



**Table 1.** Preparation <sup>a</sup> of the imines (6)

Product	R <sup>1</sup>	R <sup>2</sup>	Reaction time (h)	Yield (%) <sup>b</sup>
(6a)	Ph	Pr	14	78
(6b)	Ph	Bu	14	67
(6c)	Ph	n-C <sub>6</sub> H <sub>13</sub>	14	78
(6d)	Ph	c-C <sub>6</sub> H <sub>11</sub>	72	76
(6e) <sup>c</sup>	Ph	PhCH <sub>2</sub>	72	40
(6f)	n-C <sub>6</sub> H <sub>13</sub>	Pr	14	50
(6g)	n-C <sub>6</sub> H <sub>13</sub>	c-C <sub>6</sub> H <sub>11</sub>	72	75

<sup>a</sup> All reactions were carried out at room temperature, unless otherwise specified. <sup>b</sup> Based on alkyne. <sup>c</sup> Reaction temperature, 55 °C.

**Table 2.** Preparation <sup>a</sup> of the enamines (7) and (8)

Product	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Reaction time (h)	Yield (%) <sup>b</sup>
(7a)	Ph	Bu	Bu	—	72	71
(7b)	Ph	PhCH <sub>2</sub>	Me	—	14	43
(7c)	Ph	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	—	—	14	50
(8) <sup>c</sup>	—	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	n-C <sub>3</sub> H <sub>7</sub>	—	5	59

<sup>a</sup> All reactions were carried out in dioxan under reflux. <sup>b</sup> Based on alkyne. <sup>c</sup> 2 mmol of K<sub>2</sub>CO<sub>3</sub>/mmol HgCl<sub>2</sub> were added to the reaction mixture.

The catalytic role of the mercury(II) acetate in these processes is shown when the reaction mixture is evaporated without reduction and the gummy residue extracted with hexane; for instance, a 44% yield of (6a) and a 45% yield of (6b) were obtained in this manner after hexane elimination. Alternatively, in a test experiment, an additional 20 mmol of phenylacetylene and n-butylamine were added to the reaction mixture after the usual period for aminomercuriation, and the reaction continued for a further 24 h prior to reduction; under these conditions, 37 mmol of (6b) were obtained.

The same method, but excluding the reduction step, is suitable for the preparation in moderate yields of the corresponding enamines (7) and (8) from secondary aliphatic amines. If the reaction mixture is reduced, extremely low yields of the enamines (7) and (8) result; then, saturated tertiary amines are generated, probably by NaBH<sub>4</sub> reduction of the enamines under these reaction conditions.<sup>14</sup>

Nevertheless, the most suitable procedure for the synthesis of enamines is the reaction at *ca.* 100 °C of mercury(II) chloride (5 mmol) with a terminal alkyne (30 mmol) and a secondary aliphatic amine (150 mmol) in dioxan solution.\* Elemental mercury (*ca.* 90%) is recovered, probably due to oxidative side processes. For this reason, the reduction step becomes unnecessary in this synthesis (Scheme 3; see Table 2). † At temperatures below *ca.* 100 °C the process only affords the corresponding dialkynylmercury (5).

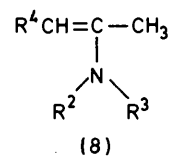
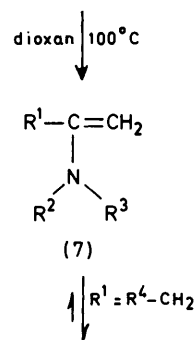
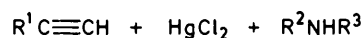
From the above results it can be inferred that the aminomercuriation only proceeds (a) if dialkynylmercury (5) is not generated ‡ or (b) once it is formed, if the second equilibrium in Scheme 1 is displaced to the left-hand side. To ascertain the second hypothesis, the following experiments were performed.

(1) Bis(phenylethynyl)mercury (5a) was recovered un-

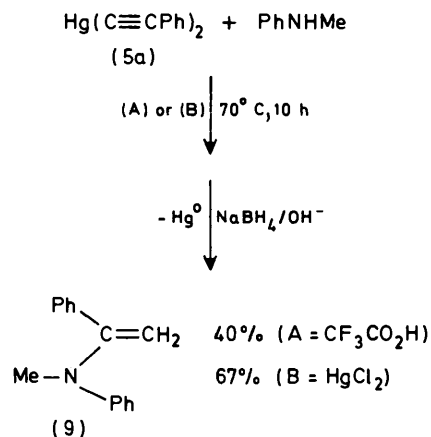
\* Primary aliphatic amines also lead to imines under these conditions. Yields are similar to those of Table 1.

† For the enamine (8) an excess of potassium carbonate was added to avoid the undesirable HCl-promoted self-condensation.<sup>15</sup>

‡ This probably occurs in the HgCl<sub>2</sub>-catalysed addition of aromatic amines to terminal acetylenes,<sup>9b</sup> the basicity of the former being insufficient for the complete displacement of the equilibria in Scheme 1 to the right-hand side.

**Scheme 3.**

changed after being heated (70 °C, 10 h) with a ten-fold excess of *N*-methylaniline. In contrast, when the same experiment was performed with addition of catalytic amounts of trifluoroacetic acid [(6a): CF<sub>3</sub>CO<sub>2</sub>H molar ratio = 5], *N*-methyl-*N*-(1-phenylvinyl)aniline<sup>8b</sup> (9) was isolated in 40% yield after NaBH<sub>4</sub> reduction (Scheme 4, A).

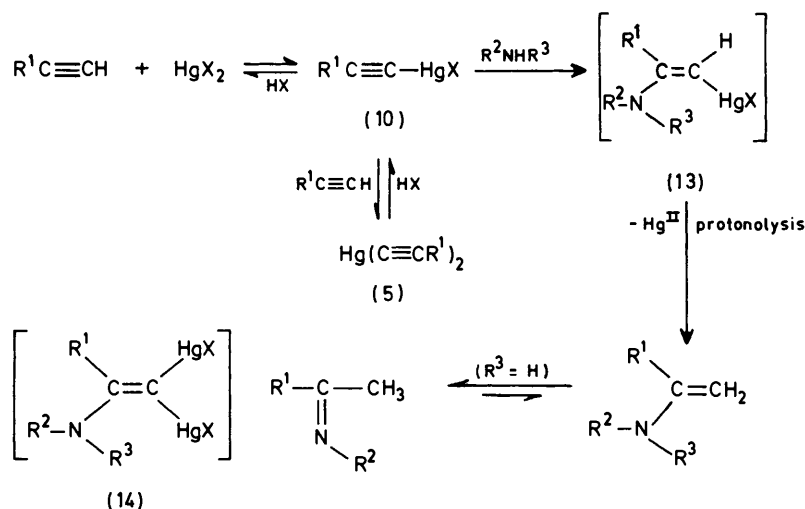
**Scheme 4.**

(2) When mercury(II) chloride was substituted for trifluoroacetic acid in the above experiment [(5a): HgCl<sub>2</sub> molar ratio = 2], the enamine (9) was obtained in 67% yield (Scheme 4, B).

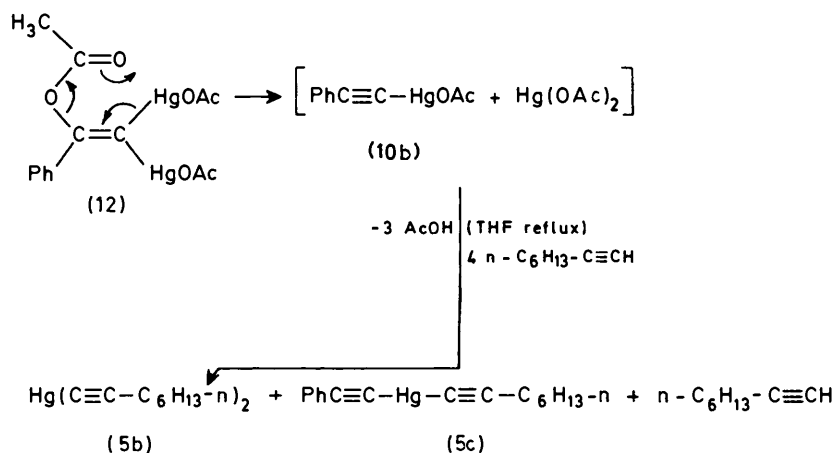
(3) Compound (5a) was allowed to react with mercury(II) acetate and a six-fold excess of n-butylamine for 10 h at room temperature [(5a): Hg(OAc)<sub>2</sub> molar ratio = 5], to give the imine (6b) in 25% yield after NaBH<sub>4</sub> reduction (Scheme 5).

All three of these experiments strongly suggest to us that alkynylmercury chloride or acetate, R<sup>1</sup>C≡C-HgX (10), are the active species able to undergo the subsequent addition of amine. It is corroborated by the fact that (phenylethynyl)mercury chloride<sup>4</sup> (10a) reacts with a 20-fold excess of *N*-methylaniline (70 °C, 1 h) or aniline (room temperature, 6 h), that is, under the conditions in which the addition of aromatic amines to terminal acetylenes is catalysed by mercury(II)





Scheme 8.



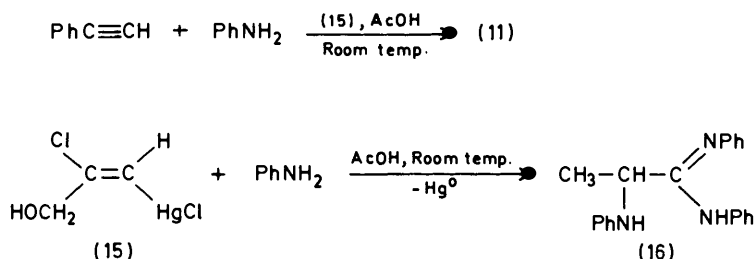
Scheme 9.

amounts of (15) promote the addition of aniline to phenylacetylene (3 : 100 : 20 molar ratio; 70 °C, 15 h) to afford the imine (11) in 78% yield. In the same way, the attack of a seven-fold excess of aniline to compound (15) in the presence of trace amounts of acetic acid (room temperature, 15 h) leads to *N,N,N'*-triphenyl-2-aminopropionamide<sup>8c</sup> (16) (Scheme 10). These results support the protonolysis of the vinylmercurial (15), in which free mercury(II) is generated, and can be regarded as an indirect proof of the possible participation of aminovinylmercurials (13) in the course of the mercury(II) salt-promoted addition of amines to terminal acetylenes.

### Experimental

I.r. spectra were recorded on a Pye-Unicam SP-1000 instrument, n.m.r. spectra on a Varian FT-80A spectrometer, and elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer.

*Preparation of the Imines (6).*—Mercury(II) acetate (4.76 g, 15 mmol) was added to a solution of phenylacetylene or oct-1-yne (20 mmol) and a primary aliphatic amine (60 mmol) in dichloromethane (50 ml), at room temperature [(6e) requires 55 °C]. After the mixture had been stirred overnight [(6d, e, g) require 72 h], a solution of sodium borohydride (0.57 g,



Scheme 10.

15 mmol) in 1.75M-aqueous potassium hydroxide (40 ml) was added and the mixture stirred for an additional 1 h. Metallic mercury (ca. 100%) was filtered off and the liquid phase extracted with dichloromethane. The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated and the volatile components were evaporated under reduced pressure (0.1 Torr); the residue was then distilled under reduced pressure to yield the imines (6).

The following compounds were obtained in this way: *N*-(1-phenylethylidene)propylamine (6a); <sup>18a</sup> *N*-(1-phenylethylidene)butylamine (6b); <sup>18a</sup> *N*-(1-phenylethylidene)hexylamine (6c); <sup>18b</sup> *N*-(1-phenylethylidene)cyclohexylamine (6d); <sup>18c</sup> *N*-(1-phenylethylidene)benzylamine (6e); <sup>18d</sup> *N*-(1-methylheptylidene)propylamine (6f) (1.69 g, 50%), b.p. 43–45 °C at 0.1 Torr;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 0.85 (m, 6 H,  $\text{CH}_2\text{CH}_2$ ), 1.15–1.6 (m, 10 H,  $\text{C}[\text{CH}_2]_2\text{C}$ ), 1.7 and 1.95 (2 s, \* 3 H,  $\text{CH}_2\text{C}=\text{N}$ ), 2.2 and 2.4 (2 t, \* 2 H,  $\text{CH}_2\text{C}=\text{N}$ ), and 3.15 (t, 2 H,  $\text{CH}_2\text{N}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 167.5 (s) (Found: C, 77.9; H, 13.8; N, 8.15.  $\text{C}_{11}\text{H}_{23}\text{N}$  requires C, 78.05; H, 13.7; N, 8.25%); *N*-(1-methylheptylidene)cyclohexylamine (6g).<sup>18e</sup>

**Preparation of Enamines (7).**—Mercury(II) chloride (1.36 g, 5 mmol) was added to a solution of phenylacetylene (3.27 ml, 30 mmol) and a secondary aliphatic amine (150 mmol) in dioxan (30 ml). After the mixture had been heated at ca. 100 °C and stirred overnight [(7a) requires 72 h], the precipitated metallic mercury (ca. 90%) was filtered off, the liquid phase treated with 1M-aqueous potassium hydroxide (15 ml) and extracted with ether. The ethereal layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated and the volatile components evaporated under reduced pressure (0.1 Torr); the residue was distilled (0.05 or 0.001 Torr) to yield the enamines (7).

The following compounds were obtained in this way: *N,N*-dibutyl-(1-phenylvinyl)amine <sup>19a</sup> (7a),  $\delta_{\text{H}}$  ( $\text{CCl}_4$ ) 0.8 (m, 8 H,  $\text{C}[\text{CH}_2]_2\text{C}$ ), 2.85 (t, 4 H,  $\text{CH}_2\text{-N}$ ), 3.95 and 4.05 (2 s, 2 H,  $\text{H}_2\text{C}=\text{C}$ ), and 7.1–7.5 (m, 5 H, ArH); *N*-benzyl-*N*-methyl-(1-phenylvinyl)amine (7b), b.p. 95–97 °C at 0.001 Torr;  $\delta_{\text{H}}$  ( $\text{CCl}_4$ ) 2.45 (s, 3 H,  $\text{CH}_3$ ), 3.85 (s, 2 H,  $\text{CH}_2\text{N}$ ), 4.0 and 4.1 (2 s, 2 H,  $\text{H}_2\text{C}=\text{C}$ ), and 7.0–7.5 (m, 10 H, ArH) (Found: C, 86.2; H, 7.7; N, 6.25.  $\text{C}_{16}\text{H}_{17}\text{N}$  requires C, 86.05; H, 7.65; N, 6.25%); *N*-(1-phenylvinyl)morpholine <sup>19b</sup> (7c).

**Preparation of the Enamine (8).**—Mercury(II) chloride (1.36 g, 5 mmol) and potassium carbonate (1.38 g, 10 mmol) was added to a stirred solution of oct-1-yne (4.4 ml, 30 mmol) and morpholine (9.0 ml, 150 mmol) in dioxan (50 ml) at ca. 100 °C. Metallic mercury (ca. 90%) and the excess of potassium carbonate were filtered off after 5 h. The liquid phase was concentrated, the volatile components evaporated under reduced pressure (0.1 Torr) and the residue distilled (0.001 Torr) to yield (8) as a ca. 7 : 3 isomeric mixture <sup>19c</sup> of *N*-(1-methylhept-1-enyl)morpholine and *N*-(1-hexylvinyl)morpholine.

**Further Characterization of Phenylethynylmercury Chloride <sup>4</sup>** (10a).—Sodium borohydride (0.30 g, 8 mmol) in 3M-aqueous potassium hydroxide (20 ml) was added to a stirred solution of (10a) (2.69 g, 8 mmol) in tetrahydrofuran (20 ml). After 30 min, metallic mercury (>95%) was filtered off and the liquid phase extracted with ether. The ethereal layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated (15 and 0.1 Torr, successively) to yield phenylacetylene (0.50 g, 61%). In addition, a solution of (10a) [ $\delta_{\text{H}}$ [( $\text{CD}_3$ )<sub>2</sub>SO] 7.35br (s, ArH)] in ( $\text{CD}_3$ )<sub>2</sub>SO was treated with water (one drop) in a n.m.r. tube, heated (50 °C, 24 h), and its <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra recorded. Under these conditions (10a) was almost quantitatively converted into acetophenone.

**Preparation of 2,2-Bis(acetoxymercurio)-1-phenylvinyl Acetate (12).**—Mercury(II) acetate (28.66 g, 90 mmol) was added to a solution of phenylacetylene (5.45 ml, 50 mmol) in chloroform (200 ml) at room temperature. After the mixture had been stirred overnight, chloroform was evaporated (0.1 Torr), and the residue treated with ether, cooled (–20 °C), and filtered, to yield (12) as a white solid (30.4 g, 99.4%), m.p. 200–205 °C (decomp.);  $\nu_{\text{max}}$  (Nujol) 1 750, 1 635, 1 585, 1 300, 1 190, 1 035, 1 020, 775, 760, 705, and 690  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [( $\text{CD}_3$ )<sub>2</sub>SO] 1.9 (s, 6 H,  $\text{CH}_3\text{CO}_2\text{Hg}$ ), 2.15 (s, 3 H,  $\text{CH}_3\text{CO}_2\text{C}$ ), 7.2–7.45 (m, 3 H, ArH), and 7.6–7.85 (m, 2 H, ArH);  $\delta_{\text{C}}$  [( $\text{CD}_3$ )<sub>2</sub>SO] 22.1 (q), 24.1 (q), 127.3, 129.0, 129.4, 129.7, 139.5, 157.6, 170.5 (s), and 175.7 (s) (Found: C, 24.9; H, 2.0.  $\text{C}_{14}\text{H}_{14}\text{Hg}_2\text{O}_6$  requires C, 24.75; H, 2.1%).

A solution of acetoxyvinylmercurial (12) (6.79 g, 10 mmol) in tetrahydrofuran (30 ml) was treated with sodium borohydride (1.0 g, 26 mmol) dissolved in 2M-aqueous potassium hydroxide (50 ml), and stirred for 30 min. Metallic mercury (3.89 g, 97%) was filtered off and the liquid phase extracted with ether; the extract was dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated (15 Torr) to yield a ca. 63 : 37 mixture (0.99 g, 87%) of acetophenone and phenylacetylene.

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\* Two signals are observed for these protons because of the presence of *E*- and *Z*-isomers.