Alkynylmercury Chloride or Acetate as Intermediates in the Mercury(II) Salt-promoted Addition of Aliphatic and Aromatic Amines to Terminal Acetylenes

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Arylaminomercuriation of terminal acetylenes has been carried out with aliphatic amines to yield amines and enamines. Phenylethynylmercury chloride is shown to be an intermediate in the mercury(II) salt-promoted addition of aliphatic and aromatic amines to terminal alkynes.

The solvomercuriation-demercuriation of olefins is an efficient method for the addition of protic substrates to alkenes which, it has been established, takes place by an ionic mechanism with formation of the cyclic mercurinium cation¹ (1). In contrast,² the mechanistic features of the solvomercuriation-demercuriation of acetylenes, known for a century and even used for industrial purposes, are virtually unexplored. For steric reasons, it has been suggested that the mercurinium ions ³ (2; R = Ph, R' = alkyl), but at least three different alternative ⁴ intermediate species containing C-Hg σ -bonds, namely mercurinium cations ⁵ (2; R' = H), mercuriated vinyl cations ⁶ (3), and alkynylmercury(II) salts ¹ (4) have been proposed on the basis of theoretical considerations. Alkynemercury(II) salt π -complexes have also been proposed.⁷

In the aminomercuriation of terminal acetylenes, only aromatic amines have been added with some generality; ⁸ for aliphatic amines only the synthesis of a tertiary amine and the preparation in low yield of an enamine by the addition of pyrrolidine or aziridine, respectively, to oct-1-yne, in the presence of stoicheiometric amounts of mercury(π) salts, have been reported.⁹

On these grounds, we were interested in studying the mechanism of the aminomercuriation of terminal acetylenes and in extending the scope of alkylaminomercuriation reactions.

The aminomercuriation of olefins with aliphatic amines requires more extreme reaction conditions ¹⁰ than the corresponding reactions with aromatic amines; this is a result of the former's enhanced ability to form very stable aminemercury(II) salts complexes,¹¹ unless the olefin bears a function capable of co-ordinating the mercury(II) salt.¹² However, in the reaction of terminal acetylenes with mercury(II) salts and an excess of aliphatic amine at temperatures below *ca.* 80 °C, the greatest difficulty seems to be the fast formation of dialkynylmercury (5). In fact, it is known that n-butylamine ¹³ and also tertiary aromatic amines ⁴ provide a medium of appropriate basicity to allow the ready formation of dialkynylmercury (5) from terminal alkynes and mercury(II) salts. This process can be explained by the following two successive equilibria ⁴ (Scheme 1).

$$R^{1}C \equiv CH + HgX_{2} \implies R^{1}C \equiv C-HgX + HX$$

$$R^{1}C \equiv C-HgX + R^{1}C \equiv CH \implies Hg(C \equiv CR^{1})_{2} + HX$$
(5) ·
Scheme 1.

We have found that the alkyne: mercury(n) salt molar ratio plays an important role in the course of the process. So, when the value of this ratio is less than 2, imines (6) are obtained



after sodium borohydride reduction from mercury(II) acetate at room temperature. In contrast, the exclusive formation of dialkynylmercury (5) is observed when this ratio has values greater than 2 (Scheme 2).

$$R^{1}C \equiv CH + Hg^{0}$$

$$\frac{1}{NaBH_{4}/OH^{-}}$$

$$Hg(C \equiv C - R^{1})_{2}$$
(5)
$$m/n \geq 2 \qquad Room temp.$$

$$CH_{2}Cl_{2} + 3mR^{2}NH_{2}$$

$$m/n \leq 2 \qquad Room temp.$$

$$CH_{2}Cl_{2}$$

$$-Hg^{0} \qquad NaBH_{4}/OH^{-}$$

$$R^{1} - C - CH_{3}$$

$$\| N \\ R^{2}$$
(6)
Scheme 2.

m

Reaction conditions and yields for the imines (6), for typical runs using mercury(II) acetate (15 mmol), terminal alkynes (20 mmol), and primary aliphatic amines (60 mmol), are summarized in Table 1.

Table 1. Preparation " of the imines (6)

Product	R ¹	R²	Reaction time (h)	Yield (%) ^b
(6a)	Ph	Pr	14	78
(6b)	Ph	Bu	14	67
(6c)	Ph	$n-C_{6}H_{13}$	14	78
(6d)	Ph	c-C ₆ H ₁₁	72	76
(6e) ^c	Ph	PhCH ₂	72	40
(6f)	n-C ₆ H ₁₃	Pr	14	50
(6g)	n-C ₆ H ₁₃	c-C ₆ H ₁₁	72	75

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

Table 2. Preparation " of the enamines (7) and (8)

Product	R¹	R²	R ³	R⁴	Reaction time (h)	Yield (%) ^b
(7a)	Ph	Bu	Bu		72	71
(7b)	Ph	PhCH₂	Me		14	43
(7c)	Ph	(CH ₂) ₂ -0)-(CH ₂) ₂		14	50
(8) ^c		(CH ₂) ₂ -0	O−(CH ₂) ₂	n-C₅H₁1	5	59

^e All reactions were carried out in dioxan under reflux. ^b Based on alkyne. ^c 2 Mmol of K_2CO_3 /mmol HgCl₂ 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 NaBH₄ reduction of the enamines under these reaction conditions.¹⁴

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 \ddagger 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-

 $R^{1}C \equiv CH + HgCl_{2} + R^{2}NHR^{3}$ dioxan 100°C



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): CF₃CO₂H molar ratio = 5], *N*-methyl-*N*-(1-phenylvinyl)aniline ^{8b} (9) was isolated in 40% yield after NaBH₄ reduction (Scheme 4, A).



Scheme 4.

(2) When mercury(II) chloride was substituted for trifluoroacetic acid in the above experiment $[(5a) : HgCl_2 molar ratio = 2]$, 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)₂ molar ratio = 5], to give the imine (6b) in 25% yield after NaBH₄ reduction (Scheme 5).

All three of these experiments strongly suggest to us that alkynylmercury chloride or acetate, $R^1C\equiv C-HgX$ (10), are the active species able to undergo the subsequent addition of amine. It is corroborated by the fact that (phenylethynyl)-mercury chloride ⁴ (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)

^{*} 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.¹⁵

[‡] This probably occurs in the HgCl₂-catalysed addition of aromatic amines to terminal acetylenes,⁸⁶ the basicity of the former being insufficient for the complete displacement of the equilibria in Scheme 1 to the right-hand side.



chloride.^{8b} After NaBH₄ reduction,* the enamine (9) and 1-

phenylethylideneaniline^{8a} (11) respectively were isolated in

(room temperature, 14 h), followed by reduction, does not

lead to the corresponding imine (6c), which, in contrast, is

The treatment of (10a) with a 15-fold excess of n-hexylamine

high yield (Scheme 6).

 $Hg(C \equiv CPh)_{2} + Hg(OAc)_{2}$ $(5a) \qquad \downarrow$ $[PhC \equiv C - HgOAc]$ $(10b) \qquad \qquad \downarrow$ $Hg(OAc)_{2}$ $AcO \qquad C = C \qquad HgOAc$ $(12) \qquad Scheme 7.$

Reactions summarized in Scheme 8 represent, at least, one of the operative reaction paths for the mercury(II) saltpromoted addition of aromatic and aliphatic amines to terminal acetylenes. The intermediacy of (13) is strongly suggested by the results contained in Scheme 6, but the hypothetical participation of an aminovinyldimercurial (14), analogous to the acetoxyvinyldimercurial (12) cannot be discounted.

Since until now we have failed to isolate the intermediate (13), probably because of its instability in a medium containing different types of acidic hydrogen atom ($R^1C\equiv CH$, R^2NHR^3 , and HX and/or ammonium salt are present), we have studied





obtained almost quantitatively in tetrahydrofuran under reflux (Scheme 6).

Comparison of these results with those in the direct reaction of terminal alkynes, mercury(II) chloride, and aliphatic amines at reaction temperatures of *ca.* 100 °C leads to the conclusion that in the latter case the formation of the corresponding dialkynylmercury (5) is the fast step. Compounds (5) will be dissociated only at temperatures above *ca.* 100 °C, probably leading to species type (10); this does not exclude the alternative intermediacy of other species such as the alkynylmercury(II) cation R¹C=C-Hg⁺.

Equimolar amounts of bis(phenylethynyl)mercury (5a) and mercury(II) acetate were allowed to react in an attempt to trap the supposed intermediate in the alkylaminomercuriation of phenylacetylene at room temperature, (phenylethynyl)mercury acetate (10b). 2,2-Bis(acetoxymercurio)-1-phenylvinyl acetate (12) however was isolated besides unchanged (5a). Compound (12) can be rationalized by addition of mercury(II) acetate to the expected intermediate (10b) (Scheme 7). For this reason, no direct proof of the intermediacy of (10b) was found. the behaviour of some vinylmercurials under similar conditions.

First of all, acetoxyvinyldimercurial (12) itself promotes the addition of a five-fold excess of N-methylaniline to phenylacetylene [PhC=CH: (12) molar ratio = 7; 60 °C, 3 h], to afford the enamine (9) in 60% yield. In the first instance, this might establish the ability of (12) to undergo protonolysis under these conditions. However, in a separate experiment we showed that the protonolysis does not take place. So, when the acetoxyvinyldimercurial (12) was treated with a four-fold excess of oct-1-yne (THF reflux, 15 min), a 1:1:1 mixture of dioct-1-ynylmercury (5b), oct-1-ynyl(phenylethynyl)mercury (5c) and oct-1-yne was obtained. This result is readily rationalized if we assume that compound (12) undergoes a $cis-\beta$ -elimination through a six-membered intermediate, a reaction favoured by the presence of oct-1-yne, since it can capture the mercury(II) acetate eliminated (Scheme 9). Doubtless, (phenylethynyl)mercury acetate (10b), which is generated in the $cis-\beta$ -elimination, is the active intermediate in the addition of N-methylaniline to phenylacetylene (see Scheme 8).

On the other hand, (*E*)-2-chloro-3-hydroxyprop-1-enylmercury chloride ¹⁷ (15), a vinylmercurial the structure of which closely resembles that of compound (13), does not undergo β -elimination; in fact it is recovered unchanged when treated with terminal acetylenes (70 °C, 8 h). Catalytic

^{*} The reduction step is introduced either to break the enamine (9)-HgCl₂ complex ¹⁶ or to avoid the HgCl₂-promoted oxidation of the imine (11) ⁸⁶ when heated during its isolation from the crude reactjon mixture by distillation under reduced pressure.



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-aminopropionamidine ^{8c} (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,

$$PhC \equiv CH + PhNH_{2} \xrightarrow{(13), ACOH} (11)$$

$$CI = C + PhNH_{2} \xrightarrow{AcOH, Room temp.} (11)$$

$$HOCH_{2} + PhNH_{2} \xrightarrow{AcOH, Room temp.} CH_{3} - CH - C + C + PhNH + PhNH + PhNH + PhNH + (15) (16)$$

(15) A-04

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 (Na₂SO₄) 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); ^{18a} *N*-(1-phenylethylidene)hexylamine (6c); ^{18b} *N*-(1-phenylethylidene)cyclohexylamine (6d); ^{18c} *N*-(1-phenylethylidene)benzylamine (6e); ^{18d} N-(1-*methylheptylidene)propylamine* (6f) (1.69 g, 50%), b.p. 43—45 °C at 0.1 Torr; $\delta_{\rm H}$ (CDCl₃) 0.85 (m, 6 H, CH₃CH₂), 1.15—1.6 (m, 10 H, C[CH₂]_nC), 1.7 and 1.95 (2 s,* 3 H, CH₃C=N), 2.2 and 2.4 (2 t,* 2 H, CH₂C=N), and 3.15 (t, 2 H, CH₂N); $\delta_{\rm C}$ (CDCl₃) 167.5 (s) (Found: C, 77.9; H, 13.8; N, 8.15. C₁₁H₂₃N requires C, 78.05; H, 13.7; N, 8.25%); *N*-(1-methylheptylidene)cyclohexylamine (6g).^{18e}

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 (Na₂SO₄) 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 ^{19a} (7a), $\delta_{\rm H}$ (CCl₄) 0.8 (m, 8 H, C[CH₂]₂C), 2.85 (t, 4 H, CH₂–N), 3.95 and 4.05 (2 s, 2 H, H₂C=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; $\delta_{\rm H}$ (CCl₄) 2.45 (s, 3 H, CH₃), 3.85 (s, 2 H, CH₂N), 4.0 and 4.1 (2 s, 2 H, H₂C=C), and 7.0–7.5 (m, 10 H, ArH) (Found: C, 86.2; H, 7.7; N, 6.25. C₁₆H₁₇N requires C, 86.05; H, 7.65; N, 6.25%); *N*-(1-phenylvinyl)morpholine ^{19b} (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 ^{19c} of *N*-(1-methylhept-1-enyl)morpholine and *N*-(1-hexylvinyl)morpholine.

Further Characterization of Phenylethynylmercury Chloride ⁴ (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 (Na₂SO₄) and concentrated (15 and 0.1 Torr, successively) to yield phenylacetylene (0.50 g, 61%). In addition, a solution of (10a) { $\delta_{H}[(CD_3)_2SO]$ 7.35br (s, ArH)} in (CD₃)₂SO was treated with water (one drop) in a n.m.r. tube, heated (50 °C, 24 h), and its ¹H and ¹³C n.m.r. spectra recorded. Under these conditions (10a) was almost quantitatively converted into acetophenone.

 Two signals are observed for these protons because of the presence of E- and Z-isomers. Preparation of 2,2-Bis(acetoxymercurio)-1-phenylvinyl Acetate (12).—Mercury(11) 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.); v_{max} . (Nujol) 1 750, 1 635, 1 585, 1 300, 1 190, 1 035, 1 020, 775, 760, 705, and 690 cm⁻¹; $\delta_{\rm H}$ [(CD₃)₂SO] 1.9 (s, 6 H, CH₃CO₂Hg), 2.15 (s, 3 H, CH₃CO₂C), 7.2—7.45 (m, 3 H, ArH), and 7.6—7.85 (m, 2 H, ArH); $\delta_{\rm C}$ [(CD₃)₂SO] 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. C₁₄H₁₄Hg₂O₆ requires C, 24.75; H, 2.1%).

A solution of acetoxyvinyldimercurial (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 (Na₂SO₄), and concentrated (15 Torr) to yield a *ca.* 63:37 mixture (0.99 g, 87%) of acetophenone and phenylacetylene.

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