Synthesis of 1,2-Diamines, 2-Imidazolidinones and 2-Imidazolidinethiones from α-Haloimines

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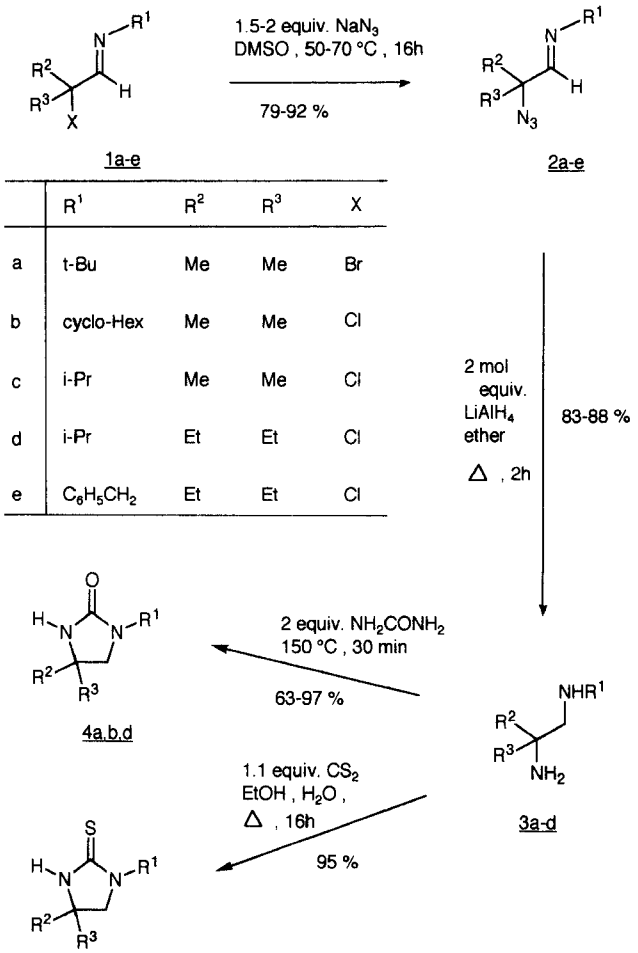
α-Bromo- and α-chloroaldimines **1** are easily converted into α-azidoaldimines **2** which are reduced by lithium aluminum hydride to afford *N*-monoalkylated 1,2-diamines **3**. In a similar way, aromatic α-bromoketimines **7** are transformed into the corresponding α-azidoketimines **8** and α-monoalkylated 1,2-diamines **9**. The 1,2-diamines, thus obtained, are converted into 2-imidazolidinones **4**, **10** and 2-imidazolidinethiones **5**, **11**.

Vicinal diamines are important bifunctional compounds in organic synthesis as they are suitable substrates for the construction of a variety of heterocyclic compounds.[1] Their ability to serve as ligands for both transition metal and main group complexes has been exploited for a long while. Besides various syntheses which allow the preparation of vicinal diamines from olefinic substrates,[2] a whole range of syntheses utilize substrates bearing two functional groups which are reductively transformed into the vicinal diamino functionality. Such transformations include the reduction of α-aminonitriles,[3-5] the reduction of α-amino amides,[6] the reductive amination of α-amino ketones,[7] and the reduction of α-aminooximes.[8] These synthetic sequences are not free from side reactions and therefore pose some problems.[9] A recent publication[10] on the transformation of α-bromooxime ethers into vicinal diamines via α-azidooxime ethers prompted us to report our results.

In this communication, we disclose an elegant entry into vicinal 1,2-diamino compounds starting from α-halogenated imines via azidation and reduction.

α-Bromoaldimine **1a** was synthesized by bromination of the appropriate aldimine with *N*-bromosuccinimide in carbon tetrachloride at 60 °C.[11] α-Chloroaldimines **1b,c** were prepared by chlorination of the appropriate aldimines with *N*-chlorosuccinimide in carbon tetrachloride at room temperature.[12] The reaction of α-haloaldimines **1** with sodium azide in dimethyl sulfoxide at 50–70 °C for 16 hours afforded α-azidoaldimines **2** in 79–92% yield. The reduction of the imino moiety and the azido function was performed with lithium aluminum hydride in diethyl ether under reflux, affording *N*-monoalkylated 1,2-diamines **3** in good yield. These 1,2-diamines **3**, carrying a sterically hindered and an unhindered amino functionality, were conveniently converted into 1,4,4-trisubstituted 2-imidazolidinones **4** and 1,4,4-trisubstituted 2-imidazolidinethiones **5** by reaction with urea or carbon disulfide, respectively (Scheme 1).

Aromatic α-bromoketimines **7** were synthesized in an alternative approach utilizing the condensation of aromatic α-bromo ketones **6** with isopropylamine in diethyl ether in the presence of stoichiometric quantities of titanium(IV) chloride.[13] α-Bromoketimines **7** were converted in a similar way into vicinal diamines **9** by azidation and subsequent reduction with lithium aluminum hydride. These *N*-monoalkylated 1,2-diamines **9** were transformed into the corresponding 5-aryl-1-isopropyl-4,4-dimethylimidazolidinones **10** and 5-aryl-1-isopropyl-4,4-dimethylimidazolidinethiones **11** by reaction with urea or thiourea, respectively (Scheme 2). Table 1 gives a survey of the synthesis of α-azidoimines **2**, **8**, vicinal diamines **3**, **9**, 2-imidazolidinones **4**, **10** and 2-imidazolidinethiones **5**, **11**. The spectroscopic data of these compounds are compiled in Table 2 (α-azidoimines **2**, **8**), Table 3 (1,2-diamines **3**, **9**) and Table 4 (2-imidazolidinones **4**, **10** and 2-imidazolidinethiones **5**, **11**). It should be pointed out that imines **1**, **2**, **7** and **8** occur as the *E* isomer exclusively.



	R¹	R²	R³	X
a	t-Bu	Me	Me	Br
b	cyclo-Hex	Me	Me	Cl
c	i-Pr	Me	Me	Cl
d	i-Pr	Et	Et	Cl
e	$C_6H_5CH_2$	Et	Et	Cl

Scheme 1

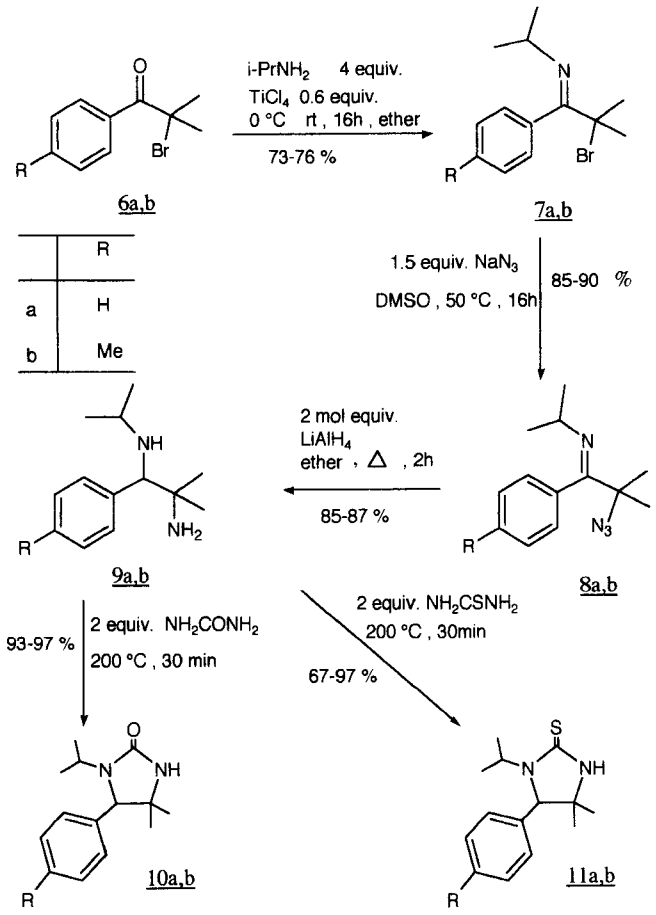
In order to determine the scope and limitations of the α-azidation of imines via α-haloimines, some additional examples in the aliphatic series were investigated. It was not possible to synthesize aliphatic α-azidoketimines by substitution of secondary or tertiary α-chloroketimines with sodium azide in dimethyl sulfoxide or dimethylformamide at 50 °C or 90 °C, respectively. The reaction of the

Table 1. Conversion of α-Haloimines **1**, **7** into α-Azidoimines **2**, **8**, Vicinal Diamines **3**, **9**, 2-Imidazolidinones **4**, **10** and 2-Imidazolidinethiones **5**, **11**

α-Haloimine	Azidation	Yield (%) **2**, **8**	Reduction of **3**, **9**	Yield (%) **3**, **9**	Reaction Conditions	Yield (%) **4**, **5**, **10**, **11**
1a	1.5 equiv. NaN_3/DMSO 50°C, 16 h	**2a** : 81	2 mol. equiv. $LiAlH_4$ ether, reflux 2 h	**3a** : 83	2 mol equiv. urea 150°C, 30 min	**4a** : 97
					1.1 equiv. CS_2 aq EtOH	**5a** : 95
1b	ibidem	**2b** : 90	ibidem	**3b** : 88	2 equiv. urea 150°C, 30 min	**4b** : 94
					1.1 equiv. CS_2 aq EtOH	**5b** : 95
1c	ibidem	**2c** : 92	ibidem	**3c** : 86	–	–
1d	2 equiv. NaN_3/DMSO 70°C, 16 h	**2d** : 84	ibidem	**3d** : 87	2 equiv. urea 150°C/30 min	**4d** : 63
1e	1.5 equiv. NaN_3/DMSO 50°C, 16 h	**2e** : 79	–	–	–	–
7a	ibidem	**8a** : 90	2 mol equiv. $LiAlH_4$ ether, reflux 2 h	**9a** : 85	2 equiv. urea 200°C, 30 min	**10a** : 97
					2 equiv. NH_2CSNH_2 200°C, 30 min	**11a** : 92
7b	ibidem	**8b** : 85	ibidem	**9b** : 87	2 equiv. urea 200°C, 30 min	**10b** : 93
					2 equiv. NH_2CSNH_2 200°C, 30 min	**11b** : 93

Table 2. Spectroscopic Data of α-Azidoimines **2**, **8**

Compound	IR (NaCl) (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ	MS (70 eV) m/z (%)
2a	2100 (N_3) 1670 (C=N)	1.17 (9H, s, *t*-Bu), 1.32 (6H, s, Me_2), 7.44 (1H, s, CH=N)	24.05 (q, Me_2), 29.59 (q, Me_3), 56.96 (s, $\underline{C}Me_3$), 62.64 (s, $\underline{C}N_3$), 157.86 (d, CH=N)	no M^+, 125 (3, M^+-CH_2=CHMe), 110 (3), 98 (5), 86 (10), 84 (28), 70 (17), 57 (100), 56 (10), 51 (7), 49 (19), 44 (9), 43 (7), 42 (9), 41 (22)
2b	2100 (N_3) 1665 (C=N)	1.0–2.0 [10H, m, $(CH_2)_5$], 1.36 (6H, s, Me_2), 3.0 (1H, m, NCH), 7.57 (1H, s, CH=N)	24.07 (q, Me_2), 24.60 [t, $(CH_2)_2$], 25.82 (t, CH_2), 34.49 [t, $(CH_2)_2$], 62.37 (s, CN_3), 68.76 (d, NCH), 161.29 (d, CH=N)	194 (M^+, 0.5), 166 (2), 165 (2), 152 (3), 123 (1), 110 (20), 83 (100), 70 (5), 67 (3), 58 (6), 55 (52), 54 (4), 53 (3), 44 (2), 43 (5), 42 (5), 41 (22)
2c	2100 (N_3) 1665 (C=N)	1.14 (6H, d, J = 6.5, $\underline{Me}_2CH$), 1.37 (6H, s, Me_2), 3.37 (1H, septet, J = 6.5, NCH), 7.56 (1H, s, CH=N)	24.05 (q, $\underline{Me}_2CN_3$), 24.13 (q, $\underline{Me}_2CH$), 60.85 (d, NCH), 62.33 (s, CN_3), 161.16 (d, CH=N)	154 (M^+, 0.5), 126 (2), 125 (2), 112 (5), 96 (2), 84 (3), 71 (4), 70 (55), 58 (4), 56 (6), 49 (4), 44 (6), 43 (100), 42 (13), 41 (20)
2d	2093 (N_3) 1660 (C=N)	0.89 (6H t, J = 7, 2 × $\underline{Me}CH_2$), 1.16 (6H, d, J = 6, $\underline{Me}_2CH$), 1.75 (4H, q, J = 7, 2 × $Me\underline{CH}_2$), 3.38 (1H, septet, J = 6, NCH), 7.48 (1H, s, CH=N)	7.92 (q, 2 × $\underline{Me}CH_2$), 24.27 (q, $\underline{Me}_2CH$), 28.54 (t, 2 × $CH_3\underline{C}H_2$), 61.45 (d, NCH), 68.39 (s, $\underline{C}N_3$), 160.53 (d, CH=N)	182 (M^+, 0.6), 154 (1), 140 (4), 139 (2), 126 (2), 111 (1), 99 (2), 98 (4), 86 (2), 85 (2), 84 (3), 71 (4), 70 (36), 69 (1), 58 (2), 57 (2), 56 (20), 55 (3), 54 (3), 44 (4), 43 (100), 42 (4), 41 (11)
2e	2095 (N_3) 1660 (C=N)	0.89 (6H, t, J = 7, 2 × $\underline{Me}CH_2$), 1.79 (4H, q, J = 7, 2 × $Me\underline{CH}_2$), 4.70 (2H, d, J = 1, NCH_2), 7.34 (5H, s, C_6H_5), 7.67 (1H, t, J = 1, CH=N)	7.96 (q, 2 × $\underline{C}H_3CH$), 28.38 (t, 2 × $CH_3\underline{C}H_2$), 64.31 (t, NCH_2), 68.85 (s, $\underline{C}N_3$), 126.94 (d, =CH para), 127.68 and 128.42 (d, =CH ortho and meta), 138.98 (s, $C_{quat.}$), 164.98 (d, CH=N)	no M^+, 198 (10), 188 (10), 148 (10), 106 (10), 92 (20), 91 (100), 86 (15), 77 (10), 65 (20), 57 (25), 55 (30), 44 (40), 43 (20), 42 (10), 41 (20)
8a	2098 (N_3) 1640 (C=N)	1.02 (6H, d, J = 6, $\underline{Me}_2CH$), 1.38 (6H, s, $\underline{Me}_2CN_3$), 3.21 (1H, septet, J = 6, NCH), 6.9–7.5 (5H, m, C_6H_5)	23.85 (q, $\underline{Me}_2CH$), 25.31 (q, $\underline{Me}_2CN_3$), 52.67 (d, NCH), 65.75 (s, CN_3), 127.12 and 128.23 (2 × d, =CH ortho and meta), 128.03 (d, =CH para), 136.16 (s, $C_{quat.}$), 168.29 (s, C=N)	230 (M^+, 0.4), 188 (1), 187 (2), 172 (1), 146 (26), 131 (2), 119 (2), 115 (2), 104 (100), 103 (12), 91 (3), 77 (11), 76 (5), 56 (6), 51 (4), 44 (2), 43 (11), 42 (6), 41 (12)
8b	2100 (N_3) 1638 (C=N)	1.01 (6H, d, J = 6, $\underline{Me}_2CH$), 1.37 (6H, s, $\underline{Me}_2CN_3$), 2.29 (3H, s, Me), 3.20 (1H, septet, J = 6, NCH), 6.83 and 7.10 (each 2H, each d, J = 8, C_6H_4)	21.17 (q, *p*-Me), 23.89 (q, $\underline{Me}_2CH$), 25.29 (q, $\underline{Me}_2CN_3$), 52.61 (d, NCH), 65.63 (s, $\underline{C}N_3$), 127.04 and 128.95 (each d, meta and ortho =$\underline{C}$H), 133.13 (s, =$\underline{C}$Me), 137.71 (s, =$\underline{C}$–C=N), 168.49 (s, C=N)	no M^+, 201 (1), 160 (19), 145 (2), 133 (3), 118 (100), 117 (6), 116 (4), 91 (7), 90 (4), 89 (3), 65 (4), 63 (3), 56 (5), 43 (7), 42 (4), 41 (9)



Scheme 2

Table 3. Spectroscopic Data of 1,2-Diamines **3** and **9**

Compound[a]	IR (NaCl) (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ	MS (70 eV) m/z (%)
3a	3000–3500 (w, NH_2, NH)	1.07 (15H, s, Me_2 and Me_3), 1.43 (3H, broad s, NH_2 and NH), 2.36 (2H, s, CH_2)	28.66 (q, Me_2), 29.30 (q, Me_3), 49.54 and 50.00 (each s, $\underline{C}NH_2$ and $Me_3\underline{C}$), 54.67 (t, CH_2N)	144 (M^+, 2), 129 (2), 112 (2), 95 (2), 88 (5), 86 (5), 84 (5), 72 (13), 70 (4), 59 (5), 58 (100), 57 (13), 51 (3), 49 (5), 44 (3), 43 (4), 42 (6), 41 (9)
3b	3100–3600 (m, NH_2, NH)	1.03 (6H, s, Me_2), 1.24 (3H, s, NH and NH_2), 1.0–2.0 [10H, m, $(CH_2)_5$], 2.40 (2H, s, CH_2), 2.4 (1H, m, $C\underline{H}N$)	25.06 [t, $(CH_2)_2$], 26.36 (t, CH_2), 34.01 [t, $(CH_2)_2$], 28.82 (q, Me_2), 49.61 (s, CNH_2), 57.40 (d, $\underline{C}HNH$), 59.38 (t, C_2)	170 (M^+, 0.4), 113 (7), 112 (26), 83 (7), 82 (9), 70 (21), 68 (6), 58 (100), 57 (7), 56 (13), 55 (19), 43 (5), 42 (14), 41 (15), 39 (4)
3c	3100–3600 (m, NH_2, NH)	1.05 (6H, d, J = 7, $\underline{Me}_2CH$), 1.11 (6H, s, Me_2), 2.14 (3H, broad s, NH_2 and NH), 2.47 (2H, s, CH_2), 2.78 (1H, septet, J = 7, $NC\underline{H}$)	23.21 (q, $\underline{Me}_2CH$), 28.59 (q, $\underline{Me}_2CNH_2$), 49.41 (d, $NH\underline{C}H$), 49.76 (s, CNH_2), 59.48 (t, CH_2)	no M^+, 97 (2), 72 (26), 58 (100), 57 (4), 56 (9), 55 (3), 50 (4), 44 (4), 43 (8), 42 (9), 41 (8)
3d	3100–3500 (m, NH_2, NH)	0.83 (6H, t, J = 7, $2\times\underline{Me}CH_2$), 1.06 (6H, d, J = 6, $\underline{Me}_2CH$), 1.39 (4H, q, J = 7, $MeC\underline{H}_2$), 2.24 (2H, s, CH_2N), 2.77 (1H, septet, J = 6, NCH), NH and NH_2 invisible (probably covered at 1.4)	7.83 (q, $2\times\underline{Me}CH_2$), 23.34 (q, $\underline{Me}_2CH$), 30.26 (t, $2\times MeC\underline{H}_2$), 49.50 (d, NCH), 53.76 (s, $Et_2\underline{C}NH_2$), 55.04 (t, CH_2N)	158 (M^+, 0.4), 129 (9), 126 (4), 112 (7), 100 (4), 87 (28), 86 (100), 85 (20), 74 (8), 72 (34), 71 (11), 70 (25), 69 (22), 58 (27), 57 (34), 56 (83), 44 (34), 43 (40), 42 (21), 41 (45)
9a	3100–3600 (m, NH, NH_2)	0.95 (6H, d, J = 6, $\underline{Me}_2CH$), 0.96 and 1.06 (each 3H, each s, $\underline{Me}_2CNH_2$), 1.53 (3H, broad, NH and NH_2), 2.52 (1H, septet, J = 6, $NC\underline{H}Me_2$), 3.44 (1H, s, $C_6H_5C\underline{H}$), 7.23 (5H, s, C_6H_5)	21.95, 24.57, 26.99 and 29.07 (4 × q, 4 × Me), 45.85 (d, NHCH), 52.33 (s, CNH_2), 69.87 (d, $C_6H_5\underline{C}H$), 126.78 (d, =CH para), 127.66 and 128.59 (each d, =CH ortho and meta), 141.79 (s, $C_{quat.}$)	no M^+, 149 (8), 148 (46), 147 (19), 132 (32), 106 (35), 105 (19), 104 (19), 91 (8), 79 (14), 77 (14), 58 (100), 43 (9), 42 (18), 41 (16)
9b	3100–3600 (m, NH, NH_2)	0.92 (6H, d, J = 6, $\underline{Me}_2CH$), 0.98 and 1.02 (each 3H, each s, 2Me), 1.6 (3H, broad, NH and NH_2), 2.24 (3H, s, *p*-Me), 2.48 (1H, septet, J = 6, $C\underline{H}N$), 3.37 (1H, s, $C_6H_5C\underline{H}$), 7.04 (4H, broad s, C_6H_4)	20.95 (q, *p*-Me), 21.95, 24.60, 26.99 and 29.07 (4 × q, 4 × Me), 45.77 (NHCH), 52.29 (s, CNH_2), 69.56 (d, $\underline{C}HC_6H_4$), 128.39 and 128.45 (each d, each =CH), 136.00 (s, $=\underline{C}Me$), 138.68 (s, $=C_{quat.}$)	no M^+, 162 (95), 146 (23), 120 (64), 119 (18), 118 (18), 105 (14), 93 (27), 91 (23), 77 (18), 65 (14), 58 (100), 44 (23), 43 (23), 42 (36), 41 (36), 40 (73)

[a] Satisfactory microanalyses obtained: C ± 0.19, H ± 0.15, N ± 0.23.

Table 4. Spectroscopic Data of 2-Imidazolidinones **4**, **10** and 2-Imidazolidinethiones **5**, **11**

Compound[a]	mp (°C)	IR (KBr) (cm^{-1})	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ	MS (70 eV) m/z (%)
4a	139	3200 (NH) 1685 (C=O)	1.24 (6H, s, Me_2), 1.33 (9H, s, *t*-Bu), 3.14 (2H, s, CH_2), 5.5 (1H, broad s, NH)	27.71 (q, Me_3), 27.87 (q, Me_2), 50.80 (s, CMe_3), 52.42 (s, CMe_2), 56.45 (t, CH_2), 161.59 (s, C=O)	170 (M^+, 13), 155 (100), 113 (16), 112 (73), 99 (27), 95 (7), 70 (15), 58 (33), 57 (21), 56 (12), 55 (24), 43 (46), 42 (20), 41 (24), 39 (10)
4b	187	3220 (NH), 1680 (C=O)	1.28 (6H, s, Me_2), 1.0–2.1 [10H, m, $(CH_2)_5$], 3.14 (2H, s, CH_2), 3.7 (1H, m, NCH), 5.5 (1H, broad s, NH)	25.59 [t, $(CH_2)_3$], 28.22 (q, Me_2), 30.42 (t, CH_2NCH_2), 50.59 (d, NCH), 52.18 (s, CMe_2), 53.75 (t, NCH_2), 160.73 (s, C=O)	196 (M^+, 42), 181 (12), 154 (15), 153 (100), 140 (28), 115 (29), 114 (24), 110 (26), 99 (27), 83 (13), 70 (14), 55 (33)
4d	215	3200 (NH), 1680–1660 (C=O)	0.90 (6H, t, J = 6, 2 × $MeCH_2$), 1.17 (6H, d, J = 6.5, Me_2CH), 1.43 (4H, q, J = 6, 2 × $MeCH_2$), 3.20 (2H, s, NCH_2), 4.44 (1H, septet, J = 6.5, NCH), 6.6 (1H, broad s, NH)	7.45 (q, 2 × $MeCH_2$), 19.99 (q, Me_2CH), 29.44 (t, $MeCH_2$), 49.09 (t, CH_2), 49.41 (d, NCH), 57.44 (s, NCH_2), 154.06 (s, C=O)	184 (M^+, 15), 169 (23), 155 (46), 149 (15), 143 (15), 113 (92), 86 (54), 85 (54), 72 (100), 70 (46), 57 (62), 56 (69), 55 (46)
10a	liq.	3100–3600 (NH), 1685 (C=O)	0.75 and 1.35 (each 3H, each s, Me_2C), 0.90 and 1.23 (each 3H, each d, J = 7, Me_2CH), 3.82 (1H, septet, J = 7, NCH), 4.21 (1H, s, C_6H_5CH), 6.34 (1H, broad s, NH), 7.20 (5H, s, C_6H_5)	20.41 (q, Me_2CH), 24.57 and 30.00 (each q, Me_2), 44.99 (d, NCH), 56.27 (s, CMe_2), 68.89 (d, CHC_6H_5), 127.69, 127.87 and 128.16 (each d, arom =CH), 139.05 (s, $C_{quat.}$), 161.71 (C=O)	232 (M^+, 7), 217 (16), 148 (18), 132 (16), 121 (9), 119 (9), 107 (7), 106 (11), 105 (11), 104 (7), 91 (11), 83 (11), 79 (9), 77 (10), 74 (10), 73 (100), 59 (7), 58 (30), 57 (7), 45 (18), 44 (9), 43 (33), 42 (9), 41 (9)
10b	146	3100–3300 (NH), 1695 (C=O)	0.78 and 1.37 (each 3H, each s, Me_2C), 0.94 and 1.25 (each 3H, each d, J = 6.5, Me_2CH), 2.33 (3H, s, *p*-Me), 3.82 (1H, septet, J = 6.5, NCH), 4.19 (1H, s, CHC_6H_4), 5.7 (1H, broad s, NH), 7.10 (4H, broad s, C_6H_4)	20.43 (q, Me_2CH), 21.07 (q, *p*-Me), 24.68 and 30.00 (each q, Me_2), 45.07 (d, NCH), 56.30 (s, CMe_2), 68,82 (d, CHC_6H_4), 127.75 and 128.91 (each d, each =CH), 135.95 (s, $C_{quat.}$), 137.50 (s, =CMe), 161.67 (s, C=O)	246 (M^+, 27), 231 (91), 189 (27), 188 (36), 174 (36), 162 (27), 161 (36), 160 (27), 146 (100), 131 (27), 119 (36), 118 (27), 105 (36), 91 (27), 77 (18), 69 (54), 42 (25), 41 (25)
5a	184	3190 (NH)	1.31 (6H, s, Me_2), 1.63 (9H, s, Me_3), 3.51 (2H, s, CH_2), 6.7 (1H, broad s, NH)	27.13 (q, Me_2), 28.17 (q, Me_3), 55.14 and 56.10 (each s, CMe_3 and CMe_2), 61.10 (t, CH_2), 181.56 (C=S)	180 (M^+, 56), 185 (23), 171 (8), 130 (14), 129 (15), 115 (38), 112 (10), 97 (5), 72 (9), 70 (9), 59 (11), 58 (95), 57 (34), 56 (11), 55 (17), 44 (13), 43 (100), 42 (21), 41 (21)
5b	236	3170 (NH)	1.31 (6H, s, Me_2), 1.0–2.1 [10H, m, $(CH_2)_5$], 3.31 (2H, s, CH_2), 4.3 (1H, m, NCH), 6.7 (1H, broad s, NH)	25.42 (t, $(CH_2)_2$), 25.54 (t, CH_2), 27.53 (q, Me_2), 29.99 [t, $(CH_2)_2$], 54.38 (d, NCH), 56.57 (s, CMe_2), 56.98 (t, NCH_2), 180.28 (s, C=S)	212 (M^+, 100), 211 (47), 197 (24), 178 (18), 169 (18), 131 (47), 130 (47), 129 (24), 115 (35), 98 (18), 81 (24), 72 (29), 71 (18), 70 (18), 69 (35), 60 (18), 59 (18), 57 (35), 56 (24), 55 (47)
11a	98	3100–3350 (NH)	0.82 and 1.46 (each 3H, each s, Me_2), 0.83 and 1.29 (each 3H, each d, J = 6.5 Hz, Me_2CH), 4.43 (1H, s, CHC_6H_5), 4.90 (1H, septet, J = 6.5 Hz, $NCHMe_2$), 6.90–7.70 (6H, m, C_6H_5 and NH)	20.17, 21.35, 23.16 and 29.85 (each q, 4 × Me), 48.16 (d, NCH), 60.81 (s, CMe_2), 70.58 (d, CHC_6H_5), 127.50, 128.32 and 128.37 (each d, arom =CH), 138.32 (s, $C_{quat.}$), 181.23 (s, C=S)	248 (M^+, 54), 132 (100), 117 (68), 111 (32), 105 (25), 99 (23), 97 (43), 95 (30), 91 (32), 85 (41), 83 (45), 81 (32), 71 (59), 69 (45), 67 (23), 57 (91), 56 (23), 55 (55)
11b	150	3200 (NH)	0.80 and 1.39 (each 3H, each s, Me_2), 0.83 and 1.26 (each 3H, each d, J = 6.5, Me_2CH), 2.33 (3H, s, *p*-Me), 4.35 (1H, s, CHC_6H_5), 4.81 (1H, septet, J = 6.5, $NCHMe_2$), 6.7 (1H, broad s, NH), 7.10 (4H, s, broad, C_6H_4)	21.12 (q, *p*-Me), 20.17, 21.39, 23.24, 29.84 (each q, each Me), 48.25 (d, NCH), 60.75 (s, CMe_2), 70.55 (d, CHC_6H_4), 127.48 and 129.08 (each d, each arom =CH), 135.25 (s, =CMe), 138.08 (s, $C_{quat.}$), 181.24 (s, C=S)	262 (M^+, 27), 146 (100), 131 (33), 117 (12), 91 (8), 69 (7), 58 (40), 43 (56), 42 (9), 41 (9)

[a] Satisfactory microanalyses obtained: C ± 0.09, H ± 0.14, N ± 0.69.

corresponding tertiary α-bromoketimines under the same conditions afforded a reaction mixture in which the desired α-azidoketimine was one of the major components.

Compounds **1a**,[11] **1b, c**,[12] **1d**,[14] **1e**[16] and **7a**[15] were reported previously.[17] α-Bromoketimine **7b** is a new compound obtained from 2-bromo-2-methyl-1-(4-methylphenyl)-1-propanone **6b** and isopropylamine in 73% yield, mp 146°C.

***N*-[2-Bromo-1-(4-methylphenyl)-1-propylidene]isopropylamine (7b):**
^1H NMR ($CDCl_3$): δ = 1.02 (6H, d, J = 6 Hz, Me_2CH), 1.93 (6H, s, Me_2CBr), 2.38 (3H, s, Me), 3.18 (1H, septet, J = 6 Hz, NCH), 7.05 and 7.21 (each 2H, each d, J = 8.5 Hz, C_6H_4).

^{13}C NMR ($CDCl_3$): δ = 21.16 (q, *p*-Me), 23.28 (q, Me_2CH), 32.34 (q, Me_2CBr), 52.48 (d, NCH), 66.34 (s, CBr), 128.23 and 128.42 (each d, meta and ortho = CHs), 132.80 (s, =CMe), 137.41 (s, =C–C=N), 168.76 (s, C=N).

IR (KBr): ν = 1627 cm^{-1} (C=N).

MS: *m/z* (%) = no M^+, 202 (7, $M^+ - Br$), 201 (4), 186 (5), 160 (46), 145 (5), 133 (8), 119 (18), 118 (100), 105 (5), 91 (8), 90 (4), 89 (3), 82 (3), 80 (3), 77 (3), 69 (7), 65 (5), 58 (30), 43 (57), 42 (7), 41 (11).

Note: All reactions with azido compounds were run behind safety shields. No decomposition of any α-azidoimine was noticed during these experiments.

α-Azidoaldimines 2 and α-Azidoketimines 8; General Procedure:
A solution of α-haloimine **1** or **7** (0.025 mol) in DMSO (30 mL) was treated with NaN_3 (0.0375–0.050 mol) and the mixture was stirred at 50–70 °C for 16 h (see Table 1). After cooling, the reaction mixture was poured into 1 N NaOH (150 mL) and extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with 1 N NaOH (50 mL), dried ($MgSO_4$), filtered and evaporated to afford α-azidoimines **2** (79–92%) and **8** (85–90%) as crude oils of sufficient purity (> 95%; NMR) in order to be used in the next reaction step. Because of safety precautions, α-azidoimines were not distilled and used as such in further experiments.

Vicinal Diamines 3 and 9 from α-Azidoimines 2, 8; General Procedure:
A solution of 0.152 g (0.004 mol) $LiAlH_4$ in Et_2O (5 mL) was treated dropwise with α-azidoimine **2** or **8** (0.002 mol), dissolved in dry Et_2O (5 mL). The mixture was refluxed for 2 h and, after cooling, the reaction mixture was poured cautiously into a separatory funnel containing water (5 mL) and Et_2O (10 mL). The latter combined layers were previously shaken vigorously. The ether layer was isolated and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined ether extracts were dried ($MgSO_4$), filtered and evaporated to give vicinal diamines **4** and **10** as clear oils (purity > 95%; GC). Yield: 83–88%. Further purification was performed on a short silica gel column using chloroform as eluent.

2-Imidazolidinones 4 and 10; General Procedure:
A mixture of 1,2-diamine **3** or **9** (0.01 mol) and urea (0.02 mol) was heated in an oil bath at 150 °C–200 °C for 30 min. After cooling, water (50 mL) was added and extracted with CH_2Cl_2 (3 × 20 mL). After drying ($MgSO_4$), the combined extracts were evaporated in vacuo to give 2-imidazolidinones **4** (63–97%) and **10** (93–97%) (purity > 95%; NMR), which were recrystallized from CCl_4/$CHCl_3$.

2-Imidazolidinethiones 5 and 11; General Procedures:
A mixture of vicinal diamine **9** (0.01 mol) and thiourea (0.02 mol) was heated at 200 °C for 30 min (oil bath). After cooling, the reaction mixture was treated with water (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). After drying ($MgSO_4$), filtration and evaporation of the combined extracts, the solid 2-imidazolidinethiones **11** were obtained in 67–92% yield. Recrystallization was performed with CCl_4/$CHCl_3$. An alternative procedure for the synthesis of 2-imidazolidinethiones **5** was worked out. A mixture of 1,2-diamine **3** (0.01 mol), EtOH (2 mL) and water (5 mL) was treated with carbon disulfide (0.011 mol). The mixture was stirred under reflux for 16 h. After cooling, water (50 mL) was added and extracted with CH_2Cl_2 (3 × 25 mL). After drying ($MgSO_4$), filtration and evaporation, the crude 2-imidazolidinethiones **5** were obtained as solids. Recrystallization was performed with CCl_4/$CHCl_3$. Yield 95% (purity > 95%; NMR).

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