# Catalytic and Non-catalytic Addition of Aromatic Amines to Terminal Acetylenes in the Presence of Mercury(II) Chloride and Acetate

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The addition of aromatic amines to terminal acetylenes in the presence of catalytic amounts of mercury(II) chloride gives imines, enamines, and 1,2,3,4-tetrahydroquinoline derivatives; mercury(II) acetate shows considerably less catalytic activity and may be used for the non-catalytic preparation of imines, enamines, *NN'*-disubstituted acetamidines, and *NN*-disubstituted acetamides.

THE addition of ammonia or amines to non-activated acetylenes can only be achieved at high temperatures and pressures and requires the presence of a catalyst.[1] For instance, acetonitrile or imines are obtained upon treatment of acetylene with ammonia or primary aliphatic amines respectively; for ammonia, the addition takes place at 300—350 °C with silica or alumina as the catalyst and, for the amines, it occurs in the presence of a mixture of zinc and cadmium acetates. The solvomercuriation–demercuriation of alkenes is probably the most important synthetic method employing intermediate organomercurials,[2-4] since it allows the addition of numerous nucleophiles to the unsaturated substrate under very mild conditions, but the mercuriation of alkynes, recently reviewed by Larock,[4] has been much less thoroughly studied and its potential synthetic utility little explored. The preparation of quinaldines, indoles, and quinolines from condensation of acetylene and amines in the presence of mercury(II) salts has been claimed,[5,6] but convencing proof was not provided.[7] The reaction of aziridine and oct-1-yne with mercury(II) acetate to afford *N*-(1-hexylethenyl)aziridine has also been described.[8]

We have already reported the synthesis of imines and enamines by treatment of phenylacetylene with primary or secondary aromatic amines and mercury(II) acetate.[9] The same products were obtained when the mercury(II) acetate was replaced by only catalytic amounts of thallium(III) acetate.[10] We now report a systematic study on the reactivity of terminal acetylenes towards aromatic amines in the presence of mercury(II) acetate and chloride. Mercury(II) chloride behaves as a catalyst in all the processes studied. However, mercury(II) acetate shows only limited catalytic activity in reactions with acetylene, without synthetic utility. The new synthetic methods now reported are outlined in Scheme 1.

The imines (3) are produced by addition of aniline to monoalkylacetylenes at room temperature, the reaction being promoted by catalytic amounts of mercury(II) chloride. In a typical experiment, a 1 : 20 : 100 ($HgCl_2$ : alkyne : amine) molar ratio is employed with cooling in a water bath to keep the temperature below 30 °C. Higher temperatures lead to extensive side reactions causing destruction of the catalyst;† these processes are much slower than the catalytic reaction at lower temperatures, but even then they do lead to final loss of the catalyst.

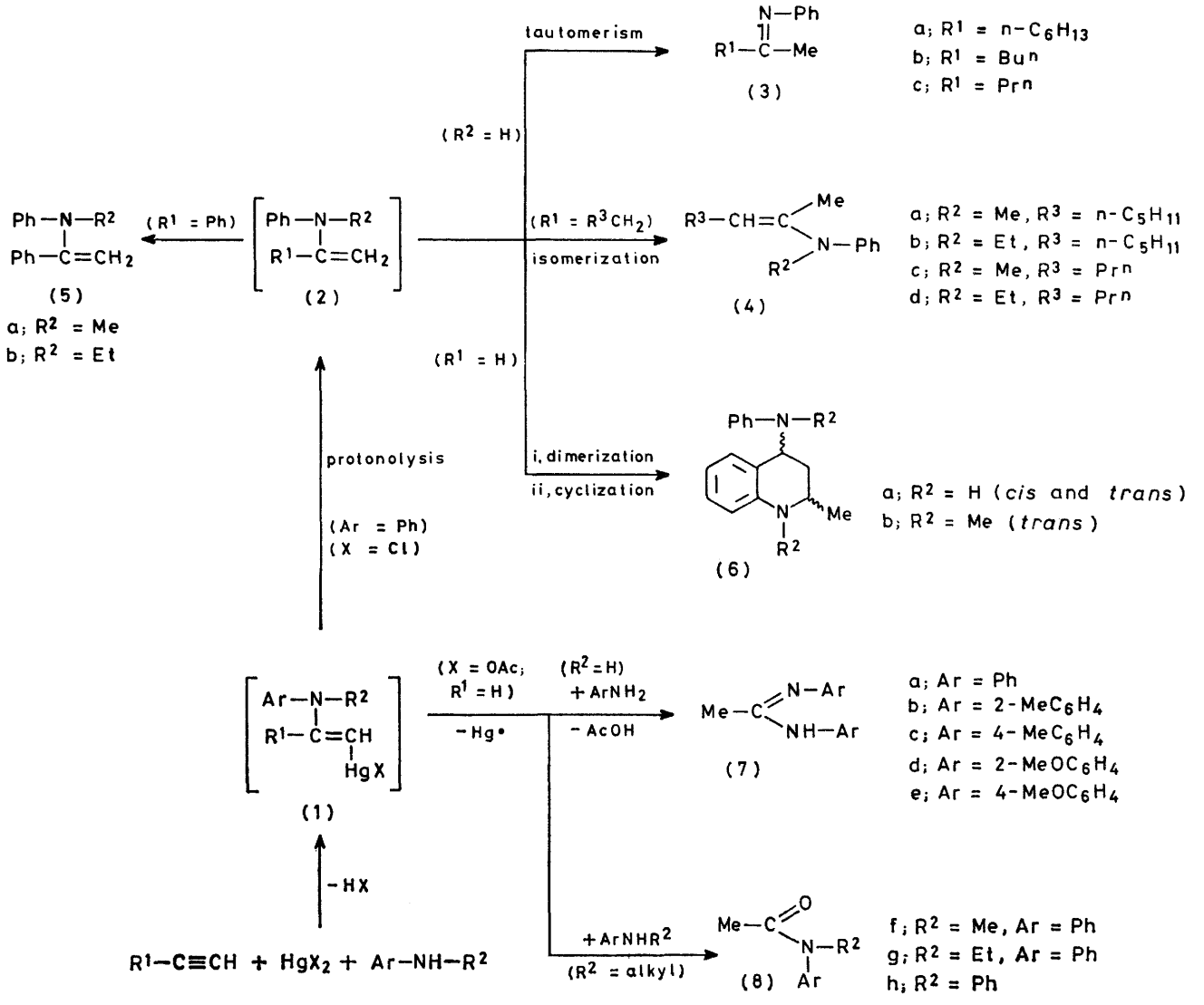
The enamines (4) are obtained as a mixture of *Z*- and *E*-isomers from the reaction of secondary aromatic amines with monoalkylacetylenes in the presence of catalytic amounts of mercury(II) chloride (1 : 20 : 100 molar ratio of $HgCl_2$ : alkyne : amine), and the products are always contaminated by $< 5\%$ of the isomer having a terminal double bond (2, $R^1 = R^3CH_2$). Compounds (2) can only be obtained pure when double bond isomerization is not possible. For instance, 1-phenylethenylamines (5) are produced by thallium(III) acetate [10] or mercury(II) chloride catalysed addition of secondary aromatic amines to phenylacetylene. The existence of terminal–internal double bond equilibration in enamines derived from secondary aromatic amines and the predominace in the latter case of the *Z*-over the *E*-isomer have been previously reported by Stradi and his coworkers.[11-13]

The enamines (4) and (5) are best synthesized in reactions at moderate temperatures (*ca.* 60 °C) for 1 h. If higher temperatures are employed, the well known self-condensation of the enamines‡ occurs to a considerable extent. The catalyst remains active after completion of the reaction, as shown by evaporation of the volatile components from the reaction mixture followed by addition of fresh reactants to the gummy residue. In a test experiment, this process was repeated four times without apparent loss of catalytic activity. In contrast with the behaviour already described for the imines (3), the enamines (4) and (5) do not lead to the precipitation of elemental mercury when are shaken with mercury(II) chloride at 60 °C.

Most of the known methods [the reaction of carbonyl compounds with secondary amines in the presence of toluene-*p*-sulphonic acid,[14] titanium(IV) chloride [15] or molecular sieves [16]] for obtaining enamines fail for those derived from aromatic amines, except for one method which uses dialkyl or alkyl aryl ketone acetals.[11,17] The mercury(II) chloride-promoted addition of aromatic amines to terminal acetylenes described here thus should provide the method of choice for these compounds.

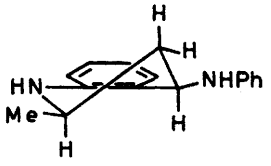
† Elemental mercury is precipitated in the reaction of (3a) with $HgCl_2$ at 60 °C for 1 h.

‡ In the case of the enamines (4), the self-condensation process always takes place between two molecules having a terminal double bond (see Experimental section). Similar behaviour has been observed for enamines derived from aliphatic amines.[11]

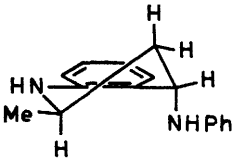



SCHEME 1

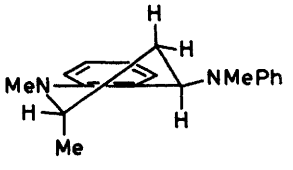
The reaction of acetylene with aromatic amines, at room temperature, in the presence of catalytic amounts of mercury(II) chloride (1 : 100 molar ratio of $HgCl_2$ : amine) leads to 2-methyltetrahydroquinoline derivatives (6). Whereas the use of aniline gives rise to a mixture of the *cis*- and *trans*-isomers of (6a) in a 1 : 2 molar ratio, with *N*-methylaniline a single product is obtained; we assume, on the basis of its $^1H$ n.m.r. parameters, that it is the *trans*-stereoisomer of (6b).*



*cis*-(6a)



*trans*-(6a)



*trans*-(6b)

The enamines (2; $R^1 = H$) or their tautomeric imines ($R^2 = H$) would be expected to result from these processes according to the reaction pathways outlined. However, they undergo a spontaneous dimerization followed by cyclization under the conditions studied by us.[19,20]

Two side reactions have been found which lead to the progressive disappearance of the catalyst by reduction of the mercury(II) salt to elemental mercury. The first is a general one and consists of the oxidation of compounds (6) by the mercury(II) chloride, affording aromatic

* Both *cis*- and *trans*-isomers of (6) can apparently exist at room temperature as two isolable conformers. Our assignments were made on the basis of previously reported $^1H$ n.m.r. data.[18]

TABLE 1

Products (3)—(6) obtained using mercury(II) chloride

| Product | Reaction time/h | Temp./°C | Yield [a] | % Yield [b] |
|---|---|---|---|---|
| (3a) | 6 | Room temp. | 13.8 | 69 |
| (3b) | 6 | Room temp. | 13.3 | 67 |
| (3c) | 6 | Room temp. | 11.0 | 55 |
| (4a) | 1 | 60 | 15.6 | 78 |
| (4b) | 1 | 60 | 16.8 | 84 |
| (4c) | 1 | 60 | 10.1 | 51 |
| (4d) | 1 | 60 | 9.5 | 48 |
| (5a) | 1 | 60 | 10.8 | 54 |
| (5b) | 1 | 60 | 7.8 | 39 |
| *cis*- and *trans*-(6a) | 48 | Room temp. | 13.4 | |
| *trans*-(6b) | 48 | Room temp. | 18.2 | |

[a] Expressed in mol of product per mol of $HgCl_2$. [b] Based on terminal acetylene.

amines and 2-methylquinoline among other products. The second process takes place only in the presence of primary aromatic amines (*i.e.*, aniline) and consists of the competitive non-catalytic reaction (1) leading to *NN'*-diphenylacetamidine (7a).

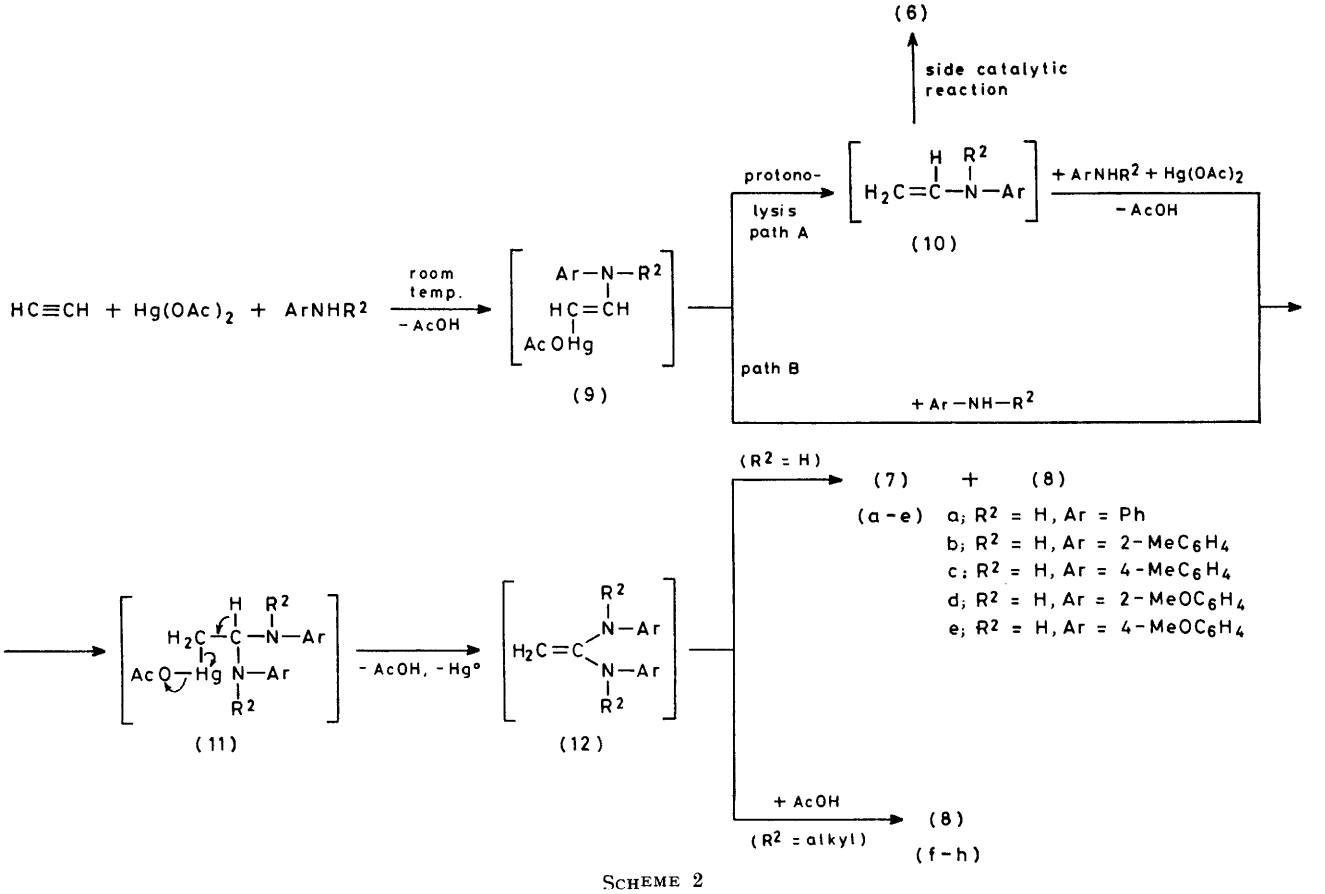
$$HC{\equiv}CH + HgCl_2 + 2\ PhNH_2 \longrightarrow (7a) + Hg^0 + 2\ HCl \quad (1)$$

Reactions conditions and yields for the catalytic production of compounds (3)—(6) are in Table 1.

Compounds (3) and (4) can also be obtained *via* aminomercuriation–demercuriation of alkynes with mercury(II) acetate, but this salt does not act as a catalyst and the intermediate organomercurial must be reduced by treatment with conventional reducing agents. A similar preparation of compounds (5) has been reported.[9]

Mercury(II) acetate shows a poor catalytic activity in the reaction between acetylene and aromatic amines to afford compounds (6). In this case, depending on the molar ratio of amine to mercury(II) acetate, the main process can be the non-catalytic formation of substituted acetamidines (7) and/or substituted acetamides (8), which takes place with spontaneous precipitation of elemental mercury. However, the use of mercury(II) acetate in the presence of a large excess of amine offers little synthetic utility. For instance, the reaction between an excess of acetylene and aniline (1.5 mol) promoted by mercury(II) acetate (15 mmol) leads to a mixture of *cis*- and *trans*-(6a) (16 mmol), (7a) (12 mmol), and (8a) (1 mmol). In contrast, when acetylene is bubbled at room temperature through a solution in tetrahydrofuran of mercury(II) acetate and a primary or secondary aromatic amine (1 : 3 molar ratio), *NN'*-diarylacetamidines (7) and *N*-alkyl-*N*-phenylacetamides (8f—h), respectively, are obtained as the major products (Scheme 2).

The pathway for the conversion of (9) into (11) could not be clearly established. In principle it could involve the intermediate (10) (path A) or take place directly by addition of a second molecule of amine (path




SCHEME 2

B); the production of trace amounts of compounds (6) suggests a major contribution of path A to the total process. The way in which (12) leads to the products depends on $R^2$. If $R^2$ is H, (12) gives the corresponding *NN'*-darylacetamidine tautomers (7) together with the *N*-arylacetamides (8a—e) as side products in $< 15\%$ yield. When $R^2$ is alkyl, the major products are the *N*-alkyl-*N*-phenylacetamides (8f—h). In the latter case, the anion linked to the mercury participates in the reaction; *e.g.* an equimolecular mixture of *NN*-disubstituted acetamides and propionamides results when mercury(II) acetate is replaced by mercury(II) propionate.

The particular behaviour of acetylene in these processes which allows the synthesis of compounds of a different nature through a catalytic or a non-catalytic reaction path* may be attributed to the particular structure of the intermediate organomercurials, which are able to undergo an internal redox process. This behaviour has also been observed when some α-functionalized acetylenes have been mercuriated.[21]

Conditions and yields for the non-catalytic production of compounds (3), (4), (7), and (8) are in Table 2.

TABLE 2

Products (3), (4), (7), and (8) obtained using mercury(II) acetate [a]

| Product | Reaction time/h | % Yield [b] |
|---|---|---|
| (3a) | 1/6 | 65 |
| (3b) | 1/6 | 45 |
| (3c) | 1/6 | 17 |
| (4a) | 1/3 | 51 |
| (7a) | 4 | 75 |
| (7b) | 10 | 77 |
| (7c) | 4 | 90 |
| (7d) | 8 | 65 |
| (7e) | 5 | 78 |
| (8f) | 4 | 81 |
| (8g) | 4 | 97 |
| (8h) | 5 | 96 |

[a] All the reactions were carried out at room temperature. [b] Based on $Hg(OAc)_2$.

## EXPERIMENTAL

I.r. spectra were recorded on a Pye–Unicam SP-1000 instrument, and $^1H$ n.m.r. spectra on a Varian EM-390 spectrometer, with tetramethylsilane as internal reference. G.l.c. analyses were performed on a Varian Aerograph 2800 instrument (Chromosorb G, 1.5%, OV-101).

*Catalytic Preparation of the Imines* (3) *using Mercury*(II) *Chloride*.—Mercury(II) chloride (1 mmol) was added to a stirred solution of an n-alkylacetylene (20 mmol) and aniline (100 mmol) in dry tetrahydrofuran (THF) (10 ml), cooled in a water bath. A solution of sodium borohydride (0.25 mmol) in 3M aqueous potassium hydroxide (10 ml) was added after 6 h and the mixture stirred for 10 min. Metallic mercury (*ca.* 100%) was filtered off and the liquid phase extracted with ether. The ethereal layer was dried ($Na_2SO_4$) and concentrated, the excess of alkyne and amine distilled off *in vacuo* (0.05 Torr), and the residue also distilled *in vacuo* to yield the *N*-(1-methylalkylidene)aniline (3).

The following compounds were obtained in this way: *N*-(1-methylheptylidene)aniline [22] (3a) (2.80 g, 13.8 mmol), b.p. 74—76 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 050, 1 660, 1 490, 750, and 700 $cm^{-1}$; δ ($CCl_4$) 0.9 (3 H, m, *Me*$[CH_2]_5$), 1.3 (8 H, m, $[CH_2]_4$Me), 1.7 and 2.1 (3 H, 2 s,† MeC=N), 2.3 and 1.9 (2 H, 2 t,† *J* 7.5 Hz, $CH_2C$=N), and 6.4—7.3 (5 H, m, ArH); N-(1-*methylpentylidene*)*aniline* (3b) (2.33 g, 13.3 mmol), b.p. 50—53 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 060, 1 670, 1 600, 1 490, 750 and 710 $cm^{-1}$; δ($CCl_4$) 1.0 (3 H, m, *Me*$[CH_2]_3$), 1.4 (4 H, m, $[CH_2]_2$Me), 1.7 and 2.1 (3 H, 2 s, MeC=N), 2.3 and 1.9 (2 H, 2 t, *J* 7 Hz, $CH_2C$=N), and 6.5—7.3 (5 H, m, ArH) (Found: C, 82.2; H, 9.85; N, 8.1. $C_{12}H_{17}N$ requires C, 82.2; H, 9.8; N, 8.0%); *N*-(1-methylbutylidene)aniline [23] (3c) (1.77 g, 11.0 mmol), b.p. 35—40 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 060, 1 660, 1 600, 1 490, 750, and 700 $cm^{-1}$; δ($CCl_4$) 0.8 and 1.0 (3 H, 2 t, *J* 7 Hz, $[CH_2]_2$*Me*), 1.5 (2 H, m, $CH_2$Me), 1.6 and 2.0 (3 H, 2 s, MeC=N), 2.3 and 1.9 (2 H, 2 t, *J* 7.5 Hz, $CH_2C$=N), and 6.4—7.3 (5 H, m, ArH).

The imines (3) were hydrolysed with 6N sulphuric acid at room temperature for 30 min, and then extracted with ether, affording the corresponding methyl alkyl ketone. The aqueous layers were treated with 3M aqueous potassium hydroxide until basic and then extracted with ether, yielding aniline. All the hydrolysis products were identified by comparison (g.l.c.) with authentic samples.

*Non-catalytic Preparation of the Imines* (3) *using Mercury*(II) *Acetate*.—Mercury(II) acetate (10 mmol) was added to a stirred solution of the n-alkylacetylene (10 mmol) and aniline (50 mmol) in dry THF (20 ml), with cooling in a water bath. A solution of sodium borohydride (2.5 mmol) in 3M aqueous potassium hydroxide (10 ml) was added after 10 min and the mixture stirred for 15 min. Mercury (90—95%) was filtered off and the liquid phase extracted with ether. The ethereal layer was dried ($Na_2SO_4$) and concentrated, the excess of alkyne and aniline distilled off *in vacuo* (0.05 Torr), and the residue also distilled *in vacuo* to yield (3a) (1.32 g, 65%), (3b) (0.79 g, 45%), or (3c) (0.27 g, 17%).

*Catalytic Preparation of the Enamines* (4) *and* (5) *using Mercury*(II) *Chloride*.—Mercury(11) chloride (1 mmol) was added to a stirred solution of the n-alkylacetylene or phenylacetylene (20 mmol) in a fivefold excess of secondary aromatic amine (100 mmol), at 60 °C. After 1 h, the excess of alkyne and amine was distilled off *in vacuo* (0.05 Torr) and the residue also distilled *in vacuo* to give (4) or (5) as a yellow liquid.

The following compounds were obtained in this way: N-*methyl*-N-(1-*methylhept*-1-*enyl*)*aniline* (4a) (3.39 g, 15.6 mmol), b.p. 65—68 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 080, 3 060, 3 020, 1 670, 1 610, 1 510, 760, and 700 $cm^{-1}$; δ($CCl_4$) 0.9 (3 H, m, *Me*$[CH_2]_4$), 1.3 (6 H, m, $[CH_2]_3$Me), 1.7 and 1.75 (3 H, 2 s, MeC=C), 2.0 (2 H, m, $CH_2C$=C), 2.9 and 2.95 (3 H, 2 s, MeN), 5.1 and 5.2 (1 H, 2 t, *J* 7.5 Hz, HC≡C), and 6.4—7.3 (5 H, m, ArH) (Found: C, 82.8; H, 10.75; N, 6.45. $C_{15}H_{23}N$ requires C, 82.9; H, 10.7; N, 6.4%); N-*ethyl*-N-(1-*methylhept*-1-*enyl*)*aniline* (4b) (3.88 g, 16.8 mmol), b.p. 72—74 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 070, 3 050, 3 020, 1 660, 1 600, 1 500, 750, and 700 $cm^{-1}$; δ($CCl_4$) 0.9 (3 H, m, *Me*$[CH_2]_4$), 1.0—1.4 (9 H, m, $[CH_2]_3$Me and *Me*$CH_2$N), 1.7 and 1.75 (3 H, 2 s, MeC=C), 2.0 (2 H, m, $CH_2C$=C), 3.1 and 3.4

* The reaction between acetylene, mercury(II) chloride, and secondary aromatic amines exceptionally takes place only *via* the catalytic path to give compounds (6). The non-catalytic reaction could lead to the production of the acetamides (8), but none of the reactants can supply the oxygen necessary for their formation.

† For compounds (3) and (4), two signals are observed for these protons because of the presence of *E*- and *Z*-isomers.

(2 H, 2 q, $J$ 7 Hz, $CH_2N$), 5.2 and 5.3 (1 H, 2 t, $J$ 6.5 Hz, (HC=C), and 6.3—7.2 (5 H, m, ArH) (Found: C, 82.95; H, 10.95; N, 6.0. $C_{16}H_{25}N$ requires C, 83.1; H, 10.9; N, 6.05%); *N-methyl-N-(1-methylpent-1-enyl)aniline* (4c) (1.91 g, 10.1 mmol), b.p. 53—54 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 060, 3 050, 3 020, 1 670, 1 590, 1 510, 760, and 710 $cm^{-1}$; $\delta(CCl_4)$ 0.9—1.0 (3 H, m, $Me[CH_2]_2$), 1.4 (2 H, m, $CH_2Me$), 1.7 and 1.75 (3 H, 2 s, MeC=C), 1.9 (2 H, m, $CH_2C$=C), 2.95 and 3.0 (3 H, 2 s, MeN), 5.15 and 5.3 (1 H, 2 t, $J$ 6.5 Hz, HC=C), and 6.4—7.2 (5 H, m, ArH) (Found: C, 82.4; H, 10.2; N, 7.4. $C_{13}H_{19}N$ requires C, 82.5; H, 10.1; N, 7.4%); *N-ethyl-N-(1-methylpent-1-enyl)aniline* (4d) (1.93 g, 9.5 mmol), b.p. 55—57 °C at 0.5 Torr; $\nu_{max.}$ (film) 3 080, 3 060, 3 020, 1 660, 1 600, 1 510, 750, and 700 $cm^{-1}$; $\delta(CCl_4)$ 0.85—0.95 (3 H, m, $Me[CH_2]_2$), 1.0—1.6 (5 H, m, $CH_2$Me and $Me$ $CH_2N$), 1.7 and 1.75 (3 H, 2 s, MeC=C), 1.9 (2 H, m, $CH_2C$=C), 3.0 and 3.3 (2 H, 2 q, $J$ 7 Hz, $CH_2N$), 5.2 and 5.3 (1 H, 2 t, $J$ 6.5 Hz, HC=C), and 6.4—7.2 (5 H, m, ArH) (Found: C, 82.65; H, 10.5; N, 6.95. $C_{14}H_{21}N$ requires C, 82.7; H, 10.4; N, 6.9%); *N*-methyl-*N*-(1-phenylethenyl)aniline [9] (5a) (2.26 g, 10.8 mmol), b.p. 73—76 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 050, 1 610, 1 500, 760, and 710 $cm^{-1}$; $\delta(CCl_4)$ 3.1 (3 H, s, MeN), 4.7 (1 H, d, $J$ < 1 Hz, HC=C), 4.85 (1 H, d, $J$ < 1 Hz HC=C), and 6.5—7.5 (10 H, m, ArH); *N*-ethyl-*N*-(1-phenylethenyl)aniline [9] (5b) (1.74 g, 7.8 mmol), b.p. 78—80 °C at 0.05 Torr; $\nu_{max.}$ (film) 3 050, 1 600, 1 570, 1 490, 750, and 700 $cm^{-1}$; $\delta(CCl_4)$ 1.2 (3 H, t, $J$ 7 Hz, $MeCH_2$), 3.6 (2 H, q, $J$ 7 Hz, $CH_2$Me), 4.8 (1 H, d, $J$ < 1 Hz, HC=C), 4.9 (1 H, d, $J$ < 1 Hz, HC=C) and 6.5—7.5 (10 H, m, ArH).

The enamines (4) and (5) were hydrolysed with 6N sulphuric acid at room temperature for 30 min, and then extracted with ether, affording the corresponding acetophenone or methyl alkyl ketone. The aqueous layers were treated with 3M aqueous potassium hydroxide until basic and then extracted with ether, yielding the corresponding *N*-alkylaniline. All the hydrolysis products were identified by comparison (g.l.c.) with authentic samples.

*Non-catalytic Preparation of* N-*Methyl*-N-(1-*methylhept*-1-*enyl*)*aniline* (4a) *using Mercury*(II) *Acetate*.—Mercury(II) acetate (10 mmol) was added under argon to a stirred solution of oct-1-yne (10 mmol) and *N*-methylaniline (30 mmol) in dry THF (50 ml) with cooling in a water bath. After 20 min, dry THF (25 ml) and an excess of lithium powder (125 mmol) were added, and the stirred mixture was heated at 60 °C for 6 h. Mercury (*ca.* 2 g) was filtered off and the liquid phase treated with methanol–water (1 : 1; 20 ml) and immediately extracted with ether. The ethereal layer was dried ($Na_2SO_4$) and concentrated, and the excess of oct-1-yne and amine distilled off *in vacuo* (0.05 Torr). The residue was also distilled *in vacuo* to yield 1.11 g (51%) of (4a).

*Self-condensation Products of the Enamines* (4a) *and* (5a).—When the enamine (4a) was stored for several weeks or heated at 80 °C for 1 day and then analysed by g.l.c., *N*-methylaniline and a product with higher molecular weight were formed. Distillation *in vacuo* (0.05 Torr) gave *N*-methylaniline, unchanged (4a), and a third fraction comprising *N*-methyl-*N*-phenyl-(1-hexylidene-3-methylnon-2-enyl)amine [$\delta(CCl_4)$ 0.8—2.3 (27 aliphatic H), 3.0 and 3.05 (3 H, 2, s, MeN), 5.0—5.7 (2 olefinic H), and 6.5—7.2 (5 aromatic H)].

Under the same conditions, the enamine (5a) yielded *N*-methyl-*N*-phenyl-(1,3-diphenylbuta-1,3-dienyl)amine [$\delta(CCl_4)$ 2.7 (3 H, s, MeN), 5.2 (2 H, m, $H_2C$=C), and 6.5—7.5 (16 H, m, 3 Ph and C=CHC=C)].

*Catalytic Preparation of Compounds* (6) *using Mercury*(II) *Chloride*.—Dry acetylene was bubbled through a stirred solution of mercury(II) chloride (5 mmol) in aniline or *N*-methylaniline (500 mmol), with cooling in a water bath. After 48 h, the mercury was filtered off. The liquid phase was treated with 3M aqueous potassium hydroxide until basic, and then extracted with ether. The ethereal layer was dried ($Na_2SO_4$) and concentrated, and the excess of amine distilled off *in vacuo* (0.05 Torr). Compounds (6a) were distilled at 0.001 Torr; the first fraction containing *NN'*-diphenylacetamidine was discarded and the second fractionally recrystallized from ether to give, successively, *cis*- and *trans*-(6a). In the case of (6b), the distillation residue was chromatographed on alumina, using cyclohexane–benzene–diethylamine (75 : 15 : 10) as eluant, and then recrystallized from hexane.

The following products were obtained in this way: *cis*-4-anilino-2-methyl-1,2,3,4-tetrahydroquinoline, *cis*-(6a), m.p. 125—126 °C (lit.,[18] 126 °C), $\nu_{max.}$ (Nujol) 3 360, 3 320, 3 040, 1 590, 1 510, 1 490, 780, and 730 $cm^{-1}$; $^1H$ n.m.r. spectrum identical with that reported; [18] *trans*-4-anilino-2-methyl-1,2,3,4-tetrahydroquinoline, *trans*-(6a), m.p. 83—84 °C (lit.,[18] 86 °C), $\nu_{max.}$ (Nujol 3 380, 3 340, 3 020, 1 600, 1 500, 770, and 720 $cm^{-1}$; $^1H$ n.m.r. spectrum identical with that reported [18] [total amount obtained of *cis*- and *trans*-(6a) 15.7 g (67 mmol)]; *trans*-1,2-dimethyl-4-(*N*-methylanilino)-1,2,3,4-tetrahydroquinoline, *trans*-(6b) (24.2 g, 91 mmol), m.p. 89—90 °C (lit.,[24] 83 °C); $M^+$, $m/e$ 266; $\nu_{max.}$ (Nujol) 3 060, 3 040, 1 610, 1 580, 1 500, 760, 750, and 700 $cm^{-1}$; $\delta(CDCl_3)$ 1.2 (3 H, d, $J$ 7 Hz, *exo*-Me), 1.8 (1 H, octet, $J$ 12, 6, and 3 Hz, *equatorial* CH–*H*CH–CH), 2.2 (1 H, sextet, $J$ 12, 12, and 4.5 Hz, *axial* CH–HC*H*–CH), 2.7 and 2.9 (6 H, 2 s, MeN), 3.5 (1 H, m, NC*H*Me), 5.1 (1 H, dd, $J$ 12 and 6 Hz, NC*H*Ar), and 6.3—7.3 (9 H, m, ArH).

*Preparation of the* NN'-*Diarylacetamidines* (7).—Mercury(II) acetate (50 mmol) was added to a stirred solution of a primary aromatic amine (150 mmol) in dry THF (50 ml) and dry acetylene was bubbled through the mixture, which was cooled in a water bath. Mercury (*ca.* 100%) was filtered off after 4—10 h. The liquid phase was treated with 2M sulphuric acid (50 ml) and then extracted with ether, yielding < 15% of the appropriate *N*-arylacetamide. The aqueous layer was treated with 3M aqueous potassium hydroxide until basic and then extracted with ether; the ether extract was dried ($Na_2SO_4$) and concentrated, and the excess of amine distilled off *in vacuo* (0.05 Torr). Recrystallization from ether yielded the *NN'*-diarylacetamidines (7).

The following products were obtained in this way: *NN'* diphenylacetamidine (7a) (7.88 g, 75%), m.p. 130—131 °C (lit.,[25a] 131—132 °C); $\nu_{max.}$ (Nujol) 3 240, 3 060, 3 020, 1 640, 1 590, 1 540, 1 500, 775, 760, 710, and 700 $cm^{-1}$; $\delta(CDCl_3)$ 1.95 (3 H, s, MeC=N), 5.0—6.7br (1 H, NH), and 6.9—7.4 (10 H, m, ArH); *NN'*-di-*o*-tolylacetamidine (7b) (9.16 g, 77%), m.p. 134—135 °C (lit.,[25b] 136 °C); $\nu_{max.}$ (Nujol) 3 300, 3 060, 3 040, 1 640, 1 600, 1 540, 1 490, 760, and 730 $cm^{-1}$; $\delta(CDCl_3)$ 1.9 (3 H, s, MeC=N), 2.2 (6 H, s, Ar*Me*), 5.0—6.2br (1 H, NH), and 6.8—7.4 (8 H, m, ArH); *NN'*-di-*p*-tolylacetamidine (7c) (10.71 g, 90%), m.p. 119—120 °C (lit.,[25c] 122 °C); $\nu_{max.}$ (Nujol) 3 300, 3 040, 1 640, 1 600, 1 540, 1 520, 840, and 820 $cm^{-1}$; $\delta(CDCl_3)$ 1.95 (3 H, s, MeC=N), 2.3 (6 H, s, Ar*Me*), 4—6br (1 H, NH), and 6.9—7.2 (8 H, m, ArH); *NN'*-di-(*o*-methoxyphenyl)acetamidine (7d) (8.87 g, 65%), m.p. 97—98 °C (lit.,[25d] 99 °C); $\nu_{max.}$ (Nujol) 3 440, 3 080, 3 060, 1 660, 1 600, 1 540, 1 500, 1 240, 1 100, and 760 $cm^{-1}$; $\delta(CDCl_3)$ 1.9 (3 H, s, MeC=N), 3.8 (6 H, s, ArO*Me*),

6.7—7.1 (8 H, m, ArH), and 7.3—8.5br (1 H, NH); *NN'*-di-(*p*-methoxyphenyl)acetamidine (7e) (10.53 g, 78%), m.p. 102—103 °C (lit.,[25e] 105 °C); $\nu_{max.}$ (Nujol 3 200, 3 060, 3 020, 1 640, 1 600, 1 550, 1 510, 1 240, 1 040, 850, and 830 $cm^{-1}$; δ($CDCl_3$) 1.9 (3 H, s, MeC=N), 3.75 (6 H, s, ArO*Me*), 5.7—6.5br (1 H, NH), and 6.7—7.2 (8 H, m, ArH).

*Preparation of the* N-*Alkyl*-N-*phenylacetamides* (8f—h).—Mercury(II) acetate (50 mmol) was added to a stirred solution of a secondary aromatic amine (150 mmol) in dry THF (50 ml) and dry acetylene was bubbled through the mixture, which was cooled in a water bath. After 4—5 h, mercury (72—80%) was filtered off, and the liquid phase treated with 3M aqueous potassium hydroxide until basic and then extracted with ether. The ethereal layer was dried ($Na_2SO_4$) and concentrated, and the excess of amine distilled off *in vacuo* (0.05 Torr). The residue was sublimed at 0.001 Torr and the sublimate recrystallized from ether to yield the *N*-alkyl-*N*-phenylacetamides (8f—h).

The following products were obtained in this way: *N*-methylacetanilide (8f) (6.03 g, 81%), m.p. 101—102 °C (lit.,[26a] 102—104 °C); $\nu_{max.}$ (Nujol) 3 040, 1 670, 1 590, 1 500, 780, and 710 $cm^{-1}$; δ($CCl_4$) 1.9 (3 H, s, MeCO), 3.3 (3 H, s, MeN), and 7.1—7.5 (5 H, m, ArH); *N*-ethylacetanilide (8g) (7.91 g, 97%), m.p. 53—54 °C) (lit.,[26b] 55 °C); $\nu_{max.}$ (Nujol) 3 060, 1 670, 1 610, 1 510, 1 480, 780 and 730 $cm^{-1}$; δ($CCl_4$) 1.1 (3 H, t, *J* 7 Hz, *Me*$CH_2$), 1.7 (3 H, s, MeCO), 3.7 (2 H, q, *J* 7 Hz, $CH_2N$), and 7.0—7.5 (5 H, m, ArH); *N*-benzylacetanilide (8h) (10.80 g, 96%), m.p. 56—58 °C (lit.,[26c] 58 °C); $\nu_{max.}$ (Nujol) 3 060, 3 040, 1 660, 1 590, 1 500, 730, and 710 $cm^{-1}$; δ($CCl_4$) 1.8 (3 H, s, MeCO), 4.8 (2 H, s, Ph$CH_2$N), and 6.9—7.3 (10 H, m, ArH).

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