# Oxidative Alkyl- and Aryl-aminomercuriation of Prop-2-ynyl Alcohols. Synthesis of $\boldsymbol{N}$-Substituted $\alpha$-Iminoketones, $\alpha$-Di-imines, and $\alpha$-Aminopropionamidines 

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#### Abstract

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(II) acetate leads to the precipitation of metallic mercury and the formation of the corresponding oxidation products. The oxidation of alcohols ( 5 a ) and ( 5 b ) in the presence of aromatic amines leads to $\alpha$-aminoketones (6), whereas $\alpha$-di-imines (7) are obtzined from aliphatic amines. The reaction of alcohol (1a) and aliphatic amines yields $\alpha$-di-imines (2); in contrast, $\alpha$-di-imines (2) or $\alpha$-aminoamidines (3) can, alternatively, be synthesized from aromatic amines. Á mechanism involving the mercury(iI) acetate-promoted addition of an amine to a carbon-carbon triple bond and an allylic oxidation, followed by the successive formation of $\alpha$-iminoketones, $\alpha$-di-imines, and $\alpha$-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 fashion ${ }^{2}$ 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 $N N^{\prime}$-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 $\alpha$-iminocarbonyl compounds was demonstrated. ${ }^{6}$ Recently efforts have been devoted to the difficult mono-imination of $\alpha$-dicarbonyl compounds ${ }^{7,8}$ and also to the synthesis of $\alpha$-diimines, ${ }^{8}$ especially in the context of transition-metal complexes, ${ }^{8 a, 9}$ 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 $N N^{\prime} N^{\prime \prime}$-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 ${ }^{1} \mathrm{H}$ n.m.r. spectrum of the crude reaction product the presence of a small singlet at $c a . \delta 8.1$. 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 $\alpha$-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 $N N^{\prime}$-diarylpropane-1,2-di-imine ( $2 ; \mathrm{R}^{1}=$ Ar) was isolated as the major product (Scheme 1).


(1) $a ; Z=0$
b; $Z=P h N$
c; $Z=2-\mathrm{MeOC}_{6} \mathrm{H}_{4} N$


$\left(3 ; R^{1}=A r\right)$
(2)

Scheme 1.

Moreover, the di-imine (2a) derived from $o$-toluidine was quantitatively converted into the corresponding $\alpha$-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 $\alpha$ 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 $\alpha$-di-imine ( $2 ; \mathbf{R}^{1}=$ alkyl); $\alpha$-aminoamidines however could not be detected. These compounds are not obtained by treatment of $\alpha$-di-imines ( $2 ; \mathbf{R}^{1}=$ alkyl) with an excess of aliphatic amine and acetic or trifluoroacetic acid, even at $67^{\circ} \mathrm{C}$ 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


Scheme 2.

Table 1. Preparation ${ }^{a}$ of $\alpha$-di-imines (2) and $\alpha$-aminoamidines (3)

| Entry | Product | $\mathbf{Z}$ in starting alkyne | $\mathrm{R}^{1}$ | Yield (\%) |
| :---: | :---: | :---: | :---: | :---: |
| 1 | (2a) ${ }^{\text {b }}$ | 0 | $2-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | 56 |
| 2 | (2b) ${ }^{\text {b }}$ | 0 | $4-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | 32 |
| 3 | (2c) $n$ | 0 | 4-MeOC6 $\mathrm{H}_{4}$ | 45 |
| 4 | (2d) ${ }^{\text {b }}$ | 0 | 2,6-Me ${ }_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ | 30 |
| 5 | (2e) | 0 | Pr | 87 |
| 6 | (2f) | 0 | Bu | 86 |
| 7 | (2g) | 0 | c- $\mathrm{C}_{6} \mathrm{H}_{11}$ | 49 |
| 8 | (2h) | 0 | $\mathrm{n}-\mathrm{C}_{6} \mathrm{H}_{13}$ | 91 |
| 9 | (3a) | 0 | $2-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | 71 |
| 10 | (3a) | PhN | $2-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | 89 |
| 11 | (3b) | 0 | $4-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | 38 |
| 12 | (3c) | 0 | $2-\mathrm{MeOC}_{6} \mathrm{H}_{4}$ | 36 |
| 13 | (3c) | $2-\mathrm{MeOC} 6 \mathrm{H}_{4} \mathrm{~N}$ | $2-\mathrm{MeOC}_{6} \mathrm{H}_{4}$ | 44 |
| 14 | (3d) | 0 | Ph | 50 |
| 15 | (3d) | PhN | Ph | 53 |

a All reactions were carried out in tetrahydrofuran, at room temperature for $5-7 \mathrm{~h}$, with an alkyne : $\mathrm{Hg}(\mathrm{OAc})_{2}$ : amine molar ratio $1: 1: 5$ [compounds (2)] or $1: 1: 20$ [compounds (3)]. ${ }^{\mathrm{b}} 2 \mathrm{Mmol} \mathrm{K} \mathrm{K}_{2} \mathrm{CO}_{3} / \mathrm{mmol} \mathrm{Hg}(\mathrm{OAc})_{2}$ 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 $\alpha$-aminoamidines (3c) and (3d). It is noteworthy that the best yield of $\alpha$-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

$$
\begin{gathered}
\mathrm{HC} \equiv \mathrm{C}-\mathrm{CH}_{2}-\mathrm{NHPh}+\mathrm{Hg}(\mathrm{OAc})_{2}+30-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{NH}_{2} \\
\text { (1b) }-\mathrm{Hg}^{\mathrm{o},-2 \mathrm{AcOH}_{1}-\mathrm{PHNH}_{2}} \\
\mathrm{Me}-\mathrm{CH}-\mathrm{C}^{2}=\mathrm{NC}_{6} \mathrm{H}_{4} \mathrm{Me}-\mathrm{o} \\
0-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{NHC} \mathrm{H}_{4} \mathrm{Me}-\mathrm{o} \\
\text { (3a) }
\end{gathered}
$$

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 $\alpha$-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 ( $2 a-d$ ) and white (3) solids during work-up. Although the $\alpha$-di-imine ( 2 g ) was isolated as a stable brown solid, the other aliphatic di-imines ( $2 \mathrm{e}, \mathrm{f}, \mathrm{h}$ ) 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 ${ }^{1} \mathrm{H}$ n.m.r. spectra. A single stereoisomer, probably $E$-s-trans- $E,{ }^{10 b}$ could be detected by n.m.r. spectroscopy for $\alpha$ -di-imines ( $2 \mathrm{a}-\mathrm{d}$ ); in the aliphatic series ( $2 \mathrm{e}-\mathrm{h}$ ) over $90 \%$ of this isomer is also formed.
$\alpha$-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 $\left[(5): \mathrm{Hg}(\mathrm{OAc})_{2}\right.$ : 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.
$\alpha$-di-imines (7) are obtained from aliphatic amines. Conversely, the use of less basic aromatic amines usually leads to the synthesis of $\alpha$-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 $\alpha$-iminoketones (6). In contrast, potassium carbonate is ineffective in this sense with aliphatic amines, and the reaction always affords $\alpha$-diimines (7).

Yields and reaction conditions for compounds (6) and (7) are summarized in Table 2. $\alpha$-Iminoketones ( $6 \mathrm{a}-\mathrm{e} ; \mathrm{R}^{2}=\mathrm{Ph}$ ) are obtained as a mixture of $E, Z$-stereoisomers in a molar ratio determined by ${ }^{1} \mathrm{H}$ n.m.r. ${ }^{14}$ (see Experimental section). N.m.r. data for the remaining $\alpha$-iminoketones ( $6 f-l ; R^{2}=$ $\mathrm{n}-\mathrm{C}_{5} \mathrm{H}_{11}$ ) show the near exclusive presence of a single stereo-

[^0]

Scheme 5.

Table 2. Preparation ${ }^{a}$ of $\alpha$-aminoketones (6) and $\alpha$-di-imines (7)

| Product | $\mathrm{R}^{1}$ | $\mathrm{R}^{2}$ | Reaction <br> time (h) | Yield <br> (\%) |
| :--- | :---: | :---: | :---: | :---: |
| (6a) | $\mathrm{Ph}^{\text {b }}$ |  |  |  |

- Unless otherwise specified, a $1: 1: 5$ alkyne $: \mathrm{Hg}(\mathrm{OAc})_{2}:$ amine molar ratio was employed. ${ }^{b}$ Yields of isolated products before distillation. ${ }^{c}$ Alkyne : $\mathrm{Hg}(\mathrm{OAc})_{2}$ : amine : $\mathrm{K}_{2} \mathrm{CO}_{3}$ molar ratio $1: 1: 2$ : 1.5. ${ }^{4}$ Yield after distillation.
isomer (probably $E^{14}$ ), although trace amounts of the $Z$ isomer cannot be excluded. The overall process leading to the $\alpha$-iminoketones (6) represents a convenient one-pot regiospecific mono-imination of methyl- $\alpha$-diketones.

The n.m.r. spectra of the $\alpha$-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 ${ }^{8 a}$ 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 $\alpha$-amino $\alpha, \beta$-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 $\mathrm{R}^{2}=\mathrm{Ph}, \mathrm{Z}=\mathrm{O}$ ) 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 $\alpha$-Di-imines (2).-Mercury(II) acetate ( 6.37 g , 20 mmol ) [and potassium carbonate ( $5.53 \mathrm{~g}, 40 \mathrm{mmol}$ ) for $\alpha$-di-imines ( $2 \mathrm{a}-\mathrm{d}$ )] was added during $c a .10 \mathrm{~min}$, at room temperature, to a stirred solution of prop-2-ynol ( 1.18 ml , 20 mmol ) and a primary amine ( 100 mmol ) in tetrahydrofuran $(50 \mathrm{ml})$. The temperature of the reaction mixture spontaneously rose to ca. $40^{\circ} \mathrm{C}$ in a few minutes. Metallic mercury ( $>90 \%$ ) was filtered off after 5-7 h. The organic phase was treated with 3 m -aqueous potassium hydroxide ( 15 ml ) and then extracted with ether and the extracts dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$. The volatile components were removed under reduced pressure ( 15 and 0.05 Torr, successively); recrystallization from cold
hexane ( $2 \mathrm{a}-\mathrm{d}$ ), boiling hexane ( 2 g ), or distillation ( $2 \mathrm{e}, \mathrm{f}, \mathrm{h}$ ) of the residues yielded the corresponding $\alpha$-di-imines. Compound (2a) was distilled under reduced pressure before recrystallization.

The following compounds were obtained in this way: $\mathrm{NN}^{\prime}$ -(1-methylethane-1,2-diylidene)di-o-toluidine (2a) ( $2.80 \mathrm{~g}, 56 \%$ ), m.p. $56-58^{\circ} \mathrm{C}$, b.p. $117-123{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (Nujol) 1625 and $1615(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CCl}_{4}\right) 2.05(\mathrm{~s}, 6 \mathrm{H}), 2.35(\mathrm{~s}$, $3 \mathrm{H})$, 6.4-7.3 (m, $8 \mathrm{H}, \mathrm{ArH}$ ), and $8.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}=\mathrm{N})$; $\delta_{\mathrm{c}}$ $\left(\mathrm{CDCl}_{3}\right) 14.2$ (q), 16.9 (q), 160.4 (d), and 166.7 (s); $m / z 250$ $\left(M^{+}\right), 132$ ( $\left.M-\mathrm{CHNC}_{6} \mathrm{H}_{4} \mathrm{OMe}\right], 100 \%$ ) (Found: C, 81.4 ; $\mathrm{H}, 7.3 ; \mathrm{N}, 11.1 . \mathrm{C}_{17} \mathrm{H}_{18} \mathrm{~N}_{2}$ requires $\mathrm{C}, 81.55 ; \mathrm{H}, 7.25 ; \mathrm{N}$, $11.2 \%$ ); $\mathrm{NN}^{\prime}$-(1-methylethane-1,2-diylidene)di-p-toluidine (2b) $\left(1.60 \mathrm{~g}, 32 \%\right.$ ), m.p. $77-79^{\circ} \mathrm{C}$; $v_{\text {max. }}$ (Nujol) 1625 and 1610 $(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CCl}_{4}\right) 2.1(\mathrm{~s}, 3 \mathrm{H}), 2.33$ and $2.35(2 \mathrm{~s}, 6 \mathrm{H})$, $6.5-7.3(\mathrm{~m}, 8 \mathrm{H}, \mathrm{ArH})$, and $8.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}=\mathrm{N}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right)$ 14.6 (q), 20.7 (q), 161.4 (d), and 167.5 (s) (Found: C, 81.35 ; $\mathrm{H}, 7.2 ; \mathrm{N}, 11.3 . \mathrm{C}_{17} \mathrm{H}_{18} \mathrm{~N}_{2}$ requires $\mathrm{C}, 81.55 ; \mathrm{H}, 7.25 ; \mathrm{N}$, $11.2 \%$ ); $\mathrm{NN}^{\prime}$-(1-methylethane-1,2-diylidene)di-p-anisidine (2c) $(2.54 \mathrm{~g}, 45 \%)$, m.p. $106-108{ }^{\circ} \mathrm{C}$; $v_{\text {max. }}$ (Nujol) 1620 and $1605(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CCl}_{4}\right) 2.2\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.78$ and $3.81\left(2 \mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3} \mathrm{O}\right), 6.55-7.3(\mathrm{~m}, 8 \mathrm{H}, \mathrm{ArH})$, and $8.15(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{CH}=\mathrm{N}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 14.7$ (q), 55.4 (q), 160.1 (d), and 167.3 (s); $m / z 282\left(M^{+}\right), 148$ ( $\left[M-\mathrm{CHNC}_{6} \mathrm{H}_{4} \mathrm{OMe}\right.$ ], $100 \%$ ) (Found: $\mathrm{C}, 71.15 ; \mathrm{H}, 6.45 ; \mathrm{N}, 10.0 . \mathrm{C}_{17} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{2}$ requires C , $72.3 ; \mathrm{H}, 6.45 ; \mathrm{N}, 9.9 \%$ ) ; 1,6-dimethyl- $\mathrm{NN}^{\prime}$-(1-methylethane-1,2-diylidene)dianiline (2d) ( $1.67 \mathrm{~g}, 30 \%$ ), m.p. $78-80{ }^{\circ} \mathrm{C}$; $v_{\text {max }}$ (Nujol) $1630 \mathrm{br}(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 2.05(\mathrm{~s}, 9 \mathrm{H}), 2.2$ $(\mathrm{s}, 6 \mathrm{H}), 6.75-7.15(\mathrm{~m}, 6 \mathrm{H}, \mathrm{ArH})$, and $8.05(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}=\mathrm{N})$; $\delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 14.8$ (q), 17.4 (q), 17.9 (q), 164.5 (d), and 167.5 (s) (Found: C, $81.9 ; \mathrm{H}, 7.8 ; \mathrm{N}, 10.15 . \mathrm{C}_{19} \mathrm{H}_{22} \mathrm{~N}_{2}$ requires C , $81.95 ; \mathrm{H}, 7.95 ; \mathrm{N}, 10.05 \%)$; $\mathrm{NN}^{\prime}-(1-$ methylethane-1,2diylidene)dipropylamine (2e) ( $2.68 \mathrm{~g}, 87 \%$ ), b.p. $32-34{ }^{\circ} \mathrm{C}$ at 0.05 Torr; $v_{\text {max }}$ (film) $1645 \mathrm{br}(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathbf{H}}\left(\mathrm{CDCl}_{3}\right) 0.8-1.2$ $\left(\mathrm{m}, 6 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.55-1.9\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 2.05(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ ), 3.45 and 3.5 ( 2 superimposed $\mathrm{t}, * 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}$ ), and $7.8\left(\mathrm{~s},{ }^{*} 1 \mathrm{H}, \mathrm{CH}=\mathrm{N}\right) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 12.6$ (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; $\mathrm{N}, 18.1$. $\mathrm{C}_{9} \mathrm{H}_{18} \mathrm{~N}_{2}$ requires $\mathrm{C}, 70.1 ; \mathrm{H}, 11.75$; $\mathrm{N}, 18.15 \%$; $\mathrm{NN}^{\prime}$-(1-methylethane-1,2-diylidene)dibutylamine ( 2 f ) $\left(3.13 \mathrm{~g}, 86 \%\right.$ ), b.p. $44-46{ }^{\circ} \mathrm{C}$ at 0.05 Torr ; $v_{\text {max. }}$ (film) $1640 \mathrm{br}(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.75-1.1\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)$, $1.2-1.85\left(\mathrm{~m}, 8 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{2} \mathrm{CH}_{3}\right), 2.05\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.45$ and $3.55\left(2\right.$ superimposed $\left.\mathrm{t},{ }^{*} 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$, and $7.8\left(\mathrm{~s},{ }^{*} 1 \mathrm{H}\right.$, $\mathrm{CH}=\mathrm{N}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 13.0(\mathrm{q}), 14.77(\mathrm{q}), 14.84(\mathrm{q}), 21.5(\mathrm{t})$, $21.8(t), 34.1(2 \mathrm{t}), 53.0(\mathrm{t}), 61.4$ (t), 165.3 (d), and 167.0 (s) (Found: C, 72.6; H, 12.05; N, 15.35. $\mathrm{C}_{11} \mathrm{H}_{22} \mathrm{~N}_{2}$ requires C, $72.45 ; \mathrm{H}, 12.15 ; \mathrm{N}, 15.35 \%$ ) ; $\mathrm{NN}^{\prime}$-(1-methylethane-1,2diylidene)dicyclohexylamine $(2 \mathrm{~g})$, $(2.29 \mathrm{~g}, 49 \%)$, m.p. $52-54$ ${ }^{\circ} \mathrm{C} ; \mathrm{v}_{\max }$ (Nujol) $1635 \mathrm{br}(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 1.1-1.9(\mathrm{~m}$, $\left.20 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{5}\right), 2.05\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.15$ and $3.5(2 \mathrm{~m}$; $2 \mathrm{H}, \mathrm{CH}-\mathrm{N})$, and $7.8\left(\mathrm{~s},{ }^{*} 1 \mathrm{H}, \mathrm{CH}=\mathrm{N}\right) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 11.5(\mathrm{q})$, 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. $\mathrm{C}_{15} \mathrm{H}_{26} \mathrm{~N}_{2}$ requires $\mathrm{C}, 76.85 ; \mathrm{H}, 11.2 ; \mathrm{N}, 11.95 \%$ ); $\mathrm{NN}^{\prime}-(1-$ methylethane-1,2-diylidene)dihexylamine ( 2 h ) ( $4.33 \mathrm{~g}, 91 \%$ ), b.p. $69-71{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) $1645 \mathrm{br}(\mathrm{CN}) \mathrm{cm}^{-1}$; $\delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.85\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.1-1.85(\mathrm{~m}, 16 \mathrm{H}$, $\left.\left[\mathrm{CH}_{2}\right]_{4} \mathrm{CH}_{3}\right), 2.05\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right.$ ), 3.45 and 3.55 ( 2 superimposed $\left.\mathrm{t},{ }^{*} 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$, and $7.8\left(\mathrm{~s},{ }^{*} 1 \mathrm{H}, \mathrm{CH}=\mathrm{N}\right) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right)$ 13.1 (q), 15.0 (2 q), 23.8 ( 2 t), 28.3 (t), 28.5 (t), 32.0 (t), 32.9 ( 2 t$), 33.1(\mathrm{t}), 53.4(\mathrm{t}), 61.8(\mathrm{t}), 165.3(\mathrm{~d})$, and 166.9 (s) (Found: C, $75.7 ; \mathrm{H}, 12.8 ; \mathrm{N}, 11.8 . \mathrm{C}_{15} \mathrm{H}_{30} \mathrm{~N}_{2}$ requires $\mathrm{C}, 75.55 ; \mathrm{H}$, 12.7; N, 11.75\%).

Preparation of $\alpha$-Aminoamidines (3).-Mercury(II) acetate $(6.37 \mathrm{~g}, 20 \mathrm{mmol}$ ) was added during ca. 10 min , at room temperature, to a stirred solution of prop-2-ynol ( $1.18 \mathrm{ml}, 20$ mmol ) [or the appropriate $N$-prop-2-ynylaniline ( 20 mmol )] in a primary aromatic amine ( 400 mmol ). The temperature spontaneously rose to ca. $40^{\circ} \mathrm{C}$ in a few minutes. Metallic mercury ( $>90 \%$ ) was filtered off after 5-7 h and the organic phase treated with 1 m -aqueous sulphuric acid ( $3 \times 25 \mathrm{ml}$ ). The aqueous layer was treated with concentrated aqueous potassium hydroxide until basic and then extracted with ether; the extracts were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ 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 $\alpha$-aminoamidine (3).
The following compounds were obtained in this way: $\mathrm{NN}^{\prime}$ $\mathrm{N}^{\prime \prime}$-tri-o-tolyl-2-aminopropionamidine (3a) $(6.35 \mathrm{~g}, 89 \%$ ), m.p. $149-150{ }^{\circ} \mathrm{C}$; $v_{\text {max. }}$ (Nujol) $3320(\mathrm{NH})$ and $1635(\mathrm{CN}) \mathrm{cm}^{-1}$; $\delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 1.4\left(\mathrm{~d}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}\right), 2.05,2.2$, and $2.3(3 \mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{CH}_{3} \mathrm{Ar}\right), 3.45 \mathrm{br}(2 \mathrm{H}, \mathrm{NH}), 4.3(\mathrm{q}, 1 \mathrm{H}, \mathrm{CHMe})$, and $6.55-$ $7.3(\mathrm{~m}, 12 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 17.2$ (2 q), 17.5 (q), $20.5(\mathrm{q})$, 49.8 (d), and 156.9 (s); $m / z 357\left(M^{+}\right), 223\left(M-\mathrm{CH}_{3} \mathrm{CHN}-\right.$ $\mathrm{HC}_{6} \mathrm{H}_{4} \mathrm{Me}$ ), $134\left(M-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{NCNHC}_{6} \mathrm{H}_{4} \mathrm{Me}\right.$ ) (Found: C, $80.85 ; \mathrm{H}, 7.5 ; \mathrm{N}, 11.65 . \mathrm{C}_{24} \mathrm{H}_{27} \mathrm{~N}_{3}$ requires $\mathrm{C}, 80.65 ; \mathrm{H}, 7.6$; $\mathrm{N}, 11.75 \%$ ) ; $\mathrm{NN}^{\prime} \mathrm{N}^{\prime \prime}$-tri-p-tolyl-2-aminopropionamidine (3b) $(2.71 \mathrm{~g}, 38 \%)$, m.p. $187-189{ }^{\circ} \mathrm{C}$; $v_{\max }$ (Nujol) 3310 and $3260(\mathrm{NH})$ and $1630(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 1.4(\mathrm{~d}, 3 \mathrm{H}$, $\left.\mathrm{CH}_{3} \mathrm{CH}\right), 2.25,2.3$, and $2.35\left(3 \mathrm{~s}, 9 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}\right), 3.5$ br $(2 \mathrm{H}$, 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. $\mathrm{C}_{24} \mathrm{H}_{27} \mathrm{~N}_{3}$ requires C, $80.65 ; \mathrm{H}, 7.6 ; \mathrm{N}, 11.75 \%$ ) ; $\mathrm{NN}^{\prime} \mathrm{N}^{\prime \prime}$-tri-(o-methoxyphenyl)-2aminopropionamidine (3c) $\left(3.56 \mathrm{~g}, 44 \%\right.$ ), m.p. $159-161{ }^{\circ} \mathrm{C}$; $v_{\text {max }}$ (Nujol) $3350(\mathrm{NH})$ and $1640(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 1.4$ (d, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}$ ), $3.4 \mathrm{br}(2 \mathrm{H}, \mathrm{NH}), 3.65$ and $3.9(2 \mathrm{~s}, 9 \mathrm{H}$, $\left.\mathrm{CH}_{3} \mathrm{O}\right), 4.0(\mathrm{q}, 1 \mathrm{H}, \mathrm{CHMe})$, and $6.65-7.2(\mathrm{~m}, 12 \mathrm{H}, \mathrm{ArH})$ (Found: C, 71.0; H, 6.6; N, 10.5. $\mathrm{C}_{24} \mathrm{H}_{27} \mathrm{~N}_{3} \mathrm{O}_{3}$ requires C , $71.1 ; \mathrm{H}, 6.7 ; \mathrm{N}, 10.35 \%$ ); $\mathrm{NN}^{\prime} \mathrm{N}^{\prime \prime}$-triphenyl-2-aminopropionamidine (3d) $\left(3.34 \mathrm{~g}, 53 \%\right.$ ), m.p. $134-135^{\circ} \mathrm{C}$; $v_{\max .}$ (Nujol) 3370 and $3340(\mathrm{NH})$ and $1635(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 1.35$ (d, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}$ ), $3.65 \mathrm{br}(2 \mathrm{H}, \mathrm{NH}), 4.1(\mathrm{q}, 1 \mathrm{H}, \mathrm{CHMe})$, and $6.45-7.5(\mathrm{~m}, 15 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 20.9(\mathrm{q}), 50.4(\mathrm{~d})$, and 156.2 (s); m/z $315\left(M^{+}\right), 195$ ( $M$ - PhNHCHMe), and 120 ( M - PhNCNHPh) (Found: C, 80.1; H, 6.85; N, 13.3. $\mathrm{C}_{21} \mathrm{H}_{21} \mathrm{~N}_{3}$ requires C, $79.95 ; \mathrm{H}, 6.7 ; \mathrm{N}, 13.3 \%$ ).

Preparation of $\alpha$-Iminoketones (6) and $\alpha$-Di-imines (7).Mercury(II) acetate ( $6.37 \mathrm{~g}, 20 \mathrm{mmol}$ ) was added during $c a$. 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 $\mathrm{mmol}) \dagger$ in tetrahydrofuran or dichloromethane ( 50 ml ). The temperature spontaneously rose to ca. $40^{\circ} \mathrm{C}$ in a few minutes. Metallic mercury [ $>80 \%$, except for (61)] was filtered off after $3-22 \mathrm{~h}$. The organic phase was treated with $3 \mathrm{~m}-$ aqueous potassium hydroxide ( 15 ml ) and then extracted with ether or dichloromethane. The extracts were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$ and the volatile components removed under reduced pressure ( 15 and 0.001 Torr, successively) to yield [except for (61)] 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 $\alpha$-iminoketone (61) only $34 \%$ of metallic mercury was precipitated and the crude product had to be purified by distillation under reduced pressure.

The following $\alpha$-iminoketones (6) were obtained in this way:
$\dagger$ For compounds (6i) and (6k), 40 mmol of amine was employed and 30 mmol of potassium carbonate was also added.

* These signals show unresolved long range coupling $\mathrm{HC}=\mathrm{N}-\mathrm{CH}_{n}$ ( $n=1$ or 2 ).

1-phenyl-2-phenyliminopropan-1-one ${ }^{19}$ (6a) $(4.19 \mathrm{~g}, 94 \%)$, as a 87: 13 mixture of $E$ - and $Z$-isomers, b.p. $110-115^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max }}$ (film) $1670 \mathrm{br}(\mathrm{CO}$ and CN$) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right)$ 2.2 and $2.45\left(2 \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right)$, $6.7-7.55(\mathrm{~m}, 8 \mathrm{H}, \mathrm{ArH})$, and $8.1-8.25(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 16.5(\mathrm{q}), 166.4(\mathrm{~s})$, and 192.7 (s); $m / z 223\left(M^{+}\right), 118(M-\mathrm{PhCO})$, and 105 ( $M$ - PhNCMe); 1-phenyl-2-(o-tolylimino)propan-1-one (6b) ( $4.0 \mathrm{~g}, 84 \%$ ), as a $93: 7$ mixture of $E$ - and $Z$-isomers; b.p. $99-101{ }^{\circ} \mathrm{C}$ at 0.001 Torr ; $v_{\max }$ (film) $1625 \mathrm{br} \mathrm{cm}^{-1}$ (CO and CN ); ${ }^{1} \mathrm{H}$ n.m.r., $\delta\left(\mathrm{CDCl}_{3}\right) 2.1$ (s, $\left.3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}\right), 2.15$ and 2.5 ( $2 \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ ), $6.6-7.65(\mathrm{~m}, 7 \mathrm{H}, \mathrm{ArH}$ ), and $8.1-8.25$ $(\mathrm{m}, 2 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 17.2$ (q), $18.8(\mathrm{q}), 167.5(\mathrm{~s})$, and 193.5 (s) (Found: C, $80.75 ; \mathrm{H}, 6.2 ; \mathrm{N}, 6.0 . \mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}$ requires $\mathrm{C}, 81.0 ; \mathrm{H}, 6.35$; N, 5.9\%); 1-phenyl-2-(m-tolylimino)propan-1one ( 6 c ) $(3.61 \mathrm{~g}, 76 \%$ ), as a mixture of $E$ - (major) and $Z$ isomers, b.p. $109-111^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) 1620 br $(\mathrm{CO}$ and CN$) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 2.2$ and $2.45(2 \mathrm{~s}, 3 \mathrm{H}$, $\mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ ), $2.35\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}\right), 6.5-7.6(\mathrm{~m}, 7 \mathrm{H}, \mathrm{ArH}$ ), and $8.05-8.2(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 17.0(\mathrm{q}), 22.1$ (q), 167.3 (s), and 193.7 (s) (Found: C, 80.8; H, 6.25; N, 5.85. $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}$ requires $\mathrm{C}, 81.0 ; \mathrm{H}, 6.35, \mathrm{~N}, 5.9 \%$ ); 2-(o-methoxyphenylimino)-1-phenylpropan-1-one ( 6 d ) ( $4.02 \mathrm{~g}, 79 \%$ ), as a $90: 10$ mixture of $E$ - and $Z$-isomers, b.p. $122-124{ }^{\circ} \mathrm{C}$ at 0.001 Torr ; $v_{\max }$ (film) $1635 \mathrm{br}(\mathrm{CO}$ and CN$) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 2.1$ and 2.5 ( $2 \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ ), $3.85\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{O}\right), 6.65-7.6(\mathrm{~m}, 7 \mathrm{H}$, $\mathrm{ArH})$, and $8.15-8.3(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 16.4(\mathrm{q}), 55.0$ (q), 167.6 (s), and 192.8 (s) (Found: C, 76.0; H, 5.8; N, 5.4. $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}_{2}$ requires $\mathrm{C}, 75.85 ; \mathrm{H}, 5.95 ; \mathrm{N}, 5.5 \%$ ); 2-(o-chlorophenylimino)-1-phenylpropan-1-one (6e) ( $4.56 \mathrm{~g}, 88 \%$ ), as a 88 : 12 mixture of $E$ - and $Z$-isomers, b.p. $111-113{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) $1620 \mathrm{br}\left(\mathrm{CO}\right.$ and CN ) $\mathrm{cm}^{-1} ; \delta_{\mathbf{H}}$ $\left(\mathrm{CDCl}_{3}\right) 2.15$ and $2.5\left(2 \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 6.6-7.65(\mathrm{~m}, 7 \mathrm{H}$, $\mathrm{ArH})$, and $8.2-8.35(\mathrm{~m}, 2 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 18.1$ (q), 170.0 (s), and 193.5 (s) (Found: C, 70.05; H, 4.75; N, 5.3. $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{ClNO}$ requires $\mathrm{C}, 69.9 ; \mathrm{H}, 4.7 ; \mathrm{N}, 5.4 \%$ ); 2-phenyl-iminooctan-3-one ( 6 f ) ( $4.17 \mathrm{~g}, 96 \%$ ), b.p. $115-120{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) $1700(\mathrm{CO})$ and $1640(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}$ $\left(\mathrm{CCl}_{4}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.2-1.8\left(\mathrm{~m}, 6 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right)$, $1.9\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-\mathrm{C}=\mathrm{N}\right), 2.9\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right)$, and $6.55-7.55$ $(\mathrm{m}, 5 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 14.7(\mathrm{q}), 14.8(\mathrm{q}), 23.5(\mathrm{t}), 24.8(\mathrm{t})$, $32.5(\mathrm{t}), 37.2(\mathrm{t}), 166.6(\mathrm{~s})$, and $198.0(\mathrm{~s})$ (Found: C, 77.6 ; H, 8.8; $\mathrm{N}, 6.6 . \mathrm{C}_{14} \mathrm{H}_{19} \mathrm{NO}$ requires $\mathrm{C}, 77.4 ; \mathrm{H}, 8.8 ; \mathrm{N}, 6.45 \%$ ); 2-(o-tolylimino)octan-3-one ( 6 g ) ( $4.46 \mathrm{~g}, 96 \%$ ), b.p. $80-82^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) $1705(\mathrm{CO})$ and $1645(\mathrm{CN}) \mathrm{cm}^{-1}$; $\delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.05-1.75(\mathrm{~m}, 6 \mathrm{H}$, $\left.\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right), 1.85\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 2.5\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}\right), 3.0$ ( $\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}$ ), and $6.4-7.3(\mathrm{~m}, 4 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right)$ $14.9(2 \mathrm{q}), 18.4(\mathrm{q}), 23.6(\mathrm{t}), 25.0(\mathrm{t}), 32.7(\mathrm{t}), 37.4(\mathrm{t}), 166.4(\mathrm{~s})$, and 198.0 (s) (Found: C, 77.8; H, 9.05; N, 6.15. $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}$ requires $\mathrm{C}, 77.9 ; \mathrm{H}, 9.15 ; \mathrm{N}, 6.05 \%) ; 2$-(m-tolylimino)octan-3one ( 6 h ) $\left(3.30 \mathrm{~g}, 71 \%\right.$ ), b.p. $102-104{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$. (film) $1710(\mathrm{CO})$ and $1645(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.9(\mathrm{~m}$, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}$ ), $1.25-1.85\left(\mathrm{~m}, 6 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right), 1.95(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 2.35\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}\right), 3.0\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right)$, and $6.45-7.4(\mathrm{~m}, 4 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 14.7$ (q), 14.9 (q), 22.1 (q), $23.6(\mathrm{t}), 24.9(\mathrm{t}), 32.7(\mathrm{t}), 37.2(\mathrm{t}), 166.5(\mathrm{~s})$, and $197.7(\mathrm{~s})$ (Found: C, $80.0 ; \mathrm{H}, 9.05 ; \mathrm{N}, 6.0 . \mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}$ requires $\mathrm{C}, 77.9$; H, 9.15 ; N, 6.05\%); 2-(p-tolylimino)octan-3-one ( 6 i ) ( 3.70 g , $80 \%$ ), b.p. $100-102{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) 1700 (CO) and $1640(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)$, $1.2-1.8\left(\mathrm{~m}, 6 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right), 2.0\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 2.35$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{Ar}$ ), $3.0\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right)$, and $6.55-7.3(\mathrm{~m}, 4 \mathrm{H}$, $\mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right) 13.2$ (2 q), $20.0(\mathrm{q}), 21.8$ (t), $23.0(\mathrm{t}), 30.9$ (t), 35.6 (t), 164.8 (s), and 195.0 (s) (Found: C, 77.85; H, 9.0; $\mathrm{N}, 6.2 . \mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}$ requires $\mathrm{C}, 77.9 ; \mathrm{H}, 9.15 ; \mathrm{N}, 6.05 \%$ ); 2-(o-methoxyphenylimino)octan-3-one ( 6 j ) $(3.40 \mathrm{~g}, 69 \%$ ), b.p. $93-95{ }^{\circ} \mathrm{C}$ at 0.001 Torr ; $v_{\text {max. }}$ (film) $1700(\mathrm{CO})$ and 1645 $(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.15-1.8(\mathrm{~m}$,
$\left.6 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right), 1.9\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.05\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right)$, $3.8\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{O}\right)$, and $6.6-7.3(\mathrm{~m}, 4 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(\mathrm{CDCl}_{3}\right)$ 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. $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NO}_{2}$ requires $\mathrm{C}, 72.85 ; \mathrm{H}, 8.55 ; \mathrm{N}, 5.65 \%$ ); 2 -(p-methoxyphenylimino)octan-3-one ( 6 k ) ( $4.64 \mathrm{~g}, 94 \%$ ), b.p. 103 $105^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) 1700 (CO) and 1645 (CN) $\mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.15-1.85(\mathrm{~m}, 6 \mathrm{H}$, $\left.\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right), 2.0\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.0\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right), 3.85$ (s, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{O}$ ), and 6.6-7.0 (m, $\left.4 \mathrm{H}, \mathrm{ArH}\right) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 14.8$ (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. $\mathrm{C}_{15} \mathrm{H}_{21^{-}}$ $\mathrm{NO}_{2}$ requires $\mathrm{C}, 72.85 ; \mathrm{H}, 8.55 ; \mathrm{N}, 5.65 \%$ ); 2-(o-chloro-phenylimino)octan-3-one (61) ( $1.50 \mathrm{~g}, 30 \%$ ), b.p. $88-90^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) $1710(\mathrm{CO})$ and $1660(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}$ $\left(\mathrm{CDCl}_{3}\right) 0.9\left(\mathrm{~m}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.2-1.8\left(\mathrm{~m}, 6 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{3} \mathrm{Me}\right)$, 1.9 (s, $3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ ), $3.0\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\right.$ ), and $6.65-7.5$ $(\mathrm{m}, 4 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 15.1(\mathrm{q}), 15.7(\mathrm{q}), 23.7(\mathrm{t}), 25.1(\mathrm{t})$, 32.7 (t), 37.8 (t), 168.8 (s), and 197.6 (s) (Found: C, 66.95; $\mathrm{H}, 7.05 ; \mathrm{N}, 5.7 . \mathrm{C}_{14} \mathrm{H}_{18} \mathrm{CINO}$ requires $\mathrm{C}, 66.8 ; \mathrm{H}, 7.2 ; \mathrm{N}$, $5.55 \%$ ).

The following $\alpha$-di-imines (7) were obtained in similar way: $\mathrm{NN}^{\prime}$-(1-methyl-2-phenylethane-1,2-diylidene)dipropylamine (7a) ( $3.13 \mathrm{~g}, 68 \%$ ), b.p. $71-73{ }^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film),
 $1.3-1.85\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 2.1\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 3.1$ and $3.35\left(2 \mathrm{t}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$, and $7.15-7.75(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{c}}$ $\left(\mathrm{CDCl}_{3}\right) 13.1$ (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 ; $\mathrm{N}, 12.3 . \mathrm{C}_{15} \mathrm{H}_{22} \mathrm{~N}_{2}$ requires $\mathrm{C}, 78.2 ; \mathrm{H}, 9.6$; $\mathrm{N}, 12.15 \%$ ); NN'-(1-methyl-2-phenylethane-1,2-diylidene)dibutylamine (7b) $(4.05 \mathrm{~g}, 78 \%)$, b.p. $78-80{ }^{\circ} \mathrm{C}$ at 0.001 Torr ; $v_{\max }$. (film) 1660 and $1630(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CCl}_{4}\right) 0.75-1.1(\mathrm{~m}, 6 \mathrm{H}$, $\mathrm{CH}_{3} \mathrm{CH}_{2}$ ), $1.2-1.85\left(\mathrm{~m}, 8 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{2} \mathrm{Me}\right), 2.0\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-\right.$ $\mathrm{C}=\mathrm{N}), 3.0$ and $3.3\left(2 \mathrm{t}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$, and $7.15-7.75(\mathrm{~m}, 5 \mathrm{H}$, $\mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 14.9$ (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: $\mathrm{C}, 79.15 ; \mathrm{H}, 10.1 ; \mathrm{N}, 10.95 . \mathrm{C}_{17} \mathrm{H}_{26} \mathrm{~N}_{2}$ requires C , $79.0 ; \mathrm{H}, 10.15 ; \mathrm{N}, 10.85 \%$ ); $\mathrm{NN}^{\prime}$-(1-methyl-2-phenylethane-1,2-diylidene)dihexylamine ( 7 c ) $\left(5.59 \mathrm{~g}, 89 \%\right.$ ), b.p. $88-90^{\circ} \mathrm{C}$ at 0.001 Torr; $v_{\text {max. }}$ (film) 1650 and $1625(\mathrm{CN}) \mathrm{cm}^{-1} ; \delta_{\mathrm{H}}$ $\left(\mathrm{CDCl}_{3}\right) 0.8\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.0-1.9\left(\mathrm{~m}, 16 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{4}-\right.$ Me), $2.0\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 2.9-3.55\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$, and $7.15-7.85(\mathrm{~m}, 5 \mathrm{H}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(\mathrm{CDCl}_{3}\right) 15.1$ (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. $\mathrm{C}_{21} \mathrm{H}_{34} \mathrm{~N}_{2}$ requires C, 80.2; $\mathrm{H}, 10.9 ; \mathrm{N}, 8.9 \%$ ); $\mathrm{NN}^{\prime}-(1-$ methyl-2-pentylethane-1 ,2-diylidene)dipropylamine (7d) ( 4.08 g , $91 \%$ ), b.p. $83-85^{\circ} \mathrm{C}$ at 0.05 Torr ; $v_{\text {max. }}$ (film) $1630 \mathrm{br}(\mathrm{CN})$ $\mathrm{cm}^{-1} ; \delta_{\mathrm{H}}\left(\mathrm{CDCl}_{3}\right) 0.7-1.1\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right), 1.15-1.85(\mathrm{~m}$, $\left.10 \mathrm{H},\left[\mathrm{CH}_{2}\right]_{4} \mathrm{Me}\right), 2.0$ and $2.05\left(2 \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right), 2.3-$ $2.85\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{N}\right)$, and $3.1-3.55\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right) ; \delta_{\mathrm{c}}$ $\left(\mathrm{CDCl}_{3}\right) 166.6$ (s), 167.5 (s), $170.0(\mathrm{~s})$, and 171.5 (s) (Found: $\mathrm{C}, 75.15 ; \mathrm{H}, 12.5 ; \mathrm{N}, 12.65 . \mathrm{C}_{14} \mathrm{H}_{28} \mathrm{~N}_{2}$ requires $\mathrm{C}, 74.95 ; \mathrm{H}$, 12.6 ; N, $12.5 \%$ ).

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[^0]:    * Not only electronic but also steric factors could probably account for the different course of the reaction. ${ }^{8}$ This aspect has not been investigated.

