Oxidative Alkyl- and Aryl-aminomercuriation of Prop-2-ynyl Alcohols. Synthesis of *N*-Substituted α-Iminoketones, α-Di-imines, and α-Aminopropionamidines

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Addition of primary aliphatic or aromatic amines to prop-2-ynol (1a), 1-phenylprop-2-ynol (5a), and oct-1-yn-3-ol (5b) in the presence of mercury(u) acetate leads to the precipitation of metallic mercury and the formation of the corresponding oxidation products. The oxidation of alcohols (5a) and (5b) in the presence of aromatic amines leads to α -aminoketones (6), whereas α -di-imines (7) are obtained from aliphatic amines. The reaction of alcohol (1a) and aliphatic amines yields α -di-imines (2); in contrast, α -di-imines (3) can, alternatively, be synthesized from aromatic amines. A mechanism involving the mercury(u) acetate-promoted addition of an amine to a carbon–carbon triple bond and an allylic oxidation, followed by the successive formation of α -iminoketones, α -di-imines, and α -aminoamidines is proposed.

Although the addition of protic compounds to carboncarbon triple bonds in the presence of mercury(II) salts was first reported several years before the now well established and synthetically useful mercuriation of carbon-carbon double bonds,¹ it received little attention. The former reaction usually takes place in a catalytic fashion² allowing the addition of water, alcohols, acids, and amines.^{2,3} The oxidation of olefins by mercury(II) salts is, however, well documented,⁴ especially the so called allylic oxidations,5 which are usually carried out with mercury(II) acetate or sulphate. To our knowledge, however, no oxidative addition on carbon-carbon triple bonds induced by mercuric salts was reported until 1980, when we showed that the mercury(II) acetate oxidation of acetylene in the presence of primary or secondary aromatic amines yields NN'-diarylacetamidines or N-alkyl-N-arylacetamides, respectively.³ Later we extended the scope of this oxidative aminomercuriation to prop-2-ynol, which is oxidized by mercury(II) acetate, in the presence of primary aromatic amines, to yield substituted propane-1,2-di-imines and 2aminopropionamidines.6

In the formation of these latter products the intermediacy of α -iminocarbonyl compounds was demonstrated.⁶ Recently efforts have been devoted to the difficult mono-imination of α -dicarbonyl compounds ^{7,8} and also to the synthesis of α -diimines,⁸ especially in the context of transition-metal complexes,^{8\alpha,9} conformational analysis,¹⁰ and the mutarotation and isomerisation of imines.¹¹

Here, we report the oxidative addition of primary aliphatic and aromatic amines to prop-2-ynol (propargyl alcohol), *N*prop-2-ynylanilines, and 3-substituted prop-2-ynyl alcohols in the presence of mercury(II) acetate.

Equimolar amounts of prop-2-ynol (1a) and mercury(II) acetate reacted with a 20-fold excess of a primary aromatic amine at room temperature to give almost quantitative amounts of elemental mercury together with the corresponding NN'N''-triaryl-2-aminopropionamidine (3) resulting from the oxidation of the starting acetylenic alcohol (Scheme 1). In some instances, when the excess of amine was less, we observed in the ¹H n.m.r. spectrum of the crude reaction product the presence of a small singlet at $ca. \delta 8.1$. This could be attributed to the existence of an azomethine proton corresponding to an intermediate compound (2), derived from the incorporation of only two molecules of amine to the starting acetylene (1a). The di-imines (2) could give rise to the α -aminoamidines (3) by acid-catalysed addition of a third molecule of aromatic amine. To corroborate this hypothesis, reactions were performed in the presence of only a five-fold excess of amine and

potassium carbonate to neutralize the acetic acid developed in the aminomercuriation step. In fact, under these conditions the corresponding NN'-diarylpropane-1,2-di-imine (2; $R^1 =$ Ar) was isolated as the major product (Scheme 1).



Scheme 1.

Moreover, the di-imine (2a) derived from *o*-toluidine was quantitatively converted into the corresponding α -aminoamidine (3a) by treatment overnight with an excess of *o*toluidine and acetic acid; that is, under conditions analogous to those resulting from the aminomercuriation step. This process can easily be understood in terms of an initial nucleophilic attack of amine on an iminium cation, followed by two tautomer equilibria (Scheme 2). A closely related nucleophilic attack of amine on the iminic carbon atom of α iminonitriles has been reported.¹²

When prop-2-ynol (1a) and mercury(II) acetate are allowed to react with an excess of primary aliphatic amine under the same initial conditions as described above, the major product is the corresponding α -di-imine (2; $\mathbb{R}^1 = alkyl$); α -aminoamidines however could not be detected. These compounds are not obtained by treatment of α -di-imines (2; $\mathbb{R}^1 = alkyl$) with an excess of aliphatic amine and acetic or trifluoroacetic acid, even at 67 °C for 24 h. In this case we assume that the excess of aliphatic amine inhibits the protonation at the aldimine nitrogen and, hence, the attack of a third molecule of amine.

Reactions conditions and yields in the synthesis of compounds (2) and (3) are summarized in Table 1. In two runs



Table 1. Preparation " of α -di-imines (2) and α -aminoamidines (3)

Entry	Product	Z in starting alkyne	R ¹	Yield (%)
1	(2a) ^b	0	2-MeC ₆ H₄	56
2	(2b) ^b	0	4-MeC ₆ H ₄	32
3	(2c) ^b	0	4-MeOC ₆ H₄	45
4	(2d) [*]	0	2,6-Me ₂ C ₆ H ₃	30
5	(2e)	0	Pr	87
6	(2f)	0	Bu	86
7	(2g)	0	c-C ₆ H ₁₁	49
8	(2h)	0	n-C ₆ H ₁₃	91
9	(3a)	0	2-MeC ₆ H₄	71
10	(3a)	PhN	2-MeC ₆ H₄	89
11	(3b)	0	4-MeC ₆ H₄	38
12	(3c)	0	2-MeOC ₆ H ₄	36
13	(3c)	2-MeOC ₆ H₄N	2-MeOC ₆ H ₄	44
14	(3d)	0	Ph	50
15	(3d)	PhN	Ph	53

^a All reactions were carried out in tetrahydrofuran, at room temperature for 5–7 h, with an alkyne : $Hg(OAc)_2$: amine molar ratio 1:1:5 [compounds (2)] or 1:1:20 [compounds (3)]. ^b 2 Mmol K₂CO₃/mmol Hg(OAc)₂ were added.

(entries 13 and 15) the N-prop-2-ynylanilines (1c) and (1b) were used respectively as the starting acetylenic system; they gave a moderate increase in the yield of the α -aminoamidines (3c) and (3d). It is noteworthy that the best yield of α -amino-amidine was obtained (entry 10) from N-prop-2-ynylaniline (1c) in which the arylamino group is different from that in the corresponding amine used in the addition process (Scheme 3). Equimolar amounts of (3a) and acetic acid were treated (3

$$HC \equiv C - CH_{2} - NHPh + Hg(OAc)_{2} + 3 o - MeC_{6}H_{4}NH_{2}$$
(1b)
$$-Hg^{o}, -2 AcOH, - PHNH_{2}$$

$$Me - CH - C - NC_{6}H_{4}Me - o$$

$$Me - CH - C - NHC_{6}H_{4}Me - o$$

$$0 - MeC_{6}H_{4} - O$$

$$MHC_{6}H_{4}Me - o$$

$$MHC_{6}H_{4}Me - o$$

Scheme 3.

days at room temperature) with a five-fold excess of *o*anisidine to check when the amine exchange takes place; compound (3a) was recovered, unchanged, which indicates that the replacement occurs in a previous step, probably on the α -iminoaminal stage type (4) (see Scheme 2). This reaction is similar to the well established exchange reaction in imines.¹³

It has been shown experimentally that compounds (2) and (3) when derived from aromatic amines can be oxidized by the action of mercury(II) acetate. This process gives rise to the formation of variable amounts of side products which appear as red oils, separable from the stable yellow (2a—d) and white (3) solids during work-up. Although the α -di-imine (2g) was isolated as a stable brown solid, the other aliphatic di-imines (2e, f, h) are brown oils which decompose in a few hours at room temperature or very fast when heated; they give rise to compounds which display no azomethine proton signal in their ¹H n.m.r. spectra. A single stereoisomer, probably *E-s*-*trans-E*,^{10b} could be detected by n.m.r. spectroscopy for α -di-imines (2a—d); in the aliphatic series (2e—h) over 90% of this isomer is also formed.

 α -Di-imines would be expected to result when 1-substituted prop-2-ynyl alcohols (5) were used as the starting acetylene. However, the reaction product $[(5) : Hg(OAc)_2 :$ amine molar ratio = 1 : 1 : 5; room temperature] depends on the aromatic or aliphatic nature of the amine (Scheme 4). In this way, the



 α -di-imines (7) are obtained from aliphatic amines. Conversely, the use of less basic aromatic amines usually leads to the synthesis of α -iminoketones (6).* When aromatic amines of enhanced basicity were used (*p*-toluidine and *p*-anisidine) in the reaction with oct-1-yn-3-ol (5b), a mixture of products (6) and (7) (molar ratio 3 : 1 and 1 : 1, respectively) was obtained. When only a slight excess of the above amines was used, and potassium carbonate was added to the reagents to neutralize the acid developed in the mercuriation step, the process stopped at the formation of the α -iminoketones (6). In contrast, potassium carbonate is ineffective in this sense with aliphatic amines, and the reaction always affords α -diimines (7).

Yields and reaction conditions for compounds (6) and (7) are summarized in Table 2. α -Iminoketones (6a—e; $\mathbb{R}^2 = \mathbb{P}h$) are obtained as a mixture of *E*,*Z*-stereoisomers in a molar ratio determined by ¹H n.m.r.¹⁴ (see Experimental section). N.m.r. data for the remaining α -iminoketones (6f—l; $\mathbb{R}^2 = n-C_5H_{11}$) show the near exclusive presence of a single stereo-

^{*} Not only electronic but also steric factors could probably account for the different course of the reaction.⁸ This aspect has not been investigated.



Table 2. Preparation " of α -aminoketones (6) and α -di-imines (7)

Product	\mathbf{R}^{1}	R²	Reaction time (h)	Yield (%) ^b
(6a)	Ph	Ph	5	94
(6b)	2-MeC ₆ H₄	Ph	3	84
(6c)	3-MeC ₆ H₄	Ph	3	76
(6d)	2-MeOC ₆ H₄	Ph	4	79
(6e)	2-ClC ₆ H₄	Ph	5	88
(6f)	Ph	n-C₅H ₁₁	7	96
(6g)	2-MeC ₆ H₄	n-C ₅ H ₁₁	10	96
(6h)	3-MeC ₆ H₄	n-C ₅ H ₁₁	5	71
(6i) ^c	4-MeC₀H₄	n-C5H11	20	80
(6j)	2-MeOC ₆ H₄	n-C₅H ₁₁	8	69
(6k) °	4-MeOC ₆ H₄	$n-C_5H_{11}$	22	94
(6l)	2-ClC₀H₄	n-C ₅ H ₁₁	11	30 ª
(7a)	Pr	Ph	22	68
(7b)	Bu	Ph	14	78
(7c)	n-C ₆ H ₁₃	Ph	11	89
(7d)	Pr	n-C ₅ H ₁₁	17	91

^a Unless otherwise specified, a 1:1:5 alkyne : Hg(OAc)₂ : amine molar ratio was employed. ^b Yields of isolated products before distillation. ^c Alkyne : Hg(OAc)₂ : amine : K₂CO₃ molar ratio 1:1:2:1.5. ^d Yield after distillation.

isomer (probably E^{14}), although trace amounts of the Zisomer cannot be excluded. The overall process leading to the α -iminoketones (6) represents a convenient one-pot regiospecific mono-imination of methyl- α -diketones.

The n.m.r. spectra of the α -di-imines (7a, b) show that they are almost pure, single stereoisomers; for (7c) and especially (7d), however, at least two stereoisomers are detected. Compounds (6) and (7) are isolated as almost pure, brown oils from the crude reaction residue. Although these compounds can be distilled under reduced pressure partial decomposition occurs^{8a} as it does when the compounds are stored open to the atmosphere. The formation of compounds (2), (3), (6), and (7) can be explained via formation of a 3-substituted alk-1-ynylmercury acetate (8) in a first step (Scheme 5). The reaction of the intermediate (8) with amine, followed by protonolysis,¹⁵ gives the allyl alcohol or allyl amine (9). During the allylic oxidation of olefins, allyl alcohols have been isolated as intermediate products.¹⁶ So, the allylic oxidation of (9) leads to α -amino α,β -unsaturated carbonyl compound (10), from which all reaction products can be explained. The participation of (16) as an intermediate has been ascertained by carrying out the reaction with a secondary aromatic amine (*i.e.* N-methylaniline) which allows (for R² = Ph, Z = O) the isolation of 2-(N-methylanilino)-1-phenylprop-2-en-1-one in high yield.¹⁷

Experimental

I.r. spectra were recorded on a Pye-Unicam SP-1000 instrument, n.m.r. spectra on a Varian FT-80 A spectrometer, and elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. M.p.s were determined with a Büchi melting point apparatus and are uncorrected.

N-Prop-2-ynylaniline (1b) and *N*-prop-2-ynyl-o-anisidine (1c) were prepared by a modification of the method reported for *N*-isopropylprop-2-ynamine.¹⁸ The other reagents were of the best commercial grade available.

Preparation of α -Di-imines (2).—Mercury(II) acetate (6.37 g, 20 mmol) [and potassium carbonate (5.53 g, 40 mmol) for α -di-imines (2a—d)] was added during *ca*. 10 min, at room temperature, to a stirred solution of prop-2-ynol (1.18 ml, 20 mmol) and a primary amine (100 mmol) in tetrahydrofuran (50 ml). The temperature of the reaction mixture spontaneously rose to *ca*. 40 °C in a few minutes. Metallic mercury (>90%) was filtered off after 5—7 h. The organic phase was treated with 3M-aqueous potassium hydroxide (15 ml) and then extracted with ether and the extracts dried (Na₂SO₄). The volatile components were removed under reduced pressure (15 and 0.05 Torr, successively); recrystallization from cold

hexane (2a—d), boiling hexane (2g), or distillation (2e, f, h) of the residues yielded the corresponding α -di-imines. Compound (2a) was distilled under reduced pressure before recrystallization.

The following compounds were obtained in this way: NN'-(1-methylethane-1,2-diylidene)di-0-toluidine (2a) (2.80 g, 56%), m.p. 56-58 °C, b.p. 117-123 °C at 0.001 Torr; v_{max.} (Nujol) 1 625 and 1 615 (CN) cm⁻¹; $\delta_{\rm H}$ (CCl₄) 2.05 (s, 6 H), 2.35 (s, 3 H), 6.4–7.3 (m, 8 H, ArH), and 8.15 (s, 1 H, CH=N); δ_c $(CDCl_3)$ 14.2 (q), 16.9 (q), 160.4 (d), and 166.7 (s); m/z 250 (M^+) , 132 ($[M - CHNC_6H_4OMe]$, 100%) (Found: C, 81.4; H, 7.3; N, 11.1. C₁₇H₁₈N₂ requires C, 81.55; H, 7.25; N, 11.2%); NN'-(1-methylethane-1,2-diylidene)di-p-toluidine (2b) (1.60 g, 32%), m.p. 77–79 °C; v_{max} (Nujol) 1 625 and 1 610 (CN) cm⁻¹; $\delta_{\rm H}$ (CCl₄) 2.1 (s, 3 H), 2.33 and 2.35 (2 s, 6 H), 6.5–7.3 (m, 8 H, ArH), and 8.15 (s, 1 H, CH=N); δ_c (CDCl₃) 14.6 (q), 20.7 (q), 161.4 (d), and 167.5 (s) (Found: C, 81.35; H, 7.2; N, 11.3. C₁₇H₁₈N₂ requires C, 81.55; H, 7.25; N, 11.2%); NN'-(1-methylethane-1,2-diylidene)di-p-anisidine (2c) (2.54 g, 45%), m.p. 106–108 °C; v_{max} (Nujol) 1 620 and 1 605 (CN) cm⁻¹; $\delta_{\rm H}$ (CCl₄) 2.2 (s, 3 H, CH₃C=N), 3.78 and 3.81 (2 s, 6 H, CH₃O), 6.55-7.3 (m, 8 H, ArH), and 8.15 (s, 1 H, CH=N); δ_c (CDCl₃) 14.7 (q), 55.4 (q), 160.1 (d), and 167.3 (s); m/z 282 (M^+), 148 ([$M - \text{CHNC}_6\text{H}_4\text{OMe}$], 100%) (Found: C, 71.15; H, 6.45; N, 10.0. C₁₇H₁₈N₂O₂ requires C, 72.3; H, 6.45; N, 9.9%); 1,6-dimethyl-NN'-(1-methylethane-1,2-diylidene)dianiline (2d) (1.67 g, 30%), m.p. 78-80 °C; v_{max} (Nujol) 1 630br (CN) cm⁻¹; δ_{H} (CDCl₃) 2.05 (s, 9 H), 2.2 (s, 6 H), 6.75-7.15 (m, 6 H, ArH), and 8.05 (s, 1 H, CH=N); $\delta_{\rm C}$ (CDCl₃) 14.8 (q), 17.4 (q), 17.9 (q), 164.5 (d), and 167.5 (s) (Found: C, 81.9; H, 7.8; N, 10.15. C₁₉H₂₂N₂ requires C, 81.95; H, 7.95; N, 10.05%); NN'-(1-methylethane-1,2divlidene)dipropylamine (2e) (2.68 g, 87%), b.p. 32-34 °C at 0.05 Torr; v_{max} (film) 1 645br (CN) cm⁻¹; δ_{H} (CDCl₃) 0.8–1.2 (m, 6 H, CH₃CH₂), 1.55–1.9 (m, 4 H, CH₂CH₃), 2.05 (s, 3 H, CH₃C=N), 3.45 and 3.5 (2 superimposed t,* 4 H, CH₂N), and 7.8 (s,* 1 H, CH=N); δ_c (CDCl₃) 12.6 (q), 12.9 (q), 13.0 (q), 24.9 (2 t), 55.0 (t), 63.4 (t), 165.2 (d), and 167.3 (s) (Found: C, 69.9; H, 11.8; N, 18.1. C₉H₁₈N₂ requires C, 70.1; H, 11.75; N, 18.15%); NN'-(1-methylethane-1,2-diylidene)dibutylamine (2f) (3.13 g, 86%), b.p. 44–46 °C at 0.05 Torr; v_{max} (film) 1 640br (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 0.75–1.1 (m, 6 H, CH₃CH₂), 1.2-1.85 (m, 8 H, [CH₂]₂CH₃), 2.05 (s, 3 H, CH₃C=N), 3.45 and 3.55 (2 superimposed t,* 4 H, CH₂N), and 7.8 (s,* 1 H, CH=N); δ_{c} (CDCl₃) 13.0 (q), 14.77 (q), 14.84 (q), 21.5 (t), 21.8 (t), 34.1 (2 t), 53.0 (t), 61.4 (t), 165.3 (d), and 167.0 (s) (Found: C, 72.6; H, 12.05; N, 15.35. C₁₁H₂₂N₂ requires C, 72.45; H, 12.15; N, 15.35%); NN'-(1-methylethane-1,2divlidene)dicyclohexylamine (2g), (2.29 g, 49%), m.p. 52-54 °C; v_{max} (Nujol) 1 635br (CN) cm⁻¹; δ_{H} (CDCl₃) 1.1—1.9 (m, 20 H, [CH₂]₅), 2.05 (s, 3 H, CH₃C=N), 3.15 and 3.5 (2 m; 2 H, CH-N), and 7.8 (s,* 1 H, CH=N); δ_c (CDCl₃) 11.5 (q), 23.8 (t), 24.0 (t), 25.0 (t), 32.5 (t), 33.4 (t), 59.4 (d), 68.0 (d), 161.7 (d), and 163.9 (s) (Found: C, 76.65; H, 11.1; N, 12.05. C15H26N2 requires C, 76.85; H, 11.2; N, 11.95%); NN'-(1methylethane-1,2-diylidene)dihexylamine (2h) (4.33 g, 91%), b.p. 69—71 °C at 0.001 Torr; v_{max} (film) 1 645br (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 0.85 (m, 6 H, CH₃CH₂), 1.1–1.85 (m, 16 H, [CH₂]₄CH₃), 2.05 (s, 3 H, CH₃C=N), 3.45 and 3.55 (2 superimposed t.* 4 H, CH₂N), and 7.8 (s.* 1 H, CH=N); $\delta_{\rm C}$ (CDCl₃) 13.1 (q), 15.0 (2 q), 23.8 (2 t), 28.3 (t), 28.5 (t), 32.0 (t), 32.9 (2 t), 33.1 (t), 53.4 (t), 61.8 (t), 165.3 (d), and 166.9 (s) (Found: C, 75.7; H, 12.8; N, 11.8. C₁₅H₃₀N₂ requires C, 75.55; H, 12.7; N, 11.75%).

Preparation of α -Aminoamidines (3).—Mercury(II) acetate (6.37 g, 20 mmol) was added during *ca*. 10 min, at room temperature, to a stirred solution of prop-2-ynol (1.18 ml, 20 mmol) [or the appropriate *N*-prop-2-ynylaniline (20 mmol)] in a primary aromatic amine (400 mmol). The temperature spontaneously rose to *ca*. 40 °C in a few minutes. Metallic mercury (>90%) was filtered off after 5—7 h and the organic phase treated with 1M-aqueous sulphuric acid (3 × 25 ml). The aqueous layer was treated with concentrated aqueous potassium hydroxide until basic and then extracted with ether; the extracts were dried (Na₂SO₄) and the volatile components eliminated under reduced pressure (15 and 0.05 Torr, successively). Recrystallization of the residues from hexanetoluene (3:1) or hexane-ether (1:1) yielded the corresponding α -aminoamidine (3).

The following compounds were obtained in this way: NN'-N"-tri-o-tolyl-2-aminopropionamidine (3a) (6.35 g, 89%), m.p. 149—150 °C; v_{max} (Nujol) 3 320 (NH) and 1 635 (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 1.4 (d, 3 H, CH₃CH), 2.05, 2.2, and 2.3 (3 s, 9 H, CH₃Ar), 3.45br (2 H, NH), 4.3 (q, 1 H, CHMe), and 6.55-7.3 (m, 12 H, ArH); δ_{c} (CDCl₃) 17.2 (2 g), 17.5 (g), 20.5 (g), 49.8 (d), and 156.9 (s); m/z 357 (M^+), 223 ($M - CH_3CHN$ - HC_6H_4Me), 134 (M – MeC_6H_4NCNHC_6H_4Me) (Found: C, 80.85; H, 7.5; N, 11.65. C₂₄H₂₇N₃ requires C, 80.65; H, 7.6; N, 11.75%; NN'N"-tri-p-tolyl-2-aminopropionamidine (3b) (2.71 g, 38%), m.p. 187–189 °C; v_{max} (Nujol) 3 310 and 3 260 (NH) and 1 630 (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 1.4 (d, 3 H, CH₃CH), 2.25, 2.3, and 2.35 (3 s, 9 H, CH₃Ar), 3.5br (2 H, NH), 4.15 (q, 1 H, CHMe), and 6.5-7.3 (m, 12 H, ArH) (Found: C, 80.5; H, 7.75; N, 11.8. C₂₄H₂₇N₃ requires C, 80.65; H, 7.6; N, 11.75%); NN'N"-tri-(o-methoxyphenyl)-2aminopropionamidine (3c) (3.56 g, 44%), m.p. 159-161 °C; v_{max} (Nujol) 3 350 (NH) and 1 640 (CN) cm⁻¹; δ_{H} (CDCl₃) 1.4 (d, 3 H, CH₃CH), 3.4br (2 H, NH), 3.65 and 3.9 (2 s, 9 H, CH₃O), 4.0 (q, 1 H, CHMe), and 6.65-7.2 (m, 12 H, ArH) (Found: C, 71.0; H, 6.6; N, 10.5. C₂₄H₂₇N₃O₃ requires C, 71.1; H, 6.7; N, 10.35%); NN'N"-triphenyl-2-aminopropionamidine (3d) (3.34 g, 53%), m.p. 134–135 °C; v_{max.} (Nujol) 3 370 and 3 340 (NH) and 1 635 (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 1.35 (d, 3 H, CH₃CH), 3.65br (2 H, NH), 4.1 (q, 1 H, CHMe), and 6.45-7.5 (m, 15 H, ArH); δ_c (CDCl₃) 20.9 (q), 50.4 (d), and 156.2 (s); m/z 315 (M^+), 195 (M – PhNHCHMe), and 120 (M - PhNCNHPh) (Found: C, 80.1; H, 6.85; N, 13.3. C₂₁H₂₁N₃ requires C, 79.95; H, 6.7; N, 13.3%).

Preparation of α -Iminoketones (6) and α -Di-imines (7).— Mercury(II) acetate (6.37 g, 20 mmol) was added during ca. 10 min, at room temperature, to a stirred solution of 1phenylprop-2-yn-1-ol or oct-1-yn-3-ol (20 mmol) and a primary aromatic [for (6)] or aliphatic [for (7)] amine (100 mmol) † in tetrahydrofuran or dichloromethane (50 ml). The temperature spontaneously rose to ca. 40 °C in a few minutes. Metallic mercury [>80%, except for (6l)] was filtered off after 3-22 h. The organic phase was treated with 3Maqueous potassium hydroxide (15 ml) and then extracted with ether or dichloromethane. The extracts were dried (Na₂SO₄) and the volatile components removed under reduced pressure (15 and 0.001 Torr, successively) to yield [except for (6l)] the corresponding compound (6) or (7) as a nearly pure, brown oil; this could be subsequently distilled under reduced pressure. In the preparation of the α -iminoketone (6) only 34% of metallic mercury was precipitated and the crude product had to be purified by distillation under reduced pressure.

The following α -iminoketones (6) were obtained in this way:

[†] For compounds (6i) and (6k), 40 mmol of amine was employed and 30 mmol of potassium carbonate was also added.

1-phenyl-2-phenyliminopropan-1-one ¹⁹ (6a) (4.19 g, 94%), as a 87:13 mixture of E- and Z-isomers, b.p. 110-115 °C at 0.001 Torr; v_{max} (film) 1 670br (CO and CN) cm⁻¹; δ_H (CDCl₃) 2.2 and 2.45 (2 s, 3 H, CH₃C=N), 6.7-7.55 (m, 8 H, ArH), and 8.1-8.25 (m, 2 H, ArH); δ_c (CDCl₃) 16.5 (q), 166.4 (s), and 192.7 (s); m/z 223 (M^+), 118 (M - PhCO), and 105 (M - PhNCMe); 1-phenyl-2-(o-tolylimino)propan-1-one (6b) (4.0 g, 84%), as a 93:7 mixture of E- and Z-isomers; b.p. 99—101 °C at 0.001 Torr; v_{max} (film) 1 625br cm⁻¹ (CO and CN); ¹H n.m.r., δ (CDCl₃) 2.1 (s, 3 H, CH₃Ar), 2.15 and 2.5 (2 s, 3 H, CH₃C=N), 6.6-7.65 (m, 7 H, ArH), and 8.1-8.25 (m, 2 H, ArH); δ_{c} (CDCl₃) 17.2 (q), 18.8 (q), 167.5 (s), and 193.5 (s) (Found: C, 80.75; H, 6.2; N, 6.0. C₁₆H₁₅NO requires C, 81.0; H, 6.35; N, 5.9%); 1-phenyl-2-(m-tolylimino)propan-1one (6c) (3.61 g, 76%), as a mixture of E- (major) and Zisomers, b.p. 109-111 °C at 0.001 Torr; v_{max.} (film) 1 620br (CO and CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 2.2 and 2.45 (2 s, 3 H, CH₃C=N), 2.35 (s, 3 H, CH₃Ar), 6.5-7.6 (m, 7 H, ArH), and 8.05—8.2 (m, 2 H, ArH); δ_c (CDCl₃) 17.0 (q), 22.1 (q), 167.3 (s), and 193.7 (s) (Found: C, 80.8; H, 6.25; N, 5.85. C₁₆H₁₅NO requires C, 81.0; H, 6.35, N, 5.9%); 2-(o-methoxyphenylimino)-1-phenylpropan-1-one (6d) (4.02 g, 79%), as a 90:10 mixture of *E*- and *Z*-isomers, b.p. 122–124 °C at 0.001 Torr; v_{max} . (film) 1 635br (CO and CN) cm⁻¹; δ_H (CDCl₃) 2.1 and 2.5 (2 s, 3 H, CH₃C=N), 3.85 (s, 3 H, CH₃O), 6.65-7.6 (m, 7 H, ArH), and 8.15-8.3 (m, 2 H, ArH); δ_c (CDCl₃) 16.4 (q), 55.0 (q), 167.6 (s), and 192.8 (s) (Found: C, 76.0; H, 5.8; N, 5.4. C₁₆H₁₅NO₂ requires C, 75.85; H, 5.95; N, 5.5%); 2-(0chlorophenylimino)-1-phenylpropan-1-one (6e) (4.56 g, 88%), as a 88:12 mixture of E- and Z-isomers, b.p. 111-113 °C at 0.001 Torr; $v_{max.}$ (film) 1 620br (CO and CN) cm⁻¹; δ_H (CDCl₃) 2.15 and 2.5 (2 s, 3 H, CH₃C=N), 6.6–7.65 (m, 7 H, ArH), and 8.2-8.35 (m, 2 H, ArH); δ_c (CDCl₃) 18.1 (q), 170.0 (s), and 193.5 (s) (Found: C, 70.05; H, 4.75; N, 5.3. C15H12CINO requires C, 69.9; H, 4.7; N, 5.4%); 2-phenyliminooctan-3-one (6f) (4.17 g, 96%), b.p. 115-120 °C at 0.001 Torr; v_{max} (film) 1 700 (CO) and 1 640 (CN) cm⁻¹; δ_{H} (CCl₄) 0.9 (m, 3 H, CH₃CH₂), 1.2–1.8 (m, 6 H, [CH₂]₃Me), 1.9 (s, 3 H, CH₃-C=N), 2.9 (t, 2 H, CH₂C=O), and 6.55-7.55 (m, 5 H, ArH); δ_{c} (CDCl₃) 14.7 (q), 14.8 (q), 23.5 (t), 24.8 (t), 32.5 (t), 37.2 (t), 166.6 (s), and 198.0 (s) (Found: C, 77.6; H, 8.8; N, 6.6. C₁₄H₁₉NO requires C, 77.4; H, 8.8; N, 6.45%); 2-(o-tolylimino)octan-3-one (6g) (4.46 g, 96%), b.p. 80-82 °C at 0.001 Torr; v_{max} (film) 1 705 (CO) and 1 645 (CN) cm⁻¹; δ_{H} (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.05–1.75 (m, 6 H, [CH₂]₃Me), 1.85 (s, 3 H, CH₃C=N), 2.5 (s, 3 H, CH₃Ar), 3.0 (t, 2 H, CH₂C=O), and 6.4–7.3 (m, 4 H, ArH); δ_c (CDCl₃) 14.9 (2 q), 18.4 (q), 23.6 (t), 25.0 (t), 32.7 (t), 37.4 (t), 166.4 (s), and 198.0 (s) (Found: C, 77.8; H, 9.05; N, 6.15. C₁₅H₂₁NO requires C, 77.9; H, 9.15; N, 6.05%); 2-(m-tolylimino)octan-3one (6h) (3.30 g, 71%), b.p. 102-104 °C at 0.001 Torr; v_{max}. (film) 1 710 (CO) and 1 645 (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.25-1.85 (m, 6 H, [CH₂]₃Me), 1.95 (s, 3 H, CH₃C=N), 2.35 (s, 3 H, CH₃Ar), 3.0 (t, 2 H, CH₂C=O), and 6.45—7.4 (m, 4 H, ArH); δ_c (CDCl₃) 14.7 (q), 14.9 (q), 22.1 (g), 23.6 (t), 24.9 (t), 32.7 (t), 37.2 (t), 166.5 (s), and 197.7 (s) (Found: C, 80.0; H, 9.05; N, 6.0. C₁₅H₂₁NO requires C, 77.9; H, 9.15; N, 6.05%); 2-(p-tolylimino)octan-3-one (6i) (3.70 g, 80%), b.p. 100-102 °C at 0.001 Torr; v_{max.} (film) 1 700 (CO) and 1 640 (CN) cm⁻¹; δ_{H} (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.2-1.8 (m, 6 H, [CH₂]₃Me), 2.0 (s, 3 H, CH₃C=N), 2.35 (s, 3 H, CH₃Ar), 3.0 (t, 2 H, CH₂C=O), and 6.55-7.3 (m, 4 H, ArH); δ_c (CDCl₃) 13.2 (2 q), 20.0 (q), 21.8 (t), 23.0 (t), 30.9 (t), 35.6 (t), 164.8 (s), and 195.0 (s) (Found: C, 77.85; H, 9.0; N, 6.2. C₁₅H₂₁NO requires C, 77.9; H, 9.15; N, 6.05%); 2-(o-methoxyphenylimino)octan-3-one (6j) (3.40 g, 69%), b.p. 93—95 °C at 0.001 Torr; v_{max} (film) 1 700 (CO) and 1 645 (CN) cm⁻¹; δ_{H} (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.15—1.8 (m,

6 H, [CH₂]₃Me), 1.9 (s, 3 H, CH₃C=N), 3.05 (t, 2 H, CH₂C=O), 3.8 (s, 3 H, CH₃O), and 6.6–7.3 (m, 4 H, ArH); δ_{c} (CDCl₃) 14.9 (q), 15.4 (q), 23.6 (t), 25.0 (t), 32.7 (t), 37.5 (t), 56.4 (q), 169.0 (s), and 197.6 (s) (Found: C, 73.0; H, 8.4; N, 5.6. C₁₅H₂₁NO₂ requires C, 72.85; H, 8.55; N, 5.65%); 2-(pmethoxyphenylimino)octan-3-one (6k) (4.64 g, 94%), b.p. 103-105 °C at 0.001 Torr; v_{max} (film) 1 700 (CO) and 1 645 (CN) cm⁻¹; δ_{H} (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.15–1.85 (m, 6 H, [CH₂]₃Me), 2.0 (s, 3 H, CH₃C=N), 3.0 (t, 2 H, CH₂C=O), 3.85 (s, 3 H, CH₃O), and 6.6-7.0 (m, 4 H, ArH); δ_c (CDCl₃) 14.8 (q), 15.0 (q), 23.6 (t), 24.9 (t), 32.6 (t), 37.2 (t), 56.0 (q), 166.0 (s), and 197.3 (s) (Found: C, 72.95; H, 8.65; N, 5.5. C₁₅H₂₁-NO₂ requires C, 72.85; H, 8.55; N, 5.65%); 2-(o-chlorophenylimino)octan-3-one (61) (1.50 g, 30%), b.p. 88-90 °C at 0.001 Torr; $\nu_{max.}$ (film) 1 710 (CO) and 1 660 (CN) $cm^{-1};\,\delta_{H}$ (CDCl₃) 0.9 (m, 3 H, CH₃CH₂), 1.2-1.8 (m, 6 H, [CH₂]₃Me), 1.9 (s, 3 H, CH₃C=N), 3.0 (t, 2 H, CH₂C=O), and 6.65-7.5 (m, 4 H, ArH); δ_{c} (CDCl₃) 15.1 (g), 15.7 (g), 23.7 (t), 25.1 (t), 32.7 (t), 37.8 (t), 168.8 (s), and 197.6 (s) (Found: C, 66.95; H, 7.05; N, 5.7. C₁₄H₁₈ClNO requires C, 66.8; H, 7.2; N, 5.55%).

The following α -di-imines (7) were obtained in similar way: NN'-(1-methyl-2-phenylethane-1,2-diylidene)dipropylamine (7a) (3.13 g, 68%), b.p. 71–73 °C at 0.001 Torr; v_{max} (film), 1 630br cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 0.9 and 1.0 (2 t, 6 H, CH_3CH_2), 1.3-1.85 (m, 4 H, CH₂CH₃), 2.1 (s, 3 H, CH₃C=N), 3.1 and 3.35 (2 t, 4 H, CH₂N), and 7.15–7.75 (m, 5 H, ArH); δ_{c} (CDCl₃) 13.1 (q), 13.2 (q), 25.1 (t), 25.4 (t), 26.3 (q), 56.6 (t), 56.8 (t), 166.2 (s), and 167.3 (s) (Found: C, 78.05; H, 9.5; N, 12.3. $C_{15}H_{22}N_2$ requires C, 78.2; H, 9.6; N, 12.15%); NN'-(1-methyl-2-phenylethane-1,2-diylidene)dibutylamine (7b) (4.05 g, 78%), b.p. 78–80 °C at 0.001 Torr; v_{max} (film) 1 660 and 1 630 (CN) cm⁻¹; $\delta_{\rm H}$ (CCl₄) 0.75–1.1 (m, 6 H, CH₃CH₂), 1.2-1.85 (m, 8 H, [CH₂]₂Me), 2.0 (s, 3 H, CH₃-C=N), 3.0 and 3.3 (2 t, 4 H, CH₂N), and 7.15-7.75 (m, 5 H, ArH); δ_c (CDCl₃) 14.9 (q), 15.0 (q), 21.7 (t), 21.9 (t), 26.3 (q), 34.1 (t), 34.4 (t), 54.6 (t), 54.7 (t), 165.7 (s), and 167.2 (s) (Found: C, 79.15; H, 10.1; N, 10.95. C₁₇H₂₆N₂ requires C, 79.0; H, 10.15; N, 10.85%); NN'-(1-methyl-2-phenylethane-1,2-diylidene)dihexylamine (7c) (5.59 g, 89%), b.p. 88-90 °C at 0.001 Torr; ν_{max} (film) 1 650 and 1 625 (CN) cm^-1; $\delta_{\rm H}$ (CDCl₃) 0.8 (m, 6 H, CH₃CH₂), 1.0–1.9 (m, 16 H, [CH₂]₄-Me), 2.0 (s, 3 H, CH₃C=N), 2.9-3.55 (m, 4 H, CH₂N), and 7.15-7.85 (m, 5 H, ArH); δ_c (CDCl₃) 15.1 (q), 23.8 (t), 26.4 (q), 28.4, 28.5, 28.7, 32.0, 32.3, 32.9, 33.1, 55.1 (t), 165.9 (s), 167.2 (s), and 170.6 (s) (Found: C, 80.4; H, 10.85; N, 8.8. C21H34N2 requires C, 80.2; H, 10.9; N, 8.9%); NN'-(1methyl-2-pentylethane-1,2-diylidene)dipropylamine (7d) (4.08 g, 91%), b.p. 83–85 °C at 0.05 Torr; v_{max} (film) 1 630br (CN) cm⁻¹; $\delta_{\rm H}$ (CDCl₃) 0.7—1.1 (m, 9 H, CH₃CH₂), 1.15—1.85 (m, 10 H, [CH₂]₄Me), 2.0 and 2.05 (2 s, 3 H, CH₃C=N), 2.3-2.85 (m, 2 H, CH₂C=N), and 3.1-3.55 (m, 4 H, CH₂N); δ_{c} (CDCl₃) 166.6 (s), 167.5 (s), 170.0 (s), and 171.5 (s) (Found: C, 75.15; H, 12.5; N, 12.65. C₁₄H₂₈N₂ requires C, 74.95; H, 12.6; N, 12.5%).

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