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THE MECHANISM OF THE STEREOISOMERIZATION OF N-ARYL KETENIMINES

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Abstract—Barriers to racemization of the o-mono and o,o'-disubstituted N-phenyl ketenimines **1a–j** were measured by dynamic NMR spectroscopy. The structures of the ketenimines **1k**, **l** were established by X-ray diffraction analysis. According to the experimental results and *ab initio* calculations (STO-3G basis set) N-aryl ketenimines and N-aryl imines in general invert their configurations by a coupled mechanism: a rotation around the N-aryl bond is coupled to inversion at nitrogen. In the transition state of nitrogen inversion the aryl π system is conjugated to the *p* lone electron pair of the nitrogen; in the ground state, however, conjugation between the aryl system and the C=N double bond is electronically preferred but may be sterically hindered.

In solution and the solid state ketenimines **1** generally show a bent C=C=N–R^3 moiety with local C_s symmetry.[1] Ketenimines with different substituents R^1 and R^2 are therefore chiral. However, in solution at room temperature open chain ketenimines racemize quickly ($\Delta G^{\ddagger} = 30$–65 kJ mol^{-1}).[2]

This topomerization proceeds through inversion at nitrogen via a transition state **1'** with a linear C–C≡N–R^3 fragment. The following arguments support this mechanism: (1) The barrier to racemization rises considerably ($\Delta G^{\ddagger} = 80$ kJ mol^{-1}) if the ketenimine is part of an eightmembered ring in which a linear transition state would be strained.[3] (2) Electron withdrawing substituents at C and N of **1** lower the barrier to configurational inversion; in extreme cases they stabilize the linear form **1'** to such an extent that it becomes more stable than the valence tautomer **1**.[4] Valence tautomers of cumulenes may be called pseudocumulenes.[5] (3) Cyanamidium salts R^1R^2N–C≡$\overset{+}{N}$–R^3 X^- being isoelectronic with **1** are pseudocumulenes with a linear N–C≡N–R^2 moiety in the ground state.[6] (4) Substituent effects on the barriers to racemization of ketenimines **1** and to geometrical isomerization of guanidines (which were shown by Kessler[7] to isomerize via nitrogen inversion) are very similar; this suggests that both classes of compounds invert their configurations by the same mechanism. (5) ^{15}N NMR chemical shifts are in accordance with significant delocalization of the nitrogen lone pair of ketenimines even in the bent ground state **1**.[8]

While topermerization via nitrogen inversion seems to be well established for N-alkyl ketenimines (**1**, R^3 = alkyl), we found evidence that N-aryl ketenimines (**1**, R^3 = aryl) and N-aryl imines in general invert their configurations by a more complicated mechanism: a rotation of the aryl group around the N-aryl bond is coupled to nitrogen inversion.

In the bent ground state **1** the aromatic π system tends to be conjugated to the C=N double bond. Accordingly, the plane of the N-aryl ring is more or less vertical to the plane passing through R^1–C–R^2. In the transition state **1'**, however, the N-aryl group lies within the plane passing through R^1–C–R^2 thus electronically stabilizing an enamine system. The following arguments support this coupled inversion-rotation mechanism: (1) -M substituents in the p-position of N-phenyl ketenimines lower the barrier to configurational inversion. The barriers correlate quite well with the Hammett σ^- constants[2] as might be expected after consideration of the canonical form **1''**. –M substituents in the p-position stabilize the transition state more than the ground state and thus lower the barrier to stereomutation. (2) Twisting the cumulene axis out of the plane of the N-phenyl ring in **1** should, according to our argumentation, result in some destabilization of the ground state and thus lower the barrier to stereomutation. In order to examine this effect the barriers to racemization of the ketenimines **1a–j** were measured by ^{1}H and ^{13}C NMR spectroscopy at various temperatures by observing the coalescence of the geminal diastereotopic methyl groups or benzylic protons. Furthermore, the structures of the ketenimines **1k**, **l** were determined by X-ray diffraction analysis.

EXPERIMENTAL—1

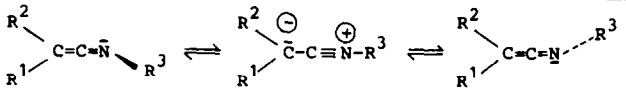
Syntheses

All ketenimines were prepared according to the methods of Stevens starting from the corresponding amides (**2a—l**). The amides were dehydrated either directly with phosphorous pentoxide (Siccapent, Merck)[9] or first transformed into the imidochlorides **3** with phosphorous pentachloride, a reaction being effectively catalyzed by dimethylformamide. Subsequent elimination of hydrogen chloride with triethylamine[10] afforded the ketenimines.

The o,o'-disubstituted N-aryl ketenimines are rather unstable compounds decomposing within two days at room temperature. We were not able to synthesize an N-(2,6-di-t-butylphenyl)ketenimine.

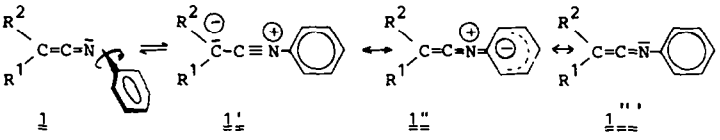
X-ray diffraction analyses of **1k**, **l**

1k, $C_{21}H_{17}N$, $M = 283.36$, orthorhombic, space group $P2_12_12_1$, $a = 787.4(1)$, $b = 1707(3)$, $c = 2381(2)$ pm, $Z = 8$, $V = 3199 \cdot 10^6$ pm^3, $d_{calc.} = 1.18$ gcm^{-3}, $T = 293$ K. μ_{MoK_α}-Radiation (0.7 cm^{-1}) was used to measure the intensities of 1409 independent significant ($I \geq 2\sigma$) reflections on a Syntex-P3-diffractometer in the ω-scan mode



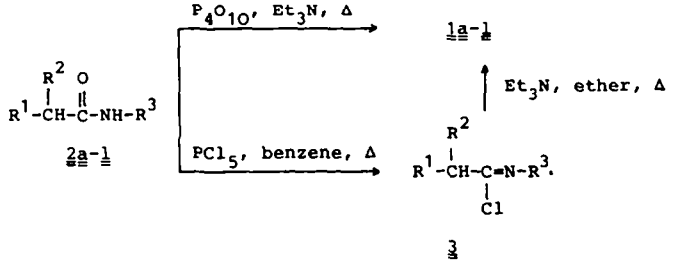
1 1'

1, 2	R^1	R^2	R^3
a	$C_5H_5CH_2(CH_3)_2C$	CH_3	C_6H_4Cl-(2)
b	$C_6H_5CH_2(CH_3)_2C$	CH_3	$C_6H_4CH_3$-(2)
c	$C_6H_5CH_2(CH_3)_2C$	CH_3	$C_6H_4[(CH_3)_2CH]$-(2)
d	$C_6H_5CH_2(CH_3)_2C$	CH_3	$C_6H_4[(CH_3)_3C]$-(2)
e	$C_6H_5CH_2(CH_3)_2C$	CH_3	$C_6H_3Cl_2$-(2,6)
f	$(CH_3)_2CH$	CH_3	$C_6H_3Cl_2$-(2,6)
g	$C_6H_5CH_2(CH_3)_2C$	CH_3	C_6H_3Cl-(2)-CH_3-(6)
h	$(CH_3)_2CH$	CH_3	C_6H_3Cl-(2)-CH_3-(6)
i	$(CH_3)_2CH$	CH_3	$C_6H_3(CH_3)_2$-(2,6)
j	$(CH_3)_2CH$	CH_3	$C_6H_3[(CH_3)_2CH]$-(2,6)
k	C_6H_5	C_6H_5	$C_6H_4CH_3$-(2)
l	C_6H_5	C_6H_5	C_6H_2Br-(4)-$(CH_3)_2$-(2,6)
m	$C_6H_5CH_2(CH_3)_2C$	CH_3	$C_6H_4CH_3$-(4)
n	$C_6H_5CH_2(CH_3)_2C$	CH_3	C_6H_4Cl-(4)
o	$C_6H_5CH_2(CH_3)_2C$	CH_3	C_6H_5
p	$(CH_3)_2CH$	CH_3	C_6H_5
q	H	H	C_6H_5



1 1' 1'' 1'''

Scheme 1.



Scheme 2.

($\Delta\omega = 1.1°$, $2.0 < \dot{\omega} < 29.3°\ min^{-1}$, $2.5° \leq 2\theta \leq 45°$, graphite monochromator, $\lambda_{MoK_\alpha} = 71.069$ pm). The cell constants were determined with the same instrument. The structure was solved by application of the program SHELXTL[11] by direct methods. Hydrogen atoms were fixed on calculated geometrically ideal positions. For the calculations form factors of neutral atoms were used. The anisotropic refinement led to agreement factors $R_1 = 0.081$ and $R_2 = 0.076$. A list of atomic coordinates with LS-computed standard deviations is given in Table 1. In Table 2 selected bond lengths, bond angles and torsional angles of **1k** are given. Figure 1 shows a molecular drawing of one of the two independent molecules of **1k** in the elementary cell.

1l, $C_{22}H_{18}BrN$, $M = 376.28$, monoclinic, space group $P2_1/c$, $a = 418.3(2)$, $b = 2958(3)$, $c = 1419(2)$ pm, $\beta = 88.93(8)$, $Z = 4$, $V = 1750 \cdot 10^6\ pm^3$, $d_{calc.} = 1.40\ g cm^{-3}$, $T = 228$ K, linear absorption coefficient for MoK_α: $\mu = 24.8\ cm^{-1}$. Measurements and solution as for **1k**. 1480 independent significant ($I \geq 2\sigma$) reflections, $\Delta\omega = 1.3°$, $1.8 < \dot{\omega} \leq 29.3°\ min^{-1}$, $2° \leq 2\theta \leq 40°$, $R_1 = 0.034$, $R_2 = 0.035$. A list of atomic coordinates with LS-computed standard deviations is given in Table 3. In Table 4 selected

Table 1. Fractional atomic coordinates and anisotropic temperature parameters of **1k***

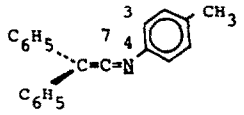
Atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
C1	0.940(2)	0.6223(7)	0.0872(5)	0.06(1)	0.052(8)	0.037(7)	-0.001(6)	-0.015(8)	0.003(9)
C2	0.863(2)	0.6047(9)	0.0404(5)	0.06(1)	0.10(1)	0.035(7)	-0.010(7)	0.007(8)	0.00(1)
N	0.780(2)	0.5986(6)	-0.0048(4)	0.064(9)	0.076(8)	0.056(7)	-0.008(6)	0.001(7)	-0.016(8)
C12	0.842(2)	0.6710(5)	0.1809(3)	0.067(7)	0.065(6)	0.042(5)	-0.010(5)	0.000(5)	0.000(7)
C13	0.756(1)	0.6611(6)	0.2297(3)	0.044(6)	0.099(7)	0.037(5)	-0.015(5)	-0.005(5)	0.009(7)
C14	0.666(2)	0.5938(7)	0.2406(4)	0.064(8)	0.12(1)	0.052(7)	0.013(6)	0.012(6)	0.009(8)
C15	0.668(2)	0.5342(6)	0.2003(5)	0.078(9)	0.078(8)	0.107(9)	0.026(7)	0.022(8)	0.013(8)
C16	0.757(2)	0.5426(6)	0.1508(3)	0.085(8)	0.076(7)	0.044(6)	0.011(5)	0.002(6)	-0.020(8)
C11	0.846(2)	0.6115(9)	0.1406(4)	0.046(9)	0.07(1)	0.023(7)	0.000(7)	-0.001(7)	-0.004(9)
C18	1.182(2)	0.6715(8)	0.0306(5)	0.05(1)	0.062(9)	0.046(8)	0.008(7)	0.008(7)	0.00(1)
C19	1.352(2)	0.6943(6)	0.0266(4)	0.084(9)	0.065(7)	0.065(6)	-0.03(5)	0.018(7)	0.007(7)
C20	1.453(1)	0.6968(5)	0.0730(4)	0.050(7)	0.045(6)	0.097(8)	-0.007(5)	-0.016(6)	0.002(6)
C21	1.387(2)	0.6771(6)	0.1245(3)	0.077(8)	0.066(7)	0.044(5)	0.008(5)	-0.014(5)	0.001(7)
C22	1.219(1)	0.6533(6)	0.1305(3)	0.040(7)	0.067(7)	0.039(5)	0.003(4)	-0.010(5)	-0.003(6)
C17	1.117(2)	0.6484(6)	0.0831(4)	0.058(9)	0.033(7)	0.035(6)	-0.003(5)	0.006(7)	0.001(7)
C31	0.766(1)	0.5279(5)	-0.0379(3)	0.049(7)	0.066(6)	0.035(5)	-0.005(4)	-0.004(5)	-0.006(6)
C32	0.834(1)	0.4594(6)	-0.0196(3)	0.090(9)	0.088(6)	0.051(6)	0.014(5)	-0.002(6)	-0.003(8)
C33	0.816(2)	0.3916(5)	-0.0529(3)	0.15(1)	0.061(7)	0.049(5)	-0.010(5)	-0.012(7)	-0.020(8)
C34	0.733(2)	0.3990(6)	-0.1023(4)	0.09(1)	0.103(9)	0.055(6)	-0.017(6)	-0.008(7)	-0.028(9)
C35	0.670(2)	0.470(1)	-0.1210(5)	0.08(1)	0.13(1)	0.049(8)	0.01(1)	-0.006(8)	-0.01(1)
C36	0.680(2)	0.538(1)	-0.0881(5)	0.06(1)	0.17(2)	0.031(7)	-0.04(1)	0.001(8)	-0.03(1)
C37	0.614(2)	0.6175(9)	-0.1095(5)	0.13(2)	0.09(1)	0.08(1)	-0.001(8)	-0.03(1)	0.06(1)
CX1	0.935(1)	0.8594(5)	0.3442(3)	0.074(7)	0.041(6)	0.045(5)	0.000(4)	-0.019(5)	-0.010(6)
CX2	0.851(2)	0.8753(7)	0.2959(5)	0.06(1)	0.044(8)	0.060(7)	-0.011(7)	-0.004(8)	-0.003(8)
NX	0.777(1)	0.8820(5)	0.2518(3)	0.057(7)	0.067(7)	0.039(5)	-0.006(5)	-0.008(5)	0.002(6)
CX12	1.184(2)	0.8070(7)	0.2877(5)	0.11(1)	0.052(8)	0.047(8)	0.004(6)	0.006(9)	0.01(1)
CX13	-0.354(2)	0.2857(5)	0.2128(4)	0.10(1)	0.050(6)	0.084(7)	0.002(5)	0.028(7)	-0.027(7)
CX14	-0.461(2)	0.2855(8)	0.1667(6)	0.07(1)	0.09(1)	0.08(1)	-0.025(8)	0.01(1)	-0.004(9)
CX15	-0.387(2)	0.3097(6)	0.1170(4)	0.081(9)	0.064(7)	0.070(7)	-0.011(5)	0.009(6)	0.010(8)
CX16	1.217(2)	0.8307(7)	0.3865(4)	0.051(9)	0.048(8)	0.070(8)	-0.002(6)	-0.008(6)	-0.001(7)
CX11	1.110(2)	0.8297(6)	0.3395(5)	0.06(1)	0.033(7)	0.044(7)	0.003(6)	-0.015(7)	-0.001(8)
CX18	0.846(1)	0.8181(5)	0.4393(3)	0.060(7)	0.072(6)	0.036(5)	0.009(5)	-0.012(5)	-0.013(7)
CX19	0.250(2)	0.3386(6)	0.0087(4)	0.088(9)	0.092(8)	0.069(6)	-0.021(6)	-0.016(7)	0.000(9)
CX20	0.335(2)	0.4050(6)	0.0049(3)	0.10(1)	0.080(8)	0.056(6)	0.021(5)	0.018(6)	0.007(8)
CX21	0.340(2)	0.4595(6)	0.0465(5)	0.071(9)	0.088(8)	0.081(8)	-0.013(7)	-0.009(7)	0.013(8)
CX22	0.764(2)	0.9415(6)	0.4023(3)	0.096(9)	0.068(7)	0.052(5)	-0.032(5)	0.005(7)	-0.011(8)
CX17	0.848(1)	0.8737(6)	0.3971(3)	0.047(7)	0.049(6)	0.038(5)	-0.003(5)	0.004(5)	-0.001(6)
CX31	0.768(1)	0.9544(6)	0.2207(3)	0.046(7)	0.069(7)	0.028(5)	0.013(5)	0.002(5)	0.020(7)
CX32	0.839(1)	1.0235(5)	0.2396(3)	0.078(8)	0.056(6)	0.041(5)	-0.016(4)	0.002(5)	0.002(6)
CX33	0.823(2)	1.0903(6)	0.2080(4)	0.073(9)	0.048(7)	0.064(7)	0.004(6)	0.015(7)	-0.001(7)
CX34	0.731(2)	1.0877(5)	0.1582(3)	0.11(1)	0.060(6)	0.061(6)	0.020(5)	0.019(7)	0.043(7)
CX35	0.665(2)	1.0188(8)	0.1389(4)	0.076(9)	0.073(8)	0.046(7)	0.008(6)	-0.007(6)	0.019(8)
CX36	0.676(2)	0.9486(7)	0.1691(4)	0.061(9)	0.083(9)	0.056(7)	0.010(6)	0.009(7)	0.016(8)
CX37	0.595(2)	0.8744(7)	0.1478(4)	0.012(1)	0.077(8)	0.071(8)	-0.025(7)	-0.035(8)	-0.001(9)

a) The anisotropic temperature parameters are defined by the expression $T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$.

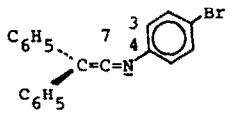
bond angles and torsional angles of **1l** are given. Figure 2 shows a molecular drawing and the bond lengths of **1l**.

DISCUSSION

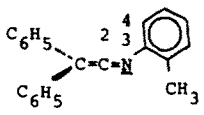
There are no unusual bond lengths or angles in the molecules **1k**, **l**. Both ketenimines show bent C=C=N moieties. Of interest are the conformations of the N-aryl rings. In diffraction analyses of N-phenyl ketenimines[1,2,12] the angle between the phenyl ring and the respective C=N–C plane was always found to be small, e.g.:



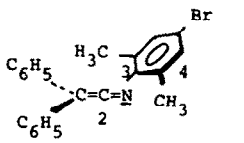
torsional angle C3-C4-N-C7 1.9° 12)



C3-C4-N-C7 1.9° 12)



C2-N-C3-C4 + 6°(2), -2°(2)



C2-N-C3-C4 -63°(1)

Scheme 3.

Deviations from this coplanarity have been discussed in terms of a low barrier to hindered rotation around the N-aryl bond and crystal packing forces.[2] Similarly, in 1,3-diphenylcarbodiimide[13–15] the N=C=N moiety lies almost in the plane of at least one phenyl ring. These findings suggest that conjugation of the N-aryl π system and the C=N double bond resulting in a coplanar conformation of C=N–C and the phenyl ring is energetically preferred to conjugation to the lone electron pair of the nitrogen. A substituent R of the phenyl group ortho to N should induce some steric strain into the ketenimine due to non bonded interactions with C=C=N or with the lone pair at

Table 2. Selected bond lengths, bond angles and torsional angles of **1k****

C1 - C2	131(2); 136(1)	C31 - C36 - C37	124(1); 124(1)
C2 - N	126(2); 121(1)	C37 - C36 - C35	122(1); 121(1)
N - C31	145(1); 144(1)	C18 - C17 - C1 - C2	+15(2); +132(1)
C17 - C1	147(2); 146(1)	C12 - C11 - C1 - C2	-132(1); -9(2)
C11 - C1	149(2); 147(2)	C18 - C17 - C1 - C11	-167(1); -49(1)
C36 - C37	154(3); 151(2)	C12 - C11 - C1 - C17	+51(2); +172(1)
C17 - C1 - C2	117(1); 118(1)	C17 - C1 - N - C31	+90 ; +89
C11 - C1 - C2	118(1); 118(1)	C11 - C1 - N - C31	-93 ; -93
C11 - C1 - C17	125(1); 124(1)	C2 - N - C31 - C32	+6(2); -2(2)
C1 - C2 - N	171(2); 174(1)	N - C31 - C36 - C37	+4(2); 0(2)
C2 - N - C31	125(1); 124(1)	C11 - C1 - C2 - N	+90 ; +63

**) The figures after the semicolon refer to the molecule marked with X.

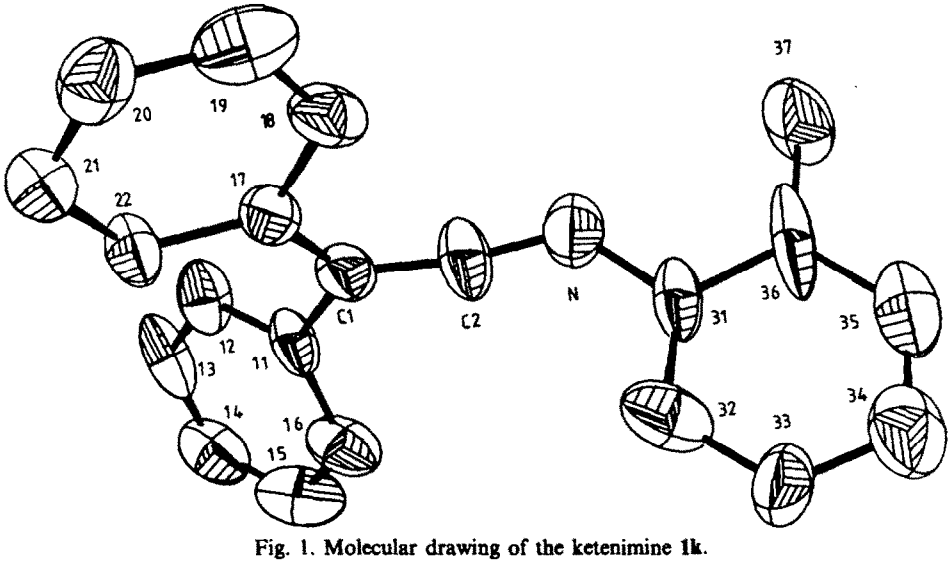


Fig. 1. Molecular drawing of the ketenimine **1k**.

Table 3. Fractional atomic coordinates and anisotropic temperature parameters of **11***

Atom	x/a	y/b	z/c	U11	U22	U33	U23	U13	U12
Br	0.0191(2)	0.30150(2)	1.23187(3)	0.0777(4)	0.0591(4)	0.0319(3)	0.0100(3)	0.0071(3)	-0.0100(3)
C1	0.327(1)	0.4172(2)	0.7183(3)	0.032(4)	0.032(3)	0.025(3)	0.004(2)	-0.001(3)	0.005(3)
C2	0.422(1)	0.3990(2)	0.7988(4)	0.034(4)	0.023(3)	0.038(4)	-0.007(3)	0.005(3)	0.001(3)
N	0.552(1)	0.3812(1)	0.8663(3)	0.044(3)	0.026(2)	0.029(3)	0.000(2)	-0.005(2)	0.001(2)
C3	0.404(1)	0.3629(2)	0.9501(3)	0.035(4)	0.037(3)	0.019(3)	0.004(3)	-0.006(3)	-0.002(3)
C4	0.231(1)	0.3906(1)	1.0124(3)	0.037(3)	0.033(3)	0.030(3)	0.000(2)	-0.007(2)	0.000(2)
C5	0.117(1)	0.3713(2)	1.0967(3)	0.046(4)	0.038(3)	0.028(3)	-0.003(2)	-0.003(2)	-0.002(2)
C6	0.176(1)	0.3264(2)	1.1154(3)	0.043(3)	0.053(3)	0.023(3)	0.006(2)	-0.006(2)	-0.012(3)
C7	0.345(1)	0.2990(2)	1.0532(3)	0.047(3)	0.028(3)	0.035(3)	0.000(2)	-0.006(2)	0.000(3)
C8	0.460(1)	0.3172(1)	0.9968(3)	0.037(3)	0.030(3)	0.028(3)	0.001(2)	-0.007(2)	0.001(2)
C41	0.170(1)	0.4398(2)	0.9927(3)	0.062(4)	0.036(3)	0.040(3)	0.001(2)	0.001(3)	0.011(3)
C81	0.638(1)	0.2881(2)	0.8974(3)	0.054(4)	0.029(3)	0.045(3)	0.000(2)	0.003(3)	0.009(2)
C11	0.292(1)	0.4668(1)	0.7087(3)	0.033(3)	0.029(3)	0.026(3)	0.002(2)	0.005(2)	0.000(2)
C12	0.441(1)	0.4964(2)	0.7718(3)	0.043(3)	0.038(3)	0.034(3)	0.001(2)	0.005(2)	-0.007(3)
C13	0.400(1)	0.5431(2)	0.7632(3)	0.049(4)	0.038(3)	0.042(3)	-0.009(2)	0.012(3)	-0.007(3)
C14	0.220(1)	0.5607(2)	0.6905(3)	0.060(4)	0.033(3)	0.040(3)	0.004(3)	0.016(3)	0.002(3)
C15	0.080(1)	0.5318(2)	0.6286(3)	0.058(4)	0.042(3)	0.034(3)	0.005(3)	0.009(3)	0.011(3)
C16	0.110(1)	0.4851(2)	0.6368(3)	0.037(3)	0.035(3)	0.032(3)	0.003(2)	0.002(2)	0.005(2)
C18	0.362(1)	0.3922(2)	0.5490(3)	0.043(3)	0.034(3)	0.028(3)	0.003(2)	0.000(2)	-0.002(2)
C19	0.295(1)	0.3611(2)	0.4783(3)	0.050(4)	0.039(3)	0.033(3)	-0.001(2)	-0.003(2)	0.001(3)
C20	0.120(1)	0.3225(2)	0.4991(3)	0.054(4)	0.035(3)	0.040(3)	-0.008(2)	-0.005(3)	-0.001(3)
C21	0.010(1)	0.3149(2)	0.5904(4)	0.055(4)	0.031(3)	0.049(3)	0.002(3)	0.000(3)	-0.009(3)
C22	0.072(1)	0.3462(2)	0.6615(3)	0.040(3)	0.032(3)	0.034(3)	0.004(2)	-0.003(2)	0.004(2)
C17	0.248(1)	0.3851(1)	0.6412(3)	0.031(3)	0.028(3)	0.027(2)	0.003(2)	0.000(2)	0.002(2)

Table 4. Selected bond and torsional angles of **11**

C11 - C1 - C2	120.9(4)	C12 - C11 - C1 - C2	+ 19(1)
C17 - C1 - C2	116.5(4)	C18 - C17 - C1 - C2	-134(1)
C11 - C1 - C17	122.6(4)	C11 - C1 - N - C3	+ 95
C1 - C2 - N	170.5(6)	C2 - N - C3 - C4	- 63(1)
C2 - N - C3	128.0(5)	C2 - N - C3 - C8	+121(1)
N - C3 - C4	120.8(4)	N - C3 - C4 - C41	+ 5(1)
N - C3 - C8	116.6(4)	N - C3 - C8 - C81	- 7(1)
C3 - C4 - C41	122.5(4)		
C3 - C8 - C81	120.7(4)		

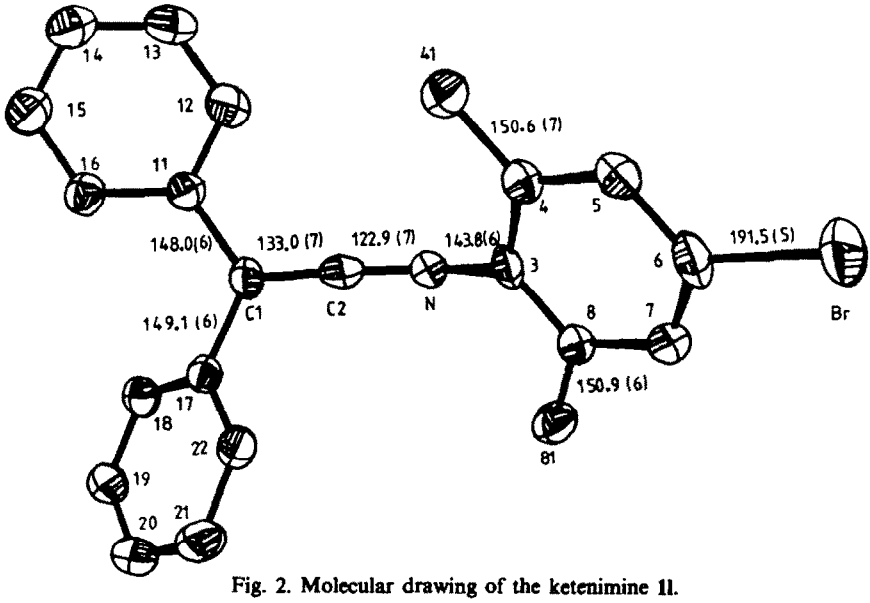


Fig. 2. Molecular drawing of the ketenimine **11**.

nitrogen. The structure of **1k** shows that a peri arrangement of R and the nitrogen lone pair is more stable than that of R and N=C. If there are two substituents ortho to C=N, the N-aryl ring is considerably twisted out of the C=N–C plane thus destabilizing the ground state of the ketenimine by loss of conjugation.

Barriers to racemization of the ketenimines **1a–j**

The barriers to racemization of the ketenimines **1a–j** as measured by dynamic NMR spectroscopy[16] are listed in Table 5. Published data for **1m–p** have been added for comparison. The temperature dependency of the spectrum of the benzylic protons of **1c** was simulated by a complete line shape analysis[17] leading to $\Delta S^{\neq} = -1 \pm 3\,JK^{-1}\,mol^{-1}$ and $\Delta H^{\neq} = 46.1 \pm 1\,kJ\,mol^{-1}$. As expected the activation entropy for the racemization is small and may be neglected. The lowering of $\Delta G^{\neq}$ in CS_2 as solvent (compare the two measurements for **1e**) is worth mentioning. This was explained[2] by complexation between CS_2 and the ketenimine.

The electronic effect of a methyl or chlorine substituent in the para position of the N-phenyl nucleus is small and barely exceeds the error limit ($\pm 1\,kJ\,mol^{-1}$) as can be seen from the $\Delta G^{\neq}$ values for **1m–p**. If however a methyl, chlorine or isopropyl substituent is ortho to nitrogen there is a decrease in the barrier of about $6\,kJ\,mol^{-1}$; if the 2-substituent is tert-butyl the decrease amounts to almost $10\,kJ\,mol^{-1}$. This behaviour must therefore be due to steric factors. The decrease in $\Delta G^{\neq}$ (as compared to the unsubstituted compound **1o**) amounts to $15\,kJ\,mol^{-1}$ if both positions ortho to N are substituted (e.g. **1j**). Similar but smaller effects were observed for the barriers to geometrical isomerization of ortho-substituted N-phenyl imines.[18,19] These findings suggest that both in the crystal and in solution C=N–C and the unsubstituted N-phenyl ring tend to be almost coplanar in the ground state of **1**. Substituents in the ortho position of the phenyl ring destabilize both the ground and the transition states of the racemization but the ground state is affected to a larger extent. Assuming that in the ground state in

Table 5. Gibbs activation energies at the coalescence temperatures T_c for the racemization of the ketenimines **1a–j, m–p** in $CHClF_2/CH_2CHCl$ (1:1)

1	observed nuclei	T_c [K]	$\Delta\nu$ [Hz] [a]	k_{T_c} [s^{-1}]	$\Delta G^{\neq}_{T_c}$ [$kJmole^{-1}$] [b]
a	$(CH_3)_2C$	218	17.4	37	46.3
b	$(CH_3)_2C$	216	15.2	34	46.0
c	CH_2 [c]		32.2		46.3
c	$(CH_3)_2CH$	197	1.3	2.9	45.9
c	$(CH_3)_2C$	221	15.4	32	47.1
c	$(CH_3)_2CH$ [d]	217	18.0	36	46.2
c	$(CH_3)_2C$	224	34.0	71	46.4
d	$(CH_3)_2C$	201	15.5	34	42.7
e	$(CH_3)_2C$	193	12.1	27	41.4
e	$(CH_3)_2C$ [e]	174	12.0	27	37.1
f	$(CH_3)_2CH$ [d]	183	5.0	5 [f]	41.5
g	$(CH_3)_2C$	179	13.0	29	38.0
h	$(CH_3)_2CH$	185	6.1	14 [f]	40.8
i	$(CH_3)_2CH$	178	4.5	7 [f]	39.9
j	$(CH_3)_2CH$-aryl	186	45	99	37.6
j	$(CH_3)_2CH$-C=	173	10	22	37.1
m [2]	$(CH_3)_2C$	240	9.5	19	52.5
n [2]	$(CH_3)_2C$	241	12.3	26	52.1
o [2]	$(CH_3)_2C$	237	10.1	21	51.6
p [2]	$(CH_3)_2CH$	222	2.1	3.5	51.5

a) Frequency difference of the diastereotopic nuclei at the coalescence temperature as obtained by linear extrapolation of the temperature dependency of $\Delta\nu$ between 50 and 10° below the coalescence temperature.

b) Error ± 1 $kJmole^{-1}$.

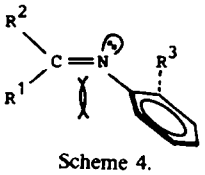
c) Complete line shape analysis between 230 and 210 K [17] gives $\Delta S^{\neq} = -1 \pm 3\ JK^{-1}mole^{-1}$ and $\Delta H^{\neq} = 46.1 \pm 1\ kJmole^{-1}$. $\Delta\nu$ is the shift difference at 193 K, $\Delta G^{\neq}$ was calculated from $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for T = 225 K.

d) Solvent CD_2Cl_2.

e) Solvent CS_2.

f) Corrected for the line width according to [16] Fig.5.

solution one ortho substituent is turned away from the C=N moiety (as suggested by the X-ray results from **1k**) a certain destabilization has to be considered due to the entropy of mixing (< 1.5 kJ mol^{-1}). In addition, there seems to be a destabilizing enthalpy effect between the ortho substituent and the lone pair of nitrogen resulting in twisting of the phenyl ring out of the C=N–C plane. This effect should be smaller for N-aryl ketenimines than for N-aryl azomethines because steric interactions between the substituents at C and the N-phenyl group in the latter hinder a coplanar arrangement of C=N–C and the phenyl ring. If both ortho positions of a N-phenyl ketenimine are substituted, steric repulsion from both the nitrogen lone pair and the C=N double bond causes the phenyl plane to be almost orthogonal to the C=N–C plane thus destabilizing the ground state by loss of conjugation. According to the measurements on **1j** (Table 5), the barrier to hindered rotation around the N-aryl single bond amounts to at least 15 kJ mol^{-1}.



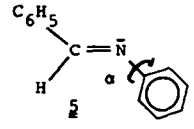
Scheme 4.

Calculations

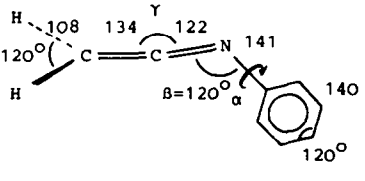
In order to support the experimental results SCF calculations employing the STO–3G basis set[20,21] were carried out on N-phenyl ketenimine **1q** and N-phenyl methylenimine **4**. The ab initio calculation of the ground state of the parent compound ketenimine with full geometry optimization has been published recently.[22] In our calculations fixed bond lengths and angles from the X-ray data of related compounds[1,2] were used. The energies of the molecules were calculated as functions of the torsional angles α (C=N–C–C) around the N-phenyl bonds for various C=N–C bond angles β. In the case of **1q** the C=C=N bond angle γ was also varied between 165 and 180° in steps of 2.5°. The main results are summarized in Figs. 3 and 4.

According to all X-ray results on ketenimines[1,2] the C=C=N unit deviates from linearity by 5–10°. It seems that this cannot be attributed to packing forces within the crystal since with $\alpha = 25°$ an energy minimum was calculated for $\gamma = 175°$ (torsional angle C=C=N–C 180° for **1q**). Assuming $\gamma = 180°$ a torsional barrier around the N-phenyl bond of 6.2 kJ mol^{-1} was found with an energy maximum at $\alpha = 90°$. The coplanar conformation ($\alpha = 0°$) is less favourable by 0.9 kJ mol^{-1} than a twisted conformation with $\alpha = 25°$; this is obviously a result of steric interactions between the ortho hydrogens of the phenyl ring and the C=C=N chain. Stereomutation via nitrogen inversion was found to be energetically preferred to rotational mechanisms. Even small deviations in the linearity of C=C=N increase the energy markedly ($\gamma = 175°$: E = 52.7 kJ mol^{-1}). In the most favourable transition state all atoms lie in one plane. The barrier to topomerization via this linear transition state was calculated to be 52.1 kJ mol^{-1} which is in good agreement with the experimental data (**1o**: $\Delta G^{+} = 51.6$ kJ mol^{-1}[2]). A linear ($\beta = 180°$) transition state in which the phenyl π system is conjugated to the C=N double bond ($\alpha = 0°$) is 12 kJ mol^{-1} higher in energy than the transition state in which the phenyl ring and the p lone pair of nitrogen are conjugated ($\alpha = 90°$). As far as a rotation of the N-phenyl bond around the C=C=N axis ($\beta = 120°$) is concerned, the transition state in which the phenyl ring is conjugated to C=N is preferred by 14 kJ mol^{-1} to that in which the phenyl ring is conjugated to the nitrogen lone pair, in contrast to the inversion process.

Quantum mechanical calculations on the mechanism of the cis-trans isomerization of imines have been the subject of long-standing interest.[23–32] Nitrogen inversion is generally calculated to be clearly preferred to rotational paths. According to MINDO/2 and PMO calculations[27] the phenyl ring stands perpendicular ($\alpha = 90°$) to the C=N–C plane in the most stable conformation of **4**. This was explained by repulsive interactions between the ortho protons of the phenyl group and CH_2. If solely the resonance energies are considered, conjugation of the aromatic π system with the C=N double bond ($\alpha = 0°$) was found to have a more stabilizing effect than conjugation with the lone electron pair on nitrogen ($\alpha = 90°$). A barrier to nitrogen inversion of 58.6 kJ mol^{-1}was calculated by MINDO/1 methods.[27] In the case of the related benzylidene aniline **5** energy minima with $\alpha = 60$–$90°$ were found in recent PSILO, INDO, MNDO and CNDO studies.[28,33,34] The calculated barrier to nitrogen inversion of 88.7 kJ mol^{-1} (CNDO/2) may be compared with the experimental value of 69.0 kJ mol^{-1}.[28] In the crystal **5** shows a twist angle of $\alpha = 55°$.[35]

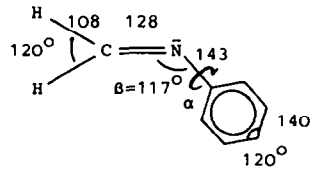


Scheme 5.



δ(H-CCN-C) = 90°

1: Bond lengths (pm) and bond angles used in the SCF calculations.



δ(H-C=N-C) = 0°

4: Bond lengths (pm) and bond angles as used in the SCF calculations.

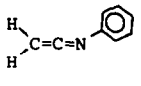
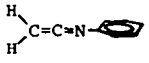
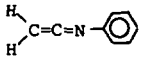
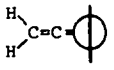
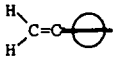
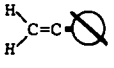
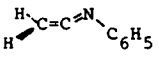
relative energy [kJmole^{-1}]	α [°]	β [°]	γ [°]	δ [°]	conformation
159.8	90	120	180	0	
146.0	0	120	180	0	
64.2	0	180	180	-	
52.1	90	180	180	-	
6.2	90	120	180	90	
0.9	0	120	180	90	
0.0 (-356.931413 au)	25	120	180	90	
-1.8	25	120	175	90	

Fig. 3. Calculated energies for various conformations of **1q**.

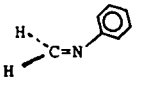
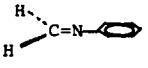
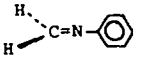
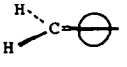
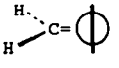
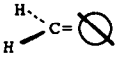
relative energy [kJmole^{-1}]	α [°]	β [°]	δ [°]	conformation
279.5	0	117	90	
154.4	0	180	-	
134.9	90	180	-	
24.4	0	117	0	
5.2	90	117	0	
0.0 (-319.578499 au)	45	117	0	

Fig. 4. Calculated energies for various conformations of **4**.

With the parameters given in the drawing of **4** a twist angle of $\alpha = 45°$ was calculated for the most stable conformation. Coplanarity of C=N–C and the phenyl plane can be better achieved for ketenimines (e.g. **1**) than for N-aryl azomethines (e.g. **4**) due to steric reasons. In the process of geometrical isomerization, nitrogen inversion is clearly preferred to rotation of the N-aryl bond around C=N. In the transition state of nitrogen inversion ($\beta = 180°$) the aryl π system again tends to be conjugated to the p lone pair of nitrogen.

These calculations support our view that a coupled mechanism of inversion at nitrogen and rotation around the N-aryl bond accounts for the topomerization of N-aryl ketenimines and of N-aryl imines more generally. In the ground state conjugation of the N-aryl π system to the C=N double bond is electronically preferred to conjugation with the lone electron pair of nitrogen. In the linear transition state, however, conjugation to the lone pair is even more strongly preferred than conjugation to the C=N double bond.

EXPERIMENTAL—2

IR spectra were recorded on a Perkin–Elmer IR 299 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Jeol JNM-MH-100 and Bruker WM-250 instruments. Coalescence temperatures were measured with a calibrated thermocouple, error $\pm 1°$. Micro-analyses were carried out by Miss R. Naserke, micro-analytical laboratory of Prof. Dr. G. Huttner, Konstanz University.

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2-chlorophenyl)-imine (**1a**)

A mixture of **2a** (3.16 g, 10 mmole) and PCl_5 (2.10 g, 10 mmole) was refluxed in dry benzene (60 ml) for 2 h. The solvent was then evaporated under reduced pressure. The remaining imido chloride was refluxed for 30 h in absol. ether (80 ml) with dry triethylamine (10 ml). After filtration and evaporation of the solvent the ketenimine was purified by column chromatography (2 cm diam, 20 cm length) on Al_2O_3 (pH 9–10, activity II-III, Brockmann) with dry CCl_4 as eluent. Work-up of the first fraction afforded 1.30 g (44%) of a yellow solid; m.p. 39°. IR (film): 2010 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.09 (2 CH_3), 1.78 (1 CH_3), 2.65 (CH_2). (Found: C, 76.74; H, 6.69; N, 4.54. Calc for $C_{19}H_{20}ClN$ (MW = 297.8): C, 76.62; H, 6.77; N, 4.70%.)

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2-methylphenyl)-imine (**1b**)

From **2b** (2.95 g, 10 mmole) as described for **1a**. The imido chloride was refluxed for 8 h with dry triethylamine (10 ml) in ether (100 ml) affording after chromatography 1.90 g (68%) of a yellow solid; m.p. 34°. IR (film): 2000 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.09 (2 CH_3), 1.77 (1 CH_3), 2.25 (1 CH_3), 2.66 (CH_2). (Found: C, 86.47; H, 8.64; N, 4.99. Calc for $C_{20}H_{23}N$ (MW = 277.4): C, 86.59; H, 8.36; N, 5.05%).

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2-isopropylphenyl) imine (**1c**)

From **2c** (3.24 g, 10 mmole) as described for **1a**. The imido chloride was refluxed for 18 h with absol. triethylamine (10 ml) in dry ether (20 ml) affording after chromatography 1.44 g (47%) of a yellow solid; m.p. 53% IR (film): 2005 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.09 (2 CH_3), 1.17 (2 CH_3, d, J = 7 Hz), 1.80 (1 CH_3), 2.69 (CH_2), 3.51 (CH, sept., J = 7 Hz); ^{13}C NMR δ (CD_2Cl_2): 13.2 ($\underline{C}H_3$–C=), 25.4 ((CH_3)$_2$CH), 29.4 (($\underline{C}H_3$)$_2$C), 30.4 (CH), 39.0 (CH_2), 48.9 ($\underline{C}\underline{C}H_2$), 72.8 (–C=), 195.1 (=C=). (Found: C, 86.34; H, 8.82; N, 4.29. Calc for $C_{22}H_{27}N$ (MW = 305.5): C, 86.50; H, 8.91; N, 4.59%.)

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2-tert-butylphenyl)imine (**1d**)

From **2d** (3.38 g, 10 mmole) as described for **1a**. The imido chloride was refluxed for 18 h with dry triethylamine (10 ml) in absol. ether (60 ml) affording after chromatography 2.50 g (78%) of a yellow solid; m.p. 35°. IR (film): 1990 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.09 (2 CH_3), 1.37 (3 CH_3), 1.81 (1 CH_3), 2.68 (CH_2). (Found: C, 86.52; H, 9.13; N, 4.28. Calc for $C_{23}H_{29}N$ (MW = 319.5): C, 86.47; H, 9.15; N, 4.39%.)

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2,6-dichlorophenyl)imine (**1e**)

From **2e** (3.50 g, 10 mmole) as described for **1a**. The imido chloride was refluxed for 84 h with dry triethylamine (25 ml) in absol. ether (20 ml) affording after chromatography 2.49 g (75%) of a yellow oil. IR (film): 2025 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.08 (2 CH_3), 1.79 (CH_3), 2.61 (CH_2). (Found: C, 68.55; H, 5.77; N, 4.47. Calc for $C_{19}H_{19}Cl_2N$ (MW = 332.3): C, 68.68; H, 5.76; N, 4.22%.)

Isopropylmethylketen-N-(2,6-dichlorophenyl) imine (**1f**)

Compound **2f** (2.60 g, 10 mmole) and 10 g Sicapent (E. Merck) were refluxed for 6 h in absol. triethylamine (150 ml). After filtration the solvent was evaporated under reduced pressure. The residue was purified by column chromatography as described for **1a** affording 1.09 g (45%) of a yellow oil. IR (film): 2025 cm^{-1} (C=C=N); ^1H NMR (CCl_4): 1.12 (2 CH_3, d, J = 7 Hz), 1.74 (1 CH_3), 2.29 (CH, sept., J = 7 Hz). (Found: C, 59.91; H, 5.58; N, 5.63. Calc for $C_{12}H_{13}Cl_2N$ (MW = 242.1): C, 59.52; H, 5.41; N, 5.79%.)

(1,1-Dimethyl-2-phenylethyl)methylketen-N-(2-chloro-6-methylphenyl) imine (**1g**)

From **2g** (3.30 g, 10 mmole) as described for **1a**. The imido chloride was refluxed for 48 h with absol. triethylamine (10 ml) in absol. ether (60 ml) affording after chromatography 1.50 g (48%) of a yellow oil. IR (film): 2015 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.05 (2 CH_3), 1.78 (1 CH_3), 2.08 (1 CH_3), 2.59 (CH_2). (Found: C, 76.87; H, 6.98; N, 4.32. Calc for $C_{20}H_{22}ClN$ (MW = 311.8): C, 77.03; H, 7.11; N, 4.49%.)

Isopropylmethylketen-N-(2-chloro-6-methylphenyl)imine (**1h**)

From **2h** (4.79 g, 20 mmole) as described for **1f**. The ketenimine was purified by distillation affording 3.20 g (72%) of a yellow oil decomposing at room temperature within a few days; b.p. 78–79°/10^{-1} torr. IR (film): 2020 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.10 (2 CH_3, d, J = 7 Hz), 1.72 (1 CH_3), 2.28 (1 CH_3), 2.24 (CH, sept., J = 7 Hz). (Found: C, 70.36; H, 7.40; N, 6.13. Calc for $C_{13}H_{16}ClN$ (MW = 221.7): C, 70.42; H, 7.27; N, 6.32%.)

Isopropylmethylketen-N-(2,6-dimethylphenyl)imine (**1i**)

From **2i** (4.39 g, 20 mmole) as described for **1a**. The imido chloride was refluxed for 24 h with dry triethylamine (40 ml) in petroleum ether (b.p. 50–70°, 20 ml). Fractional distillation afforded 1.55 g (39%) of a yellow oil; b.p. 68—69°/10^{-1} torr. IR (film): 2020 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 1.08 (2 CH_3, d, J = 7 Hz), 1.70 (1 CH_3), 2.24 (2 CH_3), 2.24 (CH, m). (Found: C, 83.42; H, 9.71; N, 7.14. Calc for $C_{14}H_{19}N$ (MW = 201.3): C, 83.53; H, 9.51; N, 6.96%.)

Isopropylmethylketen-N-(2,6-diisopropylphenyl) imine (**1j**)

To a solution of **2j** (2.76 g, 10 mmole) in dry dichloromethane (50 ml) were added PCl_5 (2.08 g, 10 mmole) and 3 drops of dimethylformamide. After stirring for 3 h at 22° the solvent was evaporated at reduced pressure. A solution of the remaining imido chloride in dry triethylamine (10 ml)

and 60 ml of absol. petroleum ether was stirred for 12 h at 22° and then refluxed for 3 h. Evaporating the solvent under reduced pressure and destillating the residue afforded 1.85 g (72%) of a yellow oil which decomposed within a few hours at room temperature; b.p. 74–76°/10^{-1} torr. IR (film): 2025 cm^{-1} (C=C=N); ^1H NMR δ (CH_2Cl_2): 1.10 (2 CH_3, d, J = 7 Hz), 1.20 (4 CH_3, d, J = 7 Hz), 1.71 (1 CH_3), 2.33 (1 CH, sept., J = 7 Hz), 3.32 (2 CH, sept., J = 7 Hz); ^{13}C NMR δ (CD_2Cl, 173 K): 11.9 (CH_3), 21.6 (gem.CH_3), 23.5, 24.3 (gem.CH_3), 28.2 (CH-phenyl), 29.4 (CH), 65.0 (C=), 123.5 (o–C), 125.0 (p–C), 139.2 (m–C), 140.4 (ipso–C), 192.1 (C=N). (Found: C, 83.80; H, 10.53; N, 5.19. Calc for $C_{18}H_{27}N$ (MW = 257.4): C, 83.99; H, 10.57; N, 5.44%).

Diphenylketen-N-(4-bromo-2,6-dimethylphenyl)imine (**1l**)

From **2l** (3.94 g, 10 mmole) as described for **1a**. After chromatography with petroleum ether/CCl_4 (1:1) as eluent the ketenimine was crystallized from petroleum ether (60 ml) affording 2.41 g (64%) of yellow needles; m.p. 59–60°. IR (Nujol): 2010 cm^{-1} (C=C=N); ^1H NMR δ (CCl_4): 2.24 (CH_3). (Found: C, 70.26; H, 4.82; N, 3.70. Calc for $C_{22}H_{18}BrN$ (MW = 376.3): C, 70.22; H, 4.82; N, 3.72%.)

N-(2-Chlorophenyl)-2,3,3-trimethyl-4-phenylbutanamide (**2a**)

A mixture of 2,3,3-trimethyl-4-phenylbutanoic acid[2] (10.3 g, 50 mmole) and thionyl chloride (11.9 g, 100 mmole) was stirred for 24 h at 5°. Excess thionyl chloride was evaporated at reduced pressure at 10°. The resulting oil was dissolved in dry ether (25 ml) and the solution added dropwise to a stirred solution of o-chloroaniline (6.4 g, 50 mmole) and dry triethylamine (10.1 g, 100 mmole) in absol. ether (50 ml). After stirring for 16 h at 22° chloroform (200 ml) was added, the organic phase was washed with aqueous $NaHCO_3$ (5%, 100 ml) and water (100 ml), dried over Na_2SO_4 and filtrated after shaking with active carbon. Evaporation of the solvent at reduced pressure afforded a red oil which crystallized from petroleum ether (100 ml). Yield 12.7 g (80%) of a colourless powder; m.p. 106°. ^1H NMR δ ($CDCl_3$): 1.00 (2 CH_3), 1.31 (CH_3, d, J = 7 Hz), 2.27 (CH, q, J = 7 Hz), 2.69 (CH_2). (Found: C, 72.20; H, 6.93; N, 4.26. Calc for $C_{19}H_{22}ClNO$ (MW = 315.7): C, 72.25; H, 7.02; N, 4.44%.)

2,3,3-*Trimethyl-N-(2-methylphenyl)-4-phenylbutanamide* (**2b**)

From o-toluidine (5.4 g, 50 mmole) as described for **2a**. Crystallization from CCl_4 (75 ml) afforded 10.5 g (71%) of colourless needles; m.p. 147°. ^1H NMR δ (CCl_4): 0.90 (2 CH_3), 1.20 (CH_3, d, J = 7 Hz), 2.12 (1 CH_3), 2.14 (CH, q, J = 7 Hz), 2.62 (CH_2, AB-q, J = 12 Hz). Found: C, 81.23; H, 8.71; N, 4.83. Calc for $C_{20}H_{25}NO$ (MW = 295.4): C, 81.31; H, 8.53; N, 4.74%.)

N-(2-Isopropylphenyl)-2,3,3-trimethyl-4-phenylbutanamide (**2c**)

From o-isopropylaniline (6.8 g, 50 mmole) as described for **2a**. Crystallization from petroleum ether (15 ml)/$CHCl_3$ (5 ml) afforded 10.1 g (62%) of a colourless powder; m.p. 113°. ^1H NMR δ ($CDCl_3$): 0.98 (2 CH_3), 1.20 (2 CH_3, d, J = 7 Hz), 1.32 (CH_3, d, J = 7 Hz), 2.36 (CH, q, J = 7 Hz), 2.65 (CH_2, AB-q, J = 12 Hz), 3.12 (CH, sept., J = 7 Hz), 7.74 (NH). (Found: C, 81.49; H, 9.03; N, 4.44. Calc for $C_{22}H_{29}NO$ (MW = 323.5): C, 81.69; H, 9.04; N, 4.33%.)

N-(2-tert-Butylphenyl)-2,3,3-trimethyl-4-phenylbutanamide (**2d**)

From o-tert-butylaniline (7.5 g, 50 mmole) as described for **2a**. Crystallization from CCl_4 (250 ml) afforded colourless needles (9.5 g, 56%); m.p. 163°. ^1H NMR δ ($CDCl_3$): 1.03 (2 CH_3), 1.33 (1 CH_3, d, J = 7 Hz), 1.38 (3 CH_3), 2.22 (CH, q, J = 7 Hz), 2.75 (CH_2). (Found: C, 81.65; H, 9.29; N, 4.16. Calc for $C_{23}H_{31}NO$ (MW = 337.5): C, 81.85; H, 9.26; N, 4.15%.)

N-(2,6-Dichlorophenyl)-2,3,3-trimethyl-4-phenylbutanamide (**2e**)

From 2,6-dichloroaniline (12.2 g, 75 mmole) and 2,3,3-trimethyl-4-phenylbutanoic acid (10.3 g, 50 mmole) as described for **2a**. Crystallization from $CHCl_3$ (15 ml) afforded colourless needles (6.3 g, 36%); m.p. 157°. ^1H NMR δ (CD_3COCD_3/CD_3SOCD_3 (3:1)): 0.98 (CH_3), 1.00 (CH_3), 1.29 (CH_3, d, J = 7 Hz), 2.62 (CH, q, J = 7 Hz), 2.78 (CH_2). (Found: C, 65.01; H, 6.00; N, 4.00. Calc for $C_{19}H_{21}Cl_2NO$ (MW = 350.3): C, 65.15; H, 6.04; N, 4.00%.)

N-(2,6-Dichlorophenyl)-2,3-dimethylbutanamide (**2f**)

From 2,6-dichloroaniline (8.1 g, 50 mmole) and 2,3-dimethylbutanoic chloride[36,37] (6.8 g, 50 mmole) as described for **2a**. Crystallization from benzene (70 ml)/petroleum ether (150 ml) afforded colourless needles (4.2 g, 32%); m.p. 191–192°. ^1H NMR δ ($CDCl_3$): 0.98 (CH_3, d, J = 7 Hz), 1.03 (CH_3, d, J = 7 Hz), 1.23 (CH_3, d, J = 7 Hz). (Found: C 55.50; H, 5.90; N, 5.36. Calc for $C_{12}H_{15}Cl_2NO$ (MW = 262.2: C, 55.40; H, 5.81; N, 5.39%.)

N-(2-Chloro-6-methylphenyl)-2,3,3-trimethyl-4-phenylbutanamide (**2g**)

From 2-chloro-6-methylaniline (10.6 g, 75 mmole) and 2,3,3-trimethyl-4-phenylbutanoic acid (10.3 g, 50 mmole) as described for **2a**. Crystallization from benzene/petroleum ether afforded a colourless powder (9.0 g, 55%); m.p. 143–144°. ^1H NMR δ ($CDCl_3$): 1.00 (2 CH_3), 1.32 (CH_3, d, J = 7 Hz), 2.19 (CH_3), 2.32 (CH, q, J = 7 Hz), 2.73 (CH_2). (Found: C, 72.75; H, 7.48; N, 4.27. Calc for $C_{20}H_{24}ClNO$ (MW = 329.9): C, 72.82; H, 7.33; N, 4.25%.)

N-(2-Chloro-6-methylphenyl)-2,3-dimethylbutanamide (**2h**)

From 2-chloro-6-methylaniline (7.3 g, 50 mmole) as described for **2f**. Crystallization from benzene (225 ml)/petroleum ether (75 ml) afforded colourless needles; m.p. 197°. ^1H NMR δ ($CDCl_3$): 0.98 (CH_3, d, J = 7 Hz), 1.03 (CH_3, d, J = 7 Hz), 1.24 (d, J = 7Hz), 2.23 (CH_3). (Found: C, 65.51; H, 7.48; N, 5.66. Calc for $C_{13}H_{18}ClNO$ (MW = 239.7): C, 63.13; H, 7.57; N, 5.84%.)

2,3-*Dimethyl-N-(2,6-dimethylphenyl)butanamide* (**2i**)

From 2,6-dimethylaniline (6.1 g, 50 mmole) as described for **2f**. Crystallization from benzene (180 ml)/petroleum ether (60 ml) afforded colourless needles (7.5 g, 68%); m.p. 220–222°. ^1H NMR δ ($CDCl_3$): 0.96 (CH_3, d, J = 7 Hz), 1.01 (CH_3, d, J = 7 Hz), 1.20 (d, J = 7 Hz), 2.17. (Found: C, 76.68; H, 9.61; N, 6.18. Calc for $C_{14}H_{21}NO$ (MW = 219.3): C, 76.67; H, 9.65; N, 6.39%.)

N-(2,6-Diisopropylphenyl)-2,3-dimethylbutanamide (**2j**)

From 2,6-diisopropylaniline (8.9 g, 50 mmole) as described for **2f**. Crystallization from benzene (225 ml)/$CHCl_3$ (225 ml) afforded colourless needles (8.1 g, 58%); m.p. 250–251°. ^1H NMR δ (CD_3COCD_3/CD_3SOCD_3 (2:1)): 0.97 (CH_3, d, J = 7 Hz), 1.02 (CH_3, d, J = 7 Hz), 1.15 (CH_3, d, J = 7 Hz), 1.16 (2 CH_3, d, J = 7 Hz). (Found: C, 78.63; H, 10.92; N, 5.12. Calc for $C_{18}H_{29}NO$ (MW = 275.4): C, 78.49; H, 10.61; N, 5.09%.)

N-(4-Bromo-2,6-dimethylphenyl)diphenylacetamide (**2l**)

From 4-bromo-2,6-dimethylaniline (10.0 g, 50 mmole) and diphenylacetyl chloride (11.5 g, 50 mmole) as described for **2a**. Crystallization from benzene (160 ml)/acetone (160 ml)/petroleum ether (160 ml) afforded a colourless powder (13.2 g, 67%); m.p. 184°. ^1H NMR δ ($CD_3SOCD_3/CDCl_3$ (4:3)): 2.03 (2 CH_3), 5.24 (CH), 9.59 (NH). (Found: C, 66.99; H, 5.16; N, 3.59. Calc for $C_{22}H_{20}BrNO$ (MW = 394.3): C, 67.01; H, 5.11; N, 3.55%.)

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