NMR ($CDCl_3$) δ 64.7 (J_{CP} = 3.9 Hz, C_4), 142.11 (J_{CP} = 2.0 Hz, C_5), 77.95 (J_{CP} = 0, C_7); ^{31}P NMR ($CDCl_3$) δ −1.55.

34b: ^1H NMR ($CDCl_3$) δ 4.00 ($^3J_{H_4H_5}$ = 3.9, $^3J_{H_4H_7}$ = 2.0, $^3J_{H_4P}$ = 4.0 Hz, H_4), 7.42 ($^3J_{H_5P}$ = 5.9 Hz, H_5), 3.66 ($^2J_{H_7P}$ = 8.8 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 64.85 (J_{CP} = 3.9 Hz, C_4), 145.46 (J_{CP} = 2.0 Hz, C_5), 76.98 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ −1.85; mass spectrum (140 °C), *m/e* (relative intensity) 318 (M, 100). Anal. Calcd for $C_{22}H_{23}P$: C, 82.99; H, 7.29; P, 9.72. Found: C, 83.11; H, 7.37; P, 9.51.

3,6,7-Triphenyl-1-phosphanorborna-2,5-diene (35). Diphenyl-2*H*-phosphole dimer **11** (0.5 g) and phenylacetylene (5 mL) were heated at 100 °C in a sealed tube for 16 h. After chromatography with toluene–hexane (20:80), both isomers **35a** (pure) and **35b** (impure) were recovered wth 70% yield (ratio **a**:**b** = 90:10).

34a: mp 112 °C; ^1H NMR ($CDCl_3$) δ 6.81 ($^4J_{H_2H_4}$ = 0.9, $^2J_{H_2P}$ = 45.6 Hz, H_2), 4.87 ($^3J_{H_4H_5}$ = 4.1, $^3J_{H_4H_7}$ = 1.8, $^3J_{H_4P}$ = 5.1 Hz, H_4), 7.73 ($^3J_{H_5P}$ = 5.9 Hz, H_5), 4.01 ($^2J_{H_7P}$ = 8.3 Hz, H_7); ^{13}C NMR ($CDCl_3$) δ 61.61 (J_{CP} = 4.9 Hz, C_4), 142.68 (J_{CP} = 2.8 Hz, C_5), 78.2 (J_{CP} = 0 Hz, C_7); ^{31}P NMR ($CDCl_3$) δ −3.89; mass spectrum (120 °C), *m/e* (relative intensity) 338 (M, 100). Anal. Calcd for $C_{24}H_{19}P$: C, 85.20; H, 5.62; P, 9.18. Found: C, 85.64; H, 5.61; P, 8.48.

35b: ^1H NMR ($CDCl_3$) δ 4.87 ($^4J_{H_4H_2}$ = 0.9, $^3J_{H_4H_5}$ = 4.1, $^3J_{H_4H_7}$ = 1.8, $^3J_{H_4P}$ = 5.1 Hz, H_4) (H_2 and H_5 under phenyl groups), 4.01 ($^2J_{H_7P}$ = 8.3 Hz, H_7); ^{31}P NMR ($CDCl_3$) δ −7.58.

Registry No. 1, 55219-61-9; **2**, 87319-14-0; **3**, 87319-15-1; **4**, 87319-16-2; **5**, 288-01-7; **6**, 87319-17-3; **7**, 82476-30-0; **8**, 82476-27-5; **9**, 87319-18-4; **10**, 87392-50-5; **11**, 87319-19-5; **12**, 87319-20-8; **14**, 87319-35-5; **15**, 87319-21-9; **16**, 87319-22-0; **23**, 87391-90-0; **25**, 87319-23-1; **28**, 87319-24-2; **29**, 87319-25-3; **30**, 87319-26-4; **31**, 87319-27-5; **32a**, 87319-28-6; **32b**, 87319-32-2; **33a**, 87319-29-7; **33b**, 87319-33-3; **34a**, 87319-30-0; **34b**, 87319-34-4; **35a**, 87319-31-1; **35b**, 87391-91-1; $W(CO)_5$, 30395-19-8; S, 7704-34-9; EtC≡CEt, 928-49-4; PhC≡CH, 536-74-3; 2,3-dimethylbutadiene, 513-81-5; tolan, 501-65-5.

Palladium-Catalyzed Oxidation of Amino Alkenes to Cyclic Imines or Enamines and Amino Ketones

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Abstract: Amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ (n = 3, 4) are cyclized to pyrrolines or piperideines under "Wacker process" conditions. Amino alkenes with a secondary amino group yield the corresponding cyclic enamines, while tertiary amino alkenes give amino ketones.

Much work has been done on the palladium-promoted amination of alkenes.[1-7] The reaction proceeds through a trans attack of the amine at the coordinated double bond.[8] However, most of these reactions cannot be catalytic, as amines usually displace alkenes coordinated to palladium(II). Known exceptions are the catalytic cyclization of *o*-allylanilines[4] and olefinic tosamides.[5]

It is known that in water most palladium–alkene complexes decompose to palladium metal, HCl, and oxidized organic products (e.g., aldehydes or ketones).[9,10] Smidt and co-workers[10] found that the palladium metal formed can easily be reoxidized by air using, e.g., copper(II) as an oxidation transfer catalyst, thus making a continuous oxidation reaction of alkenes possible. It is now shown that "Wacker process" conditions[10] can be used for the catalytic cyclization of a wide range of amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ (n = 3, 4).

Results and Discussion

The Reaction. The addition of 1 equiv of pent-4-enylamine (**3**) to a weakly acidic solution of $PdCl_4^{2-}$ results in a slow precipitation of palladium metal, and 2-methyl-1-pyrroline (**4**) can be isolated from the reaction mixture. If the reaction is run under an oxygen atmosphere and some copper(II) is added, it can be made catalytic with regard to palladium and copper.

To investigate the scope of this reaction, a series of amino alkenes were allowed to react at 60 °C under nonoptimized standard conditions, i.e., $[PdCl_2]$ = 0.005 M, $[CuCl_2]$ = 0.01 M, [NaCl] = 0.1 M, and [HCl] = 0.2 M (see Table I). Except for the reaction with a 100-fold excess of pent-4-enylamine, all reactions were run with 20 equiv of aminoalkene/mol of palladium ([amino alkene] = 0.1 M).

Table I shows that primary amino alkenes of the type $CH_2{=}CH(CH_2)_nNH_2$ give cyclic imines, if n = 3 and 4. But-3-enylamine (**1**, n = 2) is only oxidized to aminobutan-3-one (**2**) and does not cyclize under these conditions. Aminobutan-3-one (**2**) was characterized by ^1H NMR in the reaction mixture as it polymerizes on the GC column.

In the acidic reaction mixture, *N*-methylpent-4-enylamine (**5**), a secondary amino alkene, yields the stable 1,2-dimethyl-1-pyrrolinium ion (**6**), which was characterized in situ by ^1H NMR and can be deprotonated to the corresponding unstable enamine **6b**,[11,12] which was characterized by reduction to 1,2-dimethylpyrrolidine (**6c**) with H_2/Pd/C. The oxidation of tertiary amino alkenes gives only the corresponding amino ketones. The product mixtures obtained from some of the reactions indicate that double-bond isomerization must have occurred before oxidation.

Double-Bond Isomerization. It is known, that palladium(II) is a very effective catalyst for isomerization of double bonds, particularly of terminal alkenes.[13] As can be seen in Table I,

(1) Stern, E. W.; Spector, M. L. *Proc. Chem. Soc.* **1961**, 370.
(2) Hirai, H.; Sawai, H.; Makishima, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1148.
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(10) Smidt, J.; Hafner, W.; Ira, R.; Sedlmeier, J.; Sieber, R.; Rüttiger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176.
(11) Lukeš, R.; Dědek, V.; Novotný, L. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1117.
(12) Leonard, N. J.; Gash, V. W. *J. Am. Chem. Soc.* **1954**, *76*, 2781.
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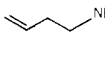
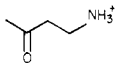
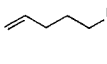
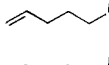
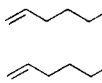
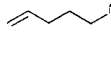
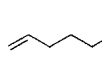
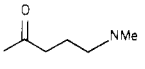
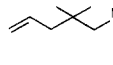
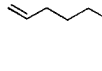
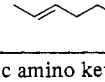
0002-7863/83/1505-6877$01.50/0

Table I. Yields of Main Products

mol of amino alkene/ mol of Pd	amino alkene	main products[a]	overall yield (%)	product ratio	reaction time (h)
20	1 	2 	80[b]		3
20	3 	4 	75[c]		6.5
100	3 	4 	70[c]		30
100	3 	4 	70[c]		20
20	5 	6 	80[b]		3.5
20	7 	8 	85[c]		6
20	9 	10 	40[c]		15[d]
20	11 	12  , 13 	75[c]	66:34	6
20	14 	12  , 13 	71[c]	66:34	6.5

[a] In most reactions isomeric amino ketones were formed as side products; see text. [b] Yield determined by ^{1}H NMR. [c] Yield determined by GLC. [d] 9 isomerizes to 2,2-dimethylpent-3-enylamine (15), which does not react under these conditions.

hex-5-enylamine (**11**) and (*E*)-hex-4-enylamine (**14**) both react to give mixtures of 2-methyl-1-piperideine (**12**) and 2-ethyl-1-pyrroline (**13**) in practically identical product ratios. This suggests that **11** and **14** isomerize to the same mixture of hexenylamines before a significant amount of oxidized product has been formed.

Except in the case of but-3-enylamine (**1**), where only one product can be detected at the end of the reaction, by-products due to double-bond isomerization are obtained with all other amino alkenes.

Thus, while pent-4-enylamine (**3**) gives 2-methyl-1-pyrroline (**4**) in about 75% yield, it also gives ca. 15% aminopentan-3-one (**15**) which does not cyclize. *N*-Methyl- and *N*,*N*-dimethylpent-4-enylamine (**5** and **7** respectively), in addition to **6** and **8**, also give *N*-methyl- and *N*,*N*-dimethylaminopentan-3-one (**16** and **17**, respectively).

Following the course of the reaction of 2,2-dimethylpent-4-enylamine (**9**) by GC, it was noticed that after a reaction time of about 30 min, no significant additional amount of 2,4,4-trimethyl-1-pyrroline (**10**) was formed. It could be shown by ^{1}H NMR that the unreacted part consists of 2,2-dimethylpent-3-enylamine (**18**). As external double bonds are more easily coordinated to metals and react faster than internal double bonds,[10,14] it is likely that, at the beginning of this reaction, 2,2-dimethylpent-4-enylamine (**9**), reacts to form both 2,4,4-trimethyl-1-pyrroline (**10**) and 2,2-dimethylpent-3-enylamine (**18**). As soon as all of **9** has been consumed, the reaction stops.

Similar observations were made in the case of pent-4-enylamine (**3**) and hex-5-enylamine (**11**), where the formation of the cyclic products is slowed down after a quick start, indicating that less reactive aminoalkenes with internal double bonds are formed at the beginning of the reaction.

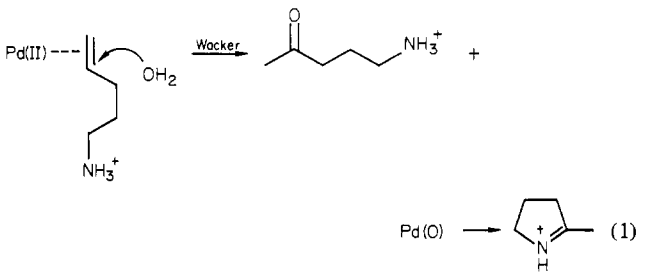
To gain further information about double-bond isomerization, standard reactions were carried out at 60 °C in D_2O with but-3-enylamine (**1**), pent-4-enylamine (**3**), *N*,*N*-dimethylpent-4-enylamine (**7**), hex-5-enylamine (**11**), and (*E*)-hex-4-enylamine (**14**); the reaction mixtures were monitored by ^{1}H NMR after 10 min. The products observed are given in Table II.

The distribution of the products obtained shows that external double bonds have a great tendency to isomerize to a thermodynamically more stable internal position. This is pointed out very clearly in the case of hex-5-enylamine (**11**) and pent-4-enylamine (**3**) where no starting material can be detected. On the other hand, the fact that 65% of but-3-enylamine (**1**), remains unreacted, and that only small amounts of compounds containing double bonds in position 2 are found in all cases, indicates that double-bond isomerization is strongly inhibited in proximity to an amino group. A comparison of *N*,*N*-dimethylpent-4-enylamine (**7**) with pent-4-enylamine (**3**) shows that double-bond isomerization is not significantly influenced by different types of amino groups.

Table II. Double-Bond Isomerization (after 10 Min Reaction Time)

	position of the double bond				
	5	4	3	2	1
but-3-enylamine (%)			65	13	–
pent-4-enylamine (%)		0	69	8	–
N,*N*-dimethyl-pent-4-enylamine (%)		0	64	7	–
hex-5-enylamine (%)	0	63	25	2	–
(*E*)-hex-4-enylamine (%)	0	58	21	4	–

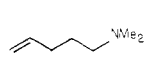
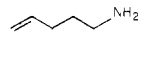
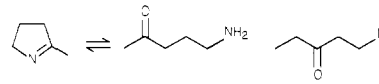
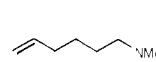
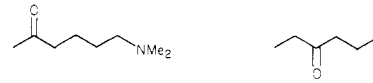
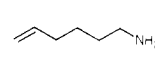
Reaction Pathway. Two fundamentally different pathways can be proposed for the reactions of amino alkenes to cyclic imines. The double bond of the amino alkene coordinated to palladium can either be attacked (a) by the solvent, e.g., OH^- or H_2O as known for the Wacker reaction,[10] where the amino alkene would be oxidized to the corresponding amino ketone, which subsequently condenses to a cyclic imine (eq 1), or (b) directly by the amino



group, which is similar to that described for the cyclization of *o*-allylanilines to indoles,[4] where a palladium–σ-alkyl complex is

(14) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1959.

Table III. Product Ratio in the Oxidation of Primary and Tertiary Amines

starting material	products	product ratio
		85:15[a]
		85:15[a]
		65:35[b]
		66:34[b]

[a] Determined by ^{1}H NMR. [b] Determined by GC.

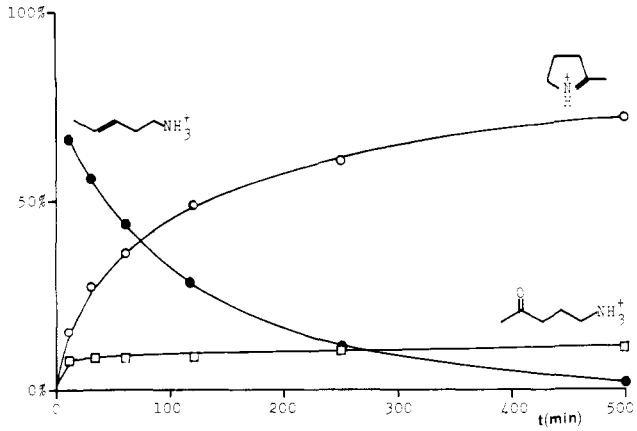


Figure 1. Product distribution during the Wacker oxidation of pent-4-enylamine (**3**) (because of fast double-bond isomerization, only internal double bonds can be detected after 10 min of reaction time).

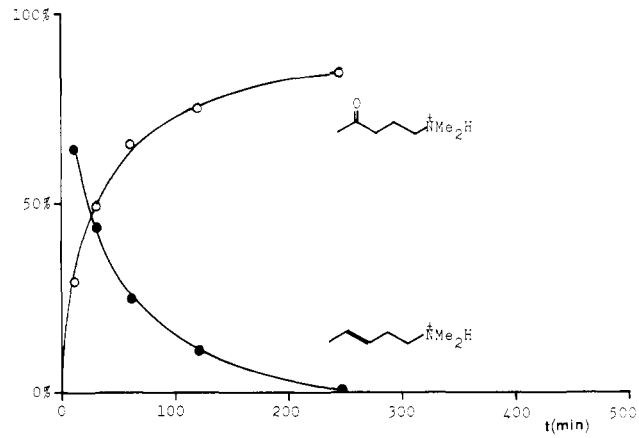
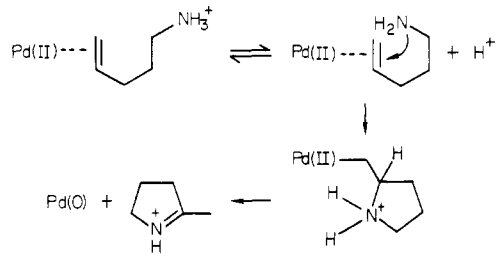


Figure 2. Product distribution during the Wacker oxidation of *N,N*-dimethylpent-4-enylamine (**7**) (because fast double-bond isomerization, only internal double bonds can be detected after 10 min of reaction time).

formed which, after β-hydrogen abstraction, decomposes to the cyclic imine or enamine and palladium metal (eq 2).



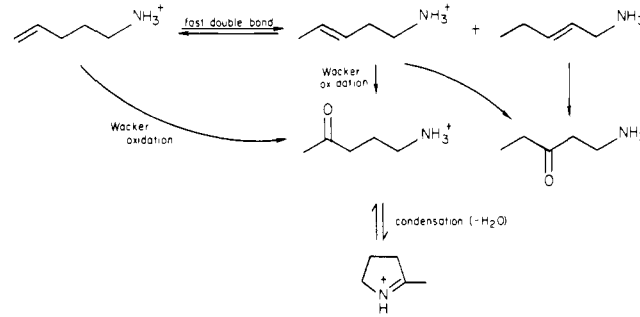
(2)

While amino ketones obtained from the reactions of but-3-enylamine (**1**) and tertiary amino alkenes can only result from a Wacker-type reaction, both pathways a and b are possible for primary and secondary amino alkenes. To obtain information as to whether primary amino alkenes also react through pathway a, the reactions of corresponding primary and tertiary amino alkenes were compared.

The course of the reaction of pent-4-enylamine (**3**) and *N,N*-dimethylpent-4-enylamine (**7**) was followed by ^{1}H NMR in a standard D_2O/DCl reaction mixture at 60 °C (see Figures 1 and 2). As can be seen, **3** and **7** behave in essentially the same way, except that the main product obtained from **3** is 2-methyl-1-pyrroline (**4**) while **7** gives only amino ketones.

A pure sample of **4**, when dissolved in 0.2 M DCl, hydrolyzes to aminopent-4-one (**19**) to an extent of about 10%. The presence of **19** in the reaction mixture (see Figure 1) cannot therefore serve as proof for pathway a. However, a comparison of the product ratios of corresponding primary and tertiary amino alkenes strongly indicates that primary amino alkenes react through pathway a as one would expect the pathways to differ in their regioselectivity. As can be seen in Table III, there are no essential differences in

Scheme I. The Reaction Pathway of Pent-4-enylamine in the Standard Aqueous Pd(II)/Cu(II) Reaction Mixture[a]



[a] Only negligible quantities of aldehydes could be detected by ^{1}H NMR at the end of the reaction.

the ratios of the main reaction products of *N,N*-dimethylpent-4-enylamine (**7**) and pent-4-enylamine (**3**), on one hand, and of *N,N*-dimethylhex-5-enylamine (**20**) and hex-5-enylamine (**11**), on the other. It is therefore likely that also primary amino alkenes are first oxidized to the corresponding amino ketones and subsequently condense to cyclic imines. Scheme I shows the proposed reaction pathway for pent-4-enylamine (**3**).

Although extensive studies have been carried out on the Wacker oxidation, the mechanism is still not completely clear.[7] Since it is known that this reaction is strongly inhibited or even stopped by strongly coordinating groups like amines,[7] the reactions were run in acidic solutions where most of the amino groups of the amino alkenes are protonated. The reaction is indeed strongly acid dependent. Its pH dependence is shown in Figure S1 (see supplementary material).

In the absence of acid, about 60% of the pent-4-enylamine (**3**) was consumed after 24 h, but only 17% 2-methyl-1-pyrroline (**4**)

could be detected. This indicates that, without acid, the reaction is very slow and that most of the pent-4-enylamine (**3**) is lost in side reactions.

With increasing amounts of acid added, the rate of the reaction increases and, after having reached a maximum, slowly drops. This rate increase is attributed to protonation of the amino group of pent-4-enylamine, which prevents the formation of inactive palladium–amino complexes. The rate decrease at high acid concentrations is also observed in the "Wacker" oxidation of ethylene.[7,15]

It has also been found[7,15] that the rate of the Wacker oxidation decreases with increasing chloride concentration. The same tendency was observed in the reaction of pent-4-enylamine (**3**) at various chloride concentrations (see Figure S2 in the supplementary material). Thus, to get a high turnover number, one should keep the chloride concentration low and protonate the amino alkene with a noncoordinating acid such as CF_3SO_3H. Thus, the reaction of 100 equiv of pent-4-enylamine in the standard reaction solution is accomplished after ca. 30 h at 60 °C if the pent-4-enylamine is added as the hydrochloric salt or after only ca. 20 h if it is protonated with CH_3SO_3H (see Table I).

Using standard reaction conditions the amount of copper(II) added to the reaction mixture was also varied. In the absence of copper, palladium metal immediately precipitated and the reaction proceeded very slowly. Within the tested range of [Cu(II)] = 0.005–0.03 M, no formation of palladium metal occurred and the rate of the reaction was not affected.

Experimental Section

Unless otherwise stated physical measurements and gas-chromatographic separations were carried out as previously described.[6,18] The ^1H NMR spectra were recorded on a Bruker 250-MHz spectrometer. The starting materials listed below were prepared as described in the references listed elsewhere:[16,17] but-3-enylamine (**1**), pent-4-enylamine (**3**), 2,2-dimethylpent-4-enylamine (**9**), hex-5-enylamine (**11**), (*E*)-hex-4-enylamine (**14**), *N*-methylpent-4-enylamine (**5**), *N*,*N*-dimethylpent-4-enylamine (**7**). *N*,*N*-Dimethylhex-5-enylamine (**20**) was prepared as described for **7**.

Standard Experimental Procedure for the Catalytic Oxidation Reaction of Amino Alkenes. The standard catalyst solution used had the following composition: $[PdCl_2]$ = 0.005 M; $[CuCl_2]$ = 0.01 M; [NaCl] = 0.1 M; [HCl] = 0.2 M. A 10-mL portion of the solution was vigorously stirred under oxygen and 1 mmol of aminoalkene (amino alkene:Pd = 20:1) was added. The solution was warmed up to 60 °C and stirring was continued for the length of time indicated in Table I. In some cases the reaction mixture did not remain completely homogeneous or some palladium metal formed; this, however, did not affect the yield.

The course of all reactions was followed by GC, except in the cases of but-3-enylamine (**1**) and N-methylpent-4-enylamine (**5**) where the ^1H NMR technique was used. Samples were taken from the reaction mixture and made alkaline with solid KOH; the organic products were extracted with diethyl ether. An internal standard (toluene or ethylbenzene) was then added to the organic phase which was analyzed by GC.

Larger scale reactions were carried out to obtain the pure products which were isolated by preparative gas chromatography. For this purpose the reaction mixture was made alkaline with KOH and extracted with several portions of diethyl ether. The organic phase was dried with solid KOH and the ether evaporated at 50 °C in a small distillation apparatus, fitted with a 20-cm Vigreux column. The residue was then worked up by preparative gas chromatography. The pure products were characterized by ^1H NMR and used as references for yield determination.

^1H NMR Experiment. Some products were characterized and some reactions were followed in situ by ^1H NMR, using standard reaction conditions, with D_2O and the same concentrations of $PdCl_2$, $CuCl_2 \cdot 2H_2O$, NaCl, and DCl. The reactions were run as described in the standard experimental procedure. Samples were taken from the reaction mixtures and cooled to room temperature; the ^1H NMR spectra were immediately measured. Most isolated products were measured in their cationic forms using D_2O solutions containing [DCl] = 0.2 M and [NaCl] = 0.1 M. In this way their spectra could be compared with those of the reaction mixture. In all D_2O spectra the H_2O peak was arbitrarily set at 4.67 ppm (δ(TSP) −0.165 ppm; TSP = 2,2,3,3-tetradeuterio-3-(trimethylsilyl)-propionic acid, sodium salt).

The spectra of $CDCl_3$ solutions were measured using $(CH_3)_4Si$ as reference.

Characterization of the Main Products and Byproducts of the Oxidation Reaction of Amino Alkenes. But-3-enylamine (1). Only aminobutan-3-one (**2**) could be detected at the end of the reaction. Since **2** polymerizes on the alkaline GC column, the latter was characterized by ^1H NMR in situ in the acidic deuterated reaction mixture. The yield was determined by ^1H NMR by adding a known amount of EtOH to the reaction mixture using the integral of the methyl group as reference.

2: ^1H NMR (deuterated reaction mixture) δ 2.08 (s, 3, CH_3), 2.84 (t, J = 6.4 Hz, 2, CH_2CO), 3.05 (br t, 2, CH_2N).

Pent-4-enylamine, (3) gave mainly 2-methyl-1-pyrroline (**4**) which was isolated by preparative GC. Its picrate was prepared and recrystallized from benzene. The yellow needles melt at 122 °C as described in the literature.[18] If pure 2-methyl-1-pyrroline (**4**) is added to a D_2O solution containing [DCl] = 0.2 M and [NaCl] = 0.1 M, the ^1H NMR measurement at ambient temperature shows a mixture of **4** and the open-chain aminopentan-4-one (**19**) in a ratio of about 9:1. Peak assignments for **19** were made by decoupling experiments and by comparison with the spectrum of isolated *N*,*N*-dimethylaminopentan-4-one (**8**). Aminopentan-3-one (**15**) is formed as a by-product in a yield of about 15%. Its ^1H NMR spectrum was measured in situ in the deuterated reaction mixture, and the assignment was made by decoupling experiments and comparison with the spectra of *N*,*N*-dimethylaminopentan-3-one (**17**) and isolated *N*,*N*-dimethylaminohexan-4-one (**22**).

4: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M]) δ 2.15 (p, J = 8.1 Hz, 2, CH_2), 2.34 (t, ^5J = 1.7 Hz, 3, CH_3), 3.00 (t of t, ^3J = 8.2 Hz, $^5J \simeq$ 2 Hz, 2, CH_2C=), 3.90 (t, of m, ^3J = 6.5 Hz, $^5J \simeq$ 2 Hz, 2, CH_2N).

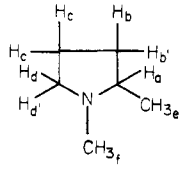
19: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 1.75 (p, J = 7.4 Hz, 2, CH_2), 2.08 (s, 3, CH_3), 2.59 (t, J = 7.1 Hz, 2, CH_2CO), 2.86 (t, J = 7.5 Hz, 2, CH_2N).

15: ^1H NMR (deuterated reaction mixture) δ 0.843 (t, J = 7.3 Hz, 3, CH_3), 2.41 (q, J = 7.3 Hz, 2, CH_3CH_2), 2.81 (t, 2, $COCH_2$), 3.06 (t, 2, CH_2N).

***N*-Methylpent-4-enylamine (5).** The reaction product was characterized as the 1,2-dimethyl-1-pyrrolinium ion **6a** by ^1H NMR in the acidic reaction mixture. The yield was determined as described for aminobutan-3-one (**2**), since the deprotonated form of **6a**, 1,2-dimethyl-pyrroline (**6b**), is relatively unstable and gives irreproducible results when analytically determined by GC. It can, however, be worked up with loss by preparative GC. A sample of **6b**, reduced with H_2/Pd/C in THF, gave exclusively one product, which was identical with 1,2-dimethylpyrrolidine (**6c**) as shown by comparison with an original sample prepared as described elsewhere.

6a: ^1H (deuterated reaction mixture) δ 2.03 (p, J = 7.9 Hz, 2, CH_2), 2.23 (s, 3, CH_3), 3.03 (t, J = 7.9 Hz, 2, CH_2C=), 3.26 (s, 3, CH_3N), 3.99 (t, J = 7.6 Hz, 2, CH_2N). At the end of the reaction a triplet at 0.85 ppm and a quartet at 2.42 ppm were observed in the reaction mixture, indicating that *N*-methylaminopentan-3-one (**16**) is formed as a by-product.

6c: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 1.22 (d, J



6c

= 6.4 Hz, 3 H_e), 1.44 – 1.64 (m, H_b), 2.04 – 2.25 (m, $H_{b'}$), 1.7 – 2 (m, 2 H_c), 2.71 (s, 3 H_f), 2.85 – 3.02 (m, H_d), 3.42 – 3.57 (m, $H_{d'}$), 3.20 (m, $J \simeq$ 6.7 Hz, H_a).

***N*,*N*-Dimethylpent-4-enylamine (7)** gave mainly *N*,*N*-dimethylaminopentan-4-one (**8**) as the reaction product which was isolated by preparative GC and characterized by ^1H NMR. The ^1H NMR spectra of the deuterated reaction mixture at the end of the reaction showed also the presence of small amounts of *N*,*N*-dimethylaminopentan-3-one (**17**) as indicated by the following signals, which are partly concealed by the signals of the main product **8**.

8: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 1.75 (p, J = 7.9 Hz, 2, CH_2), 2.03 (s, 3, CH_3), 2.53 (t, J = 6.8 Hz, 2, CH_2CO),

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2.71 (s, 6, $(CH_3)_2N$), 2.94 (t, J = 8.1 Hz, 2, CH_2N).

17: ^1H NMR (deuterated reaction mixture) δ 0.84 (t, J = 7.3 Hz, CH_3), 2.42 (q, CH_2CH_3), 2.84 (t, CH_2CO), ~3.0 (t, CH_2N).

2,2-Dimethylpent-4-enylamine (9). The course of the reaction of **9** was followed by GC. After ~30 min. the reaction stopped and no further change could be observed by GC up to 12 h reaction time. The products were worked up by preparative gas chromatography and characterized by ^1H NMR; 2,4,4-trimethyl-1-pyrroline (**10**) and isomerized **9**, 2,2-dimethylpent-3-enylamine (**18**), which was practically the same retention time as **9**, were obtained.

10: ^1H NMR ($CDCl_3$) δ 1.09 (s, 6, $C(CH_3)_2$), 1.99 (t, ^5J = 1.9 Hz, 3, CH_3), 2.31 (s, 2, CH_2), 3.51 (m, ^5J = 1.7 Hz, 2, CH_2N).

18: ^1H NMR ($CDCl_3$) δ 0.95 (s, 6, $C(CH_3)_2$), 1.69 (d, J = 4.7 Hz, 3, CH_3), 2.44 (s, 2, CH_2), 5.25–5.5 (m, 2, HC=CH).

Hex-5-enylamine (11) and (*E*)-Hex-4-enylamine (14). Both amino alkenes react to a mixture of 2-methyl-1-piperideine (**12**) and 2-ethyl-1-pyrroline (**13**). Both products were isolated by preparative GC and characterized by ^1H NMR. The assignment was made by decoupling experiments.

12: ^1H NMR ($CDCl_3$) δ 1.55 (m, J = 6 Hz, 2, CH_2CH_2N), 1.66 (m, J = 6 Hz, 2, CH_2CH_2C=), 1.90 (t, ^5J = 1.7 Hz, 3, CH_3) 2.12 (t of t, ^3J = 6.5 Hz, ^5J = 1.7 Hz, 2, CH_2C=), 3.53 (t of m, ^3J = 4.7 Hz, $^5J \simeq$ 1.7 Hz, 2, CH_2N).

13: ^1H NMR ($CDCl_3$) δ 1.16 (t, J = 7.3 Hz, 3, CH_3), 1.86 (p, J = 7.7 Hz, 2, CH_2CH_2N), 2.35 (q, J = 7.5 Hz, 2, CH_2CH_3), 2.47 (t, J = 8.2 Hz, 2, CH_2C=), 3.80 (t of m, ^3J = 7.3 Hz, ^5J = 1.7 Hz, 2, CH_2N).

***N,N*-Dimethylhex-5-enylamine (20)** gave a mixture of mainly *N,N*-dimethylaminohexan-5-one (**21**) and *N,N*-dimethylaminohexan-4-one (**22**) after complete reaction. Both products were isolated by preparative GC.

21: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 1.3–1.45 (m, 2, CH_2CH_2CO), 1.45–1.6 (m, 2, CH_2CH_2N), 2.01 (s, 3, CH_3), 2.46 (t, J = 6.8 Hz, 2, CH_2C=O), 2.68 (s, 6, $N(CH_3)_2$), 2.95 (t, J = 7.7 Hz, 2, CH_2N).

22: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 0.83 (t, J = 7.3 Hz, 3, CH_3), 1.77 (p, J = 8.1 Hz, 2, CH_2CH_2N), 2.38 (q, J = 7.3 Hz, 2, CH_2CH_3), 2.51 (t, J = 7 Hz, 2, CH_2C=O), 2.72 (s, 6, $N(CH_3)_2$), 2.95 (t, J = 8.2 Hz, 2, CH_2N).

Examination of Double-Bond Isomerization. Double-bond isomerization was investigated in D_2O using standard reaction conditions described earlier. The reaction was stopped after 10 min; the solution was cooled to room temperature and immediately examined by ^1H NMR. The quantities of products were determined using the integral of the spectrum of the reaction mixture. Some isomeric amino alkenes were isolated by preparative GC, and their ^1H NMR spectra were used for the determination of the composition of the deuterated reaction mixtures.

But-3-enylamine (1). But-2-enylamine (**23**) was characterized in situ in the deuterated reaction mixture by decoupling experiments.

23: ^1H NMR (deuterated reaction mixture) δ 1.52, (d, J = 6.4 Hz, 3 CH_3), 3.33 (d, J = 6.5 Hz, 2, CH_2), 5.2–5.9 (m, HC=CH).

Pent-4-enylamine (3). No **3** could be detected after a reaction time of 10 min; the main part had isomerized to pent-3-enylamine (**24**) and traces of pent-2-enylamine (**25**). Both isomers were characterized in the reaction mixture by decoupling experiments and by comparison with the ^1H NMR spectra of isolated *N,N*-dimethylpent-3-enylamine (**26**) and isolated *N,N*-dimethylpent-2-enylamine (**27**).

24: ^1H NMR (deuterated reaction mixture) δ 1.48 (d, J = 6.9 Hz, 3, CH_3), 2.16 (m, J = 6.9 Hz, 2, CH_2C=), 2.84 (t, J = 6.5 Hz, 2, CH_2N), 5.17–5.30 (m, 1, =$CH$$CH_2$), 5.40–5.65 (m, 1, CH_3CH=).

25: ^1H NMR (deuterated reaction mixture) δ 0.79 (t, J = 7.3 Hz, 3, CH_3), 1.92 (m, CH_2CH_3), 3.35 (d, $J \simeq$ 6 Hz, 2, CH_2N). The olefinic protons are hidden by the signals of **24**.

***N,N*-Dimethylpent-4-enylamine (7).** Pure *N,N*-dimethylpent-3-enylamine (**26**) and traces of *N,N*-dimethylpent-2-enylamine (**27**) were isolated by preparative GC.

26: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 1.48 (d, J = 5.8 Hz, 3, CH_3), 2.24 (m, J = 7.1 Hz, 2, CH_2C=), 2.67 (s, 6, $N(CH_3)_2$), 2.99 (t, J = 7.1 Hz, 2, CH_2N), 5.15–5.27 (m, 1, =$CH$$CH_2$), 5.45–5.64 (m, 1, CH_3CH=). It could be shown by decoupling technique that the coupling constant of the olefinic protons is 15.5 Hz, indicating that the double bond of **26** has *E* configuration.

27: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 0.794 (t, J = 7.5 Hz, 3, CH_3), 1.93 (p, J = 7.1 Hz, 2, CH_2CH_3), 2.62 (s, 6, $N(CH_3)_2$), 3.47 (d, J = 7.3 Hz, 2, CH_2N), 5.29–5.41 (m, 1, =$CH$$CH_2N$), 5.87–5.98 (m, 1, CH_3CH_2CH=). The coupling between the olefinic protons is 15.4 Hz, indicating *E* configuration.

Hex-5-enylamine (11) and (*E*)-hex-4-enylamine (14). Both amino alkenes gave mixtures of hex-4-enylamine (**14′**) and hex-3-enylamine (**28**). Both isomers were isolated by preparative GC.

14: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1) δ 1.47 (d, J = 5.6 Hz, 3, CH_3), 1.55 (p, J = 7.3 Hz, 2, $CH_2CH_2CH_2$), 1.92 (q, $J \simeq$ 7 Hz, 2, CH_2C=), 2.82 (t, J = 7.7 Hz, 2, CH_2N), 5.2–5.5 (m, 2, CH=CH). This spectrum is identical with the spectrum of (*E*)-hex-4-enylamine (**14**).

28: ^1H NMR (D_2O, [DCl] = 0.2 M, [NaCl] = 0.1 M) δ 0.871 (t, J = 7.5 Hz, 3, CH_3), 1.85 (p, J = 7.1 Hz, 2, CH_2CH_3), 2.18 (q, J = 7 Hz, 2, CH_2CH_2N), 2.85 (t, J = 6.9 Hz, 2, CH_2N), 5.16–5.29 (m, 1, =CH–), 5.50–5.63 (m, 1, CH_3CH_2CH=). the J value for the olefinic protons is 15.4 Hz indicating an *E* configuration. A weak doublet at 3.37 ppm could be detected in the deuterated reaction mixture. This is characteristic for a CH_2 group between an amino group and double bonds (see ^1H NMR spectra of **27** and **23**). It indicates that also traces of hex-2-enylamine are formed.

Registry No. 1, 2524-49-4; **2**, 87156-63-6; **3**, 22537-07-1; **3**·HCl, 27546-60-7; **3**·CH_3SO_3H, 87156-64-7; **4**, 872-32-2; **4**·picrate, 962-77-6; **5**, 5831-72-1; **6a**, 87156-65-8; **6b**, 5370-57-0; **6c**, 765-48-0; **7**, 1001-91-8; **8**, 43018-61-7; **9**, 73604-46-3; **10**, 2045-75-2; **11**, 34825-70-2; **12**, 1462-92-6; **13**, 1192-29-6; (*E*)-**14**, 55108-01-5; **15**, 87156-66-9; **16**, 87156-67-0; **17**, 22104-65-0; **18**, 87156-68-1; **19**, 3732-10-3; **20**, 52254-56-5; **21**, 4305-31-1; **22**, 87156-69-2; **23**, 21035-54-1; **24**, 87156-70-5; **25**, 87156-71-6; (*E*)-**26**, 87156-72-7; (*E*)-**27**, 87156-73-8; (*E*)-**28**, 87156-74-9; $PdCl_2$, 7647-10-1; $CuCl_2$, 7447-39-4.

Supplementary Material Available: Figure S1, pH dependence of rate of formation of **4**, and Figure S2, Cl dependence of rate of formation of **4** (2 pages). Ordering information is given on any current masthead page.