228. Nucleophilic Addition to C,C-Double Bonds. VI[1]). Intramolecular Addition of Primary Amines to C,C-Double Bonds Induced by Steric Compression[2])

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(30.VII.82)

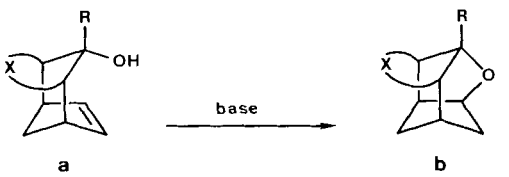
Summary

The tricyclic olefinic primary amine **1** readily cyclizes to the tetracyclic secondary amine **2** at approximately 200° in protic as well as aprotic solvents although the C,C-double bond is not activated by electron-attracting groups. This unusual intramolecular addition is the consequence of the close proximity of the nucleophile and the double bond.

For the synthesis of the sterically highly hindered amine **1**, the tricyclic oxime **4** was reduced with $TiCl_3$ to the remarkably stable imine **5** and the latter treated with AlH_3. On the other hand, reaction of **4** with AlH_3 yielded the pentacyclic aziridine **6**.

In the course of our investigations on nucleophilic additions to isolated C,C-double bonds, we reported among others about several olefinic alcohols of the general type **a** that undergo base-catalyzed intramolecular ether formation to **b** [2] *(Scheme 1)*. This uncommon reactivity is mainly due to high steric compression. Very recently we turned our attention as well to the behaviour of structurally related compounds containing other nucleophiles than alkoxide anion. In the present com-

Scheme 1



a **b**

R = H or alkyl

X = CH_2-CH_2, $CH_2-CH_2-CH_2$

[1]) For part V, see [1].

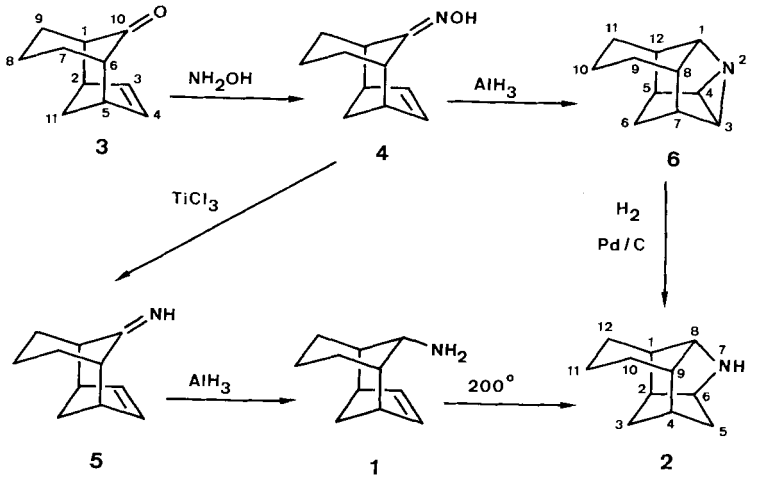
[2]) These results were first presented at the ESOC II Symposium on Organic Chemistry in Stresa (Italy), June 1–5, 1981, and at the meeting of the Swiss Chemical Society (Schweizerische Chemische Gesellschaft) on October 16, 1981 in Berne.

0018-019X/82/7/2326-07$01.00/0

munication we describe some of our preliminary results: the synthesis of the highly strained tricyclic amine **1** and its cyclization to the tetracyclic amine **2**.

Treatment of the readily available unsaturated ketone **3** [3] with excess of hydroxylamine hydrochloride in methanol in the presence of sodium hydroxide gave the oxime **4** (72%) *(Scheme 2)*. Maximum yields were achieved after approximately one day at reflux temperature, whereas longer reaction times favoured the formation of the saturated analogue **8** (*Scheme 3* in Footnote 7)[3]). Reduction of the oxime **4** with $LiAlH_4$ in dioxane at 80° or in tetrahydrofurane (THF) under reflux for 8 h led not to the desired amine **1** but only in a very poor yield to the imine **5**. The latter, however, remained unchanged on further treatment with $LiAlH_4$ in THF even under reflux for 20 h.

Scheme 2



Reaction of the oxime **4** with an excess of 0.3 M AlH_3 in THF [5], very remarkably, gave the aziridine **6** as the sole product (60%). This most striking result could be interpreted by an intramolecular addition of an intermediate alkyl nitrene to the neighbouring C,C-double bond. Due to high steric compression, the addition step has to be faster than a rearrangement to the corresponding imine **5**[4]). Finally, hydrogenolysis of **6** in the presence of 10% palladium on charcoal in ethanol [7] led to **2** (70%), the compound envisaged starting from the amine **1** (see below).

To learn if the formation of the aziridine **6** proceeds *via* **5** as an intermediate, we focused our attention to a specific preparation of the latter. Best results were obtained applying $TiCl_3$ [8]. Addition of aqueous $TiCl_3$-solution[5]) to a solution of the oxime **4** in THF/H_2O 3:1, buffered with sodium acetate, yielded quantitatively

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[3]) It has to be noted that reductive amination of **3** by a modified *Borch* procedure [4] failed to introduce the required amine functionality.

[4]) Additions of alkyl nitrenes to C,C-double bonds are practically unknown, see [6].

[5]) 15% $TiCl_3$ in 10% aq. HCl-solution.

5, a remarkably stable imine, as a consequence of the sterically highly hindered C,N-double bond[6]). Subsequent reduction with AlH_3 in THF afforded no trace of the aziridine **6** but the desired olefinic amine **1** in 55% yield besides 21% of the saturated analogue **10**[7]). These results exclude the imine **5** being an intermediate in the reaction **4** → **6** as well as a nitrene being involved in the reduction **5** → **1**[8]).

With **1** in hand we were able to study its reactivity with regard to the question of an intramolecular nucleophilic addition of the amine N-atom to the isolated C,C-double bond, and to compare the results with those of our previous work [2] on the corresponding olefinic alcohols **a** (R=H, X=CH_2–CH_2–CH_2)[9]). Initial attemps to effect the ring closure **1** → **2** with a strong base (*e.g. t*-BuOK in *t*-BuOH, 120°; BuLi in Et_2O, 0°, or $NaNH_2$ in NH_3, −78°) were unsuccessful. In a high-boiling polar solvent like ethylene glycol containing 2% of potassium hydroxide (200°, sealed tube) cyclization to the expected amine **2** took place indeed, however, **2** underwent subsequent reactions with the solvent. Isolation of **2** in practically quantitative yield was achieved by heating (200°, sealed tube) an oxygen-free solution of **1** in a protic as well as in an aprotic solvent (*t*-BuOH and toluene, respectively). The half-life of the reactant was approximately 24 h. When the cyclization was carried out in toluene containing traces of D_2O, one D-atom was incorporated regioselectively at C(5) and stereoselectively from the *exo*-side by way of antiperiplanar addition to the C,C-double bond (→ **11**)[10]). The intermolecular protonation of the double bond is obviously favoured over an intramolecular one, which would have to proceed from the *endo*-side.

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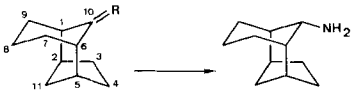
[6]) Only very few cases of such stable imines are known, see [8].

[7]) The amine **10** as sole product was easily prepared starting from the saturated ketone **7** (obtained from **3** by hydrogenation) *via* the corresponding oxime **8** (91%). Reduction of **8** with buffered $TiCl_3$-solution as well as with $LiAlH_4$ in THF produced quantitatively the imine **9**. The saturated amine **10** was obtained by AlH_3-treatment either of the imine **9** (76%) or the oxime **8** (22%).

Scheme 3



7 R = O **10**

8 R = NOH

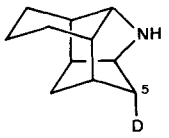
9 R = NH

[8]) These facts are compatible with the acceptor characteristics of AlH_3, which generally adds very fast to C,N-double bonds [9]. The electrophilic addition of AlH_3 to the C,N-double bond of the oxime **4** produces an intermediate (probably a nitrene), which collapses readily to the aziridine **6**. On the other hand, the reaction of the oxime **4** with $LiAlH_4$ (a donator) involves an attack of the hydride on the N,O-bond, which leads to the formation of the imine **5**, whose sterically crowded C,N-double bond is no more susceptible to a nucleophilic attack by $LiAlH_4$.

[9]) There are only a few reports on additions of amines to C,C-double bonds bearing no electron-withdrawing groups. Intermolecular cases require the presence of strong bases as well as high temperature and pressure [10]. Intramolecular examples are only known for secondary [11] and tertiary [12] amines, no addition is reported for a primary amine.

[10]) Deuterium incorporation (position, configuration and amount) was determined by 300-MHz-^{1}H-NMR., and mass spectroscopy (MS.).

Scheme 4



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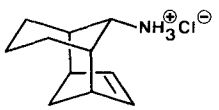
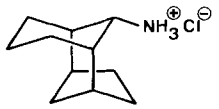
Treatment of **1** with HCl in ether yielded no trace of the cyclic amine **2** but quantitatively the hydrochloride **1** · HCl, *i.e.* protonation of the double bond in the reaction **1**→**2** must be either subsequent or simultaneous to the nucleophilic attack of the amine N-atom. The unsaturated amine **1** is actually more basic than **10**, the corresponding saturated one (see *Scheme 5*). This indicates that there is no relevant through-space charge delocalization between the N-atom and the C, C-double bond in the ground state. The pK_a-difference between **1** · HCl and **10** · HCl might arise from a better stabilization of the ammonium ion in **1** · HCl by intramolecular H-bonding with the double bond[11]).

Scheme 5



1·HCl

pK_a = 9.39



10·HCl

pK_a = 8.97

The above discussed reaction **1**→**2** is, to the best of our knowledge, the first example of an intramolecular addition of a primary amine to an unactivated C, C-double bond. As already shown in other cases [2], again the close proximity of the nucleophile and the C, C-double bond (the consequence of high steric compression) is the driving force for the cyclization, whereby a substantial amount of ground state strain is released. In contrast to our observations with olefinic alcohols [2], the amine cyclization occurs spontaneously at elevated temperature without adding base as catalyst.

Financial support for this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Ciba-Geigy AG*, Basel, is gratefully acknowledged. Mr. *G. M. R. T.* thanks for a Swiss Government Grant.

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[11]) For experimentally determined intramolecular H-bonding in related systems, see [1]. An intramolecular (N–H...π)-interaction in **1** · HCl is confirmed by X-ray structure analysis (to be published).

Analytical and spectral data. – *General.* Melting points (m.p.) were determined in sealed capillary tubes in an oil bath (*Büchi 510* apparatus) and are uncorrected. – IR. spectra were recorded in CCl_4 on a *Perkin-Elmer 297* spectrometer, bands are given in cm^{-1}. – ^{1}H-NMR. spectra ($CDCl_3$) were measured on a *Varian EM-390* or *HA-100* or *Bruker WM-300*, and ^{13}C-NMR. spectra ($CDCl_3$) on a *Varian CFT-20* or *Bruker WM-300.* Chemical shifts (δ) are given in ppm relative to TMS as internal standard; J = spin coupling constant (Hz), $W_{1/2}$ = half width at half height (Hz). – Mass spectra (MS.) were performed on a *Hitachi-Perkin-Elmer RMU-6M* instrument at 70 eV ionizing electron energy, source temperature 180°, inlet temperature 200°. The most important ions are listed as *m/z* values with relative intensities (% of base peak) in parenthesis. The pK_a-values were measured in methylcellosolve/H_2O 4:1 on a *Metrohm 636* Titroprocessor equipped with a micro glass-electrode EA 147 using tetramethylammonium hydroxide as base.

anti*[10,11]-Tricyclo[4.3.1.1^{2,5}]undec-3-en-10*endo*-amine* (**1**). – IR.: 3425*w*, 3048*w*, 1608*w*, 1484*w*, 1461*m*, 1353*m*, 1338*m*, 1274*w*, 1241*m*, 1100*m*, 1079*w*, 1062*w*, 1048*m*, 1004*w*, 950*w*, 922*m*, 912*w*, 898*w*, 879*w*, 856*w*, 616*w*. – ^{1}H-NMR. (300 MHz): 1.56 (*d*×*t*, *J(gem)* = 11, *J*(2,11*exo*) = *J*(5,11*exo*) = 8.5, H_{exo}–C(11)); 1.6–1.8 and 1.8–2.1 (2 *m*, 3 H and 5 H); 1.87 (*m*, $w_{1/2} \approx 8$, H_2N_{endo}–C(10)); *ca.* 2.6 (*m*, $w_{1/2} \approx 10$, H–C(2) and H–C(5)); 2.56 (*d*, *J(gem)* = 11, H_{endo}–C(11)); 2.79 (*m*, $w_{1/2} \approx 4$, H_{exo}–C(10)); 6.31 (*m*, $w_{1/2} \approx 4$, H–C(3) and H–C(4)). – MS.: 163 (36, M^+, $C_{11}H_{17}N$), 162 (7), 146 (10), 134 (9), 131 (5), 120 (14), 117 (8), 106 (11), 97 (12), 96 (14), 94 (10), 91 (15), 83 (10), 82 (100), 81 (17), 80 (27), 69 (48), 56 (36), 41 (15), 39 (16), 30 (16), 28 (16).

1·HCl. M.p. 260–262° (dec.), after recrystallization from a) CH_3OH/Et_2O and b) *i*-PrOH; pK_a 9.39. – IR. ($CHCl_3$): 3500–2450 br., 1595*m*, 1486*s*, 1462*w*, 1428*w*, 1364*m*, 1343*m*, 1121*w*, 1058*w*, 1030*m*, 970*m*, 925*w*, 908*m*, 889*w*, 851*m*, 826*m*. – ^{1}H-NMR. (90 MHz): 1.4–2.5 (*m*, 9 H); 2.55 (*d*, *J(gem)* = 12, H_{endo}–C(11)); 2.66 (*m*, $w_{1/2} \approx 9$, H–C(2) and H–C(5)); 3.37 (*m*, $w_{1/2} \approx 12$, H_{exo}–C(10)); 6.65 (*m*, $w_{1/2} \approx 4$, H–C(3) and H–C(4)); 8.15 (*m*, $w_{1/2} \approx 28$, $H_3N^+_{endo}$–C(10)). – ^{13}C-NMR. (75,47 MHz): 17.20 (*t*, C(8)); 27.80 (*t*, C(7) and C(9)), 31.69 and 44.56 (2 *d*, C(1), C(6) and C(2), C(5)); 37.86 (*t*, C(11)); 54.48 (*d*, C(10)); 139.82 (*d*, C(3) and C(4)).

$C_{11}H_{18}ClN$ (199.74) Calc. C 66.15 H 9.08 N 7.01% Found C 66.10 H 9.19 N 7.02%

7-Azatetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane (**2**). – IR.: 3022*w*, 1494*w*, 1464*m*, 1448*w*, 1442*w*, 1408*m*, 1389*m*, 1349*w*, 1300*m*, 1214*w*, 1174*w*, 1151*w*, 1095*w*, 1069*m*, 1055*w*, 1034*m*, 992*w*, 950*m*, 934*w*, 909*w*, 899*w*, 874*m*, 855*m*, 662*w*, 649*w*. – ^{1}H-NMR. (300 MHz): 1.22 (*d*×*d*, *J(gem)* = 12, *J*(2,3*exo*) = 6, H_{exo}–C(3)); 1.4–2.2 (*m*, 10 H); 1.6 (*d*×*d*×*d*, *J(gem)* = 11.5, *J*(4,5*exo*) = 4.5, *J*(5*exo*,6) = 4, H_{exo}–C(5)); 1.8 (*d*×*d*, *J(gem)* = 11.5, *J*(3*endo*,5*endo*) = 2.5, H_{endo}–C(5)); 2.41 (*d*×*d*, *J(gem)* = 12, *J*(3*endo*,5*endo*) = 2.5, H_{endo}–C(3)); 2.46 (*qa*, *J*(1,2) = *J*(2,3*exo*) = *J*(2,6) = 6, H–C(2)); 2.92 (*m*, $w_{1/2} \approx 8$, H–C(8)); 2.8–3.2 (*m*, H–N(7)); 3.71 (*d*×*d*, *J*(2,6) = 6, *J*(5*exo*,6) = 4, H–C(6)). – MS.: 163 (36, M^+, $C_{11}H_{17}N$), 162 (7), 146 (10), 134 (9), 131 (6), 120 (14), 117 (8), 106 (11), 97 (12), 96 (14), 94 (10), 91 (15), 83 (11), 82 (100), 81 (17), 80 (25), 79 (15), 77 (14), 69 (46), 56 (33), 55 (8), 44 (12), 43 (10), 41 (14), 39 (12), 30 (14), 28 (12).

anti*[10,11]-Tricyclo[4.3.1.1^{2,5}]undec-3-en-10-one oxime* (**4**)[12]. M.p. 165–166°, after recrystallization from CH_2Cl_2/hexane and sublimation at 72°/0.03 Torr. – IR.: 3610*m*, 3260*m* br., 3140*w* br., 3065*w*, 1674*w*, 1479*w*, 1454*m*, 1372*w*, 1348*m*, 1337*m*, 1282*m*, 1238*m*, 1217*m*, 1166*w*, 1085*w*, 1048*w*, 957*s*, 936*m*, 921*m*, 899*m*, 892*w*, 883*m*, 860*w*, 836*w*. – ^{1}H-NMR. (100 MHz): 1.3–2.2 (*m*, 7 H); 2.40 (*m*, $w_{1/2} \approx 16$, H–C(6)); 2.54 (*d*, *J(gem)* = 11, H_{endo}–C(11)); 2.5–2.7 (*m*, H–C(2) and H–C(5)); 3.41 (*m*, $w_{1/2} \approx 16$, H–C(1)); 5.9–6.15 (*m*, $w_{1/2} \approx 4$, H–C(3) and H–C(4)); 7.2–8.2 (*m*, HO–N=C(10)). – MS.: 177 (100, M^+), 176 (19), 161 (14), 160 (98), 159 (12), 158 (17), 150 (5), 149 (29), 148 (8), 145 (7), 144 (7), 143 (10), 134 (6), 133 (6), 132 (21), 131 (15), 130 (12), 128 (7), 122 (14), 118 (14), 117 (22), 112 (12), 111 (47), 110 (15), 106 (11), 104 (13), 94 (29), 91 (25), 83 (30), 79 (39), 77 (30), 67 (37), 66 (42), 65 (21), 41 (25), 39 (28), 27 (13).

$C_{11}H_{15}NO$ (177.26) Calc. C 74.54 H 8.53 N 7.90% Found C 74.53 H 8.58 N 7.80%

anti*[10,11]-Tricyclo[4.3.1.1^{2,5}]undec-3-en-10-imine* (**5**). – IR.: 3300*w* br., 3225*w*, 3150*w*, 3062*m*, 3040*w*, 1660*s*, 1480*w*, 1455*m*, 1374*s*, 1342*s*, 1314*m*, 1294*m*, 1279*m*, 1266*w*, 1242*w*, 1174*m*, 1156*w*, 1130*m*, 1084*m*,

[12]) The bridgehead C-atom towards which the hydroxy group of the oxime is oriented is numbered as C(1).

1058*w*, 1049*m*, 960*w*, 954*m*, 925*m*, 901*m*, 874*s*, 865*w*. – ^{1}H-NMR. (100 MHz): 1.3–2.3 (*m*, 7 H); 2.2–2.5 (*m*, H–C(1) and H–C(6)); 2.53 (*d*, *J(gem)* = 11, H_{endo}–C(11)); 2.5–2.7 (*m*, H–C(2) and H–C(5)); 5.6–6.6 (*m*, H–N=C(10)); 5.9–6.1 (*m*, $w_{1/2} \approx 3$, H–C(3) and H–C(4)). – MS.: 161 (78, M^+, $C_{11}H_{15}N$), 160 (56), 149 (24), 146 (20), 143 (7), 134 (21) 133 (100), 132 (71), 120 (18), 119 (10), 118 (23), 117 (10), 116 (5), 115 (7), 106 (49), 105 (10), 96 (34), 95 (46), 94 (33), 93 (17), 91 (30), 80 (19), 79 (36), 78 (13), 77 (33), 67 (30), 66 (18), 65 (18), 54 (35), 53 (13), 51 (12), 41 (29), 39 (28), 27 (14).

2-Azapentacyclo[6.4.0.0^{2,4}.0^{3,7},0^{5,12}]dodecane (**6**). – IR.: 3028*m*, 3005*w*, 1488*w*, 1474*w*, 1454*m*, 1441*w*, 1367*w*, 1343*w*, 1304*w*, 1264*w*, 1226*m*, 1182*m*, 1100*w*, 1053*w*, 992*m*, 968*w*, 954*w*, 944*m*, 918*m*, 874*m*, 861*w*, 852*w*, 646*w*, 609*w*, 590*m*. – ^{1}H-NMR. (100 MHz): 1.2–2.1 (*m*, 7 H); 2.21 (*d*, *J(gem)* = 12, H_{endo}–C(6)); 2.0–2.7 (*m*, $w_{1/2} \approx 9$, H–C(5), H–C(7), H–C(8) and H–C(12)); 3.02 (*m*, $w_{1/2} \approx 4$, H–C(3) and H–C(4)); 3.29 (*m*, $w_{1/2} \approx 12$, H–C(1)). – ^{13}C-NMR. (20 MHz): 20.23 (*t*, C(10)); 23.72 (*t*, C(9) and C(11)); 39.15 (*t*, C(6)); 43.01, 46.55 and 55.19 (3 *d*, C(3), C(4) and C(5), C(7) and C(8), C(12)); 64.32 (*d*, C(1)). – MS.: 161 (100, M^+, $C_{11}H_{15}N$), 160 (27), 146 (8), 134 (18), 133 (24), 132 (34), 120 (16), 119 (29), 118 (32), 117 (11), 106 (28), 105 (24), 95 (14), 94 (13), 93 (30), 92 (40), 91 (41), 81 (21), 80 (49), 79 (41), 78 (11), 77 (23), 67 (23), 54 (10), 53 (12), 41 (15), 39 (18).

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undecan-10-one* (**7**). – IR.: 3027*w*, 1719*s*, 1478*w*, 1464*w*, 1450*w*, 1349*w*, 1314*w*, 1276*w*, 1234*w*, 1219*w*, 1157*w*, 1086*w*, 1054*w*, 956*w*. – ^{1}H-NMR. (100 MHz): 1.0–2.6 (*m*, 14 H); 1.18 (*d*×*t*, *J(gem)* = 12, *J*(5,11*exo*) = *J*(2,11*exo*) = 4, H_{exo}–C(11)); 2.55 (*d*, *J(gem)* = 12, H_{endo}–C(11)). – MS.: 164 (90, M^+, $C_{11}H_{16}O$), 136 (38), 135 (16), 121 (31), 108 (28), 107 (33), 98 (86), 97 (43), 96 (21), 95 (86), 94 (47), 93 (62), 91 (19), 83 (28), 82 (14), 81 (48), 80 (52), 79 (69), 78 (10), 77 (24), 69 (10), 68 (43), 67 (100), 66 (31), 65 (14), 55 (24), 54 (17), 53 (24), 41 (52), 39 (40).

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undecan-10-one oxime* (**8**)[12]. M.p. 158° after recrystallization from CH_2Cl_2/hexane and sublimation at 87°/0.05 Torr. – IR.: 3610*m*, 3250*m* br., 3130*w* br., 3030*w*, 1672*w*, 1480*w*, 1468*m*, 1454*m*, 1376*w*, 1349*w*, 1328*w*, 1319*w*, 1294*w*, 1281*w*, 1264*w*, 1239*w*, 1205*w*, 1165*w*, 1089*w*, 965*s*, 935*m*, 900*m*, 880*w*, 817*m*. – ^{1}H-NMR. (100 MHz): 1.07 (*d*×*t*, *J(gem)* = 12, *J*(2,11*exo*) = *J*(5,11*exo*) = 4, H_{exo}–C(11)); 1.2–2.1 (*m*, 10 H); 2.0–2.4 (*m*, H–C(2), H–C(5), and H–C(6)); 2.38 (*d*, *J(gem)* = 12, H_{endo}–C(11)); 3.35 (*m*, $w_{1/2} \approx 16$, H–C(1)); 8.25 (*m*, $w_{1/2} \approx 9$, HO–N=C(10)). – MS.: 179 (74, M^+), 178 (13), 163 (10), 162 (67), 161 (6), 160 (27), 151 (7), 150 (8), 149 (8), 147 (6), 146 (5), 145 (7), 138 (6), 137 (15), 136 (63), 134 (16), 133 (12), 132 (12), 125 (15), 122 (10), 120 (25), 119 (18), 113 (37), 112 (17), 110 (8), 107 (9), 106 (10), 105 (11), 99 (100), 98 (22), 96 (20), 94 (18), 93 (21), 92 (12), 91 (29), 81 (34), 79 (40), 67 (54), 55 (16), 53 (16), 41 (39), 39 (24), 27 (12).

$C_{11}H_{17}NO$ (179.28) Calc. C 73.70 H 9.50 N 7.81% Found C 73.59 H 9.43 N 7.86%

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undecan-10-imine* (**9**). – IR.: 3300*w* br., 3220*w*, 3032*w*, 1658*s*, 1482*w*, 1467*m*, 1454*m*, 1445*w*, 1386*m*, 1380*w*, 1346*w*, 1318*m*, 1315*m*, 1306*m*, 1279*w*, 1270*w*, 1173*m*, 1162*w*, 1150*m*, 1129*m*, 1088*m*, 1070*w*, 1048*m*, 980*m*, 958*w*, 940*w*, 934*w*, 915*m*, 890*m*, 869*m*. – ^{1}H-NMR. (100 MHz): 1.08 (*d*×*m*, *J(gem)* = 12, $w_{1/2} \approx 8$, H_{exo}–C(11)); 1.1–2.2 (*m*, 10 H); 2.1–2.4 (*m*, $w_{1/2} \approx 8$, H–C(1), H–C(2), H–C(5) and H–C(6)); 2.36 (*d*×*m*, *J(gem)* = 12, $w_{1/2} \approx 4$, H_{endo}–C(11)); 5.3–6.9 (*m*, HN=C(10)). – MS.: 163 (47, M^+, $C_{11}H_{17}N$), 162 (14), 149 (5), 148 (9), 136 (5), 135 (16), 134 (36), 123 (27), 122 (11), 121 (9), 120 (22), 109 (8), 108 (13), 107 (21), 106 (27), 98 (20), 97 (100), 96 (77), 95 (23), 94 (24), 93 (19), 91 (13), 83 (21), 82 (37), 81 (20), 80 (22), 79 (29), 77 (14), 69 (33), 67 (35), 55 (15), 54 (21), 53 (16), 43 (16), 41 (33), 39 (21), 28 (12), 27 (10).

anti^{10,11}-*Tricyclo[4.3.1.1^{2,5}]undecan-10*endo-*amine* (**10**). – IR.: 3425*w*, 3022*w*, 1485*w*, 1466*m*, 1448*w*, 1399*w*, 1362*w*, 1275*w*, 1170*w*, 1096*m*, 893*w*, 879*w*, 599*w*. – ^{1}H-NMR. (100 MHz): 0.93 (*d*×*t*, *J(gem)* = 12, *J*(2,11*exo*) = *J*(5,11*exo*) = 4, H_{exo}–C(11)); 1.3–2.3 (*m*, 16 H); 2.24 (*d*×*m*, *J(gem)* = 12, $w_{1/2} \approx 6$, H_{endo}–C(11)); 2.83 (*m*, $w_{1/2} \approx 4$, H_{exo}–C(10)). – MS.: 165 (100, M^+, $C_{11}H_{19}N$), 164 (10), 150 (10), 148 (18), 137 (14), 136 (56), 133 (9), 122 (33), 120 (13), 119 (21), 109 (9), 108 (44), 107 (18), 106 (10), 105 (14), 97 (11), 96 (20), 95 (9), 94 (26), 93 (14), 92 (13), 91 (19), 82 (33), 81 (25), 80 (37), 79 (33), 70 (14), 69 (20), 67 (34), 66 (22), 56 (50), 43 (12), 41 (18), 39 (8), 30 (18).

10 · HCl. M.p. 280–284° (dec.), after recrystallization from CH_3OH/Et_2O; pK_a 8.97.

$C_{11}H_{20}ClN$ (201.76) Calc. C 65.49 H 9.99 N 6.94% Found C 65.38 H 9.97 N 6.94%

*7-Aza-(5*exo*-D)-tetracyclo[6.4.0.0^{2,6}.0^{4,9}]dodecane* (**11**). – ^{1}H-NMR. (300 MHz): among others: 1.6 (no signal for H_{exo}–C(5)); 1.8 (only *d*, *J*(3*endo*, 5*endo*) = 2.5, H_{endo}–C(5)); 3.71 (only *d*, *J*(2,6) = 6, H–C(6)). – MS.: 165 (12.5), 164 (100, D_I = 99%, M^+, $C_{11}H_{16}DN$), 163 (50, D_O = 1%).

We thank for their assistance: Miss *B. Brandenberg* (NMR.), Mrs. *L. Golgowsky* and Prof. *J. Seibl* (MS.), Mr. *D. Manser* (Combustion analysis), and Mr. *G. Leuenberger* (pK_a) of our analytical department.

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