Journal of Organometallic Chemistry, 214 (1981) 125—133
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PALLADIUM-PROMOTED CYCLIZATION REACTIONS OF AMINOALKENES

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(Received December 17th, 1980)

Summary

The trifluoromethanesulphonate salts of the aminoalkenes CH_2=$CH(CH_2)_3$-NH_2, its 2-methyl, 2,2-dimethyl and *N*-iso-propyl-derivatives, and CH_2=CH-$(CH_2)_4NH_2$ cyclize in the presence of $[PdCl_2(PhCN)_2]$ and a nitrogen base to produce the corresponding C- or N-substituted 2-methylpyrrolidines and 2-methylpiperidine. *E*-CH_3CH=$CH(CH_2)_3NH_2$ produces 2-ethylpyrrolidine and a small amount of 2-methylpiperidine. The regio-selectivity of these reactions differs from that observed for the cyclization of the same substrates promoted by $[PtCl_4]^{2-}$: (1) the palladium reaction with 2-methylpent-4-enylamine produces ca. a 4 : 6 ratio of *cis*- and *trans*-2,4-dimethylpyrrolidine while with platinum the converse is true; (2) there is a more marked tendency for attack of the amine at the more substituted alkene carbon atom in the palladium than in the platinum reactions.

Introduction

In recent years palladium-promoted amination reactions of alkenes have received particular attention because of their marked regioselectivity and their potential use in organic synthesis [1—4]. It has been shown that these reactions proceed through a *trans*-attack of the nucleophile at the coordinated alkene [2]. The resulting palladium—carbon σ bond can then be cleaved by a variety of reagents. In addition to intermolecular reactions of aliphatic amines with alkenes coordinated to palladium [1,2], intramolecular cyclisation of sterically favoured and less basic aminoalkenes have also been reported, e.g., indoles and isoquinolines have been obtained from the reaction of *o*-allylaniline and *o*-allylbenzylamine derivatives with $[PdCl_2(CH_3CN)_2]$ [3,4].

Other metallic compounds have also been used to promote amination of alkenes. Flexible and more basic aminoalkenes of the type CH_2=$CH(CH_2)_nNH_2$

0022-328X/81/0000—0000/$02.50,

(n = 3, 4) have been cyclized using $[PtCl_4]^{2-}$ [5,6] and HgX_2 (X = Cl, CH_3COO) [7]. Marked regio- and stereoselectivity effects have been observed for these reactions [6,7].

We were interested to establish whether the flexible aminoalkenes would also undergo a cyclisation reaction with palladium. Furthermore, as it was observed that, at least for some substrates, platinum and mercury compounds show different regioselectivities, the corresponding palladium reactions were considered worthy of investigation.

This paper describes the cyclisation reaction of aminoalkenes CH_2=CH-$(CH_2)_nNH_2$ (n = 3, 4) and some of their alkyl derivatives using $[PdCl_2(PhCN)_2]$ (I).

Results and discussion

The cyclisation reaction of pent-4-enylamine

The reaction of CH_2=$CH(CH_2)_3NH_2$ (II) with I, using standard experimental conditions [1—4], gave a low yield of III. In order to find a satisfactory method for the cyclisation of II, the products formed by the addition of II to I were investigated.

The addition of one equivalent of II to a THF solution of I at 0°C results in the immediate formation of a yellow-brown precipitate (IVa). Its infrared spectrum (see Table 1) shows the presence of free and coordinated double bonds. If, however, the reaction mixture is stirred for 30 min prior to filtration, one obtains a solid (IVb) with an infrared spectrum showing only coordinated double bonds and amino groups of II. Two bands at 335 cm^{-1} and 305 cm^{-1} are also observed and are assigned to ν(Pd—Cl). As the occurrence of two bands in this region is characteristic of complexes *cis*-$[PdCl_2L_2]$ [8] it can be assumed that a *cis* geometry is also present in IVb. Owing to its low solubility, which prevents a molecular weight determination, it is not known whether II is acting as a chelating agent, i.e., IVb is mononuclear or whether II is acting as a bridging ligand, i.e. IVb is polynuclear. Both suspensions of IVa or IVb and the isolated powders are thermally unstable and easily deposit metallic palladium at room temperature. The microanalytical data however indicate that solid IVb has the composition $[PdCl_2(II)]$.

A more thermally stable product is obtained whe CH_2=$CH(CH_2)_2NH_2$ (V) is added to a CH_2Cl_2 solution of I. The isolated powder analyzes as $[PdCl_2(V)]$

TABLE 1

MAIN INFRARED BANDS OF PALLADIUM(II) COMPLEXES WITH AMINOALKENES (cm^{-1})

Complex	ν(N—H)				C=C_{free}	C=$C_{coord.}$	Pd—Cl
Pent-4-enylamine (II) [a]	3370m,	3295m		1600w	1645s		
$[PdCl_2(II)]_x$ (IVa) [b]	3230s		3140s,	1695w	1650s,	1540w	340s
$[PdCl_2(II)_x$ (IVb) [b]	3265s,	3220s,	3150s,	1598s		1540m	335m, 305m
$[PdCl_2(II)_2]$ (VII) [b]	3280s,	3235s,	3143s,	1585s	1640m		338s
$[PdCl_2(V)]_x$ (VI) [b]	3270s, 3210s, 3100w,			1560s		1544m,	348s, 318s

[a] NaCl plates. [b] CsCl discs.

(VI). Complexes similar to IV and VI have been reported [3,4], e.g., [$PdCl_2$(*o*-allylaniline)].

As it will be shown later, V does not cyclize under conditions which give satisfactory results for II. We therefore suppose that the thermal instability of IVa and IVb is likely to be associated with the intramolecular cyclisation of II yielding a very unstable σ-bonded species, which decomposes to give a mixture of unidentified products.

Attempts were made to obtain 2-methylpyrrolidine (III) from IVa or IVb. The THF suspension of IVa or IVb was cooled to —65°C to prevent isomerisation of the double bond and β-H abstraction. In order to liberate the coordinated NH_2 group of II, needed for the nucleophilic attack at the coordinated double bond, 1 to 3 equivalents of diethylamine were added to the mixture containing IVa or IVb. The resulting yellow suspension gave, after reduction with hydrogen, yields of III which did not exceed 10%, the unreacted II being recovered as $CH_3(CH_2)_4NH_2$.

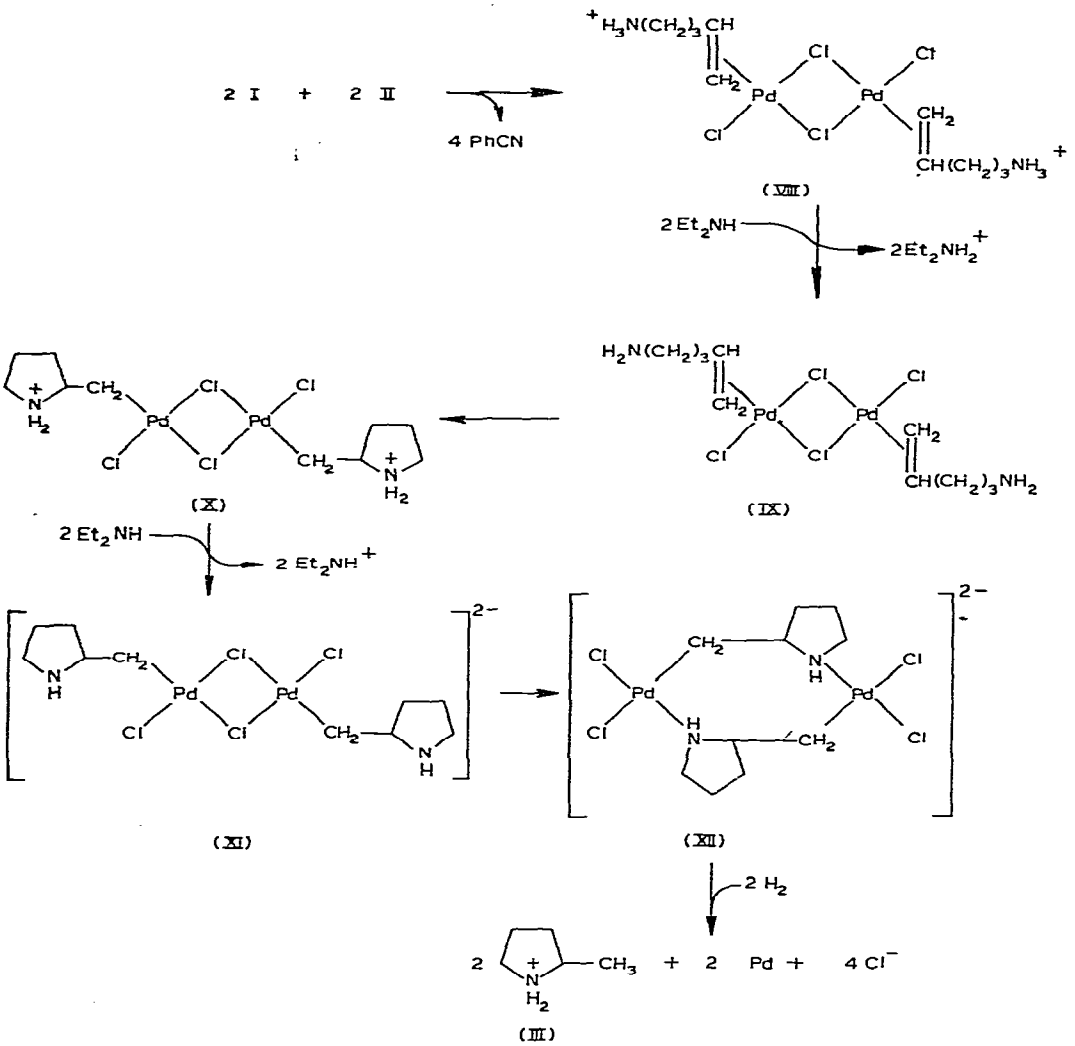
The supposition, that the added amine preferentially displaces the alkene function rather than the basic amino group of II receives support from an experiment in which a suspension of IVb is treated with one equivalent of II at ca. 25°C. This gives a yellow solution from which *trans*-[$PdCl_2$(II)$_2$] can be isolated. The infrared spectrum of this complex shows that II is coordinated only through its nitrogen atom (see Table 1). The NMR detection of the displacement of alkenes coordinated to palladium by amines has been reported elsewhere [1].

The cyclization reaction does, however, proceed with satisfactory yields if the protonated form of II is added to I followed by the addition of base. Thus, when CH_2=$CH(CH_2)_3NH_3^+$ (II′), as its $CF_3SO_3^-$ salt, is added to a THF solution of I the reaction mixture changes from red-brown to dark brown. This presumably corresponds to the formation of an alkene complex, e.g. a species such as VIII shown in Scheme 1. Base is then added to regenerate the amine function of II and the resulting complex, by analogy with VIII, can be written as IX. Intramolecular cyclisation can now occur yielding intermediate X which contains the organic moiety σ-bonded to palladium.

As can be seen from the data given in Table 2, the yield of III is base-dependent and (a) reaches a maximum when two moles of base per palladium atom are used, (b) does not change if larger amount of amine are added and (c) is practically independent of the steric requirements of amine, i.e., n-$PrNH_2$ and iso-Pr_2EtN are almost equally effective. This last result leads us to conclude that the function of the added amine is chiefly that of a base, i.e., to produce IX by deprotonation of VIII. It should be also noted that the addition of amine is carried out at —65°C to prevent olefin displacement, double bond isomerisation and β-hydrogen abstraction [1,2].

Further information about the course of the reaction is provided by the yield of III when one mole of amine per mole of palladium is used. In this case the yield of III is about one half of that obtained when two moles of base are used. This result could be accounted for as follows: Intermediate X can dissociate a proton to give intermediate XI (see Scheme 1). This species is unlikely to retain the free nitrogen donor and should transform into compound XII in which the pyrrolidine is acting as a bidentate ligand. Indeed, the tendency to

SCHEME 1 *



coordinate the nitrogen atom may provide the driving force for the deprotonation of X. Thus, as soon as X starts to form it will immediately transform into XII and the liberated proton will attack IX regenerating VIII, which will not cyclize. Thus, the addition of one mole of base will result in the cyclization of one half of the coordinated alkene and the addition of a second mole of base per palladium atom is required to bring the reaction to completion.

Earlier studies [2,9] have shown that alkyl groups which are σ-bonded to palladium are cleaved by $LiAlD_4$ giving organic compounds in which the palladium-containing moiety has been replaced by a deuterium atom. Thus, additional evi-

* Another satisfactory reaction scheme could be based on the mononuclear complexes related to species VIII to XI, e.g., for VIII $[PdCl_2(S)(CH_2{=}CH(CH_2)_3\overset{+}{N}H_3)]$ (S = PhCN or THF).

TABLE 2

CYCLIZATION REACTIONS OF AMINOALKENES

Aminoalkene		Base (equivalents)	Reaction conditions	Products		Overall yield (%)	Product ratio (%)
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	—			no cyclization		
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	Et_2NH (1)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	30	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	Et_2NH (2)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	65	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	Et_2NH (3)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	65	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	Et_2NH (4)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	64	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	n-PrH_2 (2)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	60	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	Et_3N(2)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	56	
(II)	$CH_2=CHCH_2CH_2CH_2NH_2$	iso-Pr_2EtN (2)	*a*	(III)	$HNCH_2CH_2CH_2CHCH_3$	60	
(XV)	$CH_2=CHCH_2CH(CH_3)CH_2NH_2$	Et_2NH (2)	*a*	(XX) (XXI)	*cis*-$HNCH_2CH(CH_3)CH_2CHCH_3$ *trans*-$HNCH_2CH(CH_3)CH_2CHCH_3$	72	42 58
(XVI)	$CH_2=CHCH_2C(CH_3)_2CH_2NH_2$	Et_2NH (2)	*a*	(XXII)	$HNCH_2C(CH_3)_2CH_2CHCH_3$	73	
(XVII)	$CH_2=CHCH_2CH_2CH_2NHC_3H_7$-iso	Et_2NH (2)	*b*	(XXIII)	iso-$PrNCH_2CH_2CH_2CHCH_3$	78	
(XVIII)	*E*-$CH_3CH=CHCH_2CH_2CH_2NH_2$	Et_2NH (2)	*c*	(XXIV) (XXV)	$HNCH_2CH_2CH_2CHCH_2CH_3$ $HNCH_2CH_2CH_2CH_2CHCH_3$		80 20
(XIX)	$CH_2=CHCH_2CH_2CH_2CH_2NH_2$	Et_2NH (2)	*a*	(XXV)	$HNCH_2CH_2CH_2CH_2CHCH_3$	76	
(V)	$CH_2=CHCH_2CH_2NH_2$	Et_2NH (2)	*a*		no cyclization		

[a] Standard conditions (see Experimental section). [b] Reaction time 2.5 hours (total yield after 1 hour: 67%). [c] Yield did not increase on prolonging the reaction time beyond one hour.

dence for the presence of the 2-methylpyrrolidyl group in compounds X—XII was sought by reducing the reaction mixture containing the compound formulated as XII with $LiAlD_4$. The mono-deuterocompound $HN\overline{CH_2CH_2CH_2CH}$-$CH_2D$ was the only detectable product from this reaction.

The reaction of other aminoalkenes with $[PdCl_2(PhCN)_2]$

Several C- and N-substituted pent-4-enylamines can also be cyclized as described for II and the results are summarized in Table 2. As can be seen, C- and N-alkyl substitution of II results in higher yields of cyclized products with the exception of *E*-hex-4-enylamine (XVIII). These effects have been previously observed in the platinum-promoted reaction and have been attributed, in the case of C-substitution, to changes in relative energies of the possible conformers of the coordinated alkenes [6] and in the case of N-substitution [5], to the higher basicity of the nucleophilic group.

The slower cyclization rate of XVII can be attributed to the steric retardation caused by the presence of the N-iso-propyl substituent. Steric effects are also likely to be responsible for the relatively low yield of the cyclization products XXIV and XXV obtained from XVIII. This effect has also been previously observed [5].

As found for the corresponding platinum-promoted reactions [5], (a) no cyclized product is obtained from the reaction of I with $CH_2{=}CH(CH_2)_2NH_2$ (V) and (b) $CH_2{=}CH(CH_2)_4NH_2$ (XIX) gives 2-methylpiperidine (XXV) in good yield.

Two points of interest arise from the comparison of the regio- and stereoselectivities of the palladium- and platinum-promoted reactions (see Table 2):

1. the *cis : trans* ratio of the 2,4-dimethylpyrrolidines (XX and XXI) differ in the two cases, being 42 : 58 for palladium and 62 : 38 for platinum;

2. the cyclization reaction of *N*-isopropylpent-4-enylamine (XVII) gives only N-*iso*propyl-2-methylpyrrolidine (XXIII) using I while this reaction in the presence of $[PtCl_4]^{2-}$ gives both XXIII and *N*-iso-propylpiperidine in a 71 : 29 ratio. Similarly, the reaction of XVIII with I gives 2-ethylpyrrolidine (XXIV) and 2-methylpiperidine (XXV) in an 80 : 20 ratio while, in the presence of $[PtCl_4]^{2-}$ XVIII gives XXIV and XXV in a 9 : 91 ratio.

While the slightly differing *cis : trans* ratios of the two dimethylpyrrolidines XX and XXI may tenatively be ascribed to differences in conformational energies in the palladium and platinum intermediates prior to cyclization, the marked preference for the formation of five-membered rings may reflect differences in charge distribution at the coordinated double bond [10] induced by the presence of a palladium or a platinum atom.

In conclusion, the observed differences in regioselectivity between the cyclization reactions carried out in the presence of $PdCl_2(PhCN)_2$ and of $[PtCl_4]^{2-}$ provide evidence that these cyclization reactions are worthy of further studies in order to optimize their potential for organic synthesis.

Experimental section

Unless otherwise stated physical measurements and gas-chromatographic separations were carried out as previously described [5]. The NMR data related

TABLE 3

NMR (ppm) AND MASS SPECTRAL (*m/e*) DATA OF SUBSTITUTED PYRROLIDINES AND PIPERIDINE

2-Methylpyrrolidine (III)	GC-MS:	85 (17%), 70 (100%), 57 (50%), 42 (22%), 28 (29%).
2-Methylpiperidine (XXV)	^{1}H NMR ($CDCl_3$):	3.2—2.9 (m, 1 H), 2.8—2.35 (m, 2 H), 1.85—1.2 (m, 7 H), 1.04 (d, 3 H, *J* 6.4 Hz).
cis-2,4-Dimethylpyrrolidine (XX)	^{1}H NMR ($CDCl_3$) [a]:	3.35—2.8 (m), 2.65—1.85 (m), 1.16 (d, 3 H, *J* 6.4 Hz), 1.02 (d, 3 H, *J* 6.4 Hz).
trans-2,4-Dimethylpyrrolidine (XXI)	(only methyl group):	1.13 (d, 3 H, *J* 6.4 Hz), 0.98 (d, 3 H, *J* 6.4 Hz)
2,4,4-Trimethylpyrrolidine (XXII)	^{1}H NMR (D_2O):	4.05—3.6 (m, 1 H), 3.07 (s, 2 H), 2.2—1.9 (m, 1 H), 1.8—1.5 (m, 1 H), 1.37 (d, 3 H, *J* 7.3 Hz), 1.15 (s, 3 H), 1.1 (s, 3 H).
2-methyl-1-isopropylpyrrolidine (XXIII)	^{13}C NMR (D_2O) [a]:	60.756, 53.847, 48.878, 31.354, 21.786, 18.254, 16.527, 15.091.
2-Ethylpyrrolidine (XXIV)	^{1}H NMR (D_2O):	3.7—3.2 (m, 3 H), 2.4—1.5 (m, 6 H), 1.0 (t, 3 H, *J* 8.4 Hz)

[a] Recorded on a Brucker 250 MHz spectrometer, dioxan as reference.

to the cyclic compounds described here are given in Table 3. All reactions were carried out in a nitrogen atmosphere. The amines were distilled over KOH and THF over potassium and benzophenone prior to use. The organic compounds which were not commercially available were prepared as described in the appropriate reference. Pent-4-enylamine (II) [11]; 2-methylpent-4-enylamine (XV) [6]; 2,2-dimethylpent-4-enylamine (XVI) [6]; *N*-isopropylpent-4-enylamine (XVII) [12]; *E*-hex-4-enylamine (XVIII) [6]; hex-5-enylamine (XIX) [13]; but-3-enylamine (V) [14]; 2-methylpyrrolidine (III) [15]; *cis*- and *trans*-2,4-dimethylpyrrolidine (XX and XXI) [6]; 2,4,4-trimethylpyrrolidine (XXII) [6]; 2-methyl-1-isopropylpyrrolidine (XXIII) [5] [16]; 2-ethylpyrrolidine (XXIV) [6]. $[PdCl_2(PhCN)_2]$ (I) was prepared as described elsewhere [17] and the other palladium complexes as described below.

$[PdCl_2(II)]_x$ (IVa and IVb)

66.5 mg (0.78 mmol) II were added to a solution of 300 mg (0.78 mmol) I in 15 ml THF at 0°C. The yellow-brown precipitate which formed immediately, was stirred for 1 min, filtered off and washed three times with 5 ml petroleum ether (b.p. 30—60°C). 110 mg (IVa) were thus obtained (IR, see Table 1).

If the reaction mixture obtained as described above was stirred at 0°C for 30 min before filtration, 120 mg IVb was obtained. The powder IVb, which decomposes on drying under high vacuum even at room temperature, gave the following microanalytical results: Found: C, 25.29; H, 4.33; N, 4.75; Cl, 25.97. $C_5H_{11}Cl_2NPd$ calcd.: C, 25.14; H, 4.55; N, 5.05; Cl, 25.65%. M.p.: 104°C dec.

These data are in fair agreement with a composition $[PdCl_2(II)] \cdot 0.2$ THF. The presence of THF in IVb was confirmed by a GC analysis of a sample which had been reduced with H_2 in diethyl ether.

$[PdCl_2(V)]_x$ (VI)

150 mg (0.891 mmol) I were dissolved in 15 ml CH_2Cl_2 and 1 equivalent of

V was added. The flocculent yellow precipitate was gently stirred at room temperature for two days. The resulting fine suspension was then filtered. The solid was washed several times with hexane and dried under high vacuum. A 70% yield of yellow product (decomp. pt. 145—150°C) was obtained (IR, see Table 1). Found: C, 19.54; H, 3.69; N, 5.69; Cl, 28.39. $C_4H_9Cl_2NPd$ calcd.: C, 19.33; H, 3.62; N, 5.64; Cl, 28.55%.

$[PdCl_2(II)_2]$ (VII)

51 mg (0.6 mmol) II were quickly added to a stirred solution of 100 mg (0.26 mmol) I in 2 ml THF. The yellow precipitate which initially formed redissolved to give a yellow solution. Stirring was continued for 40 min and the solvent was removed under reduced pressure. The residual oily paste was washed three times with 10 ml of a 20 : 1 mixture of petroleum ether (30—60°C) and diethyl ether. The resulting powder was dissolved in boiling ether, filtered over Celite and cooled to —20°C. A 66% yield of product (decomp. pt. 108—110°C) was thus obtained. Found: C, 34.41; H, 6.28; Cl, 20.58; N, 8.02. Mol. wt. (osmometric in CH_2Cl_2) 388. $C_{10}H_{22}Cl_2N_2Pd$ calcd.: C, 34.54; H, 6.39, Cl, 20.39; N, 8.05%. Mol. wt. 347.62. (IR, see Table 1). ^1H NMR (CD_2Cl_2, δ(ppm): 6.1—5.6 (m, 1 H) and 5.23—4.8 (m, 2 H) assignable to the sp^2 carbon atoms; 3.0—2.5 (s, broad, CH_2—N, 2 H); 2.4—1.95 (m, =CH—CH_2—, 2 H); 1.95—1.5 (m, broad, —CH_2—, NH_2, 4 H).

The cyclization reactions were carried out by the general procedure described below. Changes from this procedure are noted in Table 2.

Standard experimental procedure for the cyclization reaction

A solution of 0.39 mmol aminoalkene and 0.39 mmol trifluoromethane sulphonic acid, in 1.5 ml THF was added to a solution of 0.39 mmol I in 3.5 ml THF at 0°C. The resulting solution was stirred at 0°C for 5 min and the resulting dark brown solution was cooled to —65°C and treated with 0.78 mmol (2 equivalents) of base over 30 min. The solution was stirred for 60 min, flushed with hydrogen and then pressurized at ca. 1.8 atm for ca. 30 min while it was allowed to warm up gradually. At ca. 0°C palladium metal began to precipitate. The reaction mixture was then stirred with 3 ml 5 *M* KOH. An internal standard (ethylbenzene) was then added and the THF phase examined by GC. The yields were determined constructing a calibration curve using the appropriate pyrrolidine. For product characterization larger scale reactions (1 mmol) were carried out and the products were isolated by preparative gas chromatography. The products were identified by comparing their NMR and/or mass spectra with those of independently synthesized samples.

In all cases the cyclized products were accompanied by varying amounts of aminoalkanes formed by hydrogenation of the corresponding unreacted aminoalkenes. The amounts of aminoalkanes plus those of the corresponding cyclized product(s) added to the practical totality of aminoalkene employed in the cyclization reaction.

Deuteration experiment with $LiAlD_4$

1 mmol II was cyclized using the standard procedure described above up to the point prior to treatment with hydrogen. 2 mmol $LiAlD_4$ were added to the

reaction mixture at —65° C. This was then stirred for an additional 60 min, allowed to reach room temperature and then treated with 0.2 ml D_2O followed by 5 ml of 5 *M* KOH. The black reaction mixture was filtered off, the THF layer was separated and the aqueous phase washed several times with diethyl ether, 10 ml 3 *M* HCl were then added to the combined organic phases. The aqueous phase was separated, washed with diethyl ether and evaporated to dryness at 40° C under vacuum. The residue was dissolved in 1 ml 5 *M* KOH and repeatedly extracted with several small portions of diethyl ether. The pyrrolidine was isolated by preparative GC and characterized by its ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$, δ(ppm)): 3.2—2.6 (m, 3 H), 2.1—1.45 (m, 4 H), 1.08 (—CH_2D, d of t, ^3J(H, H) 6.4 Hz, ^2J(H, D) 1.9 Hz).

Acknowledgements

We thank Ciba-Geigy AG for support and a Studentship (to B.P.) and the Technisch-Chemisches Laboratorium, ETH Zürich, for the GC-MS studies.

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