Tetrahedron Vol. 46, No. 19, pp. 6753-6770, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

SILVER ION INDUCED REACTIONS OF α-HALOIMINES

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(*Received in UK* 14 *June* 1990)

Abstract
The silver ion induced reactions of α-haloimines are markedly different from similar reactions with the corresponding α-haloketones. The various reactions of α-haloimines, including α-alkoxylation, 1,2-dehydrohalogenation, rearrangement via α-alkoxyaziridines, Favorskii-rearrangement and Wagner-Meerwein rearrangement, are compared and evaluated with silver-induced reactions of α-haloketones. The silver ion assisted reactions of α-haloimines are best interpreted in terms of the intermediacy of α-imidoylcarbenium ions or pseudo-α-imidoylcarbenium ions.

Introduction

Silver-induced reactions of α-haloketones are well-documented in the literature and many useful synthetic applications evolved from these research efforts.[1] Classical transformations of α-haloketones with silver salts under a variety of reaction conditions involve the Favorskii rearrangement,[2,3] alcoholysis into α-alkoxyketones,[4] α-alkoxyoxirane formation,[5] 1,2-dehydrohalogenation,[6,7] etc... All these classical reactions highly depend upon the type of α-haloketone (nature of the halogen, the steric environment, the carbon skeleton) and the type of silver salt and solvent used. Very often, these reactions occur in a competitive manner leading to mixtures of reaction products, from which the desired compounds are sometimes recovered in moderate yields after extentive chromatographic efforts.

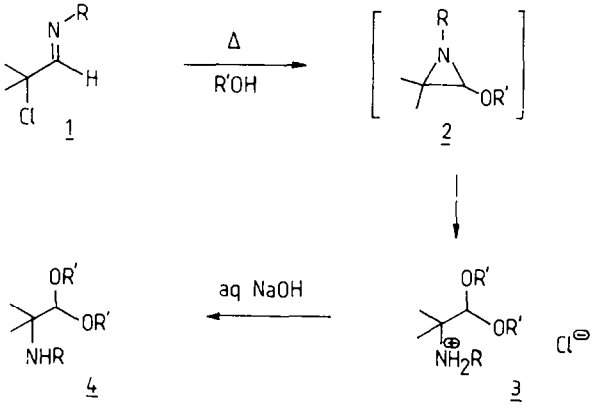
One way of altering the reactivity of α-haloketones is to convert them into a masked form, which hopefully directs the reactions to specific horizons. If reactions, different from those of the parent α-haloketones can then be obtained, these masked forms would have a high synthetic value. One such example of masked α-haloketones are the corresponding halogenated acetals which gave selective rearrangements into the medicinally important α-arylcarboxylic acids.[8] Also α-haloimines have been used recently as altered or masked α-haloketones or α-haloaldehydes.[1] Because of the latter promising results, efforts were undertaken to evaluate α-haloimines towards silver reagents in order to find a deviating and useful reactivity from the one of α-haloketones.

Results and Discussion

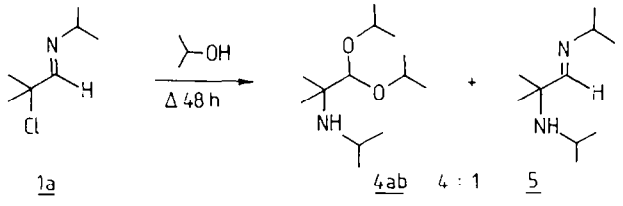
Like aldehydes, aldimines have a relatively unhindered carbon-nitrogen double bond and, therefore, when carrying out reactions with nucleophiles or in nucleophilic solvents, e.g. alcohols, the imino function of aldimines is readily attacked. This initial reactivity pattern at the imino carbon is not necessarily followed with ketimines because of more steric hindrance. For these reasons, the discussion of the reactivity of α-haloimines towards the influence of silver salts is divided into two parts. The first part deals with α-haloaldimines and the second part focusses on α-halogenated ketimines.

α-Halogenated Aldimines

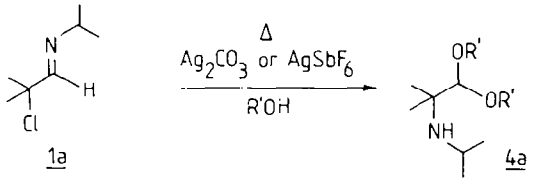
α-Chloroaldimines 1 are known to rearrange with alcohols under reflux for an extended period of time into α-(N-alkylamino)acetals, which are isolated as solid hydrochlorides 3 after evaporation of the alcohol or which provide the free bases 4 upon alkaline workup.[9] N-isopropyl α-chloroaldimine 1a



(R = i-Pr) reacted with methanol under reflux (24h) to form α-(N-isopropylamino)acetal 4aa (R = i-Pr; R' = Me) as the sole product. This study was now enlarged towards higher alcohols and the influence of silver salts. In ethanol under reflux, α-chloroaldimines 1 behaved similarly but, in some cases, α-chloroaldimine 1a (R = i-Pr) with isopropanol (reflux 48h) gave also a small amount of α-isopropylaminoaldimine 5 (ratio acetal 4ab : α-isopropylaminoaldimine 5 4:1). The α-isopropylaminoaldimine 5



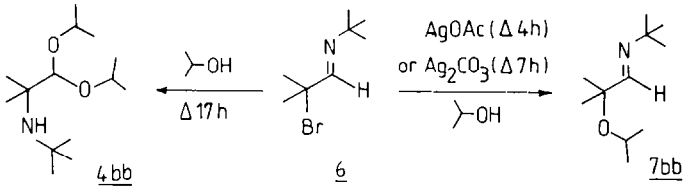
is in fact an artefact of acetal 4ab because isopropylamine can be liberated from 1a under the given reaction conditions, leading to aminolysis of acetal 4ab (cf. the liberated hydrogen chloride). This

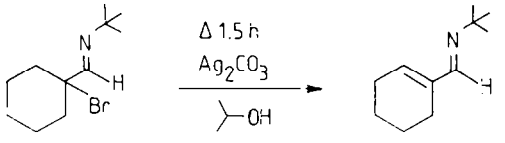


rearrangement of α-chloroaldimines 1 with alcohols via α-alkoxyaziridines 2 underwent little influence by silver salts, e.g. silver carbonate or silver hexafluoroantimonate, as far as the end products are

concerned (Table I). However, the rearrangement occurred much faster in the presence of these silver salts. The reaction with silver hexafluoroantimonate can be run at room temperature (6h) but the final product (4) was less pure and was isolated in lower yield. Silver carbonate induced also rearrangement but an extended reflux period was required.

The same absence of influence of silver ions was observed during the rearrangement of N-t-butyl α-bromoaldimine 6 into α-(N-t-butylamino)acetal 4ba with silver carbonate in methanol (reflux 2h), but an important influence was noticed with the more sterically hindered isopropanol. In isopropanol, α-bromoaldimine 6 rearranged completely into α-(N-t-butylamino)acetal 4bb (91%) but in the presence of silver carbonate or silver acetate, this reaction led to α-isopropoxyaldimine 7bb in 86% and 72% yield, respectively. The rearrangement of α-haloaldimines 1 and 6 in alcoholic medium via α-alkoxyaziridines 2 seems to be limited to isobutyraldimine derivatives as previously observed for the base-induced





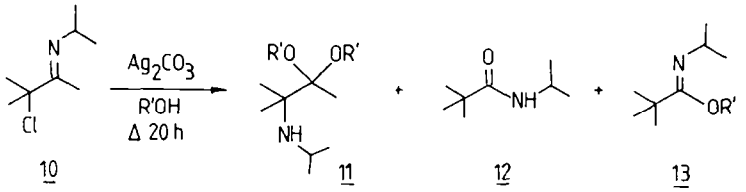
reaction of α-chloroaldimines 1 into α-(N-alkylamino)acetals 4.[9] Also the silver-induced reaction of higher α-bromoaldimines did not lead to α-alkoxylation as exemplified by the conversion of α-bromoaldimine 8 into 1-aza-1,3-diene 9 (84%) under the influence of silver carbonate in isopropanol.

α-Halogenated Ketimines

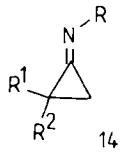
Tertiary α-chloroketimines, e.g. N-(3-chloro-3-methyl-2-butylidene)isopropylamine 10, reacted with silver carbonate in methanol under reflux to give a mixture of 28% α-(N-isopropylamino)acetal 11a (R' = Me) and 72% of a mixture of amide 12 and imidate 13 (R' = Me) in a 2:3 ratio. Without silver carbonate, no amides or imidates, were formed. The same reaction in isopropanol produced no rearranged α-aminoacetal 11b (R' = i-Pr) due to sterical hindrance, but afforded rearranged amide 12 and imidate 13 (R' = i-Pr) in a 1:1 ratio. Amides 12 and imidates 13 are formed via a Favorskii rearrangement. The base-induced Favorskii rearrangement of α-haloketimines is now well documented[10] and was shown to proceed via intermediate cyclopropylideneamines 14. In the case of the silver-induced rearrangements discussed here, it may be that the latter intermediates do not intervene and that a semi-benzil-type rearrangement (15 → 13) occurs.

Tertiary α-bromoketimines 16 readily solvolyzed into α-methoxyketimines 17 in methanol in the presence of silver carbonate under mild reaction conditions (room temperature, 4h). More sterically

hindered substrates have the tendency to give also some 1,2-dehydrobromination into 1-aza-1,3-dienes 20 (not more than 3%).



10 11 12 13



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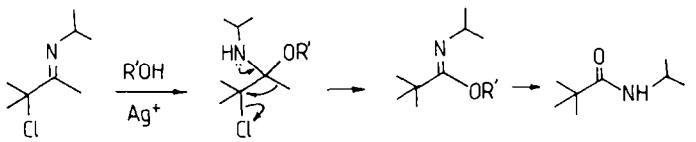
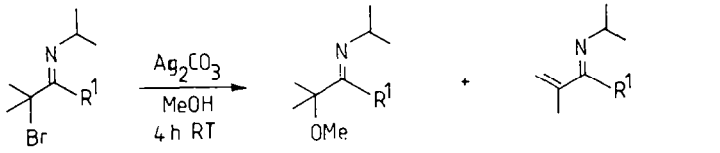


10 15 13 12

Aromatic α-bromoketimines, e.g. 19, reacted analogously with silver carbonate in alcohols into α-alkoxyketimines 20, but an increasing 1,2-dehydrobromination was observed with increasing sterical



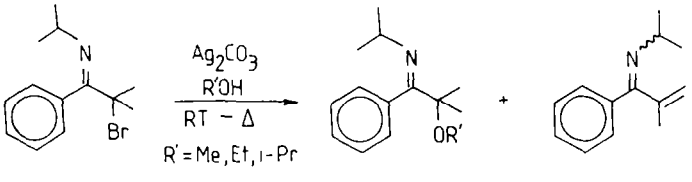
16a R^1 = Me
16b R^1 = i-Pr

17a,b (89-100 %)

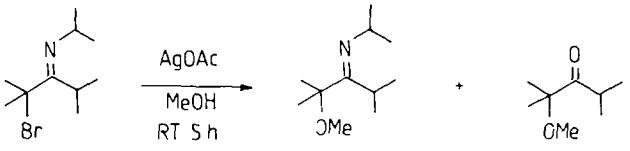
18b (R^1 = i-Pr ; 3 %)

hindrance in the alcohol because higher alcohols required higher reaction temperatures (Table II). Boron trifluoride etherate does not influence the reaction of α-bromoketimines 16 and 19 with silver carbonate in methanol, but its presence always caused some hydrolysis in the final reaction mixture. The presence of these α-methoxyketones does not disturb if these ketones are the final objective of the reaction. Accordingly, α-methoxyketimine 20a (R' = Me) was hydrolyzed with aqueous oxalic acid into α-methoxyisobutyrophenone (84%). This confirms the synthetic potential of the α-alkoxylation of α-bromoketimines. Besides silver carbonate, also silver acetate (1.5 molar equivalents) in methanol cleanly methoxylated α-bromoketimine 16b at room temperature to give 94% α-methoxyketimine 17b

and 3% α-methoxyketone 22, the latter resulting from the aqueous workup. The attempt to convert α-bromoketimine 16b with silver carbonate in 80% aqueous dimethoxyethane at room temperature into

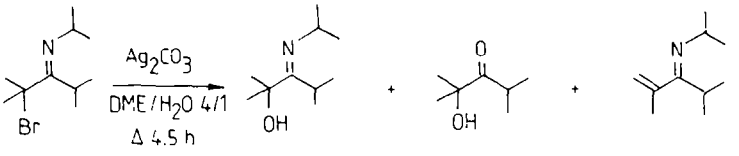


19 20a-c (70-95%) 21 (0-28%)



16b 17b (94%) 22 (3%)

the corresponding α-hydroxyketimine 23 was unsuccessful (no reaction observed). The α-hydroxylation of α-bromoketimine 16b could be accomplished using silver carbonate in 80% aqueous dimethoxyethane under reflux (4.5h) to afford 42% α-hydroxyketimine 23 and 43% α-hydroxyketone 24 (a total of 85% α-hydroxylation), together with 11% of the 1,2-dehydrobrominated 1-aza-1,3-diene 18b.

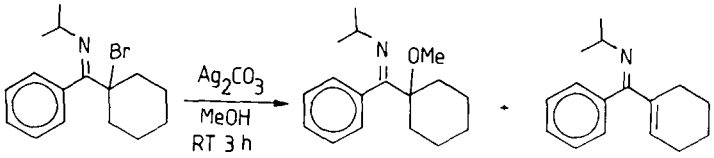


16b 23 (42%) 24 (43%) 18b (11%)

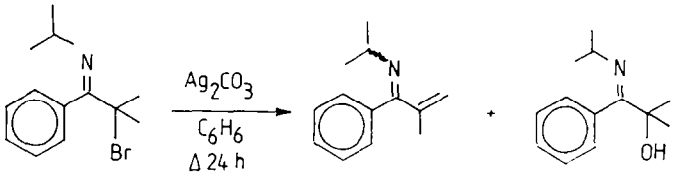
Higher substituted α-bromoketimines, e.g. cyclohexyl derivative 25, reacted with silver carbonate in methanol at room temperature (3h) to give a competition between 1,2-dehydrobromination (27, 86%) and methanolysis (26, 14%).

The reaction of α-bromoketimine 19 in benzene in the presence of silver carbonate caused a clean dehydrobromination into the α,β-unsaturated ketimine 21, which occurred as a mixture of E- and Z-isomers in solution. A small amount of α-hydroxyketimine 28 was also detected by gas chromatographic analysis. Such α-hydroxyketimines are very often present in small quantities in the reaction mixtures of the silver-induced reactions of α-bromoketimines. They are probably formed by reaction of the intermediate α-imidoylcarbenium ion or the pseudo-α-imidoylcarbenium ion with traces of water present in the reaction mixture.

α-Bromoketimines 16 and 19 solvolyze in alcohols into α-alkoxyketimines 17 and 20 under the influence of silver salts by a silver ion assisted and solvent-assistent ionisation of the carbon-bromine



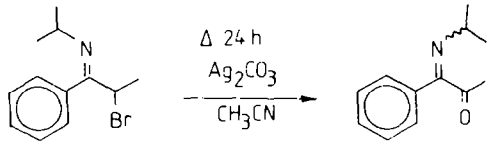
25 26 (14%) 27 (86%)



19 21 (94%) 28 (2%)

bond leading to a pseudo-α-imidoylcarbenium ion, which is neutralized by alkoxylation. Previously it was found that the mechanism of the silver ion assisted solvolysis of phenacyl bromide is best described as a highly concerted push-pull mechanism (electrophilically assisted nucleophilic displacement).[11] However, care should be taken with more bulky substrates because it was observed that the kinetic and product distribution data of the reaction of α-bromoisobutyrophenone with silver perchlorate in aqueous ethanol occurs via a mechanism involving addition of the solvent to the carbonyl group prior to the silver ion assisted solvolysis step.[31] Because of the fact that this process was found to be acid catalyzed, it probably may be ruled out to be operative during reactions of α-bromoketimines and the basic silver carbonate. The silver ion induced ionisation of α-bromoketimines is a useful addition to the area of electron deficient carbenium ions, which received considerable interest in recent years.[6,12]

Similar to secondary α-chloroketimines, secondary α-bromoketimines, e.g. 29, did not react with silver carbonate in methanol at room temperature. However, under reflux for an extended period, α-bromoketimine 29 was oxidized with silver carbonate into α-iminoketone 30, which is isolated as the main product (50%) from a rather complex reaction mixture (preparative gas chromatography). In

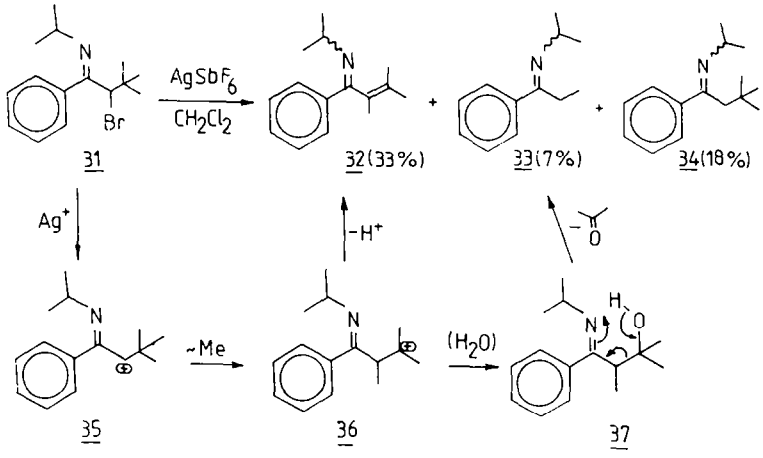


29 30 (90%)

acetonitrile, this oxidation into α-iminoketone 30 occurred cleanly. Some syntheses of carbonyl compounds from the corresponding alcohols with silver carbonate adsorbed on celite have been

described in the literature.[13-15] The conversion of α-bromoketimine 29 into α-iminoketone 30 parallels the oxidation with silver nitrate of the corresponding α-bromoketones into α-diones via α-nitratoketones.[46,47] α-Iminoketone 30 was completely identical with the same compound, prepared according to a more laborious route, involving α-fluorination of propiophenone,[16] bromination into α-bromo-α-fluoropropiophenone,[16] rearrangement with sodium methoxide into 1,1-dimethoxy-1-phenyl-2-propanone,[17] α-chloroether formation to give 1-chloro-1-methoxy-1-phenyl-2-propanone, and imination.[18]

The more sterically hindered α-bromoketimine 31, containing a neopentylic halide, did not react with silver carbonate in methanol under reflux. However, a Wagner-Meerwein type rearrangement was observed with this α-bromoketimine and silver hexafluoroantimonate in dichloromethane under reflux (48h). The reaction products were the rearranged α,β-unsaturated ketimine 32 (33%), the fragmented

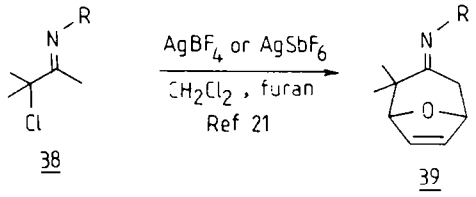


ketimine 33 (7%) and the debrominated ketimine 34 (18%). While the α,β-unsaturated ketimine 32 can be formed via rearrangement of α-imidoylcarbenium ion 35 (methyl migration into 36 and deprotonation), the fragmented ketimine 33 might result from trapping of the carbenium ion 36 by traces of water to give 37. Subsequent retroaldol type cleavage of 37 yields the propiophenone imine 33 and acetone. Similar Wagner-Meerwein rearrangements have been observed for α-acylcarbenium ions[6,33] and also for a steroidal α-imidoylcarbenium ion, generated from an azirine precursor.[19,20] The reduced product, i.e. 34, may originate from reduction of the α-imidoylcarbenium ion by a source of hydride.

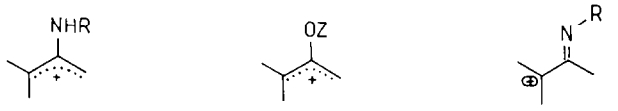
An attempt to induce a Wagner-Meerwein type rearrangement of N-(2-bromo-2-chloro-3,3-dimethyl-1-phenyl-1-butylidene)isopropylamine with silver carbonate in methanol was unsuccessful and led to a complete recovery of starting material.

In the context of the silver ion assisted reactions of α-haloimines, it deserves attention again to mention the trapping by furan of an ionized ketimine, generated from α-chloroketimine 38 with the aid of silver hexafluoroantimonate or silver tetrafluoroborate.[21] 2-Aminoallylcarbenium ions 40 were postulated as intermediates which were trapped by furan via a [4+2]-type cycloaddition to afford bicyclic adducts 39.[21] Due to the resemblance between 2-aminoallylcarbenium ions 40 and the well-known 2-oxyallyl species 41,[22] it is obvious to think in terms of a similar reactivity which gives

preference for concerted cycloadditions with dienes. However, the 2-aminoallylcarbenium ions 40 and α-imidoylcarbenium ions are isomeric species and it may be possible that the latter also intervene in the conversion of 38 into bicyclic adducts 39 via a stepwise mechanism.



38 39



40 41 (Z = H, metal, alkyl, $SiMe_3$, ..) 42

Very few silver-induced reactions of α-halogenated imino compounds have been reported hitherto. The reactivity of α-haloimines sensu strictu towards reaction conditions containing silver ions has not been studied yet, except our foregoing result on the silver-induced cycloaddition of α-chloroketimines with furan into adducts 39.[21] Other examples refer to a related field such as the α-arylation of α-bromooxime ethers with silver tetrafluoroborate in the presence of electron-rich aromatic compounds[23] and the same reaction with olefins into cycloadducts.[24] This α-arylation was explained via the intermediacy of the corresponding α-imidoylcarbenium ions. Another example involves the ionisation of 4-bromo-5-phenyl-2-isoxazolines with silver nitrate in ethanol and subsequent rearrangement of the intermediate α-imidoylcarbenium ion by phenyl group migration into isoxazoles.[25,26] A very specific report on the silver-induced generation of carbenium ions at the α-position of an imino moiety entails the formation of benzil and benzonitrile from 3-chloro-2,3-diphenylazirine.[27]

An interesting point which is raised now is the comparison between the reactivity of α-haloimines, discussed in this report, and the corresponding α-haloketones with respect to silver reagents. The chemistry of α-haloketones is well-documented in the literature.[1] If the carbonyl group is masked as an imine, then the resulting α-haloimine is a valuable synthon provided it can give rise to reactions, other than those of α-haloketones. In this way, α-haloimines act as a complementary means of reactivity allowing to broaden the synthetic potential of α-haloketones. If the reaction products from the conversions of α-haloimines still have their imino moiety, simple hydrolysis provides functionalized carbonyl compounds, which are not accessible via the known routes of α-haloketones. The following comparison makes it clear that the α-haloketimines, discussed in this article, can give rise to useful reaction products, not accessible via α-haloketones.

Tertiary α-bromoketones 44 react with alcohols in the presence of silver salts to afford the semi-benzilic Favorskii rearrangement,[2,3,5,28] while the corresponding α-bromoketimines 43 give rise to clean α-alkoxylation. Aromatic α-bromoketimines also provide mainly α-alkoxylation (70-95%) on silver-induced alcoholysis but some 1,2-dehydrobromination takes place. This useful α-alkoxylation

Table I : Silver Ion Induced Reactions of α-Haloaldimines 1, 6 and 8

Starting α-Chloroaldimine	α-Halogen	Reaction Conditions[a]	α-Amino-acetal[b] 4	α-Alkoxy-aldimine 5	1-Aza-1,3-diene 8	Remarks
1a (R = i-Pr)	Cl	MeOH/Δ 24h	95% 4aa	-	-	-
1a (R = i-Pr)	Cl	i-PrOH/Δ 48h	65% 4ab	-	-	16% 5
1a (R = i-Pr)	Cl	MeOH/1E $AgSbF_6$/RT 6h	40% 4aa	-	-	-
1a (R = i-Pr)	Cl	MeOH/1E Ag_2CO_3/Δ 6h	80% 4aa	-	-	20% α-hydroxyacetal
1a (R = i-Pr)	Cl	i-PrOH/1E Ag_2CO_3/Δ 48h	75% 4ab	-	-	+ several minor unidentified compounds
6	Br	i-PrOH/Δ 17h	91% 4bb	-	-	-
6	Br	MeOH/1E Ag_2CO_3/Δ 2h	80% 4ba	-	-	20% α-hydroxyacetal
6	Br	i-PrOH/1E Ag_2CO_3/Δ 7h	-	86% 7bb	-	-
6	Br	i-PrOH/1E AgOAc/70°C 4h	-	72% 7bb	-	-
8	Br	i-PrOH/1E Ag_2CO_3/Δ 1.5h	-	-	84%	-

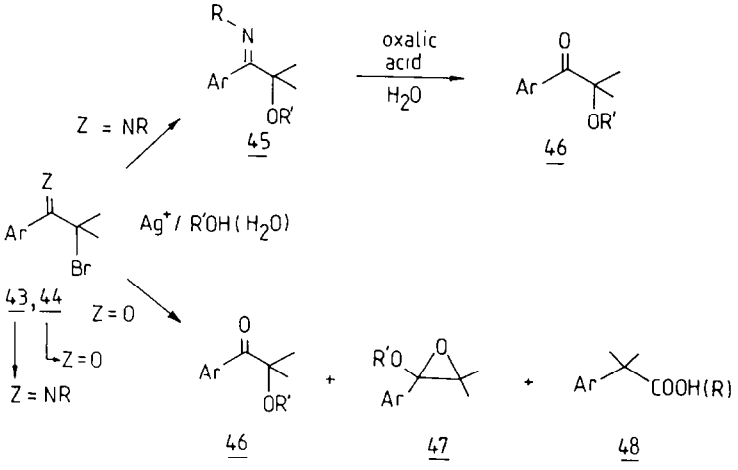
a A 10% solution (w/v) of α-haloaldimine in the given alcohol was used; Δ = reflux; E = molar equivalents; RT = room temperature.
b The first letter refers to the skeleton of the starting α-haloaldimine while the second letter points to the alcohol used (a → R' = Me; b → R' = i-Pr).

Table II : Silver Ion Induced Reactions of α-Haloketimines

Starting α-Haloketimine	α-Halogen	Reaction Conditions[a]	α-Aminoacetal	α-Alkoxyketimine	1,2-Dehydrohalogenation	Favorskii Rearrangement	Remarks
10	Cl	Me-OH/1E Ag_2CO_3/Δ 20h	28% 11 (R' = Me)	-	-	72%	43% imidate 13 (R' = Me) and 29% amide 12
10	Cl	i-PrOH/1E Ag_2CO_3/Δ 18h	-	-	-	100%	50% imidate 13 (R' = i-Pr) and 50% amide 12
16a (R^1 = Me)	Br	MeOH/1E Ag_2CO_3/RT 4h	-	100% 17a	-	-	-
16b (R^1 = Me)	Br	MeOH/0.6E Ag_2CO_3/RT 2h	-	89% 17b	3% 18b	-	-
19	Br	MeOH/0.6E Ag_2CO_3/RT 5h	-	95% 20a	-	-	-
19	Br	MeOH/1/4E $BF_3.Et_2O$/0.6E Ag_2CO_3/RT 2h	-	86% 20a	-	-	10% α-methoxyketone
19	Br	EtOH/0.6E Ag_2CO_3/RT 2h	-	40% 20b	-	-	60% 19
19	Br	EtOH/0.6E Ag_2CO_3/Δ 1.25h	-	87% 20b	13% 21	-	-
19	Br	i-PrOH/0.6E Ag_2CO_3/RT 3h	-	28% 20c	4% 21	-	68% 19
19	Br	i-PrOH/0.6E Ag_2CO_3/Δ 1h	-	70% 20c	28% 21	-	-
19	Br	CH_2Cl_2/0.6E Ag_2CO_3/RT 5h	-	-	-	-	no reaction
19	Br	CH_3CN/0.6E Ag_2CO_3/RT 5h	-	-	-	-	no reaction
19	Br	C_6H_6/0.6E Ag_2CO_3/RT 5h	-	-	-	-	no reaction
19	Br	C_6H_6/0.6E Ag_2CO_3/Δ 24h	-	-	94% 21	-	2% α-hydroxyketimine 28
29	Br	MeOH/1E Ag_2CO_3/RT 1.5h	-	-	-	-	no reaction
29	Br	MeOH/1E Ag_2CO_3/Δ 24h	-	-	-	-	50% α-iminoketone 30 + several other products
29	Br	CH_3CN/1E Ag_2CO_3/Δ 24h	-	-	-	-	90% α-iminoketone 30
25b	Br	MeOH/1.5E Ag_2CO_3/RT 3h	-	12% 26	84% 27	-	-
16b (R^1 = i-Pr)	Br	MeOH/1.5E AgOAc/RT 5h	-	94% 17b	-	-	3% α-methoxyketone 22
16b (R^1 = i-Pr)	Br	DME:H_2O 4:1/1.5E Ag_2CO_3/RT 2h	-	-	-	-	no reaction
16b (R^1 = i-Pr)	Br	DME:H_2O 4:1/1.5E Ag_2CO_3/Δ 4h 30	-	85%	11% 18bb	-	42% 23 and 43% 24
16b (R^1 = i-Pr)	Br	MeOH/$AgNO_3$/K_2CO_3/RT 2.5h	-	60% 17b	-	-	30% 16b
31	Br	CH_2Cl_2/2.6E $AgSbF_6$/Δ 48h	-	-	-	-	33% 32 + 7% 33 + 18% 34
31	Br	MeOH/1.5E Ag_2CO_3/Δ 5h	-	-	-	-	no reaction

[a] A 10% solution (w/v) of α-haloketimine in the given solvent was used, Δ = reflux; E = molar equivalents; RT = room temperature.
[b] This experiment was executed in collaboration with Dr. D. Bonnet-Delpon and Dr. M. Charpentier-Morize (CNRS, Thiais, France).

process contrasts with the silver-induced reaction of the corresponding aromatic α-bromoketones, which only afford synthetically useful α-alkoxylations when activated α-bromoketones (i.e. α-bromo-α-arylketones) are used.[4,29] In the majority of cases, aromatic α-bromoketones with alcohols in the presence of silver salts are converted into mixtures of α-alkoxy ketones (e.g. 46), α-alkoxy-epoxides (e.g. 47) and the corresponding Favorskii-rearrangement products (e.g. 48), i.e. α-arylcarboxylic acids.[5,7,30,31,45] In some cases, only the latter quasi Favorskii rearrangement takes place in moderate to low yields with silver nitrate[2,28] or in good yields with silver hexafluoroantimonate.[5]



The silver-induced 1,2-dehydrobromination of α-bromoketimines (e.g. 19) in non-nucleophilic solvents leads to 1-aza-1,3-dienes (e.g. 21), but, to the best of our knowledge, the same reaction of the corresponding α-bromoketones has been described only twice and leads to a similar 1,2-dehydrobromination into α,β-unsaturated ketones.[6,32]

In conclusion, a clean α-alkoxylation of α-bromoketones 44 has been accomplished via conversion of the latter into α-bromoketimines,[34] subsequent silver ion induced α-alkoxylation and hydrolysis. The direct conversion of α-bromoketones 44 into α-alkoxyketones 46 is problematic due to competitive side reactions, the α-alkoxylation not necessarily taking place at all.

Experimental Part

α-Chloroaldimines 1 were synthesized according to a previously published method involving chlorination of aldimines with N-chlorosuccinimide in carbon tetrachloride.[9] α-Bromoaldimines 6 and 7 were prepared similarly with N-bromosuccinimide as described earlier.[35] α-Haloketimines 10, 16, 19, 25, 29 and 31 were synthesized by condensation of the appropriate α-chloro- or α-bromoketone with a primary amine under the influence of titanium(IV) chloride.[34]

α-Bromo-α-chloroketimine 43 was prepared by chlorination with N-chlorosuccinimide in carbon tetrachloride of α-bromoketimine 36, according to a previously published procedure.[37]

Spectroscopic data of α-haloimines 1,[9] 6,[38] and 10,[34] have been described previously. The following

α-halogenated imines are new compounds (19, 25, 31) or their spectroscopic properties have not been published yet (8,[39] 16a,[40] 16b[40]).

N-[(1-Bromo-1-cyclohexyl)methylidene]t-butylamine 8

^{1}H NMR (CCl_4) 1.16 (9H,s,t-Bu); 1-2.2 (10H,m,$(CH_2)_5$); 7.55 (1H,s,CH=N). IR (NaCl) : 1655 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 29.33 (q,Me_3), 56.27 (s,N<u>C</u>Me_3); 71.99 (s,<u>C</u>-Br); 37.93 (t,$(CH_2)_2$); 23.40 (t,$(CH_2)_2$); 25.34 (t,CH_2); 158.59 (d,<u>C</u>H=N). Mass spectrum m/z (%) 245/7 (M^+, 0.2); 230/2(4); 190/2(14); 166(71); 150(7); 146(4); 136(2); 110(52); 109(9); 108(4); 106(4); 99(23); 94(4); 93(16); 91(4); 84(9); 82(4); 81(9); 67(4); 58(23); 57(100); 56(18); 43(30); 41(23); 40(21).

N-analysis : 5.69% N calcd.; 5.81% N found.

Light yellow oil (98% yield).

N-(3-Bromo-3-methyl-2-butylidene)isopropylamine 16a

^{1}H NMR (CCl_4) δ 1.05 (6H,d,J=6Hz,Me_2C-N); 1.83 (6H,s,Me_2); 2.03 (3H,s,MeC=N); 3.59 (1H,septet,NCH). IR (NaCl) : 1655 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 13.30 (q,<u>Me</u>-C=N); 23.05 (q,<u>Me</u>$_2$CH); 31.75 (q,<u>Me</u>$_2$C-Cl); 50.67 (d,N-<u>C</u>H); 69.30 (s,<u>C</u>-Br); 165.42 (s,<u>C</u>=N). Mass spectrum m/z (%) 205/7 (M^+; 0.2); 126(9); 125(17); 111(4); 110(19); 84(41); 69(15); 68(25); 67(4); 57(5); 55(5); 54(3); 53(5); 43(21); 42(100); 41(31); 40(5).

N-analysis : 6.80% N calcd.; 6.65% N found.

Bp. 55-59°C/11 mmHg (74% yield).

N-(2-Bromo-2,4-dimethyl-3-pentylidene)isopropylamine 16b

^{1}H NMR ($CDCl_3$) δ 1.90 (6H,s,Me_2C-Br); 1.10 (6H,d,J=6Hz,NCH<u>Me</u>$_2$); 1.32 (6H,d,J=7.5Hz, <u>Me</u>$_2$C-C=N); 4.25 (1H,septet,J=6Hz,NC<u>H</u>); 3.25 (1H,septet,J=7Hz,C<u>H</u>-C=N). IR (NaCl) : 1660 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 21.10 (q,<u>Me</u>$_2$C-C=N), 31.38 (d,<u>C</u>H-C=N); 23.59 (q,<u>Me</u>$_2$CN); 49.79 (d,N<u>C</u>H); 32.21 (q,<u>Me</u>$_2$C-Br); 70.44 (s,<u>C</u>-Br); 178.49 (s,<u>C</u>=N). Mass spectrum m/z (%) no M^+; 154(2); 153(5); 148/50(2); 138(2); 112(31); 110(21); 97(3); 96(3); 85(3); 82(3); 80(3); 70(100); 68(98); 55(14); 54(5); 53(3); 43(45); 42(13); 41(41); 40(12); 39(12).

N-analysis : 5.98% N calcd.; 5.79% N found.

Bp. 80-82°C/12 mmHg (82% yield).

N-(2-Bromo-2-methyl-1-phenyl-1-propylidene)isopropylamine 19

^{1}H NMR ($CDCl_3$) δ 1.93 (6H,s,<u>Me</u>$_2$C-Br); 1.02 (6H,d,J=6Hz,Me_2); 3.18 (1H,septet,J=6Hz,NC<u>H</u>); 7.1-7.5 (5H,m,C_6H_5). IR (NaCl) : 1641 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 23.29 (q,<u>Me</u>$_2$C-N); 32.41 (q,<u>Me</u>$_2$CBr); 52.64 (d,N<u>C</u>H); 66.20 (s,<u>C</u>-Br); 168.69 (s,<u>C</u>=N); 127.91 (d,para=<u>C</u>H); 128.43 and 127.80 (each d, =CH meta and ortho); 135.96 (s,$C_{quat.}$). Mass spectrum m/z (%) : 267/9 (M^+; 0.2); 188(2); 172(2); 146(36); 110(5); 104(100); 91(9); 77(13); 51(9); 43(13); 41(22).

N-analysis : 5.22% calcd.; 5.11% N found.

Colorless liquid (93%) (solidified in the refrigerator at -20°C).

N-[1-(1-Bromo-1-cyclohexyl)-1-phenylmethylidene]isopropylamine 25

^{1}H NMR ($CDCl_3$) : δ 0.98 (6H,d,J=6Hz,Me_2); 3.15 (1H,septet,J=6Hz,NCH); 1.3-1.8 (6H,m,$(CH_2)_3$); 1.8-2.2 (4H,m,$(CH_2)_2$); 7.22 (5H,s,C_6H_5). IR (NaCl) : 1632 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) : δ 23.67

(q,$\underline{Me}_2$C-N); 52.47 (d,$\underline{C}$H); 74.13 (s,$\underline{C}$-Br); 38.84 (t,$(CH_2)_2$); 23.28 (t,$(CH_2)_2$); 25.33 (t,CH_2); 168.25 (s,$\underline{C}$=N); 141.96 (s,$C_{quat.}$); 135.85, 128.48 and 127.70 (each d,o-m-p $\underline{C}$H=). Mass spectrum m/z (%) 307/9 (M^+; 1); 306/8(2); 228(40); 146(24); 104(100); 91(8); 77(12); 51(8).
N-analysis : 4.54% N calcd.; 4.63% N found.
Mp. 34°C (yield 96%).

N-(2-Bromo-3,3-dimethyl-1-phenyl-1-butylidene)isopropylamine 31
^{1}H NMR (CCl_4) : δ 1.15 (9H,s,t-Bu); 0.99 and 1.05 (each 3H,each d,J=6Hz,Me_2); 3.30 (1H,septet,J=6Hz,NCH); 4.41 (1H,s,C$\underline{H}$Br); 7.1-7.4 (5H,m,C_6H_5). IR (NaCl) : 1648 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 23.31 (q,Me_2); 52.44 (d,N$\underline{C}$H); 27.90 (q,Me_3); 36.03 (s,$\underline{C}Me_3$); 69.77 (d,$\underline{C}$HBr); 165.29 (s,C=N); 137.46 (s,$C_{quat.}$); 128.16 and 127.51 (each d,one signal is overlapped, =$\underline{C}$H o-m-p). Mass spectrum m/z (%) : no M^+; 238/40(16); 216(11); 200(11); 160(55); 104(100); 77(11); 57(16); 55(11).
N-analysis : 4.73% N calcd.; 4.91% N found.
Colorless oil (98% yield).

N-(2-Bromo-2-chloro-3,3-dimethyl-1-phenyl-1-butylidene)isopropylamine
^{1}H NMR (CCl_4) : δ 1.04 (6H,d,J=6Hz,Me_2); 3.07 (1H,septet,J=6Hz,NC$\underline{H}$); 1.53 (9H,s,t-Bu); 7.35 (5H,s,br,C_6H_5). IR (NaCl) : 1630 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) : δ 23.16 and 22.84 (each q,$\underline{Me}_2$C-N); 53.63 (d,N$\underline{C}$H); 28.30 (q,Me_3); 45.78 (s,$\underline{C}Me_3$); 95.59 (s,$\underline{C}$BrCl); 164.56 (s,$\underline{C}$=N); 135.50 (s,$C_{quat.}$); 127.3 and 129.31 (each d, =$\underline{C}$H ortho and meta); 128.00 (d,$\underline{C}$H=para). Mass spectrum m/z (%) : 329 (M^+; 1); 314(1); 272(5); 250(3); 249(5); 234(8); 194(17); 161(6); 157(5); 146(6); 104(100); 77(11); 43(2); 41(2).
N-analysis : 4.23% N calcd.; 4.18% N found.
Mp. 103°C (99% yield).

General procedure for the Reactions of α-Haloimines with Silver Reagents (Tables I and II)

A solution of 0.02 mol of α-haloimine in the given solvent (Tables I and II; 10% solution w/v) was treated with the given amount of silver reagent (mostly 0.6-1.5 molar equivalents). The reaction was run during the time and at a temperature given in Tables I and II. After cooling, the reaction mixture was poured into 100 ml of 0.5 N aqueous sodium hydroxide and the extraction was performed twice with dichloromethane. The combined extracts were dried (potassium carbonate), evaporated in vacuo to leave the reaction products as an oil. The analysis was performed by means of ^{1}H NMR and preparative gas chromatography. In cases in which a synthetically useful reaction was obtained, the reaction products were distilled in vacuo. Spectroscopic analysis of the purified compounds was performed using ^{1}H NMR, IR and mass spectrometry, sometimes together with ^{13}C NMR spectrometry. Many of the functionalized imines, obtained as reaction products, were further characterized by hydrolysis into the corresponding carbonyl compounds. The hydrolysis was performed with aqueous oxalic acid in the presence of dichloromethane as an organic phase (reflux 1-2 h).

The following compounds were identical with authentic samples described previously : 9,[9] 12,[10] 17a,[36] 30,[18] 22[43] and 24.[43]

Spectroscopic Data of Other Reaction Products

N-[(1,1-Dimethoxy-2-methyl)-2-propyl]-N-isopropylamine 4aa

^{1}H NMR δ ($CDCl_3$) 1.06 (6H,d,J=6Hz,CH$\underline{Me_2}$); 1.06 (6H,s,Me_2); 1.14 (1H,broad,N$\underline{H}$); 2.92 (1H,septet,J=6Hz,NC$\underline{H}$); 3.48 (6H,s,$(OMe)_2$); 3.92 (1H,s,C$\underline{H}(OMe)_2$). IR (NaCl) : 3360 cm^{-1} (NH). ^{13}C NMR ($CDCl_3$) : 22.39 (q,C$\underline{Me_2}$); 26.53 (q,CH$\underline{Me_2}$); 42.23 (d,N$\underline{C}$H); 57.64 (s,$\underline{C}Me_2$); 58.23 (q,$(OMe)_2$); 112.72 (d,$\underline{C}H(OMe)_2$). Mass spectrum m/z (%) 175 (M^+; 0.3); 144(5); 128(3); 112(4); 111(3); 100(71); 96(3); 86(2); 85(3); 84(4); 75(3); 70(10); 57(100); 44(4); 43(9); 42(14); 41(7).
Bp. : 64-65°C/11 mmHg.
N-analysis : 7.99% N calcd.; 7.92% N found.

N-[(1,1-Diisopropoxy-2-methyl)-2-propyl]-N-isopropylamine 4ab

^{1}H NMR δ ($CDCl_3$) 1.05 (6H,s,Me_2); 1.05 (6H,d,J=6.4Hz,N-CH$\underline{Me_2}$); 1.18 (6H,d,J=6.2Hz,OCH$\underline{Me_2}$); 1.22 (6H,d,J=6.2Hz,OCH$\underline{Me_2}$); 3.03 (1H,septet,J=6.4Hz,NC$\underline{H}$); 3.92 (2H,septet,J=6.2Hz,2xOC$\underline{H}$); 4.33 (1H,s,O-CH-O); NH invisible. IR (NaCl) : 3200-3500 cm^{-1}. Mass spectrum m/z (%) : no M^+; 152(6); 130(3); 128(1); 114(4); 112(3); 100(100;i-PrNH=CMe_2); 89(4); 88(6); 86(4); 84(12); 70(6); 57(48); 45(52); 43(24); 42(31); 41(13). ^{13}C NMR ($CDCl_3$) : 22.45, 22.70, 23.64 and 26.49 (all q,all Me's); 42.33 (d,N$\underline{C}$H); 57.48 (s,$\underline{C}Me_2$); 69.99 (d,O$\underline{C}$HMe$_2$); 105.13 (d,O-$\underline{C}$H-O).
N-analysis : 6.05% N calcd.; 6.17% N found.

N-(2-Isopropylamino-2-methyl-1-propylidene)isopropylamine 5

^{1}H NMR δ (CCl_4) 0.98 (6H,d,J=6Hz,NCH$\underline{Me_2}$); 1.08 (6H,d,J=6Hz,C=NCH$\underline{Me_2}$); 1.09 (6H,s,Me_2); 1.5 (1H,s,br,N$\underline{H}$); 2.85 (1H,septet,J=6Hz,HNC$\underline{H}$); 3.25 (1H,septet,J=6Hz,C=NC$\underline{H}$); 7.42 (1H,s,N=C$\underline{H}$). IR (NaCl) : 1660 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) : 23.95, 25.75 and 26.00 (each q,each Me_2); 43.80 (d,NH$\underline{C}$H); 56.05 (s,$Me_2\underline{C}$-NH); 60.91 (d,C=N$\underline{C}$H); 167.44 (d,$\underline{C}$H=N). Mass spectrum m/z (%) : no M^+; 113(12); 100(84); 86(5); 84(10); 70(8); 57(100); 43(84); 42(38); 40(69).

N-[(1,1-Diisopropoxy-2-methyl)-2-propyl]-N-t-butylamine 4bb

^{1}H NMR δ ($CDCl_3$) 1.20 (9H,s,Me_3); 1.15 (6H,s,Me_2); 1.1-1.3 (12H,2xd,J=6.5Hz,($\underline{Me_2}$C-O)$_2$; 3.93 (2H,septet,J=6.5Hz,(CH-O)$_2$); 4.26 (1H,s,O-CH-O). IR (NaCl) : 3350 cm^{-1} (ν_{NH}). ^{13}C NMR ($CDCl_3$) 33.06, 24.04, 23.61 and 22.46 (all q,all Me); 51.36 and 58.26 (each s,$\underline{C}$-N-$\underline{C}$); 70.24 (d,O$\underline{C}$H); 106.18 (d,O-$\underline{C}$H-O).

N-(2-Isopropoxy-2-methyl-1-propylidene)t-butylamine 7bb

^{1}H NMR δ ($CDCl_3$) 1.11 (6H,d,J=6Hz,CH$\underline{Me_2}$); 1.16 (9H,s,t-Bu); 1.27 (6H,s,Me_2); 3.70 (1H,septet,J=6Hz,OC$\underline{H}$); 7.55 (1H,s,C$\underline{H}$=N). IR (NaCl) : 1671 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) : 24.63 and 24.95 (each q,each $\underline{Me_2}$); 29.59 (q,Me_3); 56.45 (N$\underline{C}Me_3$); 65.01 (d,O$\underline{C}$H); 76.79 (s,$Me_2\underline{C}$-O-iPr); 162.08 (d,CH=N). Mass spectrum m/z (%) 185 (M^+; 0.02); 170(0.02); 128(3); 127(6); 112(3); 101(8); 86(2); 84(3); 72(2); 71(3); 70(7); 59(100); 57(31); 49(3); 43(7); 42(11); 41(8); 40(3).
N-analysis : 7.56% N calcd.; 7.41% N found.

N-(2-methoxy-2,4-dimethyl-3-pentylidene)isopropylamine 17b (R^1 = i-Pr)

^{1}H NMR δ ($CDCl_3$) 1.27 (6H,s,$\underline{Me_2}$C-O); 1.10 (6H,d,J=6Hz,$\underline{Me_2}$C-N); 1.22 (6H,d,J=7Hz, $\underline{Me_2}$C-C=N); 3.15 (3H,s,OMe); 3.11 (1H,septet,J=7Hz,C$\underline{H}$-C=N); 4.18 (1H,septet,J=6Hz,NC$\underline{H}$). IR

(NaCl) : 1667 cm^{-1} ($\nu_{C=N}$); 2820 cm^{-1} (ν_{OMe}). ^{13}C NMR ($CDCl_3$) 20.91 (q,Me_2); 24.05 (q,Me_2); 24.64 (q,Me_2); 28.27 (d,CH-C=N); 49.71 (d,NCH); 81.05 (s,C-O); 51.32 (q,OMe); 173.16 (s,C=N). Mass spectrum m/z (%) no M^+; 112(13); 73(22); 70(100); 68(7); 59(1); 58(1); 55(4); 54(2); 53(1); 43(4); 42(8); 41(18); 39(6).

N-analysis : 6.56% N calcd.; 6.42% N found.

This α-methoxyketimine 17b was further characterized by hydrolysis (aqueous oxalic acid) into 2-methoxy-2,4-dimethyl-3-pentanone 22.[43]

N-Isopropyl isopropyl 2,2-dimethylpropanimidate 13 (R' = i-Pr)

δ (CCl_4) : 1.05 (6H,d,J=6Hz,NCHMe_2); 1.15 (6H,d,J=6Hz,O-CHMe_2); 1.20 (9H,s,t-Bu); 4.17 (1H,septet,J=6Hz,NCH); 4.87 (1H,septet,J=6Hz,OCH). IR (NaCl) : 1650 cm^{-1} ($\nu_{C=N}$).

N-Isopropyl methyl 2,2-dimethylpropanimidate 13 (R' = Me)

δ ($CDCl_3$) : 1.09 (6H,d,J=6Hz,CHMe_2); 1.20 (9H,s,t-Bu); 3.56 (3H,s,OMe); 4.19 (1H,septet,J=6Hz, NCH). IR (NaCl) : 1660 cm^{-1} ($\nu_{C=N}$).

Both compounds 13 (R' = Me,i-Pr) were further characterized by hydrolysis into the corresponding carboxamide 12, which was compared with an authentic sample.

N-[(3,3-Dimethoxy-2-methyl)-2-butyl]-N-isopropylamine 11 (R' = Me)

δ (CCl_4) : 1.00 (6H,d,J=6Hz,Me_2CH); 1.00 (6H,s,Me_2); 1.23 (3H,s,Me); 3.26 (6H,s,$(MeO)_2$); 2.90 (1H,septet,J=6Hz,CH); NH invisible. IR (NaCl) : 3360 cm^{-1} (ν_{NH}). Mass spectrum m/z (%) : no M^+, 142(26); 100(76); 99(12); 84(21); 68(16); 67(37); 58(100); 44(83); 43(38); 42(85); 41(45).

N-(2,4-Dimethyl-1-penten-3-ylidene)isopropylamine 18b

^1H NMR ($CDCl_3$) δ 1.80 (3H,m,MeC=); 1.08 (6H,d,J=7Hz,Me_2C-C=N); 1.05 (6H,d,J=6.2Hz, Me_2C-N); 2.52 (1H,septet,J=7Hz,CH-C=N); 3.63 (1H,septet,J=6.2Hz,NCH); 4.60 and 5.05 (each 1H,each m,C=CH_2). IR (NaCl) : 1654 cm^{-1} (νC=N), 1635 cm^{-1} (νC=C). Mass spectrum m/z (%) 153 (M^+; 5); 138(3); 110(18); 70(13); 68(100); 55(7); 44(3); 43(20); 42(5); 41(25); 40(12); 39(7).

N-analysis : 9.14% N calcd.; 9.05% found.

This α,β-unsaturated ketimine 18b was further characterized by hydrolysis (aqueous oxalic acid) into 2,4-dimethyl-1-pentene-3-one.[43]

N-(2-methoxy-2-methyl-1-phenyl-1-propylidene)isopropylamine 20a

^1H NMR ($CDCl_3$) δ 1.33 (6H,s,Me_2C-O); 3.30 (3H,s,OMe); 1.05 (6H,d,J=6Hz); 3.30 (1H,septet,J=6Hz, NCH); 7.0-7.5 (5H,m,C_6H_5). IR (NaCl) : 1645 cm^{-1} (νC=N); 2820 cm^{-1} (ν_{OMe}). ^{13}C NMR ($CDCl_3$) δ 24.85 (q,Me_2); 23.87 (q,Me_2C-N); 52.52 (d,NCH); 78.85 (s,C-O); 169.32 (s,C=N); 137.15 (s,$C_{quat.}$); 127.94 and 127.20 (each d,CH ortho and meta); 127.56 (d,CH para). Mass spectrum m/z (%) 219 (M^+, 0.2); 189(16); 146(30); 104(100); 91(16); 77(4); 73(14); 58(8); 44(22); 40(20).

Bp. 40-42°C/0.05 mmHg.

N-analysis : 6.39% N calcd.; 6.36% N found.

N-(2-Ethoxy-2-methyl-1-phenyl-1-propylidene)isopropylamine 20b

^{1}H NMR ($CDCl_3$) δ 1.02 (6H,d,J = 6Hz,Me_2C-N); 1.14 (3H,t,J = 7Hz,Me); 1.34 (6H,s,Me_2C-O); 3.30 (1H,septet,J = 6Hz,NCH); 3.49 (2H,q,J = 7Hz,OCH_2); 6.9-7.5 (5H,m,C_6H_5). IR (NaCl) 1644 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 25.50 (q,$\underline{Me}_2$C-O); 23.87 (q,$\underline{Me}_2$C-N); 52.42 (d,N$\underline{C}$H); 78.72 (s,C-O); 58.23 (t,OCH_2); 15.81 (q,Me); 170.00 (s,$\underline{C}$=N); 137.20 (s,$C_{quat.}$); 127.27 and 127.84 (each d,$\underline{C}$H = ortho and meta); 127.47 (d,$\underline{C}$H = para). Mass spectrum m/z (%) : no M^+, 189(1); 172(1); 146(2); 131(2); 129(1); 119(1); 115(2); 104(100); 91(4); 87(12); 77(11); 76(2); 68(2); 59(4); 51(5); 43(13); 42(4); 41(14); 39(5).

N-analysis : 6.00% N calcd.; 6.11% found.

N-(2-Isopropoxy-2-methyl-1-phenyl-1-propylidene)isopropylamine 20c

^{1}H NMR ($CDCl_3$) d 1.04 (6H,d,J = 6Hz,Me_2C-N); 1.10 (6H,d,J = 6Hz,Me_2C-O); 1.32 (6H,s,Me_2); 3.33 (1H,septet,J = 6Hz,N$\underline{C}$H); 4.03 (1H,septet,J = 6Hz,O$\underline{C}$H); 7-7.5 (5H,m,C_6H_5). IR (NaCl) : 1641 cm^{-1} ($\nu_{C=N}$). ^{13}C NMR ($CDCl_3$) δ 23.78 (q,$\underline{Me}_2$C-N); 52.31 (d,N$\underline{C}$H); 26.58 (q,$\underline{Me}_2$C-O); 78.61 (s,N=C-$\underline{C}$-O); 24.91 (q,$\underline{Me}_2$CH-O); 64.81 (d,$\underline{C}$H-O); 137.52 (s,$C_{quat.}$); 127.39 (d,$\underline{C}$H = para); 127.52 and 127.75 (each d, = $\underline{C}$H ortho and meta); 170.57 (s,$\underline{C}$ = N). Mass spectrum m/z (%) : no M^+, 172(2); 146(25); 131(2); 119(2); 115(2); 104(100); 103(6); 101(4); 91(3); 77(8); 76(2); 68(1); 59(21); 51(1); 43(6); 42(2); 41(7); 39(3).

N-analysis : 5.66% N calcd.; 5.72% N found.

N-(2-Methyl-1-phenyl-2-propen-1-ylidene)isopropylamine 21

^{1}H NMR (CCl_4) E/Z 1:3 δ 1.02 (Z) and 1.15 (E) (6H,2d,J = 6Hz,Me_2); 3.26 (Z) and 3.84 (E) (1H,2 septets,J = 6Hz,N$\underline{C}$H); 1.87 (E) and 2.03 (Z) (3H,m,MeC=); 4.73 (Z) and 5.42 (Z), 4.85 (E) and 5.33 (E) (2H,m,C=CH_2); 6.8-8 (5H,m,C_6H_5). IR (NaCl) : 1640-1610 cm^{-1} ($\nu_{C=C}$ and $\nu_{C=N}$). Mass spectrum m/z (%) : 187 (M^+; 24); 186(20); 172(54); 144(12); 131(20); 129(20); 115(8); 104(100); 91(14); 77(24); 68(16); 51(12); 41(28); 40(20).

Bp. 37-43°C/0.05 mmHg.

N-analysis : 7.48% N calcd.; 7.34% found.

N-(1-Phenyl-1-cyclohexen-1-ylmethylidene)isopropylamine 27

^{1}H NMR ($CDCl_3$) E/Z 1:4 δ 1.05 (Z) and 1.21 (E) (3H,each d,J = 6Hz,Me_2); 3.35 (Z) and 3.96 (E) (1H,septet,J = 6Hz,NCH); 5.70 (1H,m,C$\underline{H}$=); 1.4-1.9 (4H,m,CH_2CH_2); 2-2.6 (4H,m,CH_2-C=C-CH_2); 7-8 (5H,m,C_6H_5). IR (NaCl) : 1606 and 1595 cm^{-1} ($\nu_{C=C}$, $\nu_{C=N}$ and $\nu_{arom.}$). ^{13}C NMR (E/Z) ($CDCl_3$) 167.33 (s,$\underline{C}$=N,major), 167.25 (s,$\underline{C}$=N,minor); 52.36 (d,N$\underline{C}$H,major); 52.59 (d,N$\underline{C}$H,minor); 127.93, 127.55, 140.24, 137.85, 136.39, 134.96, 28.08, 26.22, 25.07, 24.73, 24.39, 23.97, 23.69, 22.65, 22.30, 22.01.

N-analysis : 6.16% N calcd.; 6.06% N found.

The identity of this compound was further established by acidic hydrolysis (aqueous oxalic acid, dichloromethane, Δ 1H) into (1-cyclohexen-1-yl)phenylketone.[41]

N-[(1-methoxy-1-cyclohexyl)phenylmethylidene]isopropylamine 26

^{1}H NMR ($CDCl_3$) δ 1.05 (6H,d,J = 6Hz,Me_2); 3.3 (1H,septet,J = 6Hz,N$\underline{C}$H); 3.30 (3H,s,OMe); 1.2-2.5 (10H,m,$(CH_2)_5$); 7-7.2 and 7.3-7.5 (5H,m,C_6H_5). IR (NaCl) : 1635 cm^{-1} ($\nu_{C=N}$).

N-(2-Hydroxy-2-methyl-1-phenyl-1-propylidene)isopropylamine 28
^{1}H NMR (CCl_4) δ 1.05 (6H,d,J = 6Hz,Me_2); 3.3 (1H,septet,J = 6Hz,NCH); 1.20 (6H,s,Me_2); 6.9-7.5 (5H,m,C_6H_5). IR (NaCl) : 3300 cm^{-1} (ν_{OH}); 1648 cm^{-1} ($\nu_{C=N}$).

N-(2,3-Dimethyl-1-phenyl-2-buten-1-ylidene)isopropylamine 32
^{1}H NMR ($CDCl_3$) δ 1.28 (6H,d,J = 6Hz,Me_2;the detail of the doublet shows a fine splitting which points probably to non-equivalence of the N-i-Pr methyls;both doublets resonate with a difference of 1.2Hz); 1.56 and 1.75 (each 3H,each m,due to allylic coupling,2xMeC =); 1.85 (3H,s,br,MeC =); 3.81 (1H,septet,J = 6Hz,NCH); 7.3-7.5 (3H,m,meta/para CH =); 7.7-8.0 (2H,m,ortho CH =). IR (NaCl) : 1618 cm^{-1} ($\nu_{C=N}$), 1575 cm^{-1} ($\nu_{C=C}$ and $\nu_{arom.}$). ^{13}C NMR ($CDCl_3$) : 17.68, 18.86, 22.41, 23.63, 24.18 (all q,all Me); 52.78 (d,NCH); 167.52 (s,C = N); 126.03 and 129.00 (each s,C = CMe_2); 138.68 (s, = $C_{quat.}$); 129.44 (d,CH = para); 128.26 and 127.69 (each d, = CH ortho and meta). Mass spectrum m/z (%) : 215 (M^+, 28); 214(23); 200(98); 172(94); 157(32); 104(100); 96(23); 77(39); 69(18); 41(80). N-analysis : 6.50% N calcd.; 6.62% N found.

Hydrolysis of α-Alkoxyketimines into α-Alkoxyketones
The procedure is exemplified for the conversion of α-methoxyketimine 20a into 2-methoxy-2-methyl-1-phenyl-1-propanone 46 (Ar = C_6H_5; R' = Me). A solution of 2.19 g (0.01 mol) of 20a in 30 ml dichloromethane was treated with 40 ml water and 1.89 g (0.015 mol) of oxalic acid (2 aq.). The two-phase-system was refluxed with vigorous stirring during 1 h after which the organic layer was isolated. The aqueous phase was extracted with ether and the combined organic fractions were dried ($MgSO_4$). Evaporation under vacuo afforded α-methoxyisobutyrophenone 42 as a light yellow oil (1.50 g; 84%; purity > 97% as evidenced from GLC and ^{1}H NMR). This compound was identical in all aspects (^{1}H and ^{13}C NMR, IR, MS) with the known compound.[44]

References

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$ "Research Assistant" (Aspirant) of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" (National Fund for Scientific Research).
1. N. De Kimpe, R. Verhé, "The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines", Eds. S. Patai and Z. Rappoport, J. Wiley and Sons (1988).
2. A.C. Cope, E.S. Graham, J. Am. Chem. Soc., 73, 4702 (1951).
3. E.W. Warnhoff, C.M. Wong, W.T. Tai, J. Am. Chem. Soc., 90, 514 (1968).
4. D. Baudry, M. Charpentier-Morize, Tetrahedron Letters, 3013 (1973).
5. N. De Kimpe, L. De Buyck, R. Verhé, N. Schamp, Chem. Ber., 116, 3631 (1983) and references cited therein.
6. J.-P. Bégué and M. Charpentier-Morize, Acc. Chem. Res., 13, 207 (1980) and references cited therein.
7. C. Giordano, G. Castaldi, F. Casagrande, L. Abis, Tetrahedron Letters, 1385 (1982).
8. C. Giordano, G. Castaldi, F. Casagrande, A. Belli, J. Chem. Soc. Perkin Trans. I, 2575 (1982).
9. N. De Kimpe, R. Verhé, L. De Buyck, H. Hasma, N. Schamp, Tetrahedron, 32, 2457 (1976).
10. N. De Kimpe, P. Sulmon, L. Moëns, N. Schamp, J.-P. Declercq, M. Van Meerssche, J. Org. Chem.,

51, 3839 (1986).
11. J. Pasto, K. Garves, J. Org. Chem., 32, 778 (1967).
12. T.T. Tidwell, Angew. Chem., 96, 16 (1984).
13. Houben-Weyl, Part Oxidation, Vol. IV/1b, p. 76 (1975).
14. G. Büchi, H. Wüest, J. Org. Chem., 36, 609 (1971).
15. R.G. Buttery, L.C. King, B.O. Juliano, J.G. Turnbaugh, J. Agric. Food Chem., 31, 823 (1983).
16. N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, J. Org. Chem., 43, 2933 (1978).
17. N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, Tetrahedron Letters, 2257 (1980).
18. N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, Bull. Soc. Chim. Belg., 91, 99 (1982).
19. G. Alvernhe, S. Lacombe, A. Laurent, Tetrahedron Letters, 21, 1437 (1980).
20. R. Flammang, S. Lacombe, A. Laurent, A. Maquestiau, B. Marquet, S. Novkova, Tetrahedron, 42, 315 (1986).
21. N. De Kimpe, M. Palamareva, R. Verhé, L. De Buyck, N. Schamp, J. Chem. Research, 190 (1986).
22. H.M.R. Hoffmann, Angew. Chem., 96, 29 (1984).
23. S. Shatzmiller, R. Lidor, E. Shalom, E. Bahar, J. Chem. Soc. Chem. Commun., 795 (1984).
24. S. Shatzmiller, E. Shalom, E. Bahar, J. Chem. Soc. Chem. Commun., 1522 (1984).
25. J.F. Hansen, S.A. Strong, J. Heterocyclic Chem., 14, 1289 (1977).
26. J.F. Hansen, Y.I. Kim, S.E. McCrotty, S.A. Strong, D.E. Zimmer, J. Heterocycl. Chem., 17, 475 (1980).
27. T.C. Gallagher, R.C. Storr, Tetrahedron Lett., 2905 (1981).
28. D.N. Kevill, N.H. Cromwell, J. Org. Chem., 29, 499 (1964).
29. a) K. Takeuchi, T. Kitagawa, K. Okamoto, J. Chem. Soc. Chem. Commun., 7 (1983).
    b) F.G. Bordwell, R.G. Scamehorn, J. Am. Chem. Soc. 93, 3410 (1971).
    c) C.L. Stevens, J.J. DeYoung, J. Am. Chem. Soc., 76, 718 (1954).
30. C. Giordano, F. Minisci, Chem. Ind. (Rome), 64, 340 (1982).
31. D.J. Pasto, J.P. Sevenair, J. Am. Chem. Soc., 93, 711 (1971).
32. J.-P. Gégué, D. Bonnet, Tetrahedron, 30, 141 (1974).
33. J.F. Pazos, J. Pacifici, G.O. Pierson, D.B. Sclove, F.D. Greene, J. Org. Chem., 39, 1990 (1974).
34. N. De Kimpe, R. Verhé, L. De Buyck, L. Moëns, N. Schamp, Synthesis, 43 (1982).
35. N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, Can. J. Chem., 62, 1812 (1984).
36. N. De Kimpe, P. Sulmon, R. Verhé, L. De Buyck, N. Schamp, J. Org. Chem., 48, 4320 (1983).
37. N. De Kimpe, R. Verhé, L. De Buyck, S. Tukiman, N. Schamp, Tetrahedron, 35, 789 (1979).
38. N. De Kimpe, E. Stanoeva, R. Verhé, N. Schamp, Synthesis, 587 (1986).
39. N. De Kimpe, Z. Yao, N. Schamp, Tetrahedron Letters, 27, 1707 (1986).
40. N. De Kimpe, P. Sulmon, N. Schamp, Bull. Soc. Chim. Belg., 95, 567 (1986).
41. H.O. House, V. Paragamian, R.S. Ro, D.J. Wluka, J. Am. Chem. Soc., 82, 1457 (1960).
42. P. de Mayo, H. Ramnath, Can. J. Chem., 64, 1293 (1986).
43. H.O. House, G.A. Frank, J. Org. Chem., 30, 2948 (1965).
44. H.O. House, A.V. Prabhu, J.M. Wilkins, L.F. Lee, J. Org. Chem., 41, 3067 (1976).
45. N.H. Cromwell, P.H. Hess, J. Am. Chem. Soc., 82, 136 (1960); N.H. Cromwell, P.H. Hess, J. Am. Chem. Soc., 83, 1237 (1961).
46. W.D. Emmons, J.P. Freeman, J. Am. Chem. Soc., 77, 4415 (1955).
47. N. Vinot, Bull. Soc. Chim. Fr., 2708 (1971).