Cathodic Reduction of 1-Nitroalkenes[1] to Oximes and Primary Amines

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1-Nitroalkenes are reduced in high yields at −0.3 to −0.5 V (vs. SCE) at a mercury or graphite cathode to oximes. At higher cathodic reduction potentials (−1.1 V) primary amines are selectively obtained in fair yields. Nitroalkadienes are selectively reduced at the double bond conjugated with the nitro group to either the oxime or amine.

The double bond of 1-nitroalkenes can react as a Michael acceptor in Michael additions[2,3] or as a dienophile in Diels-Alder reactions[2,4]. The nitro group has been reduced both chemically and electrochemically. 1-Nitroalkenes with aromatic or heterocyclic substituents at C-2 afford upon treatment with iron/hydrochloric acid[5a], sodium hypophosphite/Raney nickel[5b], chromium(II)chloride, 3% hydrochloric acid[5c], or lithium tris-*sec*-butylhydridoboranate and subsequent acidic workup[5d] ketones or aldehydes in 35–92% yield. The corresponding oximes are obtained by reduction with sodium hypophosphite/palladium-charcoal[6a], chromium(II) chloride[6], sodium stannite[6c], tin(II)chloride[6d], lead[6e] or hydrogen palladium on charcoal[6f] in 15–95% yield. 2-Aryl-substituted 1-nitroalkenes have been electrochemically reduced selectively to either ketones or oximes at the lead cathode[7a] or, more unselectively, to mixtures of oximes and ketones at the platinum cathode[7b], and to nitriles[7c].

Results

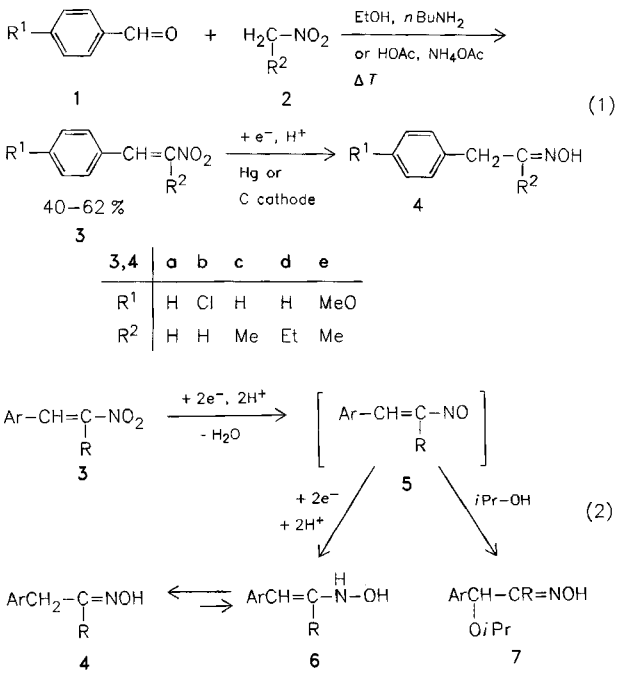
The 1-nitro-2-arylalkenes **3** are prepared by condensation of aldehydes **1** with nitroalkanes **2**[5a,8] (eq. 1). They exhibit reduction potentials between −0.17 and −0.33 V vs. SCE (Table 1). A second more cathodic reduction potential appears at −1.1 V (for **3a**), which can be attributed to the reduction of the oxime **4** to the amine **14**[9], as the oxime **4a** shows a reduction potential at −1.02 V.

The reduction of **3** at a mercury pool cathode in a divided cell in 0.1 M H_2SO_4 in 2-propanol/water(3:2, v/v) affords oximes **4** (eq. 1, Table 2). Compound **3** is probably first reduced to the 1-nitrosoalkene **5** and this subsequently to the 1-(hydroxylamino)alkene **6**, which tautomerizes to **4** (eq. 2)

Table 1. Reduction potentials of different 1-nitroalkenes

1-Nitroalkene	**3b**	**3a**	**3e**	**3d**	**3c**
$-E_{p,c}$[a] (V, SCE)	0.17	0.19	0.30	0.315	0.33
1-Nitroalkene	**12a**		**12b**		
$-E_{p,c}$[a] (V, SCE)	0.375		0.458		

[a] Cyclovoltammetry; cathode: amalgamated gold wire, scan rate: 0.1 Vs^{-1}, concentration of **3** or **12**: $1 \cdot 10^{-3}$ mol l^{-1}, electrolyte: 0.1 M H_2SO_4 in 2-propanol/water (3:2, v/v).



(1)

(2)

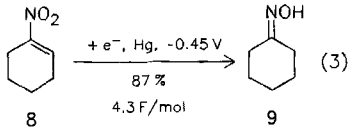
Table 2. Cathodic reduction of 1-nitroalkenes **3** to oximes **4**

3	**4**	Yield (%)[a]
a	**a**	85
b	**b**	85 (76 [44])[b]
c	**c**	91 (85 [77])[b]
d	**d**	92
e	**e**	91[c]

[a] Isolated yield, purity >98% determined by GLC, current yield corresponds to 95–100% of isolated yield. — [b] Reduction at a graphite cathode, otherwise the conditions are identical to those at the mercury cathode; numbers in brackets: current yield at graphite cathode. — [c] Contains 4% 1-isopropoxy-1-(4-methoxyphenyl)-acetone oxime determined by GLC.

The intermediate formation of **5** is supported by the formation of side product **7**, an adduct of 2-propanol to **5**. Its formation may be suppressed to as little as 4% by increasing the current density, that means by decreasing the lifetime of

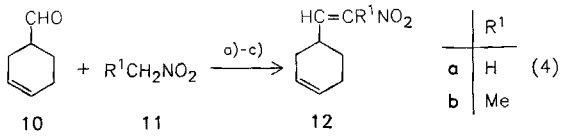
5. The oxime **4** hydrolyzes to a small extent to the corresponding ketone in the course of the electrolysis. Therefore, the electrolyte is treated with hydroxylammonium chloride before workup to reconvert the ketone into the oxime. Similarly the commercially available 1-nitro-1-cyclohexene (**8**) is reduced to the oxime **9** in 87% yield (eq. 3). The reductions can be performed also at an untoxic graphite cathode in slightly lower yields (Table 2) and decreased current yields due to a higher hydrogen evolution.



(3)

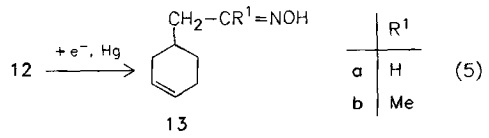
To demonstrate the chemoselective reduction of the double bond conjugated with the nitro group the nitroalkadienes **12** are prepared by addition of the nitroalkane **11** to the aldehyde **10** and subsequent acylation as decribed in ref.[10]. Elimination of acetic acid[11] followed by column chromatography affords **12** (eq. 4, Table 3).

Compound **12** is reduced in a divided cell at a mercury pool cathode in 0.1 M H_2SO_4 2-isopropanol/water (3:2, v/v) at controlled potential (−0.5 V for **12a**, −0.55 V for **12b**). After consumption of 4.27 (**12a**) or 4.02 F/mol (**12b**) the electrolyte is treated with hydroxylammonium chloride to reconvert partially hydrolyzed oximes. After workup **13** is obtained (Table 3, eq. 5).



(4)

a) KF, *i*PrOH, rt.–b) DMAP, Ac_2O, Et_2O, rt.–c) NaOAc, EtOAc, rt, flash chromatography.
(rt = room temperature)



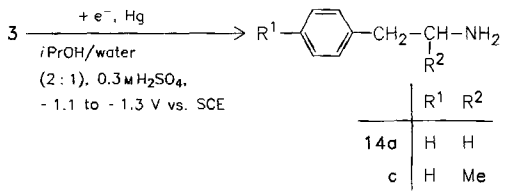
(5)

Table 3. Preparation of nitroalkadienes **12** and their reduction to **13**

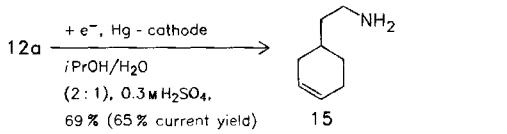
Preparation of **12**	Yield (%)	Reduction of **12** to **13**	Yield (%)[a]
a	76	**a**	88
b	62	**b**	93

[a] Isolated yield, purity >98% by GLC, current yield corresponds to 95–100% of isolated yield.

The reduction of **3** to the corresponding amines **14** is not complete due to an increasingly competing hydrogen evolution at the cathode with the progress of the electrolysis. This seems to be ascribed to the presence of hydroxylamine originating from the hydrolysis of the intermediate oxime, which decreases the hydrogen overvoltage at the cathode[12]. This leads to recovered **3**, the formation of **4** and the corresponding ketone as well as only fair yields of the amine **14** (eq. 6, Table 4).



(6)



(7)

Table 4. Reduction of 1-nitroalkenes **3** to primary alkylamines **14**

1-Nitroalkene	Alkylamine[a]	Yield (%)
3a	**14a**	66
3c	**14c**	60

[a] Reduction in a divided cell at a Hg-pool cathode at 10 to 15°C in 0.3 M H_2SO_4 in 2-propanol/water (2:1, v/v).

The chemoselectivity of this reduction has been demonstrated by the conversion of nitroalkadiene **12a** (eq. 7) into **15**, the unconjugated double bond being unaffected.

In conclusion, the present work demonstrates that 1-nitroalkenes may be converted into oximes electrochemically in high yield. The scope and selectivity of this process are larger than in earlier cathodic reductions of 1-nitroalkenes[7a,b]. Furthermore, mercury as cathode material can be replaced by graphite as shown in two cases with nearly the same product yield and a somewhat lower current yield, due to higher competing hydrogen evolution. At higher negative reduction potentials the 1-nitroalkenes are reduced to the corresponding amines. Here the conversion is incomplete and the yield of amine is only fair, due to an increasing hydrogen evolution in the course of the electrolysis. The chemoselectivity has been demonstrated by the reduction of nitroalkadienes to the oximes or amines, whereby only the conjugated double bond is reduced whilst the other remains unaffected.

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Experimental

Melting points (uncorrected): Kofler hot-stage. – Refractive indices: Zeiss refractometer. – IR: Perkin-Elmer 421, Shimadzu IR-408. – ^1H, ^{13}C NMR: Bruker WM 300, TMS for ^1H and $CDCl_3$ for ^{13}C NMR as internal standard. – MS: Varian MAT CH7A, data system SS 200, 70 eV. – Elementary analyses: Mikroanalytisches Laboratorium M. Beller, Göttingen. – GLC: Shimadzu GC-14A with integrator C-R3A, quartz capillary column 0.32 mm × 50 m, 0.25 µm SE 54 (Macherey & Nagel). – Flash

chromatography[13]: Silica gel 60 (Merck). – HPLC: Knauer 64 system, Knauer 51.78 differential refractometer, 250 mm × 8 mm Nucleosil 100-3 column (Knauer). – Electrolysis: Divided standard beaker-type cell (150 ml), cathode: mercury pool (19.5 cm^2) or graphite P 127 (9 cm^2, Sigri), anode: platinum foil (2 cm^2), reference electrode: SCE, Luggin capillary, diaphragm: glass frit (G4), current source: Wenking HP 88 (Bank Electronic).

Compounds **3a–e** were prepared according to known procedures[5a,8]. Commercially available samples (Aldrich) of 1-nitro-1-cyclohexene (**8**), 1,2,3,6-tetrahydrobenzaldehyde (**10**), and nitroalkanes **11a,b** were redistilled prior to use.

(E)-1-(3-Cyclohexen-1-yl)-2-nitroethene (**12a**): To a stirred solution of 5.51 g (50 mmol) of aldehyde **10** and 6.10 g (100 mmol) of nitromethane (**11a**) in 50 ml of 2-propanol was added 0.18 g (3 mmol) of potassium fluoride. After 20 h at room temp. the solvent was evaporated at aspirator pressure. The crude nitro alcohol[14] was dissolved in 90 ml of ether followed by addition of 6.70 g (65 mmol) of acetic anhydride and 0.30 g (2.5 mmol) of DMAP. After stirring at room temp. for 20 h the ether was evaporated and replaced by 130 ml of ethyl acetate. 10 g (120 mmol) of sodium acetate was added and stirring continued for further 12 h. Then solid material was removed by filtration and the filtrate concentrated to give an oily residue which was dissolved in ether. The solution was washed with water. After drying (magnesium sulfate) the solvent was evaporated to give 7.40 g of crude nitroalkene **12a** which was purified by flash chromatography [petroleum ether/ether (30:1)] to yield 5.83 g (76%) of **12a**[15] as a slightly yellow liquid. n_D^{20} = 1.5200. – IR (film): $\tilde{\nu}$ = 3030 cm^{-1} (=CH), 2920, 2840 (CH), 1640 (C=C), 1520, 1350 (NO_2). – ^1H NMR ($CDCl_3$): δ = 1.47–1.63 (m, 1H, ring H), 1.82–2.07 (m, 2H, ring H), 2.08–2.30 (m, 3H, ring H), 2.50–2.66 (m, 1H, C*H*–CH=C), 5.62–5.80 (m, 2H, ring HC=CH), 6.99 (dd, *J* = 13.5, allylic *J* = 1.3 Hz, 1H, CHCH=C*H*NO_2 (dd, *J* = 13.5, 7.5 Hz, 1H, CHC*H*=CHNO_2). – ^{13}C NMR ($CDCl_3$): δ = 23.70, 26.89, 29.43 (3 t, CH_2), 33.15 (d, CH), 124.23, 126.74 (2 d, ring H*C*=*C*H), 138.46 (d, H*C*=CHNO_2), 145.99 (d, HC=*C*HNO_2). – MS: *m/z* (%) = 153 (9) [M^+], 107 (24), 91 (28), 79 (79), 54 (100), 41 (38).

$C_8H_{11}NO_2$ (153.2)
Calcd. C 62.73 H 7.24 N 9.14
Found C 62.61 H 7.31 N 9.18

(E)-1-(3-Cyclohexen-1-yl)-2-nitro-1-propene (**12b**) was obtained by analogy with **12a** in 62% yield as a yellow liquid. n_D^{20} = 1.5155. – IR (film): $\tilde{\nu}$ = 3035 cm^{-1} (=CH), 2930, 2850 (CH), 1680, 1660 (C=C), 1525, 1335 (NO_2). – ^1H NMR ($CDCl_3$): δ = 1.48 to 1.64 (m, 1H, ring H), 1.72–1.84 (m, 1H, ring H), 1.89–2.04 (m, 1H, ring H), 2.08–2.28 (m, 3H, ring H), 2.20 (s, 3H, CH_3), 2.50–2.65 (m, 1H, C*H*–CH=CNO_2), 5.63–5.82 (m, 2H, HC=CH), 7.05 (d, *J* = 10.2 Hz, 1H, HC=CNO_2). – ^{13}C NMR ($CDCl_3$): δ = 12.39 (q, CH_3), 23.69, 27.39, 29.90 (3 t, CH_2), 33.19 (d, CH), 124.55, 126.70 (2 d, HC=CH), 139.80 (d, H*C*=CNO_2), 146.68 (s, HC=*C*NO_2). – MS: *m/z* (%) = 167 (1) [M^+], 79 (15), 67 (17), 55 (21), 54 (100), 41 (30).

$C_9H_{13}NO_2$ (167.2)
Calcd. C 64.65 H 7.84 N 8.38
Found C 65.54 H 7.88 N 8.37

General Procedure for the Reduction of 1-Nitroalkenes to Oximes: The cathodic compartment of the cell was charged with 30 ml of 0.1 M sulfuric acid in 2-propanol/water (3:2, v/v), subsequently by 3 mmol of substrate. Then the anodic chamber was filled with 8 ml of supporting electrolyte and introduced into the catholyte properly in order to minimize the space between the electrodes. With stirring and cooling (10 to 15°C) controlled potential electrolysis was carried out at −0.25 to −0.55 V (SCE), depending on the substrate (for the graphite cathode the potentials were about 400 mV more cathodic). After 4.0–4.2 F · mol^{-1} had been consumed (i < 10 mA) the catholyte was treated with 10 mmol of hydroxylammonium chloride in 25 ml of water and with satd. sodium hydrogencarbonate until the pH was approximately 5. After 1 h of stirring, 100 ml of water was added and the solution extracted with three portions of ether. The combined organic phases were washed with satd. aqueous NaCl and water, dried ($MgSO_4$), and concentrated to afford essentially pure oximes. Final column chromatographic purification [petroleum ether/ether (4:1 to 2:1)] afforded the oximes in yields according to Tables 2, 3 and eq. (3).

Phenylacetaldehyde Oxime (**4a**)[6b]: IR (KBr): $\tilde{\nu}$ = 3550, 3400 cm^{-1} (OH), 1630 (C=N). – ^1H NMR ($CDCl_3$): δ = 3.54, 3.75 (2 d, *J* = 6.3, 5.3 Hz, 2H, *E*-, *Z*-CH_2), 6.90, 7.55 (2 t, *J* = 5.3, 6.3 Hz, 1H, *Z*-, *E*-CH=N), 7.2–7.4 (m, 5H, aromatic H). – MS (70 eV): *m/z* (%) = 135 (31) [M^+], 118 (33), 117 (91), 91 (100), 90 (59), 65 (32).

C_8H_9NO (135.2)
Calcd. C 71.09 H 6.71 N 10.36
Found C 71.15 H 6.74 N 10.25

(4-Chlorophenyl)acetaldehyde Oxime (**4b**)[7b]: IR (KBr): $\tilde{\nu}$ = 3500–3200 cm^{-1} (OH), 1650 (C=N). – ^1H NMR ($CDCl_3$): δ = 3.51, 3.71 (2 d, *J* = 6.2, 5.4 Hz, 2H, *E*-, *Z*-CH_2), 6.85, 7.51 (2 t, *J* = 5.4, 6.2 Hz, 1H, *Z*-, *E*-CH=N), 7.12–7.19, 7.25–7.32 (2 m, 4H, aromatic H). – MS: *m/z* (%) = 169 (45) [M^+], 151 (73), 125 (86), 116 (100), 89 (72), 40 (79).

C_8H_8ClNO (169.6)
Calcd. C 56.65 H 4.75 Cl 20.90 N 8.26
Found C 56.83 H 4.73 Cl 21.09 N 8.25

Phenylacetone Oxime (**4c**)[6b]: IR (film): $\tilde{\nu}$ = 3500–3100 cm^{-1} (OH), 1660 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.80, 1.82 (2 s, 3H, *E*-, *Z*-CH_3), 3.50, 3.75 (2 s, 2H, *Z*-, *E*-CH_2), 7.2–7.4 (m, 5H, aromatic H). – MS: *m/z* (%) = 149 (80) [M^+], 131 (27), 117 (27), 116 (46), 91 (100), 65 (26).

$C_9H_{11}NO$ (149.2)
Calcd. C 72.46 H 7.43 N 9.39
Found C 72.27 H 7.31 N 9.29

1-Phenyl-2-butanone Oxime (**4d**)[7b]: IR (film): $\tilde{\nu}$ = 3500 to 3150 cm^{-1} (OH), 1665 (C=N). – ^1H NMR ($CDCl_3$): δ = 1.00, 1.06 (2 t, *J* = 7.65, 7.4 Hz, 3H, *Z*-, *E*-CH_2CH_3), 2.18, 2.32 (2 q, *J* = 7.4, 7.65 Hz, 2H, *E*-, *Z*-CH_2CH_3), 3.51, 3.76 (2 s, 2H, *Z*-, *E*-CH_2C=N), 7.18–7.40 (m, 5H, aromatic H). – MS: *m/z* (%) = 163 (12) [M^+], 117 (74), 92 (32), 91 (100), 72 (33), 65 (43).

$C_{10}H_{13}NO$ (163.2)
Calcd. C 73.59 H 8.03 N 8.58
Found C 73.52 H 8.07 N 8.61

(4-Methoxyphenyl)acetone Oxime (**4e**)[7b]: IR (film): $\tilde{\nu}$ = 3400 to 3200 cm^{-1} (OH), 1665 (C=N). – ^1H NMR ($CDCl_3$): δ = 1.81, 1.82 (2 s, 3H, *E*-, *Z*-CH_3), 3.45, 3.69 (2 s, 2H, *Z*-, *E*-CH_2), 3.81 (s, 3H, OCH_3), 6.8–6.9, 7.1–7.2 (2 m, 4H, aromatic H). – MS: *m/z* (%) = 179 (26) [M^+], 146 (30), 122 (38), 121 (100), 77 (34), 42 (34).

$C_{10}H_{13}NO_2$ (179.2)
Calcd. C 67.02 H 7.31 N 7.82
Found C 67.16 H 7.37 N 7.70

Cyclohexanone Oxime (**9**): M.p. 88–90°C (ref.[16] 90°C).

3-Cyclohexen-1-ylacetaldehyde Oxime (**13a**)[17]: IR (film): $\tilde{\nu}$ = 3500–3200 cm^{-1} (OH), 1660 (C=N). – ^1H NMR ($CDCl_3$): δ = 1.2–1.4, 1.7–1.9, 2.02–2.15 (3 m, 7H, ring H), 2.18, 2.38 (2 t, *J* = 6.5, 5.5 Hz, 2H, *E*-, *Z*-CH_2CH=N), 5.6–5.75 (m, 2H, HC=CH),

6.79, 7.46 (2 t, J = 5.5, 6.5 Hz, 2H, *Z*-, *E*-CH=N). – MS: *m/z* (%) = 139 (5), [M$^+$], 81 (40), 80 (77), 79 (55), 77 (55), 59 (100).

$C_8H_{13}NO$ (139.2)
Calcd. C 69.03 H 9.41 N 10.06
Found C 69.11 H 9.39 N 10.01

3-Cyclohexen-1-ylacetone Oxime (**13b**): IR (film): $\tilde{\nu}$ = 3400 to 3200 cm^{-1} (OH), 1660 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 1.15–1.38, 1.6–2.1 (2 m, 7H, ring H), 1.86, 1.87 (2 s, 3H, *E*-, *Z*-CH_3), 2.12, 2.34 (2 d, J = 7.3 Hz, 2H, *Z*-, *E*-CH_2C=N), 5.56–5.72 (m, 2H, HC=CH). – ^{13}C NMR ($CDCl_3$): δ = 13.56, 20.50 (2 q, *E*-, *Z*-CH_3), 24.85, 25.03, 28.40, 28.83, 31.42, 31.67 (6 t, *E*-, *Z*-CH_2CH=$CHCH_2CH_2$), 30.95, 31.00 (2 d, *E*-, *Z*-CH), 35.29, 42.34 (2 t, *Z*-, *E*-CH_2C=N), 125.99, 126.07, 126.68, 126.79 (4 d, *E*-, *Z*-HC=CH), 157.38, 157.68 (2 s, *E*-, *Z*-C=N). – MS: *m/z* (%) = 153 (9) [M$^+$], 79 (44), 74 (52), 73 (100), 42 (26), 41 (39).

$C_9H_{15}NO$ (153.2)
Calcd. C 70.55 H 9.87 N 9.14
Found C 70.70 H 9.97 N 9.02

1-Isopropoxy-1-(4-methoxyphenyl)acetone Oxime (**7e**)[6d]: Electrolysis of **3e** afforded a mixture of **4e** and **7e** (96:4, GLC). Side product **7e** was separated by HPLC [petroleum ether/ether (1:1)]. Yield: 0.017 g (2.5%). – ^{1}H NMR ($CDCl_3$): δ = 1.20, 1.23 (2 d, J = 6.06 Hz, diastereotopic CH_3), 1.75 (s, 3H, N=CCH_3), 3.62–3.75 [m, 1H, OC*H*(CH_3)$_2$], 3.82 (s, 3H, OCH_3), 5.01 (s, 1H, CHC=N), 6.85–6.93, 7.29–7.38 (2 m, 4H, aromatic H). – MS: *m/z* (%) = 237 (10) [M$^+$], 179 (34), 137 (100), 77 (15), 43 (20), 41 (24).

General Procedure for the Reduction of the 1-Nitroalkenes to the Amines: The cathodic compartment was charged with 70 ml of 0.3 M sulfuric acid in 2-propanol/water (2:1, v/v), subsequently by 6 mmol of the 1-nitro olefin. After introducing the anodic chamber, filled with 20 ml of supporting electrolyte, controlled potential (−1.1 to −1.3 V) electrolysis was performed at 10–15°C with stirring. After 7 to 8 F · mol^{-1} gas evolution increased, and the reduction was terminated. The acidic catholyte was partially evaporated at reduced pressure and the residue extracted twice with ether. To the remaining aqueous phase 2 M NaOH was added (pH 13), and the resulting emulsion was extracted with five portions of ether. The combined ethereal extracts were dried ($MgSO_4$) and concentrated to afford the amines **14a, 14b,** and **15** in 60 to 69% yield (Table 4, eq. 7).

2-Phenylethylamine (**14a**): n_D^{20} = 1.5328 (ref.[18] 1.5332).

2-Amino-1-phenylpropane (**14c**): n_D^{25} = 1.5175 (ref.[16] 1.518).

1-Amino-2-(3-cyclohexen-1-yl)ethane (**15**): Melting point and elementary analysis were obtained from the hydrochloride of **15**. M.p. (**15** · HCl) = 185–187°C. – IR (film): $\tilde{\nu}$ = 3360, 3280 cm^{-1} (NH_2), 1600 (NH). – ^{1}H NMR ($CDCl_3$): δ = 1.20–2.16 (4 m, 9H, CH, CH_2), 1.5 (br. s, 2H, exchangeable with D_2O, NH_2), 2.73 (t, J = 7.4 Hz, 2H, CH_2NH_2), 5.60–5.75 (m, 2H, HC=CH). – ^{13}C NMR ($CDCl_3$): δ = 25.03, 28.83, 31.75 (3 t, ring CH_2), 31.04 (d, CH), 39.71, 40.70 (2 t, $CH_2CH_2NH_2$), 126.28, 126.91 (2 d, HC=CH). – MS: *m/z* (%) = 125 (82) [M$^+$], 108 (34), 82 (67), 80 (100), 79 (88), 45 (87).

$C_8H_{15}N \cdot HCl$ (161.7)
Calcd. C 59.43 H 9.97 Cl 21.93 N 8.66
Found C 59.58 H 10.04 Cl 21.85 N 8.53

CAS Registry Numbers

3a: 102-96-5 / **3b**: 706-07-0 / **3c**: 705-60-2 / **3d**: 1202-32-0 / **3e**: 17354-63-1 / **4a**: 7028-48-0 / **4b**: 4410-18-8 / **4c**: 13213-36-0 / **4d**: 5368-18-3 / **4e**: 52271-41-7 / **7e**: 133777-65-8 / **12a**: 133777-63-6 / **12b**: 133777-64-7 / **13a**: 103722-77-6 / **13b**: 133777-66-9 / **14a**: 64-04-0 / **14c**: 60-15-1 / **15**: 40496-65-9 / *i*PrOH: 67-63-0 / Au, Hg: 12607-42-0 / Hg: 7439-97-6 / H_2SO_4: 7664-93-9 / graphite: 7782-42-5

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