

Scheme 2.

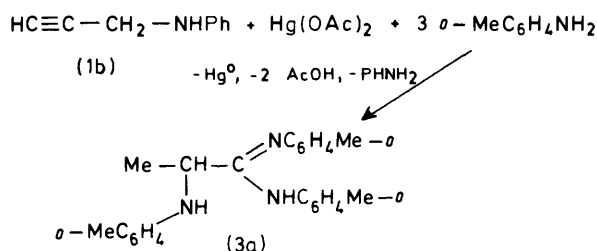
Table 1. Preparation ^a of α -di-imines (2) and α -aminoamidines (3)

| Entry | Product | Z in starting alkyne | R ¹ | Yield (%) |
|-------|-------------------|--------------------------------------|---|-----------|
| 1 | (2a) ^b | 0 | 2-MeC ₆ H ₄ | 56 |
| 2 | (2b) ^b | 0 | 4-MeC ₆ H ₄ | 32 |
| 3 | (2c) ^b | 0 | 4-MeOC ₆ H ₄ | 45 |
| 4 | (2d) ^b | 0 | 2,6-Me ₂ C ₆ H ₃ | 30 |
| 5 | (2e) | 0 | Pr | 87 |
| 6 | (2f) | 0 | Bu | 86 |
| 7 | (2g) | 0 | <i>c</i> -C ₆ H ₁₁ | 49 |
| 8 | (2h) | 0 | <i>n</i> -C ₆ H ₁₃ | 91 |
| 9 | (3a) | 0 | 2-MeC ₆ H ₄ | 71 |
| 10 | (3a) | PhN | 2-MeC ₆ H ₄ | 89 |
| 11 | (3b) | 0 | 4-MeC ₆ H ₄ | 38 |
| 12 | (3c) | 0 | 2-MeOC ₆ H ₄ | 36 |
| 13 | (3c) | 2-MeOC ₆ H ₄ N | 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 -aminoamidine 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

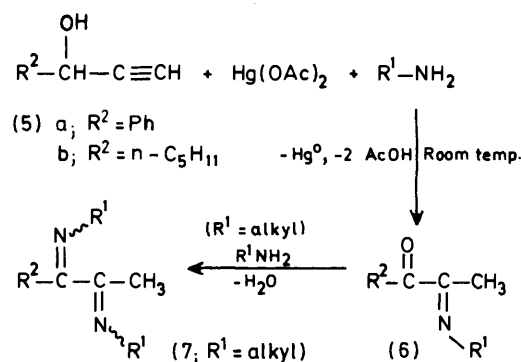


Scheme 3.

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

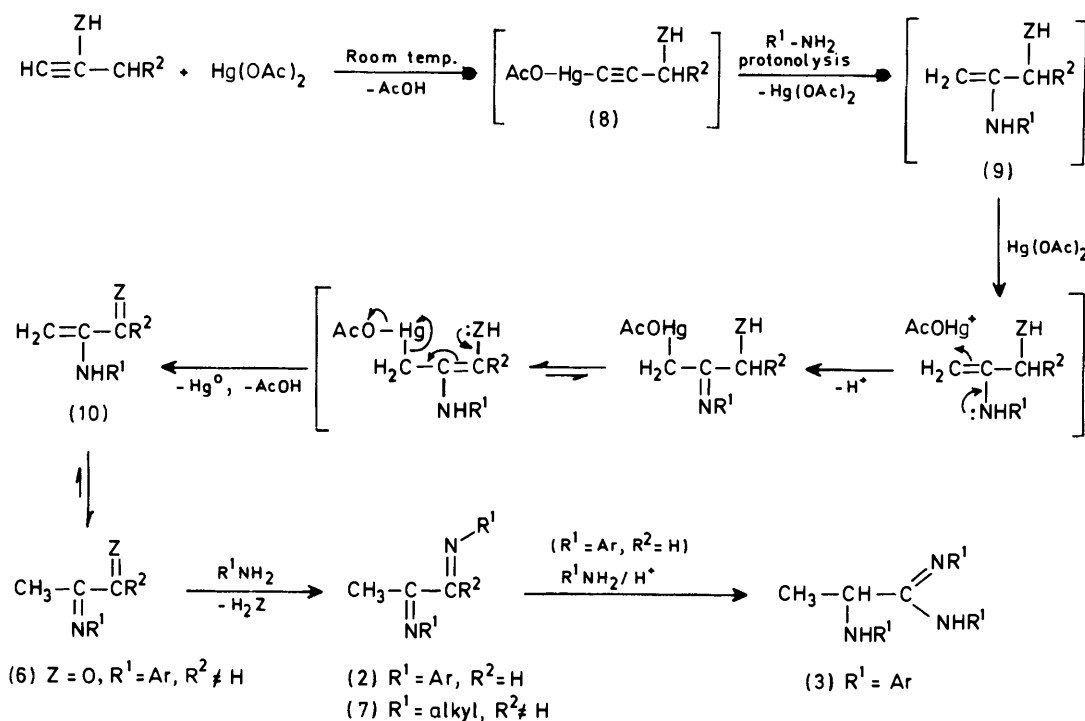


Scheme 4.

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 -di-imines (7).

Yields and reaction conditions for compounds (6) and (7) are summarized in Table 2. α -Iminoketones (6a–e; R² = Ph) 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; R² = *n*-C₅H₁₁) 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.



Scheme 5.

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

| Product | R ¹ | R ² | Reaction time (h) | Yield (%) ^b |
|-------------------|------------------------------------|----------------------------------|-------------------|------------------------|
| (6a) | Ph | Ph | 5 | 94 |
| (6b) | 2-MeC ₆ H ₄ | Ph | 3 | 84 |
| (6c) | 3-MeC ₆ H ₄ | Ph | 3 | 76 |
| (6d) | 2-MeOC ₆ H ₄ | Ph | 4 | 79 |
| (6e) | 2-ClC ₆ H ₄ | Ph | 5 | 88 |
| (6f) | Ph | n-C ₅ H ₁₁ | 7 | 96 |
| (6g) | 2-MeC ₆ H ₄ | n-C ₅ H ₁₁ | 10 | 96 |
| (6h) | 3-MeC ₆ H ₄ | n-C ₅ H ₁₁ | 5 | 71 |
| (6i) ^c | 4-MeC ₆ H ₄ | n-C ₅ H ₁₁ | 20 | 80 |
| (6j) | 2-MeOC ₆ H ₄ | n-C ₅ H ₁₁ | 8 | 69 |
| (6k) ^c | 4-MeOC ₆ H ₄ | n-C ₅ H ₁₁ | 22 | 94 |
| (6l) | 2-ClC ₆ H ₄ | n-C ₅ H ₁₁ | 11 | 30 ^d |
| (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 *Z*-isomer cannot be excluded. The overall process leading to the α -iminoketones (6) represents a convenient one-pot regio-specific mono-amination 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 (10) 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-*o*-toluidine (2a) (2.80 g, 56%), m.p. 56—58 °C, b.p. 117—123 °C at 0.001 Torr; ν_{max} . (Nujol) 1 625 and 1 615 (CN) cm^{-1} ; δ_{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} (CDCl₃) 14.2 (q), 16.9 (q), 160.4 (d), and 166.7 (s); m/z 250 (M^+), 132 ([$M - \text{CHNC}_6\text{H}_4\text{OMe}$], 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; ν_{max} . (Nujol) 1 625 and 1 610 (CN) cm^{-1} ; δ_{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; ν_{max} . (Nujol) 1 620 and 1 605 (CN) cm^{-1} ; δ_{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; ν_{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); δ_{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-1,2-diylidene)dipropylamine (2e) (2.68 g, 87%), b.p. 32—34 °C at 0.05 Torr; ν_{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; ν_{max} . (film) 1 640br (CN) cm^{-1} ; δ_{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-1,2-diylidene)dicyclohexylamine (2g) (2.29 g, 49%), m.p. 52—54 °C; ν_{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'-(1-methylethane-1,2-diylidene)dihexylamine (2h) (4.33 g, 91%), b.p. 69—71 °C at 0.001 Torr; ν_{max} . (film) 1 645br (CN) cm^{-1} ; δ_{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); δ_{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 hexane-toluene (3 : 1) or hexane-ether (1 : 1) yielded the corresponding α -aminoamidine (3).

The following compounds were obtained in this way: NN'-*tri-o*-tolyl-2-aminopropionamidine (3a) (6.35 g, 89%), m.p. 149—150 °C; ν_{max} . (Nujol) 3 320 (NH) and 1 635 (CN) cm^{-1} ; δ_{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 q), 17.5 (q), 20.5 (q), 49.8 (d), and 156.9 (s); m/z 357 (M^+), 223 ($M - \text{CH}_3\text{CHNHC}_6\text{H}_4\text{Me}$), 134 ($M - \text{MeC}_6\text{H}_4\text{NCNHC}_6\text{H}_4\text{Me}$) (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; ν_{max} . (Nujol) 3 310 and 3 260 (NH) and 1 630 (CN) cm^{-1} ; δ_{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)-2-aminopropionamidine (3c) (3.56 g, 44%), m.p. 159—161 °C; ν_{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; ν_{max} . (Nujol) 3 370 and 3 340 (NH) and 1 635 (CN) cm^{-1} ; δ_{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 ($M - \text{PhNHCHMe}$), and 120 ($M - \text{PhNCNHPH}$) (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 1-phenylprop-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 (6)] was filtered off after 3—22 h. The organic phase was treated with 3M-aqueous 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 (6)] 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:

* These signals show unresolved long range coupling HC=N—CH_n (n = 1 or 2).

† 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-one¹⁹ (6a) (4.19 g, 94%), as a 87:13 mixture of *E*- and *Z*-isomers, b.p. 110–115 °C at 0.001 Torr; ν_{\max} (film) 1 670br (CO and CN) cm^{-1} ; δ_{H} (CDCl_3) 2.2 and 2.45 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 6.7–7.55 (m, 8 H, ArH), and 8.1–8.25 (m, 2 H, ArH); δ_{C} (CDCl_3) 16.5 (q), 166.4 (s), and 192.7 (s); m/z 223 (M^+), 118 ($M - \text{PhCO}$), and 105 ($M - \text{PhNCMe}$); 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; ν_{\max} (film) 1 625br cm^{-1} (CO and CN); ^1H n.m.r., δ (CDCl_3) 2.1 (s, 3 H, CH_3Ar), 2.15 and 2.5 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 6.6–7.65 (m, 7 H, ArH), and 8.1–8.25 (m, 2 H, ArH); δ_{C} (CDCl_3) 17.2 (q), 18.8 (q), 167.5 (s), and 193.5 (s) (Found: C, 80.75; H, 6.2; N, 6.0. $\text{C}_{16}\text{H}_{15}\text{NO}$ requires C, 81.0; H, 6.35; N, 5.9%); 1-phenyl-2-(*m*-tolylimino)propan-1-one (6c) (3.61 g, 76%), as a mixture of *E*- (major) and *Z*-isomers, b.p. 109–111 °C at 0.001 Torr; ν_{\max} (film) 1 620br (CO and CN) cm^{-1} ; δ_{H} (CDCl_3) 2.2 and 2.45 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.35 (s, 3 H, CH_3Ar), 6.5–7.6 (m, 7 H, ArH), and 8.05–8.2 (m, 2 H, ArH); δ_{C} (CDCl_3) 17.0 (q), 22.1 (q), 167.3 (s), and 193.7 (s) (Found: C, 80.8; H, 6.25; N, 5.85. $\text{C}_{16}\text{H}_{15}\text{NO}$ 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; ν_{\max} (film) 1 635br (CO and CN) cm^{-1} ; δ_{H} (CDCl_3) 2.1 and 2.5 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.85 (s, 3 H, CH_3O), 6.65–7.6 (m, 7 H, ArH), and 8.15–8.3 (m, 2 H, ArH); δ_{C} (CDCl_3) 16.4 (q), 55.0 (q), 167.6 (s), and 192.8 (s) (Found: C, 76.0; H, 5.8; N, 5.4. $\text{C}_{16}\text{H}_{15}\text{NO}_2$ requires C, 75.85; H, 5.95; N, 5.5%); 2-(*o*-chlorophenylimino)-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; ν_{\max} (film) 1 620br (CO and CN) cm^{-1} ; δ_{H} (CDCl_3) 2.15 and 2.5 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 6.6–7.65 (m, 7 H, ArH), and 8.2–8.35 (m, 2 H, ArH); δ_{C} (CDCl_3) 18.1 (q), 170.0 (s), and 193.5 (s) (Found: C, 70.05; H, 4.75; N, 5.3. $\text{C}_{15}\text{H}_{12}\text{ClNO}$ requires C, 69.9; H, 4.7; N, 5.4%); 2-phenyliminoctan-3-one (6f) (4.17 g, 96%), b.p. 115–120 °C at 0.001 Torr; ν_{\max} (film) 1 700 (CO) and 1 640 (CN) cm^{-1} ; δ_{H} (CCl_4) 0.9 (m, 3 H, CH_3CH_2), 1.2–1.8 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 1.9 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.9 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 6.55–7.55 (m, 5 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{14}\text{H}_{19}\text{NO}$ 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; ν_{\max} (film) 1 705 (CO) and 1 645 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.05–1.75 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 1.85 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.5 (s, 3 H, CH_3Ar), 3.0 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 6.4–7.3 (m, 4 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{15}\text{H}_{21}\text{NO}$ requires C, 77.9; H, 9.15; N, 6.05%); 2-(*m*-tolylimino)octan-3-one (6h) (3.30 g, 71%), b.p. 102–104 °C at 0.001 Torr; ν_{\max} (film) 1 710 (CO) and 1 645 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.25–1.85 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 1.95 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.35 (s, 3 H, CH_3Ar), 3.0 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 6.45–7.4 (m, 4 H, ArH); δ_{C} (CDCl_3) 14.7 (q), 14.9 (q), 22.1 (q), 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. $\text{C}_{15}\text{H}_{21}\text{NO}$ 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; ν_{\max} (film) 1 700 (CO) and 1 640 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.2–1.8 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 2.0 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.35 (s, 3 H, CH_3Ar), 3.0 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 6.55–7.3 (m, 4 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{15}\text{H}_{21}\text{NO}$ 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; ν_{\max} (film) 1 700 (CO) and 1 645 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.15–1.8 (m,

6 H, $[\text{CH}_2]_3\text{Me}$), 1.9 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.05 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), 3.8 (s, 3 H, CH_3O), and 6.6–7.3 (m, 4 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{15}\text{H}_{21}\text{NO}_2$ requires C, 72.85; H, 8.55; N, 5.65%); 2-(*p*-methoxyphenylimino)octan-3-one (6k) (4.64 g, 94%), b.p. 103–105 °C at 0.001 Torr; ν_{\max} (film) 1 700 (CO) and 1 645 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.15–1.85 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 2.0 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.0 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), 3.85 (s, 3 H, CH_3O), and 6.6–7.0 (m, 4 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{15}\text{H}_{21}\text{NO}_2$ requires C, 72.85; H, 8.55; N, 5.65%); 2-(*o*-chlorophenylimino)octan-3-one (6l) (1.50 g, 30%), b.p. 88–90 °C at 0.001 Torr; ν_{\max} (film) 1 710 (CO) and 1 660 (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.9 (m, 3 H, CH_3CH_2), 1.2–1.8 (m, 6 H, $[\text{CH}_2]_3\text{Me}$), 1.9 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.0 (t, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 6.65–7.5 (m, 4 H, ArH); δ_{C} (CDCl_3) 15.1 (q), 15.7 (q), 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. $\text{C}_{14}\text{H}_{18}\text{ClNO}$ 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; ν_{\max} (film), 1 630br cm^{-1} ; δ_{H} (CDCl_3) 0.9 and 1.0 (2 t, 6 H, CH_3CH_2), 1.3–1.85 (m, 4 H, CH_2CH_3), 2.1 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.1 and 3.35 (2 t, 4 H, CH_2N), and 7.15–7.75 (m, 5 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{15}\text{H}_{22}\text{N}_2$ 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; ν_{\max} (film) 1 660 and 1 630 (CN) cm^{-1} ; δ_{H} (CCl_4) 0.75–1.1 (m, 6 H, CH_3CH_2), 1.2–1.85 (m, 8 H, $[\text{CH}_2]_2\text{Me}$), 2.0 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 3.0 and 3.3 (2 t, 4 H, CH_2N), and 7.15–7.75 (m, 5 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{17}\text{H}_{26}\text{N}_2$ 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} ; δ_{H} (CDCl_3) 0.8 (m, 6 H, CH_3CH_2), 1.0–1.9 (m, 16 H, $[\text{CH}_2]_4\text{Me}$), 2.0 (s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.9–3.55 (m, 4 H, CH_2N), and 7.15–7.85 (m, 5 H, ArH); δ_{C} (CDCl_3) 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. $\text{C}_{21}\text{H}_{34}\text{N}_2$ requires C, 80.2; H, 10.9; N, 8.9%); NN'-(1-methyl-2-pentylethane-1,2-diylidene)dipropylamine (7d) (4.08 g, 91%), b.p. 83–85 °C at 0.05 Torr; ν_{\max} (film) 1 630br (CN) cm^{-1} ; δ_{H} (CDCl_3) 0.7–1.1 (m, 9 H, CH_3CH_2), 1.15–1.85 (m, 10 H, $[\text{CH}_2]_4\text{Me}$), 2.0 and 2.05 (2 s, 3 H, $\text{CH}_3\text{C}=\text{N}$), 2.3–2.85 (m, 2 H, $\text{CH}_2\text{C}=\text{N}$), and 3.1–3.55 (m, 4 H, CH_2N); δ_{C} (CDCl_3) 166.6 (s), 167.5 (s), 170.0 (s), and 171.5 (s) (Found: C, 75.15; H, 12.5; N, 12.65. $\text{C}_{14}\text{H}_{28}\text{N}_2$ requires C, 74.95; H, 12.6; N, 12.5%).

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