A General Synthesis of α-Halogenated Imines[1]

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α-Halogenated imines are the nitrogen analogues of the synthetically useful α-halocarbonyl compounds. While the latter class of compounds has been studied extensively only minor attention has been given to the chemistry of α-halogenated imino compounds, due to the fact that general routes leading to these compounds were lacking. Two major approaches to the synthesis of α-halogenated imines can be considered, first, the halogenation of an imine (or the tautomeric secondary enamine), and second, the direct condensation of an α-halogenated carbonyl compound with a primary amine[2]. The first pathway can be accomplished using a variety of halogenating agents, e.g., chlorine, bromine, *N*-halosuccinimides, hypochlorites, 2,4,4,6-tetrabromocyclohexadienone, and phenyltrimethylammonium perbromide[2]. A drawback of this approach is

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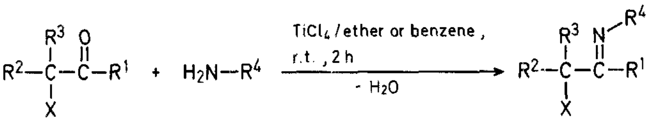
the fact that only in a few cases have regiospecific halogenations of imines been performed[2-5]. The second pathway met with major difficulties in terms of side reactions such as α-substitution, hydrogen halide elimination, Favorskii-type rearrangements, rearrangements via epoxides, etc.[2]. Thus, α-haloketones have not been condensed with primary amines to afford α-haloketimines, except for some α-fluorinated derivatives and the usual carbonyl identification reagents, e.g., hydroxylamine, hydrazines, semicarbazide, etc.[2]. On the other hand, α-haloaldehydes could be condensed with primary aliphatic amines under certain conditions (molecular sieves or Lewis catalysis) to give α-haloaldimines[6,7,8].

We now report a general synthesis of α-halogenated imines (**3**) based on the second above-mentioned approach, i.e., the condensation of an α-halocarbonyl compound (**1**) with a primary amine (**2**) in ether or benzene in the presence of titanium(IV) chloride.



1 2 3

The reaction is performed using 3-4 molar equivalents of amine (**2**) and 0.55 molar equivalents of titanium(IV) chloride. The latter reagent acts as a Lewis acid catalyst and it also removes the water formed in the reaction by formation of titanium dioxide. This method may be applied to the synthesis of α-haloaldimines and α-haloketimines. It has previously found widespread application in the synthesis of ordinary imines[9] and a modification of the method has been used for the synthesis of β-halogenated enamines[10]. The examples listed in the Table show that α-fluoro-, α-chloro-, and α-bromoimines as well as α,α-dichloro- and α,α,α-trichloroimines can be prepared by the present method which may be performed in two modifications: In Method A, a solution of titanium(IV) chloride in pentane is added to a solution of the α-halocarbonyl compound (**1**) and the amine (**2**) in ether or benzene; in Method B, the amine (**2**) is added to a solution of the α-halocarbonyl compound (**1**) and titanium(IV) chloride in ether to avoid undesired side reactions between **1** and **2** such as α-substitution and Favorskii-type rearrangements which might occur with reactive α-halocarbonyl compounds (e.g., with α-bromoketones and α-chloroaldehydes).

The scope of the method seems to be limited by steric factors. While no limitations were observed with α-haloaldehydes, sterically hindered α-haloketones such as α-brominated dineopentyl and diisopropyl ketone could not be condensed with isopropylamine to afford the corresponding ketimines. Surprisingly, some undesired side reactions were observed in the case of the condensation of 1-chloro-1-phenylpropanone and 3-chloro-3-methylbutanone with *t*-butylamine, making the isolation of the pure *N*-*t*-butyl-α-chloroketimine impossible.

Most of the α-haloimines described here were obtained as one geometrical isomer, i.e. in the (*E*)-form with respect to the imino function, as

Table 1. α-Haloaldimines and α-Haloketimines (**3**)

3	R^1	R^2	R^3	R^4	X	Method	Yield [%]	m.p. or b.p./ torr [°C]	Molecular formula[a] or Lit. data
a	H	C_6H_5	CH_3	i-C_3H_7	Cl	B	93	— (dec.)	$C_{12}H_{16}ClN$ (209.7)
b	H	t-C_4H_9	Cl	t-C_4H_9	Cl	A	82	m.p. 31°	$C_{10}H_{19}Cl_2N$ (224.2)
c	H	Cl	Cl	t-C_4H_9	Cl	A	73	b.p. 58-62°/13	b.p. 67°/12[11]
d	CH_3	CH_3	H	i-C_3H_7	Cl	A	78	b.p. 47-48°/14	$C_7H_{14}ClN$ (147.6)
e	CH_3	CH_3	H	t-C_4H_9	Cl	A	77	b.p. 57-59°/14	$C_8H_{16}ClN$ (161.7)
f	CH_3	CH_3	H	c-C_6H_{11}	Cl	A	68	b.p. 109-114°/14	$C_{10}H_{18}ClN$ (187.7)
g	CH_3	H	H	i-C_3H_7	Cl	A	86	— (dec.)[b]	$C_6H_{12}ClN$ (133.6)
h	CH_3	H	H	t-C_4H_9	Cl	A	72	— (dec.)[b]	$C_7H_{14}ClN$ (147.6)
i	CH_3	C_6H_5	H	i-C_3H_7	Cl	A	90	b.p. 76-78°/0.03	$C_{12}H_{16}ClN$ (209.7)
j	n-C_3H_7	H	H	i-C_3H_7	Cl	A	98	—[d]	$C_8H_{16}ClN$ (161.7)
k	CH_3	CH_3	CH_3	i-C_3H_7	Cl	B	88	b.p. 42-45°/11	$C_8H_{16}ClN$ (161.7)
l	CH_3	CH_3	CH_3	c-C_6H_{11}	Cl	B	56	b.p. 100-103°/11	$C_{11}H_{20}ClN$ (201.7)
m	CH_3	C_6H_5	CH_3	i-C_3H_7	Cl	A	93	b.p. 52-54°/0.04	$C_{13}H_{18}ClN$ (223.7)
n	CH_3	C_6H_5	Cl	i-C_3H_7	Cl	A	57	b.p. 78-80°/0.03	$C_{12}H_{15}Cl_2N$ (244.2)
o	i-C_4H_9	Cl	H	i-C_3H_7	Cl	A	82	—[d]	$C_9H_{17}Cl_2N$ (210.1)
p	CH_3	CH_3	H	C_6H_5	Cl	A	33	b.p. 53-58°/0.15	$C_{10}H_{12}ClN$ (181.7)
q	H	C_2H_5	H	t-C_4H_9	Cl	A	47	b.p. 56-58°/12	b.p. 27-28°/0.4[6]
r	C_6H_5	CH_3	Cl	C_2H_5	Cl	A	86	—[c]	—[12]
s	C_6H_5	CH_3	Cl	i-C_3H_7	Cl	A	89	—[c]	—[12]
t	C_6H_5	CH_3	Cl	c-C_6H_{11}	Cl	A	88	—[c]	—[12]
u	4-Cl—C_6H_4	CH_3	Cl	i-C_3H_7	Cl	A	91	m.p. 41°	—[12]
v	C_2H_5	CH_3	H	i-C_3H_7	Br	B	79	— (dec.)	$C_8H_{16}BrN$ (206.1)
w	C_6H_5	CH_3	H	i-C_3H_7	Br	A	87	—[d]	$C_{12}H_{16}BrN$ (254.2)
x	C_6H_5	CH_3	H	i-C_3H_7	F	A	89	—[d]	$C_{12}H_{16}FN$ (193.3)

[a] C, H, Cl, N analyses were performed with **3b, d, e, i, k, l**; C, H, N analyses were performed with **3w, x**; Cl, N analyses were performed with **3f, n, p**; N analyses only were performed with **3a, j, m, o**. These microanalyses were in good agreement with the calculated values: C, ±0.15; H, ±0.20; Cl, ±0.15; N, ±0.19.

[b] Compounds **3g** and **3h** should be used directly in further experiments as they decompose rapidly and exothermically in neat form. Storing the pure compounds in a closed vessel, even at low temperature (−20 °C) may be cause serious explosions. Similar behavior of **3g** and **3h** was observed on attempted vacuum distillation.

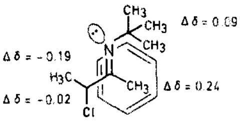
[c] Compounds **3r-t** were not distilled; these products were shown to be free of impurities and were used as such in further experiments.

[d] Not distilled, crude yields given.

Table 2. Spectral Data of Compounds **3**

3	M.S. (70 eV) *m/e* (rel. int.)	I.R. (NaCl) $\nu_{C=N}$ [cm^{-1}]	^{1}H-N.M.R. (CCl$_4$/TMS$_{int}$, 60 MHz) δ [ppm]
a		1665	1.20, 1.21 (2d, 6H, $J=6.5$ Hz, 2 $C\underline{H}_3$); 3.46 [sept, 1H, $J=6.5$ Hz, $C\underline{H}(CH_3)_2$]; 2.00 (s, 3H, $C\underline{H}_3$); 7.1-7.6 (m, 5H_{arom}); 7.75 (s, 1H, CH=N)
b	no M$^+$, 167/69/71 (0.5); 152/4/6 (1); 111/3/5 (3); 99 (6); 84 (6); 57 (100); 41 (36)	1660-1675	1.22 [s, 18H, 2$C(C\underline{H}_3)_3$]; 7.58 (s, 1H, $C\underline{H}$=N)
c	[11]	[11]	[11]
d	147/9 (M$^+$, 0.5); 132/4 (2); 112 (2); 96 (1); 90 (1); 89 (1); 84 (33); 70 (5); 55 (3); 54 (2); 43 (19); 42 (100); 41 (6)	1660	1.05, 1.07 [2d, 6H, $J=6.5$ Hz, 2 CH_3]; 1.57 (d, 3H, $J=6.5$ Hz, $C\underline{H}_3$); 1.88 (s, 3H, N=C=$\underline{H}_3$); 3.60 [sept, 1H, N—$C\underline{H}(CH_3)_2$]; 4.41 (q, 1H, $J=6.5$ Hz, $C\underline{H}$—Cl)
e	161/3 (M$^+$, 0.5); 146/8 (6); 110 (4); 106 (5); 105 (4); 98 (15); 70 (15); 57 (100); 42 (28); 41 (38)	1665	1.23 [s, 9H, $C(C\underline{H}_3)_3$]; 1.54 (d, 3H, $J=6.5$ Hz, $C\underline{H}_3$); 1.98 (s, 3H, N=C—$C\underline{H}_3$); 4.33 (q, 1H, $J=6.5$ Hz, $C\underline{H}$—Cl)
f	187/9 (M$^+$, 1); 152 (12); 124 (24); 108 (2); 106 (4); 83 (100); 70 (5); 68 (4); 67 (4); 55 (44); 54 (5); 53 (4); 42 (34); 41 (20); 39 (4)	1663	1.57 (d, 3H, $J=7$ Hz, $C\underline{H}_3$); 1.90 (s, 3H, N=C—$C\underline{H}_3$); 1-2 [m, 10H, $(C\underline{H}_2)_5$]; 3.2 (m, 1H, N—$C\underline{H}$); 4.41 (q, 1H, $J=7$ Hz, $C\underline{H}$—Cl)
g	—	1661	1.05 [d, 6H, $J=6.5$ Hz, $CH(C\underline{H}_3)_2$]; 1.90 (s, 3H, N=C—CH_3); 3.56 [sept, 1H, $J=6.5$ Hz, $C\underline{H}(CH_3)_2$]; 3.92 (s, 2H, $C\underline{H}_2$—Cl)
h	— —	1665	1.23 [s, 9H, $C(C\underline{H}_3)_3$]; 2.04 (s, 3H, N=C—$C\underline{H}_3$); 3.91 (s, 2H, $C\underline{H}_2$—Cl)
i	no M$^+$, 175 (0.5); 151 (0.5); 149 (0.5); 117 (2); 115 (1); 91 (6); 84 (23); 77 (1); 65 (2); 63 (1); 58 (1); 51(2); 43 (15); 42 (100); 41 (7)	1657	1.06, 1.14 [2d, 6H, $J=6$ Hz, $CH(C\underline{H}_3)_2$]; 1.71 (s, 3H, N=C—CH_3); 3.56 [sept, 1H, $J=6$ Hz, $C\underline{H}(CH_3)_2$]; 5.47 (s, 1H, $C\underline{H}$—Cl); 7-7.5 (m, 5H_{arom})
j	161/3 (M$^+$, 0.3); 146/8 (1); 133/5 (2); 126 (2); 112 (2); 110 (2); 104 (1); 98 (2); 84 (10); 76 (2); 70 (39); 69 (3); 68(3); 67 (2); 58 (2); 57 (2); 56 (2); 55 (3); 54 (3); 43 (39); 42 (100); 41 (33); 40 (4); 39 (13)	1658	0.95 (covered, 3H, CH_3); 1.10, 1.12 [2d, ratio (*E/Z*) 70/30, 6H, $CH(C\underline{H}_3)_2$]; 1.2-1.9 (m, 2H, $C\underline{H}_2$); 2.2-2.6 (m, 2H, $C\underline{H}_2$—C=N); 3.3-4 [m, 1H, $C\underline{H}(CH_3)_2$]; 4.00, 3.89 [2s, ratio (*E/Z*) 70/30, 2H, $C\underline{H}_2$—Cl]
k	161/3 (M$^+$, 1); 146/8 (2); 126 (4); 125 (7); 110 (7); 84 (26); 69 (11); 68 (15); 43 (23); 42 (100); 41 (28)	1657	1.07 [d, 6H, $J=6$ Hz, $CH(C\underline{H}_3)_2$]; 1.66 (s, 6H, 2$C\underline{H}_3$); 1.98 (s, 3H, H=C—CH_3); 3.60 [sept, 1H, $J=6$ Hz, $C\underline{H}(CH_3)_2$]
l	no M$^+$, 166/8 (7); 150 (6); 124 (12); 122 (15); 108 (11); 96 (15); 84 (27); 83 (73); 69 (21); 68 (35); 67 (21); 55 (78); 42 (69); 41 (100); 39 (27)	1661	1.62 (s, 6H, 2CH_3); 1.94 (s, 3H, N=C—$C\underline{H}_3$); 1-2 [m, 10H, $(C\underline{H}_2)_5$]; 3.2 (m, 1H, N—$C\underline{H}$)
m	—	1660	1.18 [d, 6H, $J=6$ Hz, $CH(C\underline{H}_3)_2$]; 1.75 (s, 3H, CH_3); 1.94 (s, 3H, N=C—CH_3); 3.73 [sept, 1H, $J=6$ Hz, $C\underline{H}(CH_3)_2$]; 7.1-7.6 (m, 5H_{arom})
n	243/5/7 (M$^+$, 2); 208/10 (18); 207/9 (10); 191 (6); 173 (8); 166 (12); 165 (8); 158 (10); 131 (18); 130 (13); 118 (3); 117 (10); 116 (5); 115 (20); 91 (5); 89 (15); 84 (100); 77 (10); 63 (8); 51 (4); 43 (48); 42 (75); 41 (20)	1666	1.13 [d, 6H, $J=6.5$ Hz, $CH(C\underline{H}_3)_2$]; 1.97 (s, 3H, N=C—CH_3); 3.66 [sept, 1H, $J=6.5$ Hz, $C\underline{H}(CH_3)_2$]; 7.2-7.7 (m, 5H_{arom})
o	no M$^+$, 126 (10); 84 (100); 57 (10); 43 (21); 42 (17); 41 (17)	1650	1.00 [d, 6H, $J=6$ Hz, C—$CH(C\underline{H}_3)_2$]; 1.13 [d, 6H, $J=6$ Hz, N—$CH(C\underline{H}_3)_2$]; ~2.4 (m, 2H, $C\underline{H}_2$—C=N); 3.80 [sept, 1H, $J=6$ Hz, N—$C\underline{H}(CH_3)_2$]; 6.10, 6.56 [2s, ratio (*E/Z*) 85/15, $C\underline{H}Cl_2$]
p	181/3 (M$^+$, 5); 118 (100); 77 (66); 51 (26)	1662	1.72 (d, 3H, $J=6.5$ Hz, CH_3); 1.89 (s, 3H, N=C—CH_3); 4.60 (q, 1H, $J=6.5$ Hz, $C\underline{H}$—Cl); 6.5-6.7 (m, 2H_{ortho}); 6.8-7.4 (m, 3$H_{meta+para}$)
q	[6]	[6]	[6]
r	[12]	[12]	[12]
s	[12]	[12]	[12]
t	[12]	[12]	[12]
u	[12]	[12]	[12]
v	205/7 (0.5, M$^+$); 134/6 (2); 98 (39); 84 (3); 69 (15); 57 (5); 56 (100); 55 (5); 54 (5); 43 (15); 42 (6); 41 (10)	1652	1.06 [d, 6H, $J=6.5$ Hz, $CH(C\underline{H}_3)_2$]; 1.11 (t, 3H, $J=7$ Hz, CH_3); 1.76 (d, 3H, $J=7$ Hz, CH_3); 2.38 (q, 2H, $J=7$ Hz, $C\underline{H}_2$—C=N); 3.70 [sept, 1H, $J=7$ Hz, $C\underline{H}(CH_3)_2$]; 4.55 (q, 1H, $J=7$ Hz, $C\underline{H}$—Br)
w	no M$^+$, 146 (2); 104 (100); 77 (2); 51 (1); 43 (3); 41 (2); 39 (1)	1638	0.97, 1.03 [2d, 6H, $J=6$ Hz, $CH(C\underline{H}_3)_2$]; 1.76 (s, 3H, $J=6.8$ Hz, CH_3); 3.31 [sept, 1H, $C\underline{H}(CH_3)_2$]; 4.75 (q, 1H, $J=6.8$ Hz, $C\underline{H}$—Br)
x	193 (M$^+$, 3); 192 (2); 178 (6); 173 (2); 158 (3); 146 (32); 135 (2); 130 (2); 117 (4); 115 (4); 104 (100); 77 (7); 51 (4); 43 (6); 42 (2); 41 (4); 39 (3)	1650	0.98, 1.03 [2d, 6H, $J=6$ Hz, $CH(C\underline{H}_3)_2$]; 1.43 (dd, 3H, $J_{HH}=6.4$ Hz, $J_{HF}=23$ Hz, CH_3); 3.37 [sept, 1H, $J=6$ Hz, $C\underline{H}(CH_3)_2$]; 5.13 (dq, 1H, $J_{HH}=6.4$ Hz, $J_{HF}=47.2$ Hz, $C\underline{H}$—F); 6.9-7.4 (m, 5H_{arom})

evidenced by the ^{1}H-N.M.R. spectra of α-chloroaldimines **3a, q**, α,α-dichloroalkyl aryl ketimines **3r–u**, α-chloroalkyl methyl ketimines **3d, e, f, i, k, l, m, p**, α-bromoketimines **3v, w**, and α-fluoroketimine **3x**. However, chloromethyl ketimine **3j** and dichloromethyl ketimine **3o** exist as an equilibrium mixture of the (*E*)- and (*Z*)-isomers which was investigated by ASIS (Aromatic Solvent Induced Shift) measurements[3,5] by which the variations in chemical shifts are determined on going from a carbon tetrachloride solution to a benzene solution. The upfield "benzene solvent shift" of protons *trans* to the lone pair of electrons at the N-atom is more pronounced than that of the *cis* protons. This phenomenon was explained in terms of a repulsive effect between the lone pair of electrons at the N-atom and the benzene solvent molecule whereby the latter is pushed away from the N-atom as far as possible and, on the other hand, is attracted by the partial positive charge of the sp^2-hybridized C-atom.



3e

As exemplified for *N*-*t*-butyl-3-chloro-2-butanimine (**3e**), the remarkable shielding effect of the protons remote from the lone pair of electrons at the N-atom, expressed by the benzene solvent shift

$$\delta^{C_6H_6}_{CCl_4} = \delta^{CCl_4} - \delta^{C_6H_6} \text{ [ppm]},$$

is indicative for the (*E*)-configuration.

The α-halocarbonyl compounds **1** were prepared by literature methods. Secondary and tertiary α-chloroketones were prepared by chlorination of the parent ketones with sulfuryl chloride[13] while α-bromoketones were synthesized by standard brominations with bromine[14]. 1-Chloro-2-pentanone was obtained from the reaction of the parent α-diazoketone with hydrogen chloride[15] while 1,1-dichloro-4-methyl-2-pentanone[16], 2-fluoro-1-phenyl-1-propanone[12], and α,α-dichloroalkyl aryl ketones[17] were prepared as previously described.

α-Haloimines (3); General Procedures:

Method A: To a vigorously stirred ice-cooled solution of the α-halogenated carbonyl compound **1** (0.1 mol) in a tenfold volume of dry ether (distilled from sodium wire), the primary amine **2** (0.4 mol; in the case of aniline 0.3 mol) is added followed by the dropwise addition of a solution of titanium(IV) chloride (10.435 g, 0.055 mol) in pentane (20 ml) [*Caution!* all reactions are exothermic; the rate of addition should therefore be carefully controlled to ensure smooth reaction]. After the addition is complete the ice bath is removed and the heterogeneous mixture stirred for another 2 h at room temperature. The mixture[a] is then poured into aqueous 0.5–1 normal sodium hydroxide (100 ml) covered by a layer of ether (50 ml). The system is vigorously shaken, the ether layer isolated, and the aqueous layer extracted with ether (2 × 50 ml). The combined ether phase is dried with potassium carbonate and evaporated. The residual product is distilled in vacuo. The α-halocarbonyl compounds thus obtained should be kept under an inert atmosphere at low temperature (−20 °C) to avoid decomposidion.

Method B: To a vigorously stirred ice-cooled solution of the α-halogenated carbonyl compound **1** (0.1 mol) in a tenfold volume of dry ether (distilled from sodium wire), a solution of titanium(IV) chloride (10.435 g, 0.055 mol) in pentane (20 ml) is added followed by the dropwise addition of the amine **2** (0.4 mol) [*Caution!* the reaction is exothermic; the rate of addition should therefore be carefully controlled to ensure smooth reaction]. After the addition is complete, stirring is continued for 2 h at room temperature and the mixture then worked up as in Method A.

Using Methods A or B, the α-haloimines (**3**) are obtained in a purity of >98% (as evidenced by G.L.C. analysis). In most cases, impurities cannot be detected.

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[a] Work-up of the reaction mixture may also be performed by filtering off the precipitated titanium dioxide and amine hydrochloride using a sintered glass filter but in many cases a slow filtration rate is noticed. This can be circumvented to some extent by filtration through a bed of magnesium oxide, florisil, or celite; this leads to considerable loss of product, however.

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[1] This is Part 25 of our series of communications on the chemistry of α-halogenated imino compounds. For Part 24, see: N. DeKimpe et al., *Tetrahedron Lett.* **22**, 1837 (1981).

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