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Formation of α-Iminoketones and α-Diimines Versus Favorskii Rearrangement Products from the Reaction of α,α'-Dibromoketones and Primary Amines

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ABSTRACT

The reaction of aliphatic acyclic α,α'-dibromoketones with primary amines gave rise to α-iminoketones and α-diimines. Both reaction products could be selectively obtained under appropriate reaction conditions. Sterically hindered α,α'-dibromoketones did not react with primary amines, although, under forcing conditions the Favorskii rearrangement could be induced. In aqueous methanol, α,α'-dibromoketones reacted with primary amines to give the Favorskii rearrangement instead of the α-iminoketone formation. Alicyclic α,α'-dibromoketones behave differently towards primary amines in that five-membered rings afford 2-(N-alkyl)amino-2-cyclopentenones, while six-membered rings give rise to a Favorskii ring contraction.

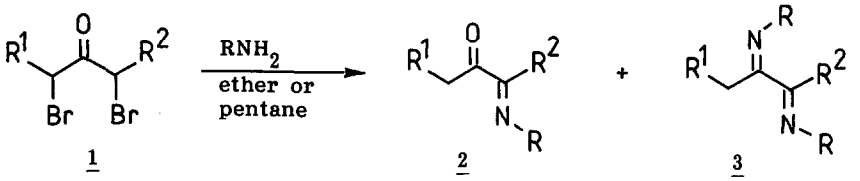
INTRODUCTION

α,α'-Dibromoketones have been the subject of considerable study in the last years and, as a result, they have been developed as valuable substrates for the synthesis of a variety of reaction products, including functionalized 1,3-dioxolanes,[4,5] α-iminocyclobutanones,[6] cyclopropanone adducts,[7] 3-thietanones,[8] α-acetoxyketones,[9] 4-cycloheptenones,[10] bicyclo-[3.2.1]oct-6-en-3-ones and (heterocyclic) analogues,[10-15] cyclopentenones,[16] and many natural products.[17] Also the reaction of α,α'-dibromoketones with amines received considerable attention. Depending upon the type of α,α'-dibromoketone and the type of amine used, a great variety of reactions was observed. Classical mechanistic possibilities of these reactions are the Favorskii rearrangement, 1,2-dehydrobromination, aminolysis resulting from various types of nucleophilic substitution, 1,3-dehydrobromination and attack of the carbonyl group by the amine (imination). The reaction of cyclic α,α'-dibromoketones with primary amines was reported to afford the ring-contracted α,β-unsaturated carboxylic amides, according to the Favorskii rearrangement.[18] A competition between

Favorskii rearrangement and enaminoketone formation was observed when these substrates were brought into reaction with secondary amines.[19] On the other hand, α,α'-dibromoketones and tertiary amines (or pyridines) have been shown to give rise to α,β-dehydrobromination[20] or α,α'-dehydrobromination,[21] yielding α,β-unsaturated ketones or cyclopropenones, respectively. The reaction of aliphatic α,α'-dibromoketones 1 with primary amines is, to our knowledge, not studied hitherto, apart from our preliminary communication.[22] The latter report described some initial research on the surprising conversion of α,α'-dibromoketones with primary amines into α-iminoketones 2 and α-diimines 3. In the present article, more details and extensions of this novel synthesis of α-iminoketones and α-diimines are reported, with special focus on the observed competition with the Favorskii rearrangement. The scope and limitations of these transformations are reported.

RESULTS AND DISCUSSION

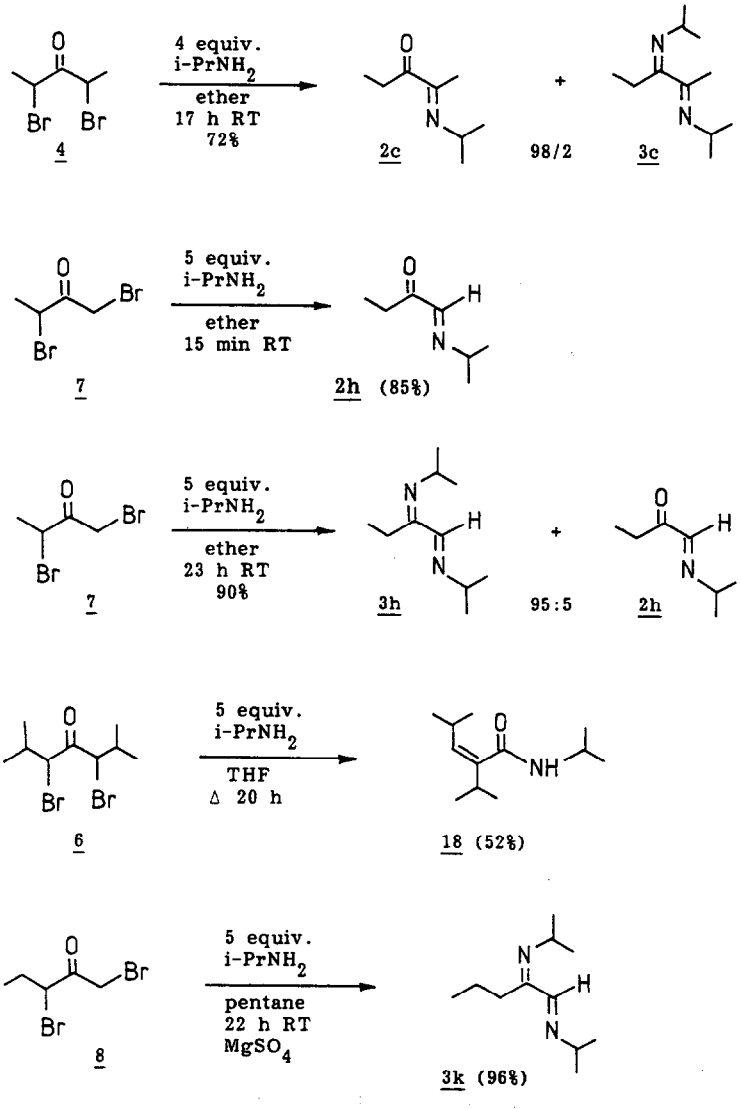
The reaction of aliphatic α,α'-dibromoketones 1 with an excess of primary amines in ether at room temperature leads to the instanteneous precipitation of the amine hydrochloride. Depending on the substrate, the amine and the reaction time, variable ratios of α-iminoketones 2 and α-diimines 3 were observed (Table I). Unhindered amines, e.g. methylamine



1 2 3

and ethylamine, give rise to mixtures of α-iminoketones 2 and α-diimines 3 (entries 1, 2, 5). On the other hand, the more hindered isopropylamine forms α-iminoketones 2 by far as the major reaction products (entries 3, 10, 19), even with relatively unhindered α,α'-dibromoketones 1 (R^1, R^2 = H, Me). It is clear that a relatively fast conversion into α-iminoketones 2 occurs, followed by a slow imination into α-diimines 3. With α-ketoaldimines 2 (R^2 = H) the latter process is still occurring smoothly but α-ketoketimines 2 (R^2 = Me, Et) are only very slowly converted into α-diimines 3 or almost not at all (entries 3, 6). The slow conversion of 2 into 3 was monitored by ^1H NMR and GC analysis for the reaction of 1,3-dibromo-2-butanone 4 (R^1=Me; R^2=H) with isopropylamine in ether at room temperature (entries 11-14). A fast reaction to afford α-iminoketone 2h (85%) in 15 min occurred, while a 2:1 ratio of α-iminoketone 2h and

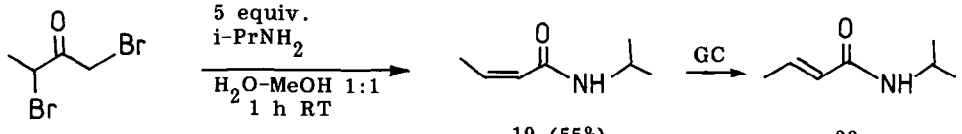
α-diimine 3h was noticed after 40 min. This ratio changed to 2:3 after 100 min and was gradually built up to 5:95 after 23 h. Sterically hindered α,α'-dibromoketones 1 (R^1=R^2=i-Pr,t-Bu) and hindered amines, e.g. isopropylamine, did not react (entries 7, 9, 46). However, under more forcing conditions, i.e. reflux in tetrahydrofuran for 20 h (entry 8), a Favorskii rearrangement could be induced to produce the corresponding



α,β-unsaturated amide 18. Less hindered α,α'-dibromoketones, e.g. 1 (R^1=Me; R^2=H) do not give the Favorskii rearrangement upon heating with isopropylamine in ether but they give rise to α-diimines 3 as the major reaction product (entry 15).

As can be judged from the results in table I, α,α'-dibromomethylketones 1 (R^2=H) react with primary amines in a regiospecific way to produce α-ketoaldimines 2 (R^2=H) and/or α-iminoaldimines 3 (R^2=H). No trace of the isomeric compounds $R^1C(=NR)COCH_3$ or the corresponding α-diimines were detected in any cases (entries 10-16, 18-30). The selective formation of α-ketoaldimines 2 (R^2=H) is at best accomplished with 3 molar equivalents of the primary amine in ether (entry 19), while the selective formation of the corresponding α-diimine 3 (R^2=H) is most conveniently performed with an excess (5 molar equiv.) of the primary amine in ether or pentane (22-23 h RT) in the presence of magnesium sulfate as drying agent (entries 14 and 27).

The solvent plays an important role in the conversion of α,α'-dibromoketones 1 into 2 and 3. With an excess of isopropylamine (5 molar equiv.), 1,3-dibromo-2-pentanone 8 (R^1=Et; R^2=H) could not be converted completely into α-diimine 3k when dichloromethane (17 h, room temperature) of carbontetrachloride (70 h, room temperature) were used as solvents (entries 25, 26). With isopropylamine as solvent, this conversion into 3k was complete but some unidentified products were also formed. The most complete conversion into α-diimine 3k was accomplished in pentane as solvent (entry 27). More polar solvents, e.g. methanol, induce an exothermic conversion of 1,3-dibromo-2-butanone 7 (R^1=Me; R^2=H) with isopropylamine (5 equiv.) into the α-diimine 3h and α-iminoketone 2h (ratio 1:9). However, the yield was rather low (50%) and the reaction mixture contained several unidentified compounds. Surprisingly, when the same reaction was run in 50% aqueous methanol, the reaction product was the Favorskii amide 19 (55% yield), together with varying amounts (5-15%) of methyl-3-(N-isopropylamino)butyrate (Favorskii ester which underwent Michael addition). The stereospecifically formed (Z)-amide 19 was converted partially into the (E)-amide 20 upon preparative gas chromatography (entry 17).



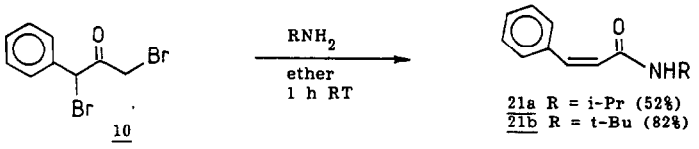
7 19 (55%) 20

Titanium(IV) chloride in benzene could not direct the reaction of α,α'-dibromoketone 7 (R^1=Me; R^2=H) with isopropylamine into the formation of the corresponding α,α'-dibromoketimine (entry 18), as opposed to the general synthesis of α-haloketimines from α-haloketones.[23]

A striking influence in the primary amine is observed when using sterically hindered α,α'-dibromoketones 1. The reaction of 1,3-dibromo-4-methyl-

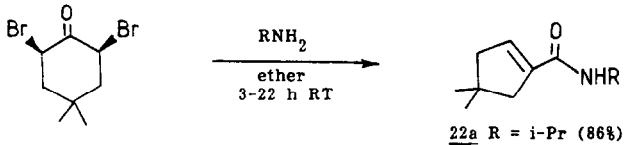
2-pentanone 9 with isopropylamine in ether at room temperature gave rise to the α-iminoketone 21 exclusively (entries 28, 29). However, the same substrate, upon reaction with n-propylamine in ether was converted smoothly into the α-diimine 31 exclusively, indicative of the steric requirements in the primary amine.

α,α'-Dibromoketones 1 having an activating substituent at the α-position, such as in 1,3-dibromo-1-phenyl-2-propanone 10, react with primary amines in ether to afford the Favorskii rearrangement products, i.e. (Z)-α,β-



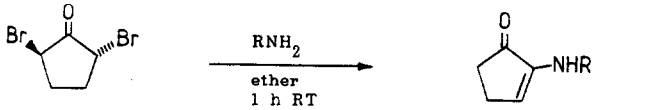
10

21a R = i-Pr (52%)
21b R = t-Bu (82%)



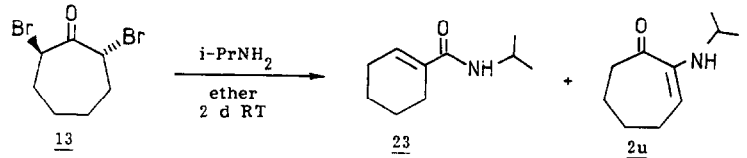
11

22a R = i-Pr (86%)
22b R = t-Bu (95%)
22c R = n-Pr (98%)



12

2s R = i-Pr (60%)
2t R = t-Bu (55%)



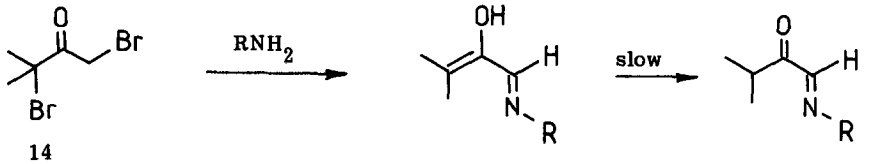
13 23 2u

unsaturated carboxylic amides 21, exclusively (entries 31, 32).

Cyclic α,α'-dibromoketones react with primary amines in ether in different ways depending upon the ring size. Cis-2,6-Dibromo-4,4-dimethyl-2-cyclohexanone 11 reacts smoothly with primary amines to afford ring-contracted Favorskii rearrangement products, i.e. 4,4-dimethyl-1-cyclopentenecarboxylic amides 22 in 86-98% yield (entries 33-35). This result parallels the reaction of analogous substrates such as 3,5-dibromo-2,2,6,6-tetramethyl-

4-piperidone[18a,b,d] and 2,6-dibromo-3,3,5,5-tetramethyl-1,4-cyclohexanedione[18c] with ammonia into ring-contracted Favorskii compounds. On the other hand, trans-2,5-dibromocyclopentanone 12 condensed with isopropylamine or t-butylamine in ether at room temperature to give "α-iminoketones", which occurs entirely under the enamine form 2s,t (entries 36, 37). Thus, primary amines, like secondary amines,[19b] give a similar type of reaction as observed for acyclic aliphatic α,α'-dibromoketones. The absence of Favorskii rearrangement is certainly due to the impossibility of 2,5-dibromocyclopentanone 12 to generate a very strained bicyclic cyclopropanone, i.e. a bicyclo[2.1.0]pentane-5-one.[24] It is indeed known that the ring size in α,α'-dibromoketones is important for the outcome of the reaction with secondary amines;[19] under certain reaction conditions, it was possible to convert 2,6-dibromocyclohexanone into the Favorskii rearrangement product or the corresponding 2-(dial-kylamino)-2-cyclohexenone.[19b] The reaction of trans-2,7-dibromocycloheptanone 13 with isopropylamine in ether at room temperature for 2 days was more complicated (after 5 h, there was no conversion of starting material yet). The major product proved to be the Favorskii carboxylic amide 23, which was accompanied by a minor reaction product, tentatively identified as the ketoenamine 24 (entry 38).

From the mechanistic point of view the reaction of α,α'-dibromoketones, having an extra alkyl substituent at the α-position, was most interesting. The reaction of 1,3-dibromo-3-methyl-2-butanone 14 with a large excess of isopropylamine (10 molar equiv.) in pentane (room temperature 45 h) in the presence of magnesium sulfate as drying agent afforded 1-(N-isopropyl)imino-3-methyl-2-butanone 2v in 71% yield after vacuum distillation



14

24a R = i-Pr
24b R = n-Pr

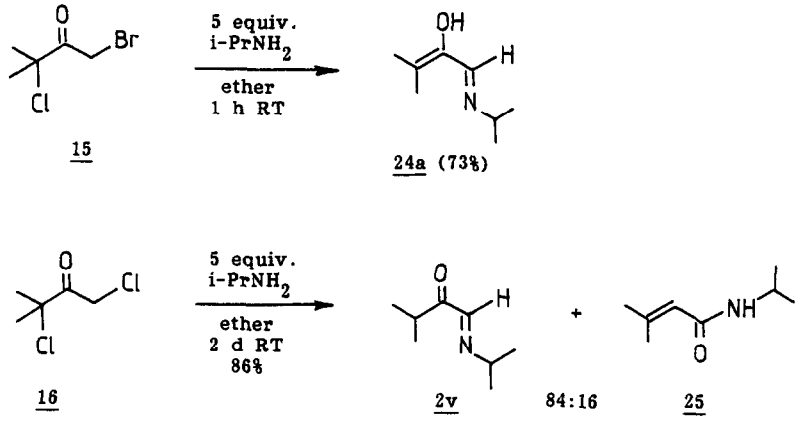
2v
2w

(entry 39). When the reaction was run for a shorter period (reflux 2.5 h, pentane, 10 molar equiv. isopropylamine), the starting α,α'-dibromoketone 14 was converted into the α-iminoketone 2v in about 40%, and, in addition, a substantial amount of the corresponding enol 24a was formed (entry 40). Upon standing at room temperature, this enol was converted very slowly into the α-iminoketone 2v (final yield 75%).

The same reaction type was observed with the α,α'-dibromoketone 14 and n-propylamine but, in all cases, very unstable reaction products were for-

med. After 1 h at room temperature, α,α'-dibromoketone 14 and n-propylamine (5 molar equiv.) in ether produced about 20% of α-iminoketone 2w together with substantial amounts of the corresponding unstable enol 24b, i.e. N-(2-hydroxy-3-methyl-2-buten-1-ylidene)n-propylamine, and the starting material (entry 41). After a similar reaction in pentane at room temperature for 24 h a complex reaction mixture was formed, consisting of α-iminoketone 2w and the corresponding α-diimine 3w in a 55:45 ratio, respectively (entry 41). Again this result expresses the influence of the steric requirements of the amine and the α,α'-dibromoketone in the formation of α-iminoketones 2 and α-diimines 3. As mentioned before, isopropylamine and α-iminoketone 2v are too much sterically hindered for a further conversion into the corresponding α-diimine 3v.

In order to investigate the mechanism of the reaction (vide infra) in more detail, one bromine in the starting material 1 was replaced by chlorine. 1-Bromo-3-chloro-3-methyl-2-butanone 15 reacted with isopropylamine (5 molar equiv.) in ether for 1 h at room temperature to afford the pure enol 24a in 73% yield (entry 44). The complete tautomerization of this enol into α-iminoketone 2v was accomplished after standing for 5 days at room temperature.



It is obvious that the reaction of the corresponding α,α'-dichloroketone, i.e. 1,3-dichloro-3-methyl-2-butanone 16, with primary amines would be much slower than the previous bromo analogues. Compound 16 reacted indeed very slowly with isopropylamine in ether, as visualized by the slow precipitation of isopropylamine hydrochloride. After 2 days at room temperature the reaction mixture consisted of 72% α-iminoketone 2v and 14% Favorskii carboxylic amide 25, together with 12% of an unstable compound which decomposed upon standing of the reaction mixture (entry 45).

Table I : Reaction of α,α'-Dibromoketones 1 with Primary Amines

Entry	Starting Material	Substitution Pattern	R^1	R^2	R	Reaction Conditions[a]	Reaction Products (Distribution; %)			Remarks[b]
							α-Iminoketone 2	α-Diimine 3	Favorskii product	
1	4	(a)	Me	Me	Me	6 Equiv.; 17 h RT	56	44	0	63% yield (dist.)
2	4	(b)	Me	Me	Et	6 Equiv.; 22 h RT	18	82	0	68% yield (dist.)
3	4	(c)	Me	Me	i-Pr	4 Equiv.; 17 h RT	98	2	0	72% yield (dist.)
4	4	(d)	Me	Me	n-Pr	5 Equiv.; 2 h RT	95	5	0	93% crude yield; 65% yield (dist.)[c]
5	5	(e)	Et	Et	Me	6 Equiv.; 24 h RT	55	45	0	-[c]
6	5	(f)	Et	Et	Et	6 Equiv.; 24 h RT	100	0	0	60% yield (dist.)
7	6	(g)	i-Pr	i-Pr	i-Pr	5 Equiv.; 24 h RT or 24 h Δ	0	0	0	no reaction
8	6	(g)	i-Pr	i-Pr	i-Pr	5 Equiv.; THF; 20 h Δ	0	0	100	52% 18
9	6	(g)	i-Pr	i-Pr	i-Pr	5 Equiv.; THF; 24 h RT	0	0	0	no reaction
10	7	(h)	Me	H	i-Pr	5 Equiv.; 2 h RT	77	23	0	42% 2h and 19% 3h (dist.)
11	7	(h)	Me	H	i-Pr	5 Equiv.; 15 min RT	85	0	0	^{1}H NMR and GC analysis
12	7	(h)	Me	H	i-Pr	5 Equiv.; 40 min RT	67	33	0	^{1}H NMR and GC analysis
13	7	(h)	Me	H	i-Pr	5 Equiv.; 100 min RT	40	60	0	^{1}H NMR and GC analysis
14	7	(h)	Me	H	i-Pr	5 Equiv.; 23 h RT	5	95	0	^{1}H NMR and GC analysis (crude yield : 90%)
15	7	(h)	Me	H	i-Pr	5 Equiv.; THF; 40 min Δ	20	80	0	^{1}H NMR and GC analysis
16	7	(h)	Me	H	i-Pr	5 Equiv.; MeOH; 1 h RT	10	90	0	50% crude yield; formation of a complex reaction mixture
17	7	(h)	Me	H	i-Pr	5 Equiv.; MeOH:H_2O 1:1; 1 h RT	0	0	100	55% 19 (cryst.) and 5-15% methyl-3-(N-isopropylamino)butyrate GLC caused E/Z isom.
18	7	(h)	Me	H	i-Pr	6 Equiv.; C_6H_6; 0.6 Equiv. $TiCl_4$; 4 h Δ	0	100	0	85% crude yield
19	7	(h)	Me	H	i-Pr	3 Equiv.; 4 h RT	97	3	0	91% crude yield
20	7	(h)	Me	H	i-Pr	10 Equiv.; pentane; 17 h RT $MgSO_4$	0	100	0	94% crude yield
21	7	(i)	Me	H	n-Pr	5 Equiv.; 1 h RT	15	85	0	95% crude yield
22	7	(j)	Me	H	t-Bu	5 Equiv.; 1.25 h RT	85	0	0	20% yield
23	8	(k)	Et	H	i-Pr	5 Equiv.; 22 h RT	25	75	0	40% (dist.)[c]
24	8	(k)	Et	H	i-Pr	i-$PrNH_2$ as solvent (10% w/v); 21 h RT	0	100	0	80% crude yield; formation of unidentified compounds

25	8	(k)	Et	H	i-Pr	5 Equiv.; CH_2Cl_2; 17 h RT	23	77	0	
26	8	(k)	Et	H	i-Pr	5 Equiv.; CCl_4; 70 h RT	9	91	0	
27	8	(k)	Et	H	i-Pr	5 Equiv.; pentane; 22 h RT $MgSO_4$	0	100	0	96% yield
28	9	(l)	i-Pr	H	i-Pr	5 Equiv.; 2 h RT	100	0	0	88% yield (dist.)
29	9	(l)	i-Pr	H	i-Pr	5 Equiv.; 15 h RT	100	0	0	95% crude yield 72% (dist.)
30	9	(m)	i-Pr	H	n-Pr	5 Equiv.; 2 h RT	0	100	0	71% yield (dist.) (unstable)
31	10	(n)	Ph	H	i-Pr	5 Equiv.; 1 h RT	0	0	100	52% (dist.) 21a
32	10	(o)	Ph	H	t-Bu	5 Equiv.; 1 h RT	0	0	100	82% (cryst.) 21b
33	11	(p)	$CH_2C(Me_2)CH_2$		i-Pr	5 Equiv.; 3 h RT	0	0	100	86% (cryst.) 22a
34	11	(q)	$CH_2C(Me_2)CH_2$		t-Bu	5 Equiv.; 22 h RT	0	0	100	95% (cryst.) 22b
35	11	(r)	$CH_2C(Me_2)CH_2$		n-Pr	5 Equiv.; 20 h RT	0	0	100	98% (crude yield) 22c
36	12	(s)	CH_2CH_2		i-Pr	5 Equiv.; 1 h RT	100	0	0	60% crude yield
37	12	(t)	CH_2CH_2		t-Bu	5 Equiv.; 1 h RT	100	0	0	55% crude yield
38	13	(u)	$(CH_2)_4$		i-Pr	5 Equiv.; 2 d RT	10[d]	0	90	81% crude yield
39	14	(v)	-[e]	-[e]	i-Pr	10 Equiv.; pentane; $MgSO_4$ 45 h RT	100	0	0	71% yield (dist.) 2v
40	14	(v)	-[e]	-[e]	i-Pr	10 Equiv.; pentane; $MgSO_4$ 2.5 h Δ	100[f]	0	0	75% yield 2v
41	14	(w)	-[e]	-[e]	n-Pr	5 Equiv.; 1 h RT	100[f]	0	0	20% starting material; decomposition upon glc; ^1H NMR analysis
42	14	(w)	-[e]	-[e]	n-Pr	5 Equiv.; pentane; $MgSO_4$ 24 h RT	55	45	0	unstable reaction products
43	14	(v)	-[e]	-[e]	i-Pr	7 Equiv.; pentane; $MgSO_4$ 5 d RT	63	37	0	84% yield
44	15	(v)	-[g]	-[g]	i-Pr	5 Equiv.; 1 h RT	100[h]	0	0	73% yield
45	16	(v)	-[i]	-[i]	i-Pr	5 Equiv.; 2 d RT	84	0	16	86% yield; 12% unidentified compound
46	17	(x)	t-Bu	t-Bu	i-Pr	5 Equiv.; 24 h Δ	0	0	0	no reaction

[a] Solvent : ether except otherwise stated; Equiv. = molar equivalents primary amine used; RT = room temperature; Δ = reflux.

[b] Isolated yields after distillation or crystallization unless otherwise stated; yields of crude products are always nearly quantitative, unless otherwise stated.

[c] Substantial decomposition during distillation.

[d] Tentatively assigned.

[e] 1,3-Dibromo-3-methyl-2-butanone 14.

[f] This compound was accompanied by a substantial amount of the corresponding enol (slow formation of the keton upon standing at room temperature).

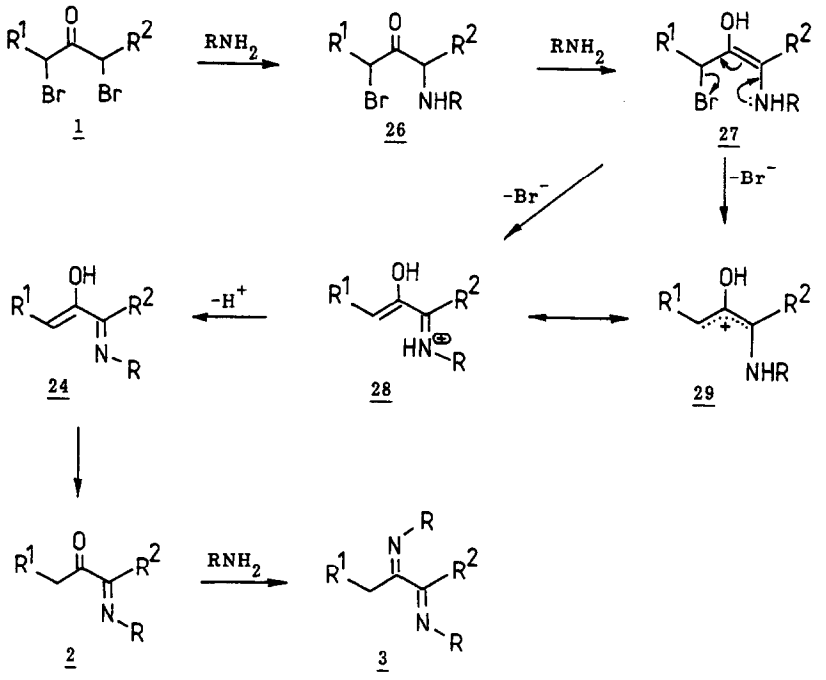
[g] 1-Bromo-3-chloro-3-methyl-2-butanone 15.

[h] Isolated as the pure enol, which slowly tautomerized to the α-iminoketone 2v within 5 days at room temperature.

[i] 1,3-Dichloro-3-methyl-2-butanone 16.

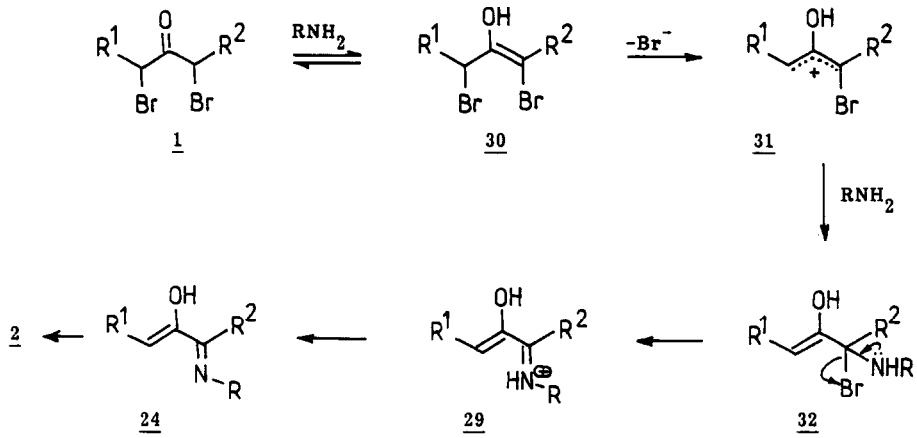
Mechanisms of the Reactions

From the mechanistic point of view, the rather unexpected formation of α-iminoketones 2 and α-diimines 3 from the reaction of α,α'-dibromoketones 1 with primary amines can be explained in the following way. Primary amines are more apt to give nucleophilic substitution (aminolysis) with α-haloketones as compared to secondary amines, which are more sterically hindered and more basic. The latter features of secondary amines explain the ready formation of Favorskii rearrangement products.[19] The aminolysis of α,α'-dibromoketones 1 with primary amines can be explained by a nucleophilic substitution of the least hindered bromoatom to form 26, followed by base-induced enol formation and expulsion of the bromide anion. When



written as a spontaneous loss of a bromide anion from enol 27, the positive charge of the resulting allylic carbenium ion 28 is best stabilized as an iminium species such as in structure 29. Loss of a proton and tautomerization of the enol 24 into α-iminoketone 2 forms one end product, which is slowly converted into α-diimine 3. Nucleophilic substitution of a primary α-bromoketone by a primary amine is a reasonably fast process, as supported by the experiment that 1-bromo-3-methyl-2-butanone reacted with isopropylamine (1 h room temperature) in ether to give 1-(N-isopropyl)amino-3-methyl-2-butanone in 85% yields. Secondary α-bromoketones also give rise to nucleophilic substitution with primary amines,[25] but tertiary

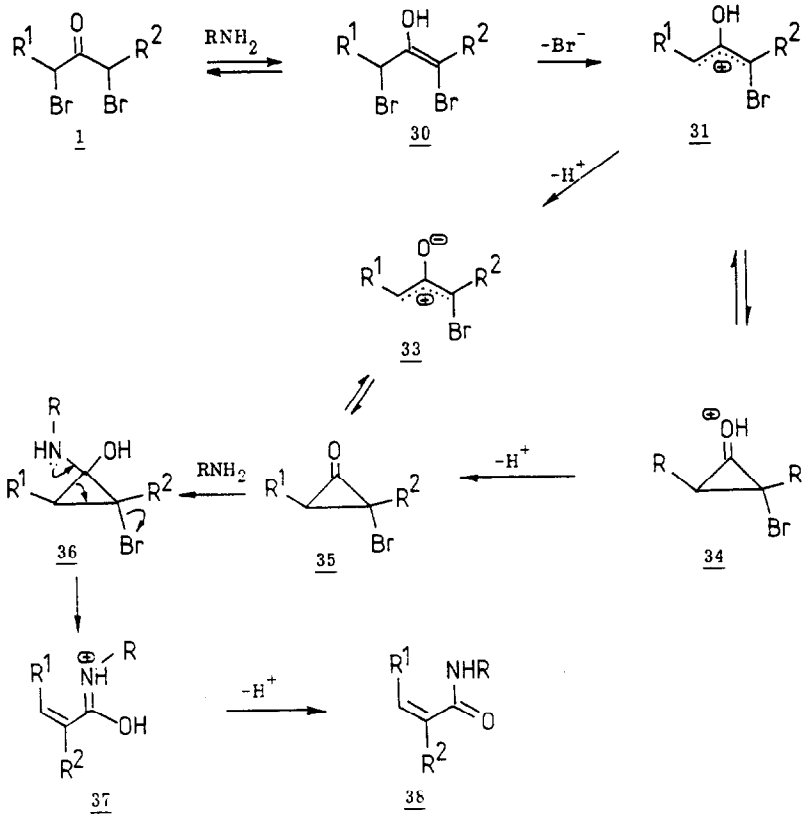
α-bromoketones react very slowly. For instance, 3-bromo-3-methyl-2-butanone reacts only with isopropylamine in ether after a period of 2 days at room temperature to yield 3-(N-isopropyl)amino-3-methyl-2-butanone (86%). The more sterically hindered 2-bromo-2,4-dimethyl-3-pentanone and 2,4-dibromo-2,4-dimethyl-3-pentanone did not react with isopropylamine (5 equiv.) in ether under reflux for 3 days. It follows that, depending upon the type of bromide in the starting α,α'-dibromoketones 1, it is not necessarily a fast nucleophilic substitution which initiates the reaction sequence. A viable alternative route is certainly the enolization of α,α'-dibromoketone 1 followed by loss of a bromide anion from the allylic intermediate 30. The positive charge is better stabilized at the carbon



bearing the allyl group and the bromo atom, although this centre exerts some steric hindrance. Aminolysis of this allylic carbenium ion then gives adduct 32 which expels hydrogen bromide and tautomerizes subsequently to α-iminoketone 2.

The regiospecific formation of α-ketoaldimines 2 from dibrominated methylketones 1 (R^2=H) can also be explained via the two mechanistic schemes presented above. The former mechanism concentrates on an initial nucleophilic substitution of a primary bromide to give α-bromo-α'-aminoketone 26, which eliminates the bromide anion via an activated allylic structure 27. This selective nucleophilic substitution is certainly a viable route in the light of the previous model experiments with regiospecifically α-monobrominated 3-methyl-2-butanone. An alternative explanation results from the latter mechanism in which enolization plays a crucial role. α,α'-Dibromoketones 1, derived from methylketones (R^2=H), react regiospecifically with primary amines at the carbon at position 1 because the hydrogens of the bromomethyl group are more acidic than the hydrogens, if

any, at the 3-position. This fact initiates the reaction at the 1-position, delivering finally α-ketoaldimines 2 (R^2=H).
In both mechanisms discussed above, the role of the enol 24 is evident. It is therefore no surprise that an intermediate enol 24a, carrying maximum stabilization from the double methyl substitution at the 3-position, was isolated from the reaction of α,α'-dihalogenated ketones (entries 39, 40, 42).



Although the end products from the aminolysis and the Favorskii rearrangement seem to be very different, their formation is mechanistically linked. Under the influence of bases, α,α'-dibromoketones 1 tautomerize into enols 30, which lose a bromide anion under the conditions of the aminolysis. The resulting 2-hydroxyallylic carbenium ion 31 is in equilibrium with the ringclosed form, i.e. protonated cyclopropanone 34. In similar way the corresponding deprotonated intermediates, i.e. oxyallyl zwitter ion 33 and cyclopropanone 35 can be considered as transient forms in these reactions. Such allylic species 31 have been already the subject of considerably study and a link to cyclopropanone type chemistry has been established in

the literature.[14,15] Therefore the conversion of allylic species 31 into cyclopropanones 35 is acceptable and this route further explains the formation of Favorskii-derived products. Addition of the primary amine across the reactive carbonyl of cyclopropanone 35 gives an adduct which undergoes ring-opening in a regiospecific way, as established previously with the alkoxide-induced Favorskii rearrangement of α,α-dichloromethylketones.[26] The stereospecificity of the conversion of α,α'-dibromoketones into (Z)-α,β-unsaturated carboxylic derivatives 38 (see entries 30, 31) is an old point of discussion in the Favorskii rearrangement. More or less accepted is the fact that the stereospecificity would depend on the mere elimination of the halogen anion from the least hindered rotamer of the carbanion formed on opening of the cyclopropanone intermediate.[26,27] The other Favorskii-rearrangements mentioned above (see Table) are explained in a similar way and obey the known general trend in the mechanism of this reaction. At the moment, the influence of the solvent on the course of the reaction is not clear but it is certainly related to the equilibrium of the oxyallyl species 31, 33 and the cyclopropanones 34, 35.

In conclusion, a suitable and fairly general route to α-iminoketones 2 and α-diimines 3 has been developed from the reaction of α,α'-dibromoketones 1 with primary amines. The synthetic potential of these scarcely reported bifunctional compounds is under current study. Simple α-diimines, e.g. 1,2-ethanediimines and 1,2-propanediimines, are accessible by condensation of α-ketoaldehydes with amines.[28] α-Iminoketones cannot be synthetisized conveniently except from symmetrical α-diones[29,30] or alkyl aryl α-diones.[30] The oxidation of aldimines with selenium(IV) oxide into α-ketoaldimines was not reproducible in our hands,[31] while the photolysis[32] or thermolysis[33] of α-azidoketones offers an alternative route. Other methods for the synthesis of α-diimines include $TiCl_4$-mediated synthesis from α-diones,[34] reaction of propargyl alcohol with amines in the presence of mercury(II) acetate[35] and photolysis of 1,2-diazidoalkanes.[36] α-Diimines, often referred to as 1,4-diaza-1,3-dienes, have numerous applications in the coordination chemistry because of their ready formation of complexes with an enormous variety of metals (e.g. zinc, nickel, aluminium, iron, copper, palladium, ruthenium, cobalt, platinum, etc...).[37] Their use as building blocks for several classes of heterocycles, e.g. imidazolines[38] and pyrimidines,[39] make them very attractive substrates. Special focus deserves the use of 3-(N-methyl)imino-2-butanone as flavor for the commercial preparation of corn flakes.[40] As a matter of fact, the α-iminoketones 2 and α-diimines 3 described in this paper, displayed pleasant, fruity flavors, resembling banana's and the like. On the other hand, some N-n-propyl derivates did not reveal this flavor character at all but could be rather classified as stenches.

Experimental Part

Infrared spectra were recorded with a Perkin Elmer model 1310 spectrophotometer. ^1H NMR spectra were measured with a Varian T-60 NMR spectrometer. Mass spectra were obtained with a Perkin MAT 112 mass spectrometer using the direct inlet system and GC-MS coupling (70 eV). Melting points were recorded with a Kofler hotstage and are uncorrected.

Synthesis of α,α'-Dibromoketones 1

α,α'-Dibromoketones 1 were synthesized by bromination of appropriate ketones (1 mol) with bromine (2 molar equivalents) in glacial acetic acid (100 ml) at room temperature under vigorous stirring. CAUTION! Although hundreds of these syntheses were performed on a molar scale (especially with the cheap aliphatic acyclic ketones) with success without any difficulty, one experiment caused a dramatic explosion (no fire) with serious injury to the researcher (severe skin and eye irritation and oedeme as a result of contact with the reaction mixture; the recovery of the casualty took several weeks, leaving damage to the sight to some extent). The dramatic experiment concerned a preparation of 2,4-dibromo-3-pentanone on a molar scale. After initial discoloration of the little amount of added bromine to the solution of the ketone in glacial acetic acid, the remaining amount of bromine was added dropwise over a period of two hours. The progress of the reaction was visualized by the continuous exhaust of a fume of hydrogen bromide gas. After addition of half the amount of bromine, the reaction mixture did not discolorize any more (as usual). A heavy explosion, due to a sudden pressure built up, occurred, breaking the whole glass apparatus (a 1 liter three-necked flask; reflux condensor, separatory funnel, magnetic stirring bar) and spreading around the reaction mixture as far as 2 meters. Because the reaction started smoothly and continued as expected, the reason of this accident is not clear but must be associated to a blow-up of the apparatus due to a substantial amount of gaseous hydrogen bromide.

All other experiments leading to α,α'-dibromoketones were worked up (after addition of bromine, stirring was continued for 1 h at room temperature; some reaction mixtures were light yellow, others were dark red) by pouring the reaction mixture in a large amount of water. The mixture was extracted with carbon tetrachloride and the combined extracts were washed with aqueous sodium bicarbonate and brine. After drying ($MgSO_4$) and evaporation of the solvent in vacuo, the α,α'-dibromoketone was distilled in vacuo over a Vigreux column in order to separate it from monobromo-, tribromo and isomeric dibromoketones. When the 1,3-dibromoketone is a solid material, it is purified by crystallization from the reaction mixture. 2,4-Dibromo-3-pentanone 4, bp 75-76°C/13 mmHg (76%), Lit.[8] bp 63-

65°C/10 mmHg; 3,5-dibromo-4-heptanone 5, bp 104-109°C/13 mmHg (75%), Lit.[41] bp 118-121°C/25 mmHg; 3,5-dibromo-2,6-dimethyl-4-heptanone 6 (72%), bp 120-123°C/11 mmHg, Lit.[41] bp 145-147°C/28 mmHg; 1,3-dibromo-2-butanone 7 (75%), bp 85-90°C/12 mmHg, Lit.[42] bp 76.5-77°C/10 mmHg; 1,3-dibromo-2-pentanone 8 (86%), bp 86-90°C/16 mmHg, Lit.[43] bp 88-89°C/10 mmHg; 1,3-dibromo-4-methyl-2-pentanone 9 (81%), bp 103-107°C/13 mmHg, Lit.[44] bp 118-130°C/25 mmHg; 1,3-dibromo-1-phenyl-2-propenone 10 (54%), bp 110-115°C/0.2 mmHg, Lit.[9] bp 138°C/1.8 mmHg; cis-2,6-dibromo-4,-dimethylcyclohexanone 11 (68%), mp 96°C, Lit.[45] mp 95-96°C; trans-2,5-dibromocyclopentanone 12 (47%)[19b,46,47] and trans-2,7-dibromocycloheptanone 13[47,84] were prepared according to the literature; 1,3-dibromo-3-methyl-2-butanone 14 (81%), bp 86-88°C/12 mmHg, Lit.[49] bp 87°C/10 mmHg; 1-bromo-3-chloro-3-methyl-2-butanone 15 was prepared in 79% yield by bromination of 3-chloro-3-methyl-2-butanone with bromine (1.1 molar equiv.) in methanol at room temperature (1 h), bp 81-83°C/18 mmHg, Lit.[50] bp 83-83.5°C/20 mmHg; 1,3-dichloro-3-methyl-2-butanone 16 was prepared by chlorination of 3-methyl-2-butanone with sulfuryl chloride (2 molar equiv.) in dichloromethane at ambient temperature, bp 66-75°C/15 mmHg, Lit.[50] bp 72-73°C/20 mmHg.

Reaction of α,α'-Dibromoketones 1 with Primary Amines

According to the reaction conditions mentioned in Table I, the condensation of α,α'-dibromoketones 1 with primary amines are executed following the protocol given below. A 10% w/v solution of α,α'-dibromoketone 1 (0.01 mol) in dry ether (distilled from Na wire), cooled in an ice-bath, was treated dropwise under stirring with an excess (usually 5 molar equivalents) of the appropriate primary amine. After stirring for the time indicated in Table I, the reaction mixture was triturated with pentane (half the volume of ether), after which the precipitated amine hydrobromide was removed by filtration. The filtrate was most of all worked up by simple evaporation in vacuo. Alternatively, the filtrate was poured into water, shaken, and the organic phase was isolated. After a second extraction with ether, the combined organic phases were dried (K_2CO_3), filtered and evaporated in vacuo. Both work-up procedure give rise to a reaction mixture which is investigated by ^1H NMR in order to determine the composition. This attribution is always verified by preparative gas chromatography (3 m, 5-10% SE 30, H_2 carrier gas, Varian models 1700 and 920 or Intersmat IGC 120 ML gas chromatographs). A large number of α-iminoketones 2 and α-diimines 3 were prepared on a larger scale (0.1 mol) and distilled. In many cases, considerable decomposition occurred during the distillatioin under vacuo. α-Iminoketones 2 and α-diimines 3 are labile compounds, decomposing to dark tarry liquids upon standing. However, when freshly prepared they can easily be characterized and handled, except some

less hindered substrates, e.g. with R^1=Me and especially R^2=Me, Et, n-Pr. Some representative examples of preparations on a preparative scale are given here.

Synthesis of 2-(N-Isopropyl)imino-3-pentanone 2c (entry 3)

A cooled (0°C) solution of 9.76 g (0.04 mol) of 2,4-dibromo-3-pentanone 4 in 100 ml dry ether was treated dropwise with 9.44 g (0.16 mol) of isopropylamine. After stirring for 17 h at ambient temperature, pentane (50 ml) and magnesium sulfate (5 g) were added and the mixture was stirred for 15 min. Filtration and evaporation of the solvent gave a light yellow oil, which consisted of α-iminoketone 2c and α-diimine 3c in a 98:2 ratio (^{1}H NMR; GC). Distillation in vacuo provided 2-(N-isopropyl)imino-3-pentanone 2c in 72% yield, bp 61-62°C/15 mmHg. ^{1}H NMR (CCl_4) : 1.03 (3H,t,J=7Hz, CH_3-C-CO); 1.15 (6H,d,J=6Hz,Me_2); 1.92 (3H, s,CH_3C=N); 2.83 (2H,q,J=7Hz, CH_2); 3.78 (1H,septet,J=6Hz,NCH). IR (NaCl) : 1702 cm^{-1} (CO); 1645 cm^{-1} (C=N). Mass spectrum m/z (%) : 141 (M^+; 0.5); 126 (1); 84(34); 70(1); 57(6); 43(18); 42(100); 41(9); 40(10). ^{13}C NMR ($CDCl_3$) : 8.15 (q,Me); 11.26 (q,Me); 23.04 (q,Me_2); 29.63 (t,CH_2); 52.17 (d,NCH); 162.56 (s,C=N); 203.79 (s,C=O). Elem. anal. : calcd. 9.92% N, found 9.78% N.

Regiospecific Synthesis of 1-(N-Isopropyl)imino-2-butanone 2h (entry 19)

1,3-Dibromo-2-butanone 7 was reacted with 3 molar equivalents of isopropylamine in ether for 4 h at room temperature. Workup as described above afforded a reaction mixture (91% crude yield) which consisted of 97% α-iminoketone 2h and 3% of the corresponding α-diimine 3h (GC, ^{1}H NMR). Distillation in vacuo gave pure 2h (70%), bp 53-65°C/12 mmHg. Preparative gas chromatographic of the reaction mixture allowed the characterization of the major 2h and the minor α-diimine 3h.

1-(N-Isopropyl)imino-2-butanone 2h

^{1}H NMR (CCl_4) : 1.07 (3H,t,J=7.5Hz,CH_3); 2.80 (2H,q,J=7.5Hz,CH_2); 1.23 (6H,d, J=6Hz,Me_2); 3.55 (1H,septet,J=6Hz,NCH); 7.56 (1H,s,CH=N). IR (NaCl) : 1699 cm^{-1} (C=O); 1635-1639 cm^{-1} (C=N). Mass spectrum m/z (%) : 127 (M^+; 0.1); 112 (5); 109(0.3); 94(0.5); 84(0.5); 82(0.4); 70(50); 69(0.5); 68(0.7); 67(0.7); 57(26); 56(4); 55(2); 54(1.2); 53(0.5); 52(0.5); 51(0.4); 43(100); 42(6); 41 (24); 40(3); 39(6).
Elem. anal. : calcd. 11.01% N; found 10.79% N.

Bis(N-isopropyl)butane-1,2-diimine 3h

Bp. 68-70°C/12 mmHg (entry 20); bp 30-35°C/0.08 mmHg.
^{1}H NMR (CCl_4) : 1.00 (3H,t,J=7.5Hz,Me); 2.51 (2H,q,J=7.5Hz,CH_2); 1.12 and 1.18 (each 6H,each d,each J=6Hz,2Me_2); 3.5 (2H,m,2NCH); 7.57 (1H,s,CH=N).

IR (NaCl) : 1633 and 1644 cm^{-1} (C=N). Mass spectrum m/z (%) : 168 (M^+; 1); 153 (7); 125(2); 111(9); 110(1); 109(1); 108(1); 98(5); 96(5); 94(3); 84(2); 83 (3); 82(1); 70(4); 69(1); 68(2); 67(1); 56(100); 55(3); 54(3); 53(1); 52(1); 43(28); 42(11); 41(20); 40(3); 39(7).
^{13}C NMR ($CDCl_3$) : 12.25 (q,Me); 19.58 (t,CH_2); 23.89 (q,Me_2); 50.89 (d, NCH); 60.78 (d,NCH); 161.17 (d,CH=N); 168.84 (s,C=N).
Elem. anal. : calcd. 16.65% N, found 16.54% N.

Synthesis of Bis-(N-isopropyl)butane-1,2-diimine 3h (entry 20)
1,3-Dibromo-2-butanone 7 (0.002 mol) was reacted with 10 molar equivalents of isopropylamine in pentane (10% w/v) in the presence of $MgSO_4$ (0.5 g). After stirring for 17 h at ambient temperature, the mixture was filtered and evaporated to leave pure α-diimine 3h (94% crude yield; GC; see data above). Bp 68-70°C/12 mmHg.

Rearrangement of bis-2,6-dibromo-4,4-dimethylcyclohexanone 11 into N-t-butyl-4,4-dimethyl-1-cyclopentenecarboxylic Amide 22b
A stirred solution of 0,71 g (0.0025 mol) of cis-2,6-dibromo-4,4-dimethylcyclohexanone 11 in 10 ml dry ether was treated dropwise with 0.91 (0.0125 mol) t-butylamine. After stirring for 22 h at room temperature, 5 ml pentane was added. The precipitate was filtered and washed with little pentane. After evaporation of the solvent, the solid residue was recrystallized (-20°C) from CCl_4 to give 0.46 g (95%) of pure carboxyl amide 22b, mp 128°C. ^1H NMR ($CDCl_3$) : 1.40 (9H,s, tBu); 1.13 (6H,s,Me_2); 2.2-2.4 (4H,m,2CH_2); 5.4 (1H,s,broad,NH); 6.36 (1H,m, =CH). IR (KBr) : 3340 cm^{-1} (NH); 1646 cm^{-1} (C=O); 1611 cm^{-1} (C=C). Mass spectrum m/z (%) : 195 (M^+; 8); 181(8); 140(22); 139(10); 124(30); 123(100); 106(8); 95(28); 81(24); 79(20); 77(14); 67(22); 58(30); 57(30); 56(28); 55 (40); 53(24); 44(12); 43(10); 42(12); 41(98); 40(20); 39(40). ^{13}C NMR ($CDCl_3$) : 28.93 (q,Me_3); 29.75 (q,Me_2); 39.07 (s,$\underline{C}Me_2$); 46.69 and 48.06 (each t,2CH_2); 51.06 (s,$\underline{C}Me_3$); 139.10 (s,=$\underline{C}$-C=O); 135.36 (d,=CH); 165.09 (s,C=O).
Elem. anal. : calcd. 73.80% C, found 73.59% C; calcd 10.84% H, found 10.65% H; calcd. 7.17% N, found 7.31% N.

Synthesis of 2-(N-Isopropyl)amino-2-cyclopentenone 2s (entry 36)
A solution of 0.48 g (0.002 mol) trans-2,5-dibromocyclopentanone 12 in 10 ml ether was treated dropwise with 0.59 g (0.01 mol) of isopropylamine. After stirring 1 h at room temperature, the reaction mixture was filtered and evaporated to give a dark viscous oil and some precipitate. The oil was taken up in dry ether, filtered and evaporated to afford a dark oily residue which consisted of almost pure (> 92%) compound 2s (^1H NMR) (50% crude yield). Preparative GC revealed 2s as the sole product.

^{1}H NMR ($CDCl_3$) : 1.17 (6H,d,J=6Hz,Me_2); 2.3-2.6 (4H,m,CH_2CH_2); 3.45 (1H, septet,J=6Hz,NCH); 3.6 (1H,s,broad,NH); 5.98 (1H,t,J=2.8Hz,=CH). IR (NaCl) : 3360 cm^{-1} (NH); 1706 cm^{-1} (C=O); 1638 cm^{-1} (C=C). Mass spectrum m/z (%) : 139 (M^+; 35); 124(100); 96(10); 82(15); 69(17); 68(35); 54(40); 43(30); 42 (25); 41(85); 39(40). ^{13}C NMR ($CDCl_3$) : 22.40 (q,Me_2); 23.62 and 33.42 (each t,$CH_2\underline{C}H_2$); 45.23 (d,NCH); 120.61 (d,=CH); 145.13 (s,C=$\underline{C}$-N); 205.08 (s,$\underline{C}$=O).

Conversion of 1-Bromo-3-chloro-3-methyl-2-butanone 15 into N-(2-Hydroxy-3-methyl-2-but-1-ylidene)isopropylamine 24a (entry 43)

A stirred solution of α-chloro-α'-bromoketone 15 (0.01 mol) in dry ether (10% w/v) was treated dropwise with isopropylamine (0.05 mol). After stirring for 1 h at room temperature, the solvent was evaporated and the residue treated with pentane. Filtration of the solid material and evaporation of the filtrate afforded a residual liquid which consisted of pure enol 24a (> 96% pure; 73% yield).

Enol 24a : ^{1}H NMR (CCl_4) : 1.15 (6H,d,J=6Hz,$\underline{Me}_2$CH); 1.80 (6H,s,$\underline{Me}_2$C=C); 3.56 (1H,septet,J=6Hz,NCH); 5.8 (1H,broad,OH); 8.08 (1H,s,CH=N). IR (NaCl) : 3380 cm^{-1} (OH); 1620 cm^{-1} (C=N). ^{13}C NMR ($CDCl_3$) : 16.48 (q,$\underline{Me}$-C=C); 18.00 (q,$\underline{Me}$-C=N); 24.22 (q,Me_2); 58.85 (d,NCH); 115.25 (s,$Me_2\underline{C}$=C); 142.29 (s,=$\underline{C}$-OH); 150.27 (d,CH=N). This enol tautomerized slowly into 2v upon standing at room temperature (complete after 5 d).

1-(N-Isopropyl)imino-3-methyl-2-butanone 2v

Bp 49-50°C/12 mmHg. ^{1}H NMR (CCl_4) : 1.09 (6H,d,J=7Hz,Me_2); 1.25 (6H,d, J=6Hz, Me_2); 3.2-3.8 (2H,2x septet,overlap,2CH); 7.46 (1H,s,CH=N). IR (NaCl) : 1700 cm^{-1} (C=O); 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 141 (M^+; 0.5); 126(5); 110(0.5); 108(0.5); 99(0.5); 98(1); 84(1); 82(0.5); 80(0.5); 71(7); 70(50); 69(1); 56(2); 55(1); 54(1); 43(100); 42(6); 41(16); 40(4); 39(5). ^{13}C NMR ($CDCl_3$) : 18.28 (q,$\underline{Me}_2$CHCO); 23.53 (q, $\underline{Me}_2$CH-N); 34.43 (d,$\underline{C}$H-CO); 61.12 (d,NCH); 156.53 (s,C=N); 205.82 (s,C=O). Elem. anal. : calcd. 9.92% N; found 9.75% N.

Spectroscopic Data of the Remaining α-Iminoketones 2, α-Diimines 3 and Favorskii Rearrangement Products

2-(N-Methyl)imino-3-pentanone 2a

Bp. 51-56°C/14 mmHg (no separation from the corresponding α-diimine 3a); very labile compound. Mass spectrum m/z (%) : no M^+; 57(5); 56(100; Me-C≡N-Me); 55(2); 54(2); 42 (4); 41(3).

Bis-(N-methyl)pentane-2,3-diimine 3a

Bp. 51-56°C/14 mmHg (no separation from the corresponding α-iminoketone 2a); very labile compound. ^{1}H NMR (CCl_4) : 0.92 (3H,t,J=7.5Hz,MeCH_2); 1.93 (3H,q, J=0.3Hz,CH_3C=N); 2.60 (2H,q,J=7.5Hz,CH_2); 2.95 and 3.25 (each m,N-Me,17% and 83%,resp.,E/Z isomerism). IR (NaCl) : 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 126 (M^+; 8); 125(27); 111(3); 70(100); 57(5); 56(100); 55(5); 54(5); 42 (48); 41(6).

2-(N-Ethyl)imino-3-pentanone 2b

Bp. 73-82°C/15 mmHg (no separation from the corresponding α-diimine 3b); very labile compound. ^{1}H NMR (CCl_4) : 1.03 (3H,t,J=7.5Hz,CH_3-C-C=O); 1.27 (3H,t, J=7.5Hz,CH_3-C-N); 1.90 (3H,t,J=1Hz,CH_3C=N); 2.80 (2H,q,J=7.5Hz, CH_2CO); 3.47 (2H,qxq,J=7.5Hz,J=1Hz,NCH_2). IR (NaCl) : 1702 cm^{-1} (C=O); 1645 cm^{-1} (C=N). Mass spectrum m/z (%) : 127 (M^+; 1.5); 112(1); 84(1); 70(73); 57(3); 56(1.5); 55(1); 42(100); 41(3); 40(8). This compound was obtained as the major reaction product (crude yield 86%) from the reaction of 1,3-dibromo-2-butanone 7 with ethylamine (3 molar equiv.) in ether for 20 h at room temperature (no α-diimine 3b observed).

Bis-(N-Ethyl)pentane-2,3-diimine 3b

Bp. 73-82°C/15 mmHg (no separation from the corresponding α-iminoketone 2b); very labile compound. ^{1}H NMR (CCl_4) : 0.95 (3H,t,J=7.5Hz,CH_3); 1.24 (2x3H, 2xt,J=7.5Hz,2xN-C-CH_3); 1.97 (3H,s,CH_3C=N); 2.62 (2H,q,J=7.5Hz, CH_2C=N); 3.45 (2H,q,J=7.5Hz,NCH_2); 3.50 (2H,q,J=7.5Hz,NCH_2). IR (NaCl) : 1635 cm^{-1} (C=N). Mass spectrum m/z (%) : 154 (M^+; 2); 153(2); 139(46); 125(3); 111(2); 110(2); 96(4); 85(4); 84(65); 70(58); 69(2); 68(3); 56(100); 55(3); 54(3); 44(2); 43 (3); 42(82); 41(6).

Bis-(N-isopropyl)pentane-2,3-diimine 3c

Bp. 84-88°C/14 mmHg. ^{1}H NMR (CCl_4) : 0.97 (3H,t,J=7.5Hz,MeCH_2); 1.15 (12h,d, J=6Hz,2Me_2); 2.02 (3H,s,MeC=N); 2.68 (2H,q,J=7.5Hz,CH_2); 3.78 and 3.81 (2H,2x septet,2xJ=6Hz,2xNCH); IR (NaCl) : 1630 cm^{-1} (C=N). Mass spectrum m/z (%) : 182 (M^+; 3); 167(50); 139(6); 125(17); 110(6); 98(22); 84(28); 57(7); 56 (100); 43(17); 42(69); 41(14); 40(14). ^{13}C NMR ($CDCl_3$) : 12.03 (q,MeC=N); 12.51 (q,Me); 18.91 (t,CH_2); 23.30 and 23.89 (each q,2xMe_2); 50.80 and 51.32 (each d,each NCH); 163.55 and 169.39 (each s,N=C-C=N). Elem. anal. : calcd. 15.37% N; found 15.28% N.

2-(N-n-Propyl)imino-3-pentanone 2d

Bp. 76-81°C/13 mmHg; ^{1}H NMR (CCl_4) : 1.03 (3H,t,J=7Hz,CH_3-C-CO); 0.98 (3H, t, J=6.5Hz,CH_3-C-C-N); 2.80 (2H,q,J=7Hz,CH_2CO); 3.37 (2H,t,broad,J=6.5Hz, NCH_2); 1.65 (2H,quintet,J=6.5Hz,CH_2-C-N); 1.90 (3H,t,J=0.8Hz,CH_3C=N). IR

(NaCl) : 1700 cm^{-1} (C=O); 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 141 (M^+; 0.5); 112 (1); 108(1); 84(33); 70(1); 68(1); 67(0.5); 57(4); 56(2); 55(2); 54(1); 53 (0.5); 44(2); 43(27); 42(100); 41(11); 40(2). ^{13}C NMR ($CDCl_3$) : 8.18 (q,Me); 11.72 (q,Me); 12.12 (q,Me); 23.84 (t,CH_2); 29.61 (t,$\underline{C}H_2C$=O); 54.58 (t,NCH_2); 165.50 (s,C=N); 202.99 (s,C=O).

3-(N-Methyl)imino-4-heptanone 2e

Decomposed completely upon vacuum distillation. ^1H NMR (CCl_4) : 0.91 (3H, t, J=7Hz,CH_3-C-C-C=O); 0.95 (3H,t,J=7.5Hz,CH_3-C-C=N); 1.2-1.8 (2H,m, Me$\underline{H}_2$); 2.47 (2H,q,J=7.5Hz,CH_2C=N); 2.72 (2H,t,J=7Hz,CH_2C=O); 3.34 (3H,br s,NCH_3). IR (NaCl) : 1698 cm^{-1} (C=O); 1645 (C=N). Mass spectrum m/z (%) : no M^+; 125(5); 124(5); 84(25); 70(90); 56(15); 43(37); 42(100); 41(25).

Bis-(N-Methyl)heptane-3,4-diimine 3e

Decomposed completely during vacuum distillation. ^1H NMR (CCl_4) : 0.91 (2x3H,2xt,J=7.5Hz,2xMe); 1.2-1.9 (2H,m,CH_2); 2.3-2.8 (2H,m,CH_2C=N); 2.95 and 3.30 (3H,broad s,28% and 72% resp.,E/E,NCH_3). IR (NaCl) : 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 154 (M^+; 2); 153(6); 84(55); 72(36); 70(74); 57(6); 56(6); 54(5); 43(16); 42(100); 41(18).

3-(N-Ethyl)imino-4-heptanone 2f

Bp. 73-75°C/15 mmHg. ^1H NMR (CCl_4) : 0.90 (3H,t,J=7Hz,CH_3-C-C-CO); 0.95 (3H, t,J=7.5Hz,CH_3-C-C=N); 1.27 (3H,t,J=7.5Hz,CH_3-C-N); 1.6 (2H,m, $CH_2CH_2CH_3$); 2.45 (2H,q,J=7.5Hz,CH_2C=N); 2.70 (2H,q,J=7Hz,CH_2C=O); 3.53 (2H,q,J=7.5Hz,NCH_2). IR (NaCl) : 1698 cm^{-1} (C=O); 1641 cm^{-1} (C=N). Mass spectrum m/z (%) : 155 (M^+; 2); 140(1); 98(58); 84(85); 70(77); 57(10); 56(100); 55(5); 54(6); 44 (7); 43(31); 42(5); 41(15).

N-Isopropyl 2-Isopropyl-4-methyl-2-pentenamide 18

Mp 120°C. ^1H NMR ($CDCl_3$) : 0.97 and 1.05 (each 6H,each d,J=6.2Hz,J=6.5Hz, resp.,$\underline{Me}_2$CHCH=C-CH$\underline{Me}_2$); 1.18 (6H,d,J=6.7Hz,$\underline{Me}_2$CHN); 4.15 (1H,m,NCH); 5.3 (1H, s,broad,NH); 2.2-2.8 (2H,m,C$\underline{H}$-C=C-C$\underline{H}$); 5.09 (1H,dxd,J=10Hz,J=1.7Hz, CH=C). IR (KBr) : 3250 cm^{-1} (NH); 1615-1650 cm^{-1} (C=O and C=C). Mass spectrum m/z (%) : 197 (M^+; 18); 182(52); 154(14); 140(20); 139(14); 123(10); 95(31); 81 (10); 69(70); 67(17); 58(17); 55(64); 53(17); 44(20); 43(100); 42(15); 41(10); 39(22). ^{13}C NMR ($CDCl_3$) : 21.55, 22.91 and 23.36 (each q,each Me); 28.59 and 32.04 (each d,each $Me_2\underline{C}H$); 41.22 (d,NCH); 133.69 (d,$\underline{C}$H=C); 142.44 (s,=$\underline{C}$-CO); 169.82 (s,C=O).
Elem. anal. : calcd. 7.10% N, found 6.92% N.

(Z)-N-Isopropyl 2-butenamide 19

Mp. 95°C (subl.). ^{1}H NMR ($CDCl_3$) : 1.08 (6H,d,J=6.8Hz,Me_2); 2.11 (3H,dxd, J=6.5Hz,J=1Hz,CH_3); 4.15 (1H,m,NCH); 5.3 (1H,broad,NH); 5.75 (1H,dxq, J=12Hz, J=1Hz,=CH-C=O); 6.17 (1H,dxq,J=12Hz,J=6.5Hz,MeC<u>H</u>=C); IR (NaCl/ $CDCl_3$) : 3270 cm^{-1} (NH); 1660 and 1630 cm^{-1} (C=C and C=O). Mass spectrum m/z (%) m/z (%) : 127 (M^+; 13); 112(17); 86(2); 85(4); 84(1); 69(100); 68(10); 67(3); 58(10); 57(1); 56(1); 55(1); 44(32); 43(14); 42(10); 41(40); 40(9); 39(18).

The stereochemical assignment of compounds 19 and 20 is in complete agreement with ^{1}H NMR data of analogues in the literature.[51]

(E)-N-Isopropyl 2-butenamide 20

Mp. 90°C (Lit.[53] mp. 89-90°C). ^{1}H NMR ($CDCl_3$) : 1.21 (6H,d,J=6.5Hz,Me_2); 3.8-4.6 (2H,m,NH-CH); 1.87 (3H,dxd,J=6.5Hz,J=1.3Hz,Me); 5.88 (1H,dxq,J=16 Hz,=CH-CO); 6.95 (1H,dxq,J=16Hz,J=6.5Hz,MeC<u>H</u>=C); IR (NaCl/$CDCl_3$) : 3250 cm^{-1} (NH); 1672 and 1628 cm^{-1} (C=C and C=O). Mass spectrum m/z (%) : 127 (M^+) etc.; MS is completely identical to the mass spectrum of compound 19.

Methyl-3-(N-isopropylamino)butyrate

^{1}H NMR ($CDCl_3$) : 1.04 (6H,d,J=6.5Hz,Me_2); 1.14 (3H,d,J=6.5Hz,Me); 3.71 (3H,s, OMe); 2.3-2.5 (2H,m,CH_2); 2.7-3.4 (2H,m,C<u>H</u>-N-C<u>H</u>). IR (NaCl) : 1730 cm^{-1} (C=O).

This compound was identical in all aspects with the compound prepared from Michael addition across methyl crotonate (i-$PrNH_2$/C_6H_6/Δ 30 h).

Bis-(N-n-Propyl)butane-1,2-diimine 3i

Very labile compound (decomposition during preparative GC). ^{1}H NMR (CCl_4) : 0.7-1.1 (9H,m,overlap,3Me); 2.53 (4H,q,J=7.5Hz,CH_2C=N); 1.3-2 (4H,m,2xCH_2-C-N); 3.2-3.6 (4H,m,2xNCH_2); 7.60 (1H,t,J=1Hz,CH=N). IR (NaCl) : 1640-1650 cm^{-1} (C=N).

1-(N-t-Butyl)imino-2-butanone 2j

This compound could not be characterized completely due to its lability and contamination with unidentified reaction products. ^{1}H NMR (CCl_4) : 1.23 (9H, s,tBu); 1.05 (3H,t,J=7.5Hz,CH_3); 2.78 (2H,q,J=7.5Hz,CH_2); 7.45 (1H,s,CH=N).

1-(N-Isopropyl)imino-2-pentanone 2k

Bp. 62-70°C/13 mmHg. ^{1}H NMR (CCl_4) : 0.93 (3H,t,J=6Hz,CH_3); 1.22 (6H,d,J= 6Hz, Me_2); 1.4-2 (2H,sextet,J=6Hz,MeC<u>H_2</u>); 2.73 (2H,t,J=6Hz,CH_2CO); 3.52 (1H, septet,J=6Hz,NCH); 7.52 (1H,s,CH=N). IR (NaCl) : 1706 cm^{-1} (C=O); 1645 cm^{-1} (C=N). Mass spectrum m/z (%) : no M^+; 126(4); 99(1); 98(0.5);

84(2); 71(14); 70(57); 57(1); 56(9); 55(2); 54(1); 44(5); 43(100); 42(7); 41(17); 40(3); 39 (5).

Bis-(N-isopropyl)pentane-1,2-diimine 3k

Bp. 70-80°C/13 mmHg. ^{1}H NMR (CCl_4) : 0.92 (3H,t,CH_3); 1.11 and 1.18 (2x6H, 2xd,J=6Hz,2Me_2); 2.50 (2H,t,J=7Hz,CH_2C=N); 3.84 (1H,septet,J=6Hz, NCH); 3.56 (1H,septet,J=6Hz,NCH); 7.61 (1H,s,CH=N). IR (NaCl) : 1629 and 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 182 (M^+; 1); 167(9); 139(3); 125(8); 112(4); 97(3); 96(3); 94(5); 82(3); 71(5); 70(100); 56(3); 55(4); 54(4); 44(5); 43 (50); 42(11); 41(22); 40(3); 39(6).
Elem. anal. : calcd. 15.37% N, found 15.55% N.

1-(N-Isopropyl)imino-4-methyl-2-pentanone 2l

Bp. 65-69°C/13 mmHg. ^{1}H NMR (CCl_4) : 0.91 (6H,d,J=6.5Hz,Me_2C-C); 1.22 (6H,d, J=6.2Hz,Me_2C-N); 2.1 (1H,m,C-CHMe$_2$); 2.62 (2H,d,J=6.2Hz,CH_2CO); 3.48 (1H,septet,J=6.2Hz,NCH); 7.44 (1H,s,CH=N). IR (NaCl) : 1702 cm^{-1} (C=O); 1640 cm^{-1} (C=N). Mass spectrum m/z (%) : 155 (M^+; 1); 140(3); 111(1); 99(4); 98(2); 94 (1); 85(8); 70(83); 69(2); 68(1); 57(22); 56(3); 55(2); 54(1); 53(1); 44(3); 43(100); 42(7); 41(22); 40(5); 39(7). ^{13}C NMR ($CDCl_3$) : 22.68 (q,Me_2); 23.51 (q,Me_2); 24.73 (d,CH_2CH); 45.68 (t,CH_2); 60.98 (d,NCH); 157.71 (d,CH=N); 202.18 (s,C=O).
Elem. anal. : calcd. 9.02% N, found 9.28% N.

Bis-(N-n-propyl)pentane-1,2-diimine 3m

Bp. 103-105°C/12 mmHg. Very unstable (complete decomposition upon GC-MS analysis). ^{1}H NMR (CCl_4) : 0.91 (6H,2t,overlap,2Me); 1.3-2.1 (5H,m,2xCH_2-C-N and CHMe$_2$); 3.2-3.6 (4H,m,2xCH_2N); 2.42 (2H,d,J=6.5Hz,CH_2C=N); 7.58 (1H,t,J=1.2Hz,CH=N). IR (NaCl) : 1649 and 1634 cm^{-1} (C=N). ^{13}C NMR ($CDCl_3$) : 12.09 and 11.79 (each q,xMe-C-C-N); 22.84 (q,Me_2); 23.93 and 24.29 (each t,2CH_2); 27.04 (d,CH); 54.10 and 62.84 (each t,2xNCH_2); 35.28 (t,CH_2C=N); 164.53 (d, CH=N); 169.79 (s,C=N).

(Z)-N-isopropyl-3-phenylpropenamide 21a (R=i-Pr)

^{1}H NMR (CCl_4) : 0.98 (6H,d,J=7Hz,Me_2); 3.90 (1H,broadened septet,J=7Hz, NCH); 6.4 (1H,s,broad,NH); 5.80 (1H,d,J=12.5Hz,=CH-CO); 6.51 (1H,d,J=12.5 Hz,=CH-Ph); 7.1-7.5 (5H,m,Ph). IR (NaCl) : 1655 cm^{-1} (C=O); 1625 cm^{-1} (C=C). Mass spectrum m/z (%) : 189 (M^+; 36); 176(7); 146(11); 131(100); 104(9); 103(39); 102(7); 91(5); 78(25); 58(36); 51(11); 44(29); 43(14); 41(7). As a reference material, the corresponding (E)-N-isopropyl-3-phenylpropenamide was prepared as described in the previous experiment, mp. 104°C (Lit.[52] mp 102-103°C). This compound showed the following typical ^{1}H NMR data ($CDCl_3$) : 1.26 (6H,d,J=7Hz,Me_2); 4.2 (1H,m,NCH); 6.85 (1H,d,

J=15.8Hz, =CH-CO); 7.75 (1H, d,J=15.8Hz,=CH-Ph); 7-7.8 (6H,m,Ph and NH).

(Z)-N-t-Butyl-3-phenylpropenamide 21b (R=t-Bu)

Mp. 71°C; ^{1}H NMR ($CDCl_3$) : 1.22 (9H,s,tBu); 5.3 (1H,s,broad,NH); 5.89 (1H, d, J=12.5Hz,=CH-CO); 6.66 (1H,d,J=12.5Hz,=CH-Ph); 7.1-7.4 (5H,m,Ph). IR (NaCl/ $CDCl_3$) : 1655 cm^{-1} (C=O); 1625 cm^{-1} (C=C). Mass spectrum m/z (%) : 203 (M^+; 34); 188(42); 146(47); 131(100); 103(37); 77(20); 58(18).
Elem. anal. : calcd. 6.89% N, found 6.61% N.
As a reference material, the corresponding (E)-N-t-butyl-3-phenylpropenamide was prepared from cinnamoyl chloride and t-butylamine in dichloromethane (room temperature 15 h), mp 149°C (Lit.[52] mp 148-49°C). This compound showed the following typical ^{1}H NMR data ($CDCl_3$) : 6.45 (1H,d,J=15.5 Hz,=CH-CO); 7.62 (1H,d,J=15.5Hz,CH=C-CO).

N-Isopropyl-4,4-dimethyl-1-cyclopentenecarboxylic Amide 22a

Mp. 116°C (ether). ^{1}H NMR ($CDCl_3$) : 1.13 (6H,s,Me_2); 1.19 (6H,d,J=7Hz, Me_2); 2.2-2.4 (4H,m,CH_2-C=C-CH_2); 4.1 (1H,septet,broadened,J=7Hz,NCH); 5.4 (1H, broad,NH); 6.8 (1H,m,=CH). IR (KBr) : 3275 cm^{-1} (NH); 1644 cm^{-1} (C=O); 1602 cm^{-1} (C=C). Mass spectrum m/z (%) : 181 (M^+; 16); 166(10); 125(30); 124(26); 123(100); 95(32); 81(55); 79(24); 77(16); 67(28); 58(22); 55(35); 53(28); 43 (76); 42(22); 41(75); 40(24); 39(40). ^{13}C NMR ($CDCl_3$) : 22.85 (q,Me_2C-N); 29.74 (q,Me_2); 39.10 (s,Me_2C); 41.22 (d,NCH); 46.62 and 48.12 (each t,each CH_2-C=); 135.47 (d,CH=C); 138.27 (s,=C-CO); 164.82 (s,C=O). Elem. anal. : calcd. 72.88% C, found 73.06% C; calcd. 10.56% H, found 10.68% H; calcd. 7.73% N, found 7.60% N.

N-n-Propyl-4,4-dimethyl-1-cyclopentenecarboxylic Amide 22c

Mp. 69°C (CCl_4/pentane). ^{1}H NMR ($CDCl_3$) : 1.14 (6H,s,Me_2); 0.94 (3H,≈t, CH_3); 1.3-1.8 (2H,m,CH_2-C-N); 2.2-2.5 (4H,m,CH_2-C=C-CH_2); 3.30 (2H,t, broadened,J=6 Hz,NCH_2); 6.0 (1H,broad,NH); 6.44 (1H,m,=CH). IR (NaCl/ $CDCl_3$) : 3200 cm^{-1} (NH); 1647 cm^{-1} (C=O); 1613 cm^{-1} (C=C). Mass spectrum m/z (%) : 181 (M^+; 10); 167(9); 125(22); 124(20); 123(97); 97(11); 96(12); 95(32); 81(60); 79 (28); 77(19); 67(32); 55(34); 53(28); 51(10); 44(32); 43(80); 42(15); 41(73); 40(100). ^{13}C NMR ($CDCl_3$) : 11.40 (q,Me-C-C-N); 22.95 (t,CH_2-C-H); 41.21 (t, CH_2N); 29.74 (q,Me_2); 39.06 (s,CMe_2); 46.59 and 48.09 (each t,CH_2C=C-CH_2); 136.06 (d,=CH); 138.13 (s,=C-CO); 165.72 (s,C=O). Elem. anal. : calcd 7.73% N, found 7.86% N.

2-(N-t-Butyl)amino-2-cyclopentenone 2t

^{1}H NMR (CCl_4) : 1.23 (9H,s,t-Bu); 2-2.6 (4H,m,CH_2CH_2); 3.8 (1H,s,broad, NH); 5.83 (1H,t,J=2.8Hz,=CH). ^{13}C NMR ($CDCl_3$) : 28.62 (q,Me_3); 23.77 and 32.43 (each t,CH_2CH_2); 50.06 (s,CMe_3); 121.04 (d,CH=); 142.62 (s,=C-N);

205.93 (s,C=O). IR (NaCl) : 3370 cm^{-1} (NH); 1709 cm^{-1} (C=O); 1635 cm^{-1} (C=C). Mass spectrum m/z (%) : 153 (M^+; 33); 138(100); 97(60); 96(10); 69(84); 68(19); 57(54); 56(18); 55(20); 54(19); 53(10); 43(13); 42(21); 41 (86); 40(14); 39(33). Elem. anal. : calcd. 9.14% N, found 9.21% N.

N-Isopropyl-1-cyclohexenecarboxylic Amide 23

Mp. 71°C. ^1H NMR ($CDCl_3$) : 1.19 (6H,d,J=6.5Hz); 1.5-1.8 (4H,m,CH_2CH_2); 2-2.4 (4H,m,CH_2-C= and CH_2CO); 4.15 (1H,septet,broadened,J=6.5Hz,NCH); 5.5 (1H,s, broad,NH); 6.67 (1H,m,C<u>H</u>=C). IR (NaCl) : 3300 cm^{-1} (NH); 1666 and 1625 cm^{-1} (C=C and C=O). ^{13}C NMR ($CDCl_3$) : 22.87 (q,Me_2); 41.38 (d,NCH); 21.70, 22.31, 24.44 and 25.39 (each t,each CH_2); 132.66 (d,=CH); 133.80 (s,<u>C</u>=CH); 167.78 (s,C=O). Mass spectrum m/z (%) : 167 (M^+; 35); 152(17); 138(15); 109(100); 81(90); 79(35); 67(12); 58(15); 53(25); 49(15); 44(45); 43(30); 41(40). Elem. anal. : calcd. 8.37% N, found 8.52% N.

2-(N-Isopropyl)amino-2-cycloheptenone 2u

^1H NMR ($CDCl_3$) : 1.12 (6H,d,J=7Hz,Me_2); 1.5-2.0 (4H,m,CH_2CH_2); 2.2-2.9 (4H,m, C<u>H</u>$_2$CO and C<u>H</u>$_2$C=C); 3.4 (1H,m,NCH); 5.4 (1H,m,CH=). IR (NaCl) : 1670-1640 cm^{-1} (C=O,C=C).

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