 mg, 5.77 mmol) and 18-crown-6-ether (153 mg, 0.58 mmol) in Et_2O (20 ml). After 10 min, the resulting colorless suspension was cooled to 10° and a suspension of *1-(chloromethyl)-1*H*-benzimidazole* (**8**; 957 mg, 5.74 mmol) [3a] in dry Et_2O (60 ml) was added over a period of 40 min. The resulting mixture was allowed to reach r.t., and was stirred for a further 15 h. KCl was filtered off, and the remaining org. soln. reduced *i.v.* MPLC (silica gel, 40–63 μm, AcOEt) of the resulting yellow oil gave **9** (860 mg, 76%) as colorless crystals. M.p. 100–103°. IR (CCl_4): 3020*w*, 2980*w*, 1520*m*, 1505*m*, 1300*s*, 1260*m*, 1100*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 6.13 (*s*, 2 H); 6.20, 6.82 (pyrrolic *AA'MM'*); 7.31 (*m*, 2 H); 7.41 (*m*, 1 H); 7.80 (*m*, 1 H); 7.98 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 57.5 (CH_2); 109.4 (CH); 110.4 (CH); 120.4 (CH); 120.7 (CH); 122.9 (CH); 123.8 (CH); 132.9 (C); 142.1 (CH); 143.8 (C). MS: 197 (62, $C_{12}H_{11}N_3$), 131 (100), 104 (8), 80 (55), 67 (10), 53 (15).

*3-Methyl-1-[(pyrrol-1-yl)methyl]-1*H*-benzimidazolium Iodide* (**10**). A soln. of **9** (100 mg, 0.51 mmol) in MeCN (5 ml) was allowed to react at 40° under N_2 for 20 h with MeI (430 mg, 3.03 mmol). Removal of the solvent and excess MeI *i.v.* left crude **10** which was recrystallized from EtOH to give colorless prisms (161 mg, 93%). M.p. 129–131° (dec.). IR (CH_2Cl_2): 3040*w*, 2960*w*, 1580*m*, 1305*m*, 1100*m*. ^{1}H-NMR (CD_3CN, 400 MHz): 4.05 (*s*, 3 H); 6.17, 7.14 (pyrrolic *AA'MM'*); 6.62 (*s*, 2 H); 7.67 (*m*, 2 H); 7.83 (*m*, 1 H); 7.94 (*m*, 1 H); 9.60 (*s*, 1 H). ^{13}C-NMR

(CD_3CN, 100 MHz): 34.7 (CH_3); 59.9 (CH_2); 111.4 (CH); 114.3 (CH); 114.6 (CH); 122.6 (CH); 128.2 (CH); 128.4 (CH); 131.2 (C); 133.3 (C); 142.6 (CH).

*1-[(Pyrrol-1-yl)methyl]-1*H*-benzotriazole* (**11**). A soln. of freshly distilled pyrrole (1.13 g, 16.8 mmol) in dry THF (10 ml) was added dropwise under N_2 and with stirring to a soln. of *t*-BuOK (2.0 g, 17.8 mmol) and 18-crown-6-ether (0.51 g, 1.9 mmol) in dry THF (20 ml). After 15 min a soln. of **8** (3.0 g, 17.9 mmol) [10] in dry THF (20 ml) was slowly added to the resulting mixture. Stirring at r.t. was continued overnight. Filtration of KCl, followed by removal of the solvent *i.v.* and recrystallization of the crude product from MeOH gave **11** (2.6 g, 81%) as colorless crystals. M.p. 140–143°. ^{1}H-NMR ($CDCl_3$, 200 MHz); 6.19, 6.91 (pyrrolic *AA'MM'*); 6.59 (*s*, 2 H); 7.30–7.50 (*m*, 3 H); 8.04 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 60.1 (CH_2); 109.1 (CH); 110.5 (CH); 120.3 (CH); 124.4 (CH); 128.2 (CH); 132.1 (C); 146.2 (C). MS: 198 (20, M^+), 132 (43), 104 (20), 80 (30), 77 (100), 53 (28), 51 (24). Anal. calc. for $C_{11}H_{10}N_4$: C 66.65, H 5.09, N 28.26; found: C 66.62, H 4.98, N 28.06.

*1-[(Pyrrol-1-yl)methyl]-1*H*-[1,2,4]triazole* (**12**). Compound **12** was prepared by an analogous route to the procedure given above for **11** but using 1-(chloromethyl)-1*H*-[1,2,4]triazole [3b] as the starting material. Yield 74%. Colorless leaflets. M.p. 81–83°. IR (CCl_4): 3000*w*, 1520*m*, 1510*s*, 1300*s*, 1290*m*, 1210*m*, 1150*s*, 1100*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 6.12 (*s*, 2 H); 6.28, 6.88 (pyrrolic *AA'MM'*); 7.98 (*s*, 1 H); 8.09 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 61.2 (CH_2); 110.8 (CH); 120.8 (CH); 142.4 (CH); 152.5 (CH). MS: 148 (72, $C_7H_8N_4$), 120 (66), 93 (15), 82 (26), 80 (88), 67 (34), 55 (100), 53 (44).

N,N-*Dimethyl*-N-*[(pyrrol-1-yl)methyl]anilinium Chloride* (**14**). A soln. of trioctylphosphine (5.8 g, 15.6 mmol) in dry Et_2O (10 ml) was added dropwise under N_2 to a cooled (−10°) soln. of *(pyrrol-1-yl)methanol* (**13**; 1.4 g, 14.4 mmol) [5], *N,N*-dimethylaniline (7.27 g, 60 mmol), and CCl_4 (10 ml, 103 mmol) in dry Et_2O (25 ml). This resulted in the precipitation of the desired salt. The mixture was allowed to warm slowly to 10°, whereupon the precipitate was filtered, washed with cold Et_2O, and dried unter N_2 to give **14** as a greyish powder (1.96 g, 58%). IR (CD_3CN): 2980*s*, 2850*s*, 1610*m*, 1510*m*, 1500*m*, 1280*m*, 1120*s*. ^{1}H-NMR (CD_3CN, 400 MHz, shows an equilibrium of **14**, **17**, and *N,N*-dimethylaniline) assignment to **14**: 3.56 (*s*, Me_2N); 5.93 (br. *s*, NCH_2N); 6.12, 6.61 (pyrrolic *AA'MM'*); 7.60 (*m*, 3 H); 7.72 (*m*, 2 H). Assignment to **17**: 5.83 (*s*, 2 H); 6.15, 6.86 (pyrrolic *AA'MM'*). Assignment to *N,N*-dimethylaniline: 2.90 (*s*, 6 H); 6.65–6.85 (*m*, 3 H, exchange-broadened); 7.15–7.25 (*t*, exchange-broadened, 2 H). Anal. calc. for $C_{13}H_{17}ClN_2$ (**14**): C 65,95, H 7.24, Cl 14.97, N 11.84; found: C 65.76, H 7.34, Cl 14.52, N 11.53.

N,N-*Dimethyl*-N-*[(pyrrol-1-yl)methyl]*-p-*toluidinium Chloride* (**15**). The salt **15** was prepared by analogy with the procedure given above for **14** but using *N,N*-dimethyl-*p*-toluidine as the intercepting base: greyish powder in 55% yield. IR (CD_3CN): 2995*s*, 2900*s*, 1620*m*, 1525*m*, 1500*m*, 1280*m*, 1120*s*. ^{1}H-NMR (CD_3CN, 200 MHz, shows an equilibrium of **15**, **17**, and *N,N*-dimethyl-*p*-toluidine) assignment to **15**: 2.40 (*s*, 3 H); 3.57 (*s*, Me_2N); 6.02 (br. *s*, NCH_2N); 6.12, 6.65 (pyrrolic *AA'MM'*); 7.4 (br. *d*, *J* = 8, 2 H); 7.62 (br. *d*, *J* = 8, 2 H). Assignment to **17**: 5.83 (*s*, 2 H); 6.17, 6.88 (pyrrolic *AA'MM'*). Assignment to *N,N*-dimethyl-*p*-toluidine: 2.20 (*s*, 3 H); 2.85 (*s*, 6 H); 6.6 (exchange-broadened *d*, 2 H); 7.02 (exchange-broadened *d*, 2 H). For the equilibrium constant see text. Anal. calc. for $C_{14}H_{19}ClN_2$ (**15**): C 67.05, H 7.64, Cl 14.14, N 11.17; found: C 66.87, H 7.79, Cl 13.91, N 11.02.

*6,7,8,9-Tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindole* (**21a**), *5a,6,7,8-Tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindole* (**22a**), *and 1-(Morpholinomethyl)pyrrole* (**23**). A soln. of **14** (239 mg, 1.01 mmol) in anh. MeCN (10 ml) was added slowly under N_2 and with stirring to a soln. of *4-(cyclohex-1-enyl)morpholine* (**20a**; 253 mg, 1.52 mmol) [9] in MeCN (5 ml) kept at 60°. Stirring at 60° was continued for 100 min. The mixture was hydrolyzed by adding sat. Na_2CO_3 soln. (50 ml), and extracted three times with Et_2O. The combined Et_2O fractions were washed with sat. aq. Na_2CO_3 soln. and brine, and then dried (Na_2CO_3). Et_2O was removed *i.v.*, and the *N,N*-dimethylaniline was distilled off under low pressure (10^{-3} Torr). Final separation of the remaining oil by MPLC (silica gel, 220–440 mesh, hexane/Et_2O 9:1) gave **21a** and **22a** which were eluted simultaneously (total yield 64 mg, *i.e.* 20% each), and **23** (83 mg, 50%).

The spectroscopic data for **21a**/**22a** were obtained with the 1:1 mixture and are not assigned to one or the other isomer. The ^{1}H-NMR spectra, however, have been assigned individually by 2D techniques (COSY-45 [11] [12]). A fortuitous rearrangement of **22a** to **21a** in $CDCl_3$ (not purified over alumina) provided support to our assignment.

21a/**22a** (colorless oil): IR ($CDCl_3$): 2930*m*, 2855*w*, 1710*m*, 1435*w*, 1255*w*. ^{1}H-NMR ($CDCl_3$, 400 MHz) assignment to **21a**: 1.7–1.8 (*m*, 4 H); 2.2–2.36 (*m*, 4 H); 4.26 (*s*, 2 H); 5.76, 6.17, 6.85 (pyrrolic *ABC*). Assignment to **22a**: 1.38–1.7 (*m*, 2 H); 1.9–2 (*m*, 1 H); 2.06–2.14 (*m*, 1 H); 2.2–2.4 (*m*, 2 H); 3.2–3.3 (*m*, 1 H); 3.57 (*dd*, *J* = 9.5, 9, 1 H); 4.2 (*dd*, *J* = 9.5, 8.5, 1 H); 5.8 (*m*, 1 H); 6.10, 6.29, 6.68 (pyrrolic *ABC*). MS for **21a**/**22a**: 159 (98, M^+), 158 (48), 131 (100), 130 (48), 105 (42), 84 (41). HR-MS: calc. for $C_{11}H_{13}N$: 159.1048; found: C 159.1055.

Data of **23**: (colorless oil): IR ($CDCl_3$): 2975*w*, 2940*w*, 1455*w*, 1265*m*, 1115*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.48 (*t*, *J* = 4.5, 4 H); 3.69 (*t*, *J* = 4.5, 4 H); 4.58 (*s*, 2 H); 6.16, 6.69 (pyrrolic *AA'BB'*). ^{13}C-NMR ($CDCl_3$, 50 MHz): 50.37 (CH_2); 66.77 (CH_2); 71.25 (CH_2); 108.3 (CH); 121.4 (CH). MS: 166 (5, $C_9H_{14}N_2O$), 100 (100), 80 (34), 56 (74), 53 (27).

7,8,9,10-Tetrahydro-5H,6H-cyclohepta[a]pyrrolizine (**21b**) *and 5,5a,6,7,8,9-Hexahydrocyclohepta[a]-pyrrolizine* (**22b**). A tautomeric mixture **21b**/**22b** (ratio 0.45:1) was prepared and isolated (colorless oil, total yield 44%) by analogy with the procedure given above for **21a**/**22a** but using *4-(cyclohept-1-enyl)morpholine* (**20b**) [13] as the starting enamine. Spectral data for **21b**/**22b** were obtained with the mixture. ^{1}H-NMR assignment is supported by COSY-45 [11] [12]. Slow rearrangement of **21b** to **22b** in $CDCl_3$ (not purified over alumina) suggests that **22b** is the thermodynamically more stable isomer, and provided additional support to the ^{1}H-NMR assignment. ^{1}H-NMR ($CDCl_3$, 400 MHz) assignment to **21b**: 1.2–2.5 (10 H mostly hidden by major isomer); 4.30 (*s*, 2 H–C(5)); 5.77, 6.09, 6.81 (pyrrolic *ABC*). Assignment to **22b**: 1.1–1.9 (*m*, 5 H); 2.06 (*m*, 1 H); 2.20 (*m*, 1 H); 2.33 (*m*, 1 H); 3.48 (*m*, 1 H); 3.63 (*dd*, J = 10.5, 5.5, 1 H); 4.30 (*dd*, J = 10.5, 8.9, 1 H); 6.01, 6,26, 6.58 (pyrrolic *ABC*); 6.06 (*m*, 1 H).

6,7,8,9,10,11-Hexahydro-5H-cycloocta[a]pyrrolizine (**21c**) *and 5a,6,7,8,9,10-Hexahydro-5H-cycloocta[a]-pyrrolizine* **22c**. A tautomeric mixture **21c**/**22c** (ratio 4:1) was prepared and isolated (colorless oil, total yield 42.4%) by analogy with the procedure given above for **21a**/**22a** but using *4-(cyclooct-1-enyl)morpholine* (**20c**) [13] as the starting enamine. Spectral data for **21c**/**22c** were obtained with the mixture. ^{1}H-NMR ($CDCl_3$, 200 MHz) assignment to **21c**: 1.3–1.9 (*m*, 8 H); 2.42 (*m*, 2 H); 2.53 (*m*, 2 H); 4.30 (*s*, 2 H–C(5)); 5.76, 6.21, 6.86 (pyrrolic *ABC*). Assignment to **22c**: (high-field region of 10 H mostly hidden by the major isomer); 3.42 (*m*, 1 H); 3.62 (*dd*, J = 10.5, 3.0, 1 H); 4.18 (*dd*, J = 10.5, 6.5, 1 H); 5.75–5.83 (*m*, 1 H, partially hidden); 6.06, 6.27, 6.60 (pyrrolic *ABC*). MS: 187 (98, $C_{13}H_{17}N$), 159 (66), 144 (100), 132 (63), 131 (60), 130 (68), 119 (63), 118 (68), 104 (34), 91 (26), 80 (42), 77 (48), 65 (31), 51 (44).

2,3-Dihydro-2,2-dimethyl-1-(2,3,4,5-tetrahydropyrrol-1-yl)-1H-pyrrolizine (**25**) *and 2-methyl-2-(2,3-dihydro-2,2-dimethyl-1H-pyrrolizin-1-yl)propionaldehyde* (**26**). *2,3,4,5-Tetrahydro-1-(2-methylprop-1-enyl)pyrrole* **24** [9] was allowed to react with **14** in a procedure similar to that described above for the preparation of **21a**/**22a**. The analogous workup left a crude oil from which *N,N*-dimethylaniline was removed *i.v.* (10^{-3} Torr). Flash chromatography (silica gel 220–440 mesh, hexane/Et_2O 9:1) gave **25** + **26** in 31% and 20% yield, resp., and **27** (16%). The latter was shown by NMR to be identical with authentic material [1a]. Anal. samples of **25** were obtained by CC on basic alumina (hexane/Et_2O 9:1). Triple CC of **25**/**26** on silica gel (hexane/Et_2O 9:1) gave a very small anal. sample of **26**.

Data of **25**: (colorless oil): IR (CCl_4): 3090*w*, 2960*s*, 2920*s*, 2875*s*, 1600*m*, 1500*m*, 1484*m*, 1460*s*, 1365*m*, 1290*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.16 (*s*, 3 H); 1.24 (*s*, 3 H); 1.68 (*m*, 4 H); 2,32 (*m*, 2 H); 2.62 (*m*, 2 H); 3.65 (*s*, 1 H); 3.56, 3.73 (*AB*, J = 10); 5.93, 6.19, 6.57 (pyrrolic *ABC*). ^{13}C-NMR ($CDCl_3$, 50 MHz): 21.85 (CH_3); 23.21 (CH_2); 29.21 (CH_3); 46.89 (C); 50.60 (CH_2); 58.41 (CH_2); 68.52 (CH); 102.7 (CH); 110.7 (CH); 114.0 (CH); 135.3 (C). MS: 204 (60), $C_{13}H_{20}N_2$), 148 (43), 134 (56), 119 (100), 104 (14), 93 (60), 80 (3), 55 (22).

Data of **26**: (colorless oil): ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.98 (*s*, 3 H); 1.11 (*s*, 3 H); 1.18 (*s*, 3 H); 1.19 (*s*, 3 H); 2.91 (*s*, 1 H); 3.51, 3.72 (*AB*, J = 10); 5.88, 6.21, 6.60 (pyrrolic *ABC*); 9.73 (*s*, CHO).

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