AZOBRIDGES FROM AZINES XIII.[1] AZOBRIDGED POLYCYCLES: SKELETAL REARRANGEMENTS BY DENITROGENATION OF TRIAZOLINES AND SOLVOLYSES OF AZIRIDINES

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Abstract - Triazolines (**2**, **6** and **12**) derived from the corresponding azobridged polycycles undergo rapid denitrogenation in the presence of several heterogeneous acids (e.g. silica gel) with formation of the aziridines (**3**, **7**, and **13**) together with the rearrangement products (**4**) and (**8**). In addition to **7** and **8**, further products are formed on extrusion of nitrogen from **6** by dissolved acids, especially formic acid. In these reactions the azo group of **6** is involved, and hydrazine (**9**) and enamine (**10**) are produced. These two products are also isolated from the very slow acid catalyzed rearrangement of aziridine (**7**). The most likely reaction paths are exemplified with triazoline (**6**) in Scheme 1.

In earlier papers of this series we have described a rather general Diels-Alder reaction with reversed electron demand between cyclic azines and alkenes or alkadienes.[3] The [4+2] adducts with dienes constitute a special class of rigid skeletons in which an N=N and an C=C group are located in a parallel fashion within a definite distance. To these systems the well established 1,3-dipolar [3+2] cycloaddition between olefins and azides[4] can easily be applied. We concentrate here on those triazolines which are derived from systems which contain a norbornene moiety together with an azo bridge and azidoformic acid ester as the 1,3-dipole. The well documented extrusion of dinitrogen from these triazolines is of special interest, since this reaction may trigger skeletal rearrangements or lead to aziridines[5] which again may rearrange under solvolytic conditions.[6] We wondered, if the nature of our systems would influence the different reaction paths and if even the azo group present would be involved.

Triazolines and their denitrogenation

Addition of azidoformic acid ester to system (**5**) and the smooth decomposition of the triazoline (**6**) by silica gel

in dichloromethane has already been described.[6] Azirudine (**7**) and the rearranged urethane (**8**) are the only reaction products which could be isolated by chromatography.

System **1**,[5] in which the positions of the N=N and C=C compared to **5** are exchanged again is smoothly transformed into the corresponding triazoline (**2**), which, however, decomposes easily. Therefore crude **2** was subjected to denitrogenation by silica gel, yielding the expected aziridine (**3**) together with urethane (**4**). These results demonstrate that the different geometry of triazolines (**2**) and (**6**) is not reflected in the course of the nitrogen extrusion reactions catalyzed by silica gel. So far, the urethane (**4**) is the only representative of this skeleton which contains the N=N and C=C groups in exo/exo position. The corresponding isomers are **1** (exo/endo),[7] **5** (endo/exo, basic system known)[3a] and **8** (endo/endo).[6] As to be expected from earlier investigations,[3d,8] only **8** undergoes a smooth [2+2] photocycloaddition.[6]

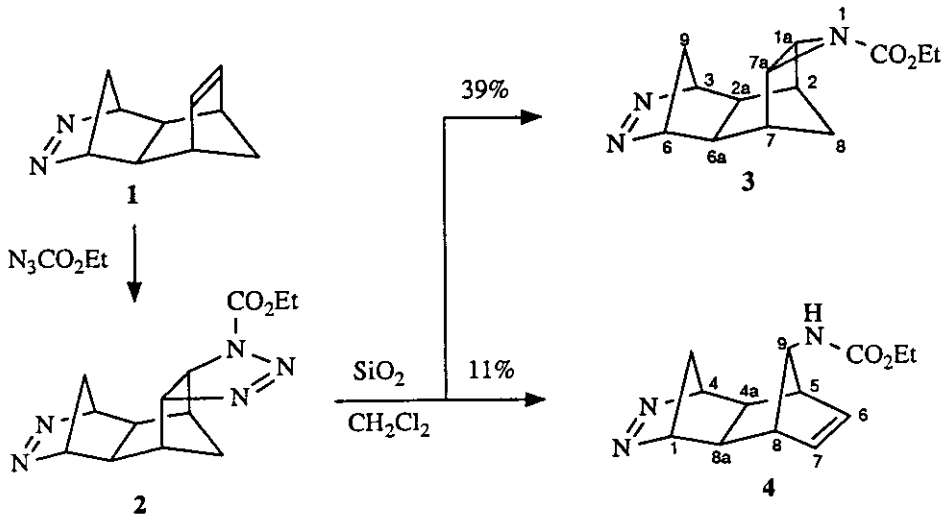
Nitrogen extrusion from triazolines (**2**) and (**6**) by silica gel is very convenient. In case of **6** the overall yield and the ratio of products (**7**) and (**8**) remains nearly constant with Lewatit SPC 112[9] and the Montmorillonit K 10 as catalysts, whereas with Alox S[10] the overall yield was reduced to 42%.[6]

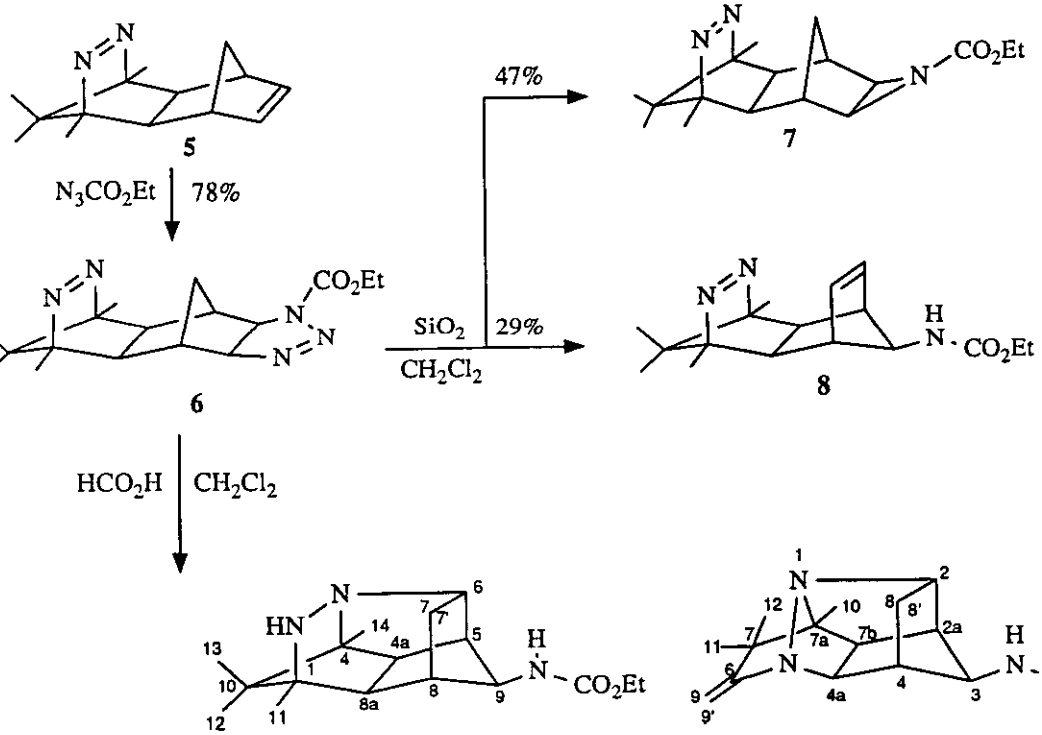
All the above mentioned acidic catalysts act in the solid state. We wondered, how dissolved (Lewis) acids, rarely applied so far,[11] would behave. Indeed, with triazoline (**6**) as a model not only products (**7**) and (**8**) are observed, but also the transanular products (**9**) and (**10**): In acetone with 2 N HCl, in dichloromethane with HCO_2H, CF_3CO_2H (**8** and **10**) and $BF_3 \bullet Et_2O$ (**7** and **9**).

This unexpected behavior of **6** has been studied in more detail with formic acid at 0°C and 25°C by hplc when all four products (**7** - **10**) are observed. Whereas the amount of aziridine (**7**) remains constant, at the lower temperature **9** is formed in much higher, **8** and **10** in much lower yield.

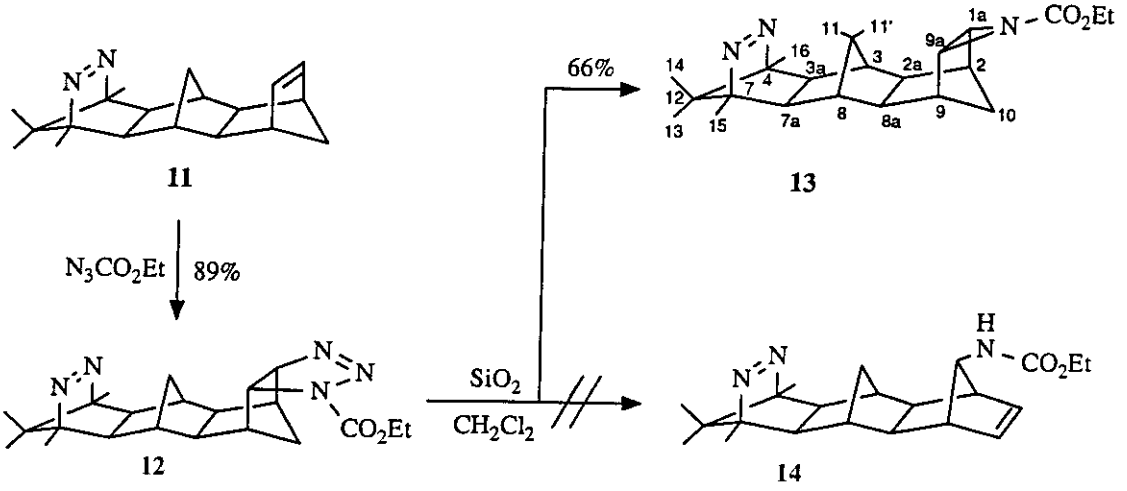
Triazoline (**12**), easily obtained from the olefin (**11**)[2,12] and azidoformic acid ester, was also subjected to silica gel in dichloromethane. Interestingly, only the corresponding aziridine (**13**) could be isolated, but rearranged product, e.g. urethane (**14**), was not detected. At first glance the structural pattern around the triazoline moieties in **2** and **12** look rather similar. However, the different orientation and the larger distance of the azo group in **12** obviously suppress rearrangements.

The well established photo denitrogenation of triazolines[4,10,13] cannot be applied to **2**, **6** and **12**. The $n \rightarrow \pi^*$ transition of the azo group is located at longer wave length than that of the triazoline moiety. Therefore, as exemplified with **6**[6], irradiation by a mercury lamp removes two equivalents of dinitrogen yielding the aziridine (**16**) exclusively. On applying the 365 nm line of an Argon laser, however, the azo group in **6** is expelled selectively leaving the triazoline moiety in **15** completey intact. Consecutive irradiation of **15** or even better

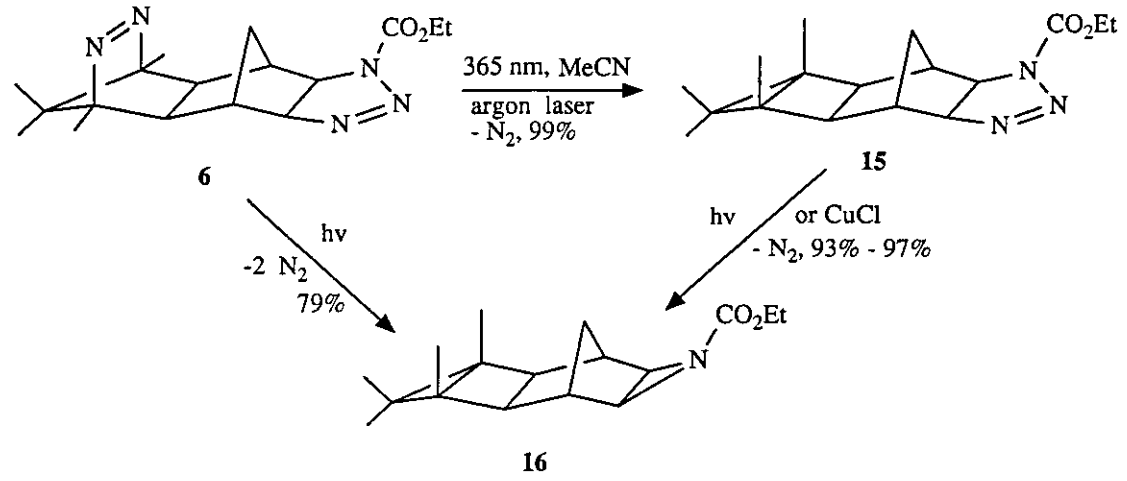




	7 + 8	+ 9	+ 10
0 °C	33% (<3%)	58%	6%
25 °C	33% 23%	19%	24%



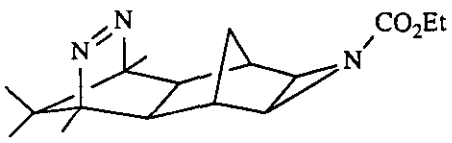
treatment with CuCl yields **16** quantitatively.[6] Nitrogen extrusion from triazolines by CuCl, obviously not described so far, may gain general importance.



Ring Opening of Aziridines by Acids

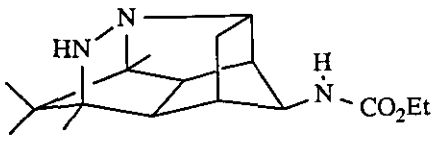
Acid catalyzed dinitrogen extrusion from triazolines is known to occur rather rapidly[11] whereas the corresponding ring opening of aziridines proceeds extremely slowly.[14] If these aziridines are derivatives of azatricyclo[3.2.1.$0^{2,4}$]octane, solvolyses provoke Wagner-Meerwein rearrangements[14,15] which therefore are also expected for our model (**7**).

Aziridine (**7**) reacts very slowly under different conditions (tlc monitoring) and mostly with partial decomposition. Reaction products are the rearranged compounds (**9**) or (**10**), depending on the acid employed as demonstrated by the following reaction sequence.

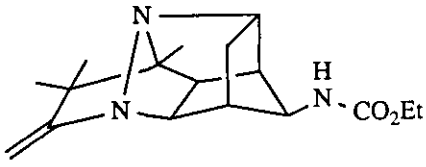


7

CH_2Cl_2 | 20°C



9



10

acids			
2 N HCl	6 months	32%	—
$BF_3 \cdot Et_2O$	6 months	—	15%
CF_3CO_2H	5 months	—	48%
HCO_2H	3 days	76%	—

The very slow reaction with 2 N HCl originates not from the two phase conditions, since the homogeneous reactions with $BF_3 \cdot Et_2O$ and CF_3CO_2H are not faster. The much higher activity of formic acid is hard to comprehend.

It is remarkable that in these four experiments either **9** or **10**, but none of the rearrangement product (**8**), could be isolated. The norbornene derivative (**8**) does not act as a precursor for **9** or **10** since treatment of **8** under the same acidic conditions leaves this compound untouched even after 30 days (hplc). The high yield of **9** which is achieved with formic acid may result from the short reaction time. But the reducing properties of the acid could also be important since the formation of **9** must include a reduction step (*vide infra*).

Structure elucidation of the products

Routine ^1H- and ^{13}C-nmr spectra of **2** - **4**, **12**, and **13** are completely in accord with the structures given above. Their features correspond well with those of **6** - **8** and similar compounds obtained previosly in this series.

Besides, all products, exept **9** and **10** exhibit an uv absorption at 362 - 368 nm (lg ε = 2.15 - 2.56) which is typical for a diazabicyclo[2.2.1]hepten-2-ene system integrated into the rigid frameworks under discussion. Structures (**9**) and (**10**) could be assigned from their ^{1}H-nmr spectra after several NOE experiments and by comparison with certain models reported in the literature.[16] However, it was not possible to discriminate between a "parallel" cyclization as given in **9**, and a "cross" cyclization. The former seems to be more likely since in similar systems "parallel" cyclization is the preferred one.[13a] The rather unexpected structure of **10** is supported by the ^{1}H-nmr dubletts at 4.83 ppm and 4.36 ppm with a typical geminal coupling constant of 0.6 Hz for exo-methylene groups[18] and the ^{13}C-nmr signals at 165.2 (s) and 95.5 (t) indicative for 1,1-disubstituted olefins.[19] The persistance of that enamine against acid hydrolysis is another argument for structure (**10**): Formation of the immonium ion would violate Bredt's rule

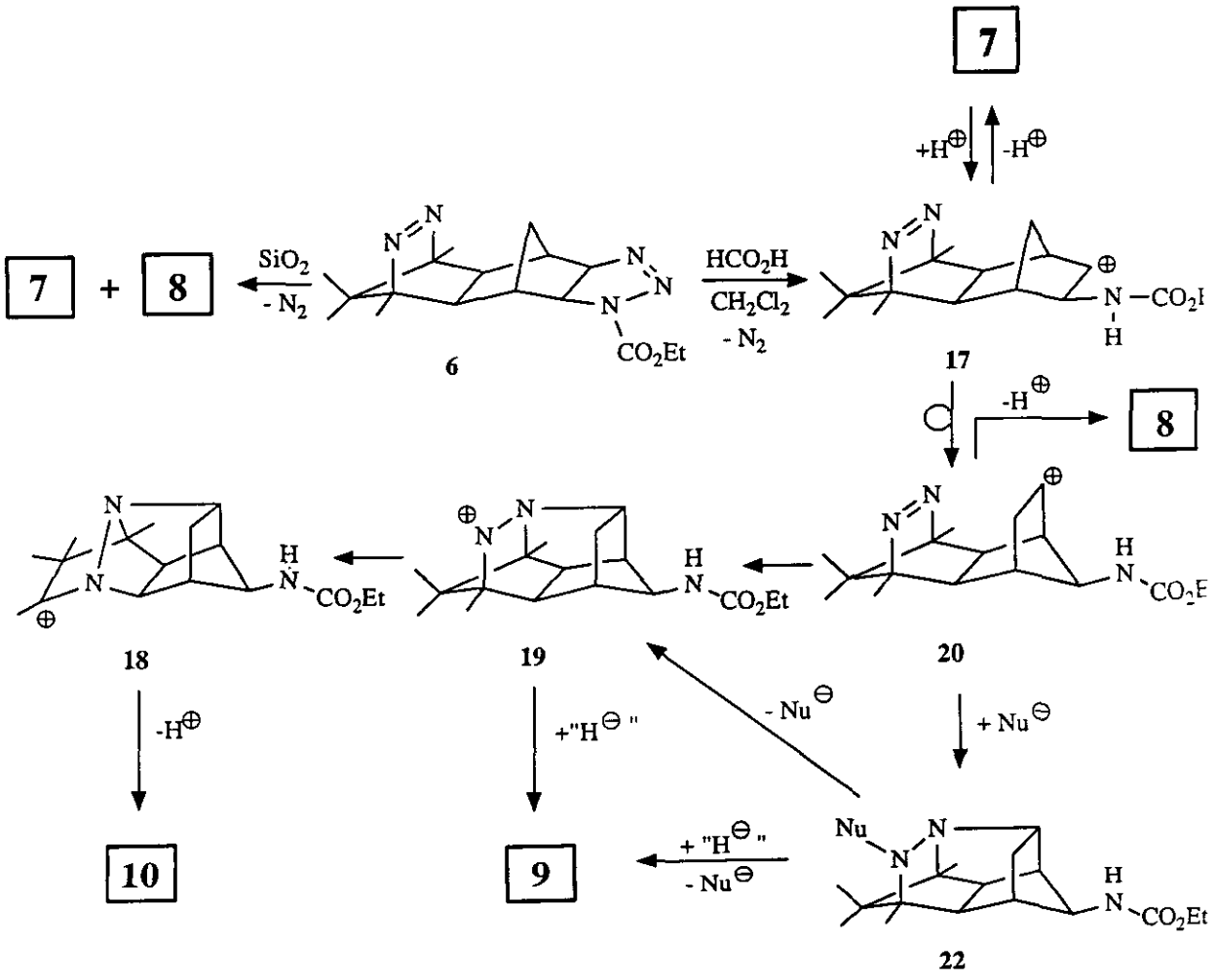
Discussion of the rearrangements

As described above, silica gel is a useful catalyst for nitrogen extrusion from triazolines (**2**, **6**, and **12**) whereby the aziridines (**3**, **7**, and **13**) are formed together with the urethanes (**4**) and (**8**). The mechanism of these reactions should be close to the well documented thermal decomposition.[20] These two types of products together with an amine and an imine[13a] have also been observed with the rather similar triazoline obtained from norbornene and azidoformate. Since the reaction of the *exo*-anellated *exo*-triazolinonorbornane (**6**) gives rise to the *endo*-anellated norbornene derivative (**8**), *endo*-anellated *exo*-triazolinonorbornene (**2**) consequently yields the *exo*-anellated norbornene derivative (**4**).

As reported above, decomposition of triazoline (**6**) with dissolved acids produces not only aziridine (**7**) and urethane (**8**), but also the cage compounds (**9**) and (or) (**10**) by including the azo group into the rearrangement. The most probable competing reaction routes for **6** are collected in Scheme 1. There, only classical structures of the cations are presented, although we are aware of their non classical nature.

After extrusion of nitrogen by the protic acid (e.g. formic acid) the crucial intermediate is supposed to be the norbornyl cation (**17**). Its ring closure to aziridine (**7**) is doubtlessly a dead end reaction under the applied conditions. Its proton catalyzed reopening to **17** proceeds much more slowly but consequently also produces the rearrangement products (**9**) and (**10**).

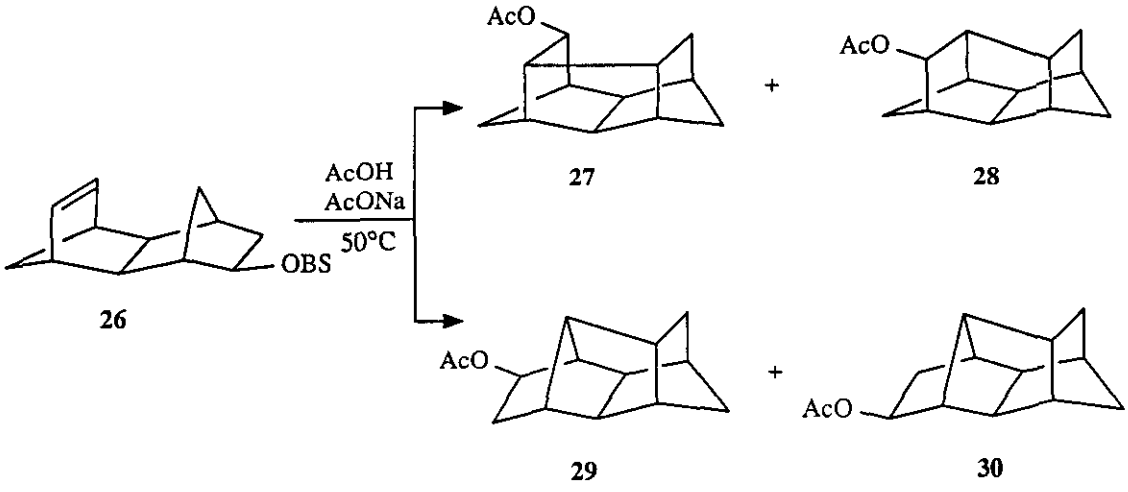
Scheme 1



Wagner-Meerwein rearrangement of **17** occurs on a similar time scale yielding the new norbornyl cation (**20**) which on deprotonation ends up as **8**. However, attack of the carbenium ion in **20** on the azobridge should form the nitrenium ion (**19**) which after another skeletal rearrangement to **18** and deprotonation yields enamine (**10**). Since no isomeric enamine was detected the rearrangement **19** → **18** must occur stereospecifically. It is not clear if the steric requirements in **19** cause such a clean rearrangement or if first a nucleophile is added to **22** which after protonation provoke a concerted "anti"-rearrangement to **18**.

The formation of **9**, which includes a reductive step, may occur by two different routes. Both formal addition of a hydride ion to **19** and formal substitution of the nucleophile on route **20** → **22** → (**19**) should be possible. According to earlier reports[21-24] on formal nitrenium ions radical pathways are likely too.

Alkylation of a nitrogen atom in diazabicycloalkene derivatives together with consecutive redox reactions has already been reported. In all these cases the lone pair of the nitrogen is approached by the electrophile. Now the rigid structure of intermediate (**20**) only allows intramolecular electrophilic attack on the π bond of the azo group, perhaps the first example of this type of reaction. On the basis of the very weak nucleophilicity of the azo group it is remarkable that compounds (**9**) and (**10**) are formed at all in addition to the "normal" products of triazoline denitrogenation, **7** and **8**.



The reaction sequence **17** → **20** → **19** or **22** compares well with results from the solvolysis of brosylate (**26**).[27] This can be judged from products (**27** - **30**) which are formed besides some others. It should be mentioned, that with the carbocyclic system cross coupling **28** as well as parallel coupling **27** is observed, whereas in case of **6** only one reaction mode is found as discussed above.

EXPERIMENTAL

Melting points are taken under a microscope and are corrected. Ir: Perkin Elmer 1420; uv: Perkin Elmer 330; ^{1}H-nmr: Bruker WM 400, AC 250 [vs. $CDCl_3$ (δ = 7.27), toluene (δ = 2.32) or benzene (δ = 7.29)]; ^{13}C-nmr: Bruker WM 400, AC 250 [vs. $CDCl_3$ (δ = 77.0)]; ms: Varian MAT CH7 (70 eV). Flash chromatography (FC) on silica gel 32 - 63 μm (WOELM). Medium pressure chromatography (MPC) on Lichrosorb 15 - 25 μm (Merck), column 25 x 2.4 cm (N = 7200). Solvent: ethyl acetate/petroleum ether (E/P).Uv detection at 340 nm. All solvents were purified and dried according to common procedures.

Ethyl (3at,4ac,8ac,9at)-3a,4,4a,5,8,8a,9,9a-Octahydro-4r,9c;5t,8t-dimethano[1,2,3]triazolo[4,5-g]phthalazine-1-carboxylate (triazoline 2)

A solution of **1**[5] (335 mg, 2.09 mmol) and N_3CO_2Et (313 mg, 2.94 mmol) in 5 ml of CH_2Cl_2 is reacted for 4 d (tlc monitoring). After removal of the solvent, crude **2** is stirred with a mixture of SiO_2 (1 g) and CH_2Cl_2 (5 ml) for 45 min. The filtered pale yellow solution is separated in portions (~ 50 mg product) by mpc (E/P = 1:1). Fraction I: **3**, fraction II: **4**.

Ethyl (1at,2ac,6ac,7at)-1a,2,2a,3,6,6a,7,7a-Octahydro-2r,7c;3t,6t-dimethanoazirino[2,3-g]phthalazine-1-carboxylate (aziridine 3)

3: 171 mg (39%), colorless crystals, mp 114 - 115 °C, decomp. with evolution of gas. Ir (KBr): ν = 2990, 2960, 2920 (C-H), 1705 (C=O), 1390, 1370, 1270, 1230, 1180, 1105 cm^{-1}; uv (hexane): λ_{max} (log ε) = 343 (2.40), 338 (2.12) nm; MeCN: λ_{max} (log ε)= 343 (2.22) nm; EtOH: λ_{max} (log ε) = 342 (2.18) nm; ^{1}H-nmr ($CDCl_3$, 200 MHz): δ = 0.89 (d, 1H, 8-H, J=10.2 Hz), 1.03 (d, 1H, 9-H, J=12.0 Hz), 1.17 (t, 3H [ethyl]), J=7.1 Hz), 1.51 (br s, 2H, 2a-H, 6a-H), 1.60 (d, 1H, 8'-H, J = 10 Hz), 1.90 (d, 1H, 9'-H, J = 12 Hz), 2.57 (br s, 4H, 1a-H, 7a-H, 2-H, 7-H), 4.01 (q, 2H [ethyl], J = 7 Hz), 4.96 (br s, 2H, 3-H, 6-H) ppm; ^{13}C-nmr ($CDCl_3$, 50.3 MHz): δ = 14.02 (q, [ethyl]), 32.73, 36.26 (t, C-8, C-9), 37.31, 37.61, 40.50 (3d, C-2, C-7, C-1a, C-7a, C-2a, C-6a), 62.11 (t, [ethyl]), 76 00 (d, C-3, C-6), 162.0 (s, C=O) ppm; ms (70 eV): m/z (%) = 154 (5), 153 (30), 152 (100), 130 (10), 124 (23), 108 (41), 92 (17), 91 (30), 81 (14), 80 (100), 67 (24), 66 (28), 53 (26), 41 (23), 39 (22), 29 (90), 27 (81), 27 (27). Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 63.25; H, 7.12; N, 16.94.

Ethyl([(4at,8at)-1,4,4a,5,8,8a-Hexahydro-1r,4c;5c,8c-dimethanophthalazine-9-yl])-9-carbamate (carbamide ester **4**)

4: 48.0 mg (11%) colorless crystals, mp 108-110 °C decomp. with evolution of gas. - Ir (KBr): ν = 3360 (N-H), 3000-2980, 2920 (C-H), 1690 (C=O), 1540, 1470, 1370, 1345, 1250, 1230, 1215, 1110, 1050, 700 cm^{-1}; uv (EtOH). λ_{max} (log ε) = 344 (2 09) nm; ^{1}H-nmr ($CDCl_3$, 200 MHz): δ = 0.84 (br d, 1H, 10-H, J=12.8 Hz), 1.19 (3H, [ethyl], J=7.1 Hz), 1.34 (pseudo t, 2H, 4a-H, 8a-H, band widths 1.3 Hz), 2.13 (d, 1H, 10'-H, not fully resolved), 2.73-2.75 (mc, 2H, 5-H, 8-H), 4.03 (q, 2H [ethyl], J = 7 Hz), 4.63 (d, 1H, 9-H, $J_{9,N-H}$=9.1), 4.98 (d, 3H, 1-H, 4-H, N-H, J=1.2 Hz), 6.14 (br s, 2H, 6-H, 7-H) ppm; ^{13}C-nmr ($CDCl_3$, 50.3 MHz): δ=14.51 (q, [ethyl]), 29.60 (t, C-10), 42.86, 46.69 (2d, C-5, C-8, C-4a, C-8a), 60.75 (t, [ethyl]), 62.27 (d, C-9), 76.36 (d, C-

1, C-4), 136.57 (d, C-6, C-7), 156.28 (s, C=O) ppm; ms (70 eV): m/z (%)= 153 (14), 146 (6), 131 (14), 129 (55), 128 (16), 117 (31), 115 (33), 102 (13), 94 (15), 91 (31), 82 (21), 81 (44), 80 (44), 66 (75), 65 (21), 39 (23), 30 (38), 29 (100), 28 (58), 27 (39). Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 63.53; H, 7.10; N, 16.77.

*Reaction of Triazoline(***6***)*[6] *with Formic Acid*

A solution of **6** (200 mg, 0.60 mmol) in CH_2Cl_2 (2 ml) is reacted with 33 mg (0.66 mmol) of HCO_2H at 20°C until **6** is consumed (tlc monitoring, 23 h). The solution is extracted with sat. $NaHCO_3$, the aqueous phase with 2x3 ml of CH_2Cl_2, and the organic phase dried with K_2CO_3. After evaporation the product mixture is separated by mpc (E/P 1:1). Fraction I: 61.0 mg (33%) aziridine (**7**) (mp, ^{1}H-nmr). Fraction II: 41.0 mg (23%) carbamate ester (**8**) (^{1}H-nmr).[6] Final elution with CH_2Cl_2/MeOH/conc. NH_3 100:10:1, and FC of the crude product with the same eluent yields 44 mg (24%) of enamine (**10**) and 35 mg (19%) of urethane (**9**) (purifications of **9** and **10** by sublimation under reduced pressure).

Ethyl(1,4,10,10-Tetramethyloctahydro-2,7-cyclo-1,4;5,8-dimethanophthalazine-9-anti-yl)carbamate (urethane **9**)

Colorless crystals, mp 207-208 °C. Ir (KBr): ν= 3330 (N-H), 2950 (C-H), 1680 (C=O), 1540, 1250 (C-O), 975 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 400 MHz): δ= 0.82 (s, 3H, 11-H), 0.92 (s, 3H, 13-H), 1.08 (s, 3H, 14-H), 1.17 (s, 3H, 12-H), 1.20 (t, 3H, [ethyl], J=6.7 Hz), 1.35 (dd, 1H, 7'-H, $J_{7',8}$=6 Hz, $J_{7',6}$=6 Hz), 2.35 (d, 1H, 8-H, J = 12 Hz), 2.42 (d, 1H, 7-H, $J_{7,7'}$=12.0 Hz), 2.55-2.60 (m, 1H, 4a-H), 2.63-2.68 (m, 1H, 5-H), 3.24 (br s, 1H, NH), 3.40 (dd, 1H, 8a-H, $J_{8a,8}$=5.1 Hz, $J_{8a,4a}$=5.1 Hz), 3.45 (ddd, 1H, 6-H, $J_{6,7'}$=5.1 Hz, $J_{6,5}$=5.1 Hz, $J_{6,4a}$=1.8 Hz), 3.78 (d, 1H, 9-H, not fully resolved), 4.06 (q, 2H, [ethyl], J = 7 Hz), 4.78 (d, 1H, NH, $J_{NH,9}$=5.0 Hz) ppm; ^{13}C-nmr ($CDCl_3$, 100.6 MHz): δ= 12.27, 14.54, 17.65, 21.88, 23.19 (5q, C-11), C-12, C-13, C-14 [ethyl]), 26.44 (t, C-7), 42.11 (d, C-9), 47.52 (s, C-10), 51.80, 52.59 (2d, C-5, C-8), 55.16 (d, C-6), 59.07, 59.50 (2d, C-4a, C-8a), 60.74 (t, [ethyl]), 78.43 (s, C-4), 91.45 (s, C-1), 156.19 (s, C=O) ppm; ms (70 eV): m/z (%)= 306 (8), 247 (14), 125 (100), 108 (25), 107 (18), 94 (13), 82 (15), 81 (18), 56 (20), 43 (26), 41 (16). Anal. Calcd for $C_{17}H_{27}N_3O_2$: C, 66.88; H, 8.85; N, 13.77. Found: C, 67.08; H, 8.66; N, 13.51.

Ethyl (7,7,7a-Trimethyl-6-methyleneoctahydro-1,5-diaza-1r,5c-cyclo-2c,4c-methanocyclopenta[cd]indene-3c-yl)carbamate (enamine **10**)

Colorless crystals, mp 200-202 °C. Ir (KBr): ν= 3195 (N-H), 3015, 2960 (C-H), 1710 (C=O), 1670, 1550, 1245

(C-O), 1170, 1095, 1045, 910, 875 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 400 MHz): δ= 1.03, 1.06, 1.15 (3s, each 3H, 10-H), 12-H, 13-H), 1.20 (t, 3H, |ethyl], J=5.9 Hz), 1.43 (dd, 1H, 8'-H, J = 8 Hz), 2.35-2.45 (m, 2H, 4-H, 8-H), 2.60-2.70 (m, 1H, 7b-H), (m, 1H, 2a-H), 3.13 (dd, 1H, 4a-H, $J_{4a,4}$=5.9 Hz, $J_{4a,7}$=5.9 Hz), 3.48 (ddd, 1H, 2-H, $J_{2,3'}$=5.2 Hz, $J_{2,2a}$=5.2 Hz, $J_{2,7b}$=2.0 Hz), 3.79 (d, 1H, 3-H, not fully resolved), 4.06 (q, 2H [ethyl], J = 7 Hz), 4.41 (1H, 9-H), 4.83 (1H, 9'-H, $J_{9,9'}$=0.6 Hz), 4 93 (d, NH, $J_{NH,3}$=5 5 Hz) ppm; ^{13}C-nmr ($CDCl_3$, 100.6 MHz): δ= 11.69, 14.52, 24.89, 26.28 (4q, C-10, C-11, C-12 |ethyl|), 26.23 (t, C-8), 41.94 (d, C-3), 45.06 (s, C-7), 52 28, 52.33 (2d, C-2a, C-4), 54.92 (d, C-2), 60.65 (t |ethyl|), 59.20, 69.17 (2d, C-4a, C-7b), 78.24 (s, C-7a), 96.86 (t, C-9), 156.23 (s, C=O), 165.17 (s, C-6) ppm; ms (70 eV): m/z (%)= 303 (100, M^+), 288 (39), 257 (14), 242 (13), 216 (10), 215 (57), 199 (34), 180 (20), 162 (17), 150 (21), 147 (22), 135 (46), 125 (20), 124 (25), 109 (33), 106 (25), 94 (21), 91 (30), 80 (18), 79 (18). Hplc: purity >99.5%. Silica, λ=210 nm, methyl *t*-butyl ether/methanol 140:3, t_R=16 07 min) *Anal Calcd for* $C_{17}H_{25}N_3O_2$, *exact mass* $C_{17}H_{25}N_3O_2^+$: 303 1946. Found· 303.1946

Ethyl 6,9,14,14-tetramethyl-(3at,4ac,5ac,9ac,10ac,11at)-3a,4,4a,5,5a,6,9,9a,10,10a,11,11a-dodecahydro-4r,11c,5t,10t:6c,9c-trimethano[1,2,3]triazolo[4,5-g]benzo[1,2-g]phthalazine-1-carboxylate (triazoline **12**)

A solution of **11**[2,12] (500 mg, 1 77 mmol) and N_3CO_2Et (265 mg, 2.32 mmol) in CH_2Cl_2 (5 ml) is reacted for 4 days at 20 °C (tlc monitoring). Evaporation of the solvent yields crude **12** (690 mg, 98%). From petrol ether at -78 °C **12** is isolated as a pale yellow solid (629 mg, 89%) which is stirred in CH_2Cl_2 (5 ml) with SiO_2 (1.0 g) for 5 h After filtration FC (E/P 1:4) yields 385 mg (66%) of **13** (sublimation at 180°C/0.8 torr).

Ethyl 4,7,12,12-Tetramethyl-(1at,2ac,3ac,7ac,8ac,9at)-1a,2,2a,3,3a,4,7,7a,8,8a,9,9a-dodecahydro-2r,9c;-3t,8t,4c,7c-trimethanoaziino[4,5]benzo[1,2-g]phthalazine-1-carboxylate (aziridine **13**)

Colorless crystals, mp 174-176 °C. Ir (KBr): ν=2980-2920 (C-H), 1740 (C=O), 1490, 1440, 1375, 1360, 1275, 1250, 1170, 1100, 1040 cm^{-1}, uv (hexane): λ_{max} (log ε)= 363 (2.27) nm; (MeCN): λ_{max} (log ε)= 363 (2.12) nm; EtOH: λ_{max} (log ε)= 362 (1.99) nm; ^{1}H-nmr ($CDCl_3$, 200 MHz): δ= 0.29 (s, 3H, 14-H), 0.63 (d, 11'-H, J=10.0 Hz), 0.70 (s, 3H, 13-H), 1.17 (t, 3H |ethyl|, J=7.1 Hz), 1.34 (br s, 2H, 10-H), 1.44 (d, 1H, 11-H, partly disguised by the following signal), 1.46 (br s, 2H, 2a-H, 8a-H), 1.56 (s, 6H, 15-H, 16-H), 1.64 (br s, 2H, 3a-H, 7a-H), 2.25 (br s, 2H, 3-H, 8-H), 2.50 (br s, 2H), 2.55 (br s, 2H, 1a-H, 2-H, 9-H, 9a-H), 4.00 (q, 2H |ethyl|, J = 6 Hz), ppm; ^{13}C-nmr ($CDCl_3$, 50.3 MHz): δ= 12.38 (q, 2C, C-15, C-16), 14.11 (q), 15.42 (q), 17 36 (q, C-13, C-14, |ethyl|), 30.44 (t), 32.00 (t, C-10, C-11, 35.64 (d), 38.58 (d), 40.42 (d), 52.20 (d), 54 43

(d, C-3a, C-7a, C-3, C-8, C-2a, C-8a, C-2, C-9, C-1a, C-9a), 61.10 (s, C-12), 61.95 (t [ethyl]), 90.34 (s, C-4, C-7), 162.32 (s, C=O) ppm; ms (70 eV): m/z (%)= 327 (23), 326 (100), 280 (16), 237 (30), 218 (11), 199 (15), 173 (31), 153 (36), 152 (74), 147 (88), 131 (22), 129 (32), 123 (56), 122 (87), 108 (33), 107 (67), 105 (34), 91 (64), 80 (62), 79 (44), 67 (31), 29 (94), 28 (67) Anal. Calcd for $C_{22}H_{31}N_3O_2$: C, 71.51; H, 8.46; N, 11.37. Found: C, 71.61; H, 8.59; N 11.47.

Rearrangement of Aziridine (**7**)

Reaction of **7** in dichloromethane with different acids at room temperature is run until all **7** is consumed (tlc monitoring). The reaction mixture is washed with sat. aqueous Na_2CO_3, dried over K_2CO_3 and evaporated. Flash chromatography (fc) or mpc (conditions see above) of the complex mixtures yields rearranged product (**9**) or (**10**).

A) A solution of **7** (200 mg, 0.66 mmol) in 2 ml of CH_2Cl_2 and 2 ml of 2 N HCl is violently stirred for 6 months. After work up **9** (59.0 mg, 89%, ^{1}H-nmr, mp) is isolated. B) A mixture of **7** (200 mg, 0.66 mmol) and BF_3•Et_2O (140 mg, 0.90 mmol) is stirred for 6 months. From the brown residue (136 mg) **10** (30.0 mg, 15%, ^{1}H-nmr, mp) is isolated by mpc. C) Reaction of **7** (200 mg, 0.66 mmol) with CF_3CO_2H (83 mg, 0.73 mmol) in 2 ml of CH_2Cl_2 for 6 months yields a brown oil (184 mg). After fc **10** (96.0 mg, 48%, ^{1}H-nmr, mp) is isolated. D) Reaction of **7** (150 mg, 0.50 mmol) with HCO_2H (40 mg, 0.87 mmol) in 2 ml of CH_2Cl_2 complets in 3 days. The crude is purified by fc (Al_2O_3, MeOH/CH_2Cl_2 1.60) and then recrystallized from CCl_4, yielding **9** (112 mg, 76%, ^{1}H-nmr, mp).

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REFERENCES

1 Paper XII: U. Brand, S Hünig, K Peters, and H. G von Schnering, *Chem. Ber.*, 1991, **124**, 1187.

2 Ph.D. Thesis, *P. Kraft*, University of Würzburg, 1989

3 a) K. Beck, A. Höhn, S Hünig, and F Prokschy, *Chem Ber.*, 1984, **117**, 517.

b) S. Hünig and F Prokschy, *Chem. Ber*, 1984, **117**, 534.

c) W. Berning, S. Hünig, and F. Prokschy, *Chem. Ber.*, 1984, **117**, 1455.

d) K. Beck and S. Hünig, *Chem Ber.*, 1987, **120**, 477.

3 e) K. Beck, S. Hünig, F.-G. Klärner, P. Kraft, and U. Artschwager-Perl, *Chem. Ber.*, 1987, **120**, 2041.

4 Cf. A. Padwa, *1,3-Dipolar Cycloaddition Chemistry*, eds. E.C. Taylor, A. Weissberger, New York (John Wiley & Sons) 1984, Vol. 1, p. 559.

5 Detailed discussion: lit.[3e]

6 S. Hünig and P. Kraft, *J. Prakt. Chemie*, 1990, **332**, 133.

7 Ph D Thesis, *B. Albert*, University of Würzburg, 1981

8 B. Albert, W. Berning, Ch. Burschka, S. Hünig, and F. Prokschy, *Chem. Ber.*, 1984, **117**, 1465.

9 Acidic ion exchanger from BAYER AG, Leverkusen.

10 Decomposition of triazolines during chromatography on aluminium oxide has been described: R. J. Stedman, A. C. Swift, and J. R. Hoover, *Tetrahedron Lett.*, 1965, 2525 M. Christl and H. Leininger, *Tetrahedron Lett.*, 1979, 1553.

11 E Funakubo, I. Moritani, H. Taniguchi, T. Yamamoto, and T. Tsuchiya, *Chem. Ber.*, 1963, **96**, 2035.

12 Submitted to *Chem. Ber.*

13 a) A. C. Oehlschlager, R. S. McDaniel, A. Thakore, P Tillman, and L. H. Zalkow, *Can. J. Chem.*, 1969, **47**, 4367. R. S. McDaniel, and A. C Oehlschlager, *Tetrahedron*, 1969, **25**, 1381. A. C. Oehlschlager, P. Tillman, and L M. Zalkow, *J. Chem. Soc., Chem. Commun.*, 1965, 569

b) P. Scheiner, *Tetrahedron*, 1968, **24**, 2757 R Huisgen, L. Möbius, G. Müller, H. Stange, G. Szeimies, and J. M Vernon, *Chem. Ber.*, 1965, **98**, 3992. P. Scheiner, *J. Org. Chem.*, 1965, **30**, 7.

14 K. Wiesner, P.-T Ho, R C. Jain, S. F Lee, S Oida, and A. P Philipp, *Can. J. Chem.*, 1973, **51**, 1448.

15 R. Huisgen, L. Möbius, G. Müller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, 1965, **98**, 3992. L. H Zalkow and R. M Calhoun, *Tetrahedron Lett.*, 1975, 2149. L. H Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, 1963, **28**, 3303. H. Tanida, T.Tsuji, and T. Irie, *J. Org. Chem.*, 1966, **31**, 3941. K. Fukunaga and C. Rüchardt, *Synthesis*, 1987, 1097.

16 S. Freund, H. Henneberger, and M. Christl, *Chem. Ber.*, 1988, **121**, 1665.

17 U Brand, S. Hunig, K Peters, and H. G. von Schnering, *Chem. Ber.*, 1991, **124**, 1187.

18 H Günther, nmr-*spectroscopy*, 2nd edition, p. 100, Georg Thieme Verlag, Stuttgart, 1983.

19 H.-O. Kalinowski, S Berger, and S Braun, *^{13}C-Nmr-Spectroscopy*, 1st edition, p. 115, Georg Thieme Verlag, Stuttgart, 1984.

20 Compare P. Scheiner, *Sel. Org. Transform.*, 1970, **1**, 327.

21 C. A. Grob and P Flury, *Tetrahedron Lett.*, 1983, **24**, 3195.

22 P. G. Gassman and R. L. Cryberg, *J. Am. Chem Soc* , 1969, **91**, 5176.

23 E. M. Kosower, *Progr Phys. Org. Chem.*, 1965, 3, 81. M. L. Heyman and J. P. Snyder, *J. Am. Chem. Soc.*, 1975, **97**, 4416.

24 A. G. Anastassiou, *J Am. Chem. Soc.*, 1966, **88**, 2322.

25 J. P. Snyder, M. L. Heymann, and M. Gudestrup, *J. Chem. Soc., Perkin Trans. I*, 1977, 1551. S. F. Nelsen and R. T. Landis, *J. Am Chem. Soc.* 1974, **96**, 1788.

26 S Hünig and M Schmitt, *Tetrahedron Lett.*, 1984, **25**, 1725. S. Hünig and F. Prokschy, *Chem. Ber.*, 1984, **117**, 2099. K. Beck, S. Hünig, and P Reinold, *Tetrahedron*, 1988, **44**, 3295. S. Hünig and M. Schmitt, *Israel J Chem* , 1989, **29**, 213

27 L. de Vries and S. Winstein, *J Am Chem. Soc.*, 1960, **82**, 5363.

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