Regio- and Stereo-selectivity of Acetoxymercuration of Acetylenes

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Acetoxymercuration of alkylphenylacetylenes (PhC≡CR; R = Me, Et, Pr^n, or Bu^n) (1) in acetic acid at 20—60 °C proceeds completely in a *trans*-fashion to afford a regioisomeric mixture of two vinylmercury(II) compounds, Ph(OAc)C=C(HgCl)R (2) and Ph(HgCl)C=C(OAc)R (3), the extent of attack of Hg at the carbon α to alkyl group to form (2) being increased upon increasing the carbon chain length of the alkyl group [(2)/(3) = 3.0—16.5]. In the case of R = Pr^i (2) is the sole product, while no acetoxymercuration occurs when R = Bu^t. A bridged mercurinium ion intermediate in which phenyl and alkyl groups are bent toward the attacking side of acetate anion is proposed for explaining a marked dependence of the isomer ratio (2) : (3) on the kind of alkyl groups. Similar treatment of diphenylacetylene at 20—95 °C gives only the *cis*-adduct as reported previously, while that of diethyl-acetylene affords the *trans*-adduct and a mixture of *trans*- and *cis*-adduct at 20 °C and at 65 °C, respectively. The NaBH$_4$ reduction of (2; R = Me) in neutral condition produces a mixture of (Z)- and (E)-1-acetoxy-1-phenyl-propene (*ca.* 3—5 : 1) in contrast to the reduction of thallium analogue of (2) which gives only the Z-isomer.

OXIDATIONS and/or hydrations of acetylenes by metal ions such as mercury(II),[1] thallium(III),[2,3] lead(IV),[4] and gold(III)[5] are known, especially the mercury(II)-catalysed hydration of acetylene to acetaldehyde, which was an important industrial process.[1,5] These reactions are generally considered to proceed *via* oxymetallation, and in fact, the intermediate vinylmetal compounds have been isolated in the former two cases. Although the stereochemistry of oxythallation of acetylenes has been studied recently,[6,7] that of oxymercuration has not yet been thoroughly studied.[8] Thus, acetoxymercur-ation of diphenylacetylene with mercury(II) acetate gave completely the *cis*-adduct,[9] while dimethylacetylene afforded the *trans*- and *cis*-adducts, the ratio depending on the temperature.[8,10] Furthermore, no data are yet available on the regiospecificity of oxymercuration of asymmetrical acetylenes. In order to study both the stereo- and regio-specificity of oxymercuration of

acetylenes and to compare the results with those of oxythallation, we have carried out acetoxymercuration of various acetylenes, especially alkylphenylacetylenes. We now report the results in detail and discuss the mechanistic difference between both oxymetallations.[11,12]

RESULTS AND DISCUSSION

Reaction of the alkylphenylacetylene (1; R = Me, Et, Pr^n, or Bu^n) with mercury(II) acetate [(1) : Hg-(OAc)$_2$ = 2 : 1] in acetic acid at 55—60 °C for 5 h, followed by treatment of the resulting mixture with aqueous potassium chloride, produced an isomeric mixture of vinylmercurials, (2) and (3), in 44—96% yield. Under these conditions formation of hydration products such as ketones and esters was negligible. Although the yields of (2) + (3) were somewhat lower for (1) when R = Pr^n and Bu^n, the reactions were incomplete in these cases and the unchanged mercury(II) acetate could be recovered. Here, the yield increased

TABLE 1

Acetoxymercuration of acetylenes

Acetylene	Temp. (°C)	Time (h)	Yield ^{a} of (2) + (3) or (7) + (8) (%)	Isomer ratio ^{b} (2) : (3)	M.p. (d) (°C)	M.p. (d) of (2) and/or (3) (°C)	Analysis (%) Found (reqd.) C	H	Isomer ratio,^{c} of (9) : (10)
(1; R = Me)	55—60	5	96	3.0 : 1	104—108	(2; R = Me) 120	32.1 (32.1)	2.6 (2.6)	2.5—2.8 : 1
(1; R = Me)	55—60	1	81	3.0 : 1		(3; R = Me) 155—157			
(1; R = Me)	20	5	76	3.0 : 1					
(1; R = Et)	55—60	5	88	5.0 : 1	95—98	(2; R = Et) 99—100	33.7 (33.9)	3.05 (3.1)	1.8 : 1
(1; R = Pr^n)	55—60	5	74	11.0 : 1	100—104	(2; R = Pr^n) 103—104	35.5 (35.5)	3.5 (3.4)	1.9 : 1
(1; R = Bu^n)	55—60	5	44	16.5 : 1	94—97	(2; R = Bu^n) 83—84	37.0 (37.1)	3.7 (3.8)	1.9 : 1
(1; R = Bu^n)	55—60	7	55	16.5 : 1					
(1; R = Pr^i)	55—60	5	52	only (2)	127—129		35.4 (35.5)	3.4 (3.4)	
(6; R = Ph)	95	2	80	only (7)	137—142 ^{d}				
(6; R = Ph)	60	5	63	only (7)					
(6; R = Ph)	20	20	28	only (7)					
(6; R = Et)	65	5	44 ^{e}	(8)/(7) = 3.0	56—60		25.05 (25.5)	3.4 (3.5)	
(6; R = Et)	20	1	80	only (8)	66—68		25.4 (25.5)	3.4 (3.5)	

^{a} Based on Hg(OAc)$_2$ consumed. ^{b} Determined by n.m.r. spectroscopy by comparison of the intensity of the acetoxymethyl protons. ^{c} Obtained in the reaction at 60—65 °C for 1—3 h.[6] ^{d} Lit.,[9] m.p. 141 °C. ^{e} Other product; hexan-3-one 10%. ^{f} Only the *trans*-adduct,[7] obtained in the reaction at 60 °C for 3 h.

with longer reaction times at the same temperature without affecting the ratio of (2) : (3). The reaction proceeded even at 20 °C for (1; R = Me), the isomer ratio of (2) : (3) remaining the same. In the case of R = Pr^i (2) is the sole product, while neither (2) nor (3) was formed from (1; R = Bu^t). Typical results are shown in Table 1. Treatment of terminal acetylenes such as

(5) have already been established [6] and these demetal-lations are known to proceed generally with retention of configuration,[6,13] this finding shows that both (2) and (3) have the structures shown; namely, acetoxymercuration of (1) occurred completely in a *trans*-fashion giving a regioisomeric vinylmercury(II) compounds. Coupling constants $J($^{199}Hg–Me$)$ of 190 Hz in (2) and of 26 Hz in
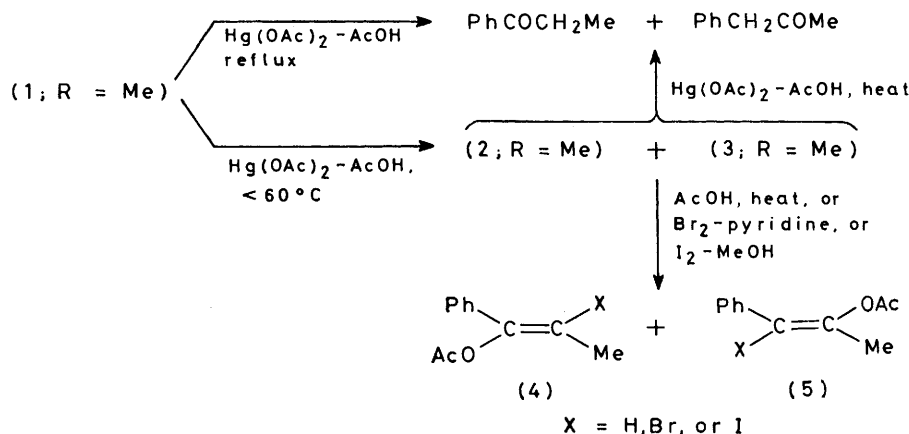
SCHEME

(1; R = H) and oct-1-yne at 20 °C in acetic acid or, more preferably, in chloroform, resulted in almost quantitative formation of bis(phenylethynyl)mercury and bis(oct-1-ynyl)mercury, respectively.

When a 3 : 1 mixture of (2; R = Me) and (3; R = Me) (the ratio being determined by n.m.r. spectra by comparing the intensity due to the acetoxy-methyl protons) was heated under reflux in acetic acid for 2 h, proto-demercuration occurred almost quantitatively to give a 3 : 1 mixture of the corresponding esters, (4; X = H) and (5; X = H).

(3) are also reasonable for each structure. The latter value is smaller than the observed value in (Z)-MeCH= C(R)HgCl [R = CH(OMe)Me or C(OMe)Me$_2$],[14] but both values agree quite well with the calculated ones for RHgX from $J($RHgX$) = 2.2 \times J($R$_2$Hg$)$ [15] using $J($^{199}Hg–Me$)$ of 88.2 and 12.0 Hz for (CH$_2$=CMe)$_2$Hg and (MeCH=CH)$_2$Hg (Hg and Me, *cis*-position); [16] 194 Hz and 26 Hz respectively. The i.r. spectra showed strong absorption bands at 1 740 ($\nu_{C=O}$) and 1 640 ($\nu_{C=C}$) cm^{-1} due to vinyl ester group.

As described above it has been reported by Nesmeyanov
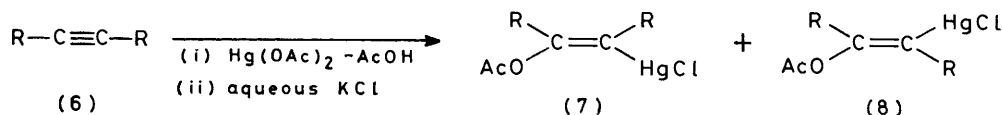
Similar treatment of the mixture in the presence of mercury(II) acetate gave a 3 : 1 mixture of propiophenone and benzyl methyl ketone in quantitative yield. The ketones consisting of the same isomer ratio were directly obtained by heating a mixture of (1; R = Me) and mercury(II) acetate in acetic acid at reflux temperature for 2 h, clearly showing that hydration of (1; R = Me)

et al.[9,10] that acetoxymercuration of diphenylacetylene (6; R = Ph) gave the *cis*-adduct, while that of dimethyl-acetylene (6; R = Me) afforded the *trans*- and *cis*-adducts, the isomer ratio depending on the reaction temperature. In order to know what the kinetically controlled products are in these cases, we carried out acetoxymercuration of (6; R = Ph) and diethylacetylene
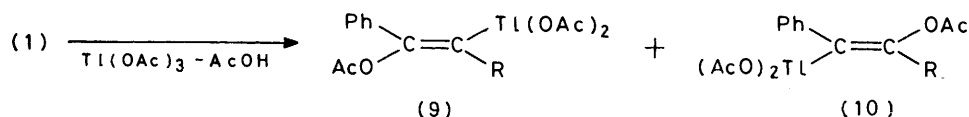
to give ketones proceeded through acetoxymercuration. Halogenodemercuration of (2; R = Me) with iodine in methanol or bromine in pyridine at 15—20 °C for 2—3 h gave the corresponding vinyl halides, (4) and (5) (X = I or Br), quantitatively. All these reactions are summarized in the Scheme. Since the structures of (4) and

(6; R = Et) under several conditions. As a result it was found that (6; R = Ph) gave only the same *cis*-adduct (7; R = Ph) even at lower temperatures (20 and 60 °C) as that obtained at 95 °C for 2 h by the reported method, although the reactions were slow. On the contrary, from (6; R = Et) a mixture of (7; R = Et) and (8;

R = Et) was obtained at 65 °C, while only (8; R = Et), the trans-isomer, was formed at 20 °C in a good yield. Although it seems that the trans-isomer may convert into the cis-isomer by heating, the attempt of isomerization of (8; R = Et) in acetic acid at 60 °C resulted in a decomposition to the corresponding ketone and esters, and no (7; R = Et) was detected in the reaction products. Typical results are shown in Table 1. All organomercury(II) compounds obtained in this report are white solids, stable in air, and soluble in polar solvents. The pure isomer could be obtained by recrystallization from ethanol or chloroform–n-hexane.

The results described above show that acetoxymercuration of a triple bond generally proceeds in a trans-fashion except in the case of diphenylacetylene. Contrary to acetoxythallation of (1), where the ratio of (9) : (10) [the thallium analogues of (2) and (3), respect-

attack of the anion are shown by the two arrows. Since back-side attack of acetate anion on this intermediate (trans-acetoxymercuration) should occur in the same plane containing phenyl, alkyl, and C=C groups, increased carbon chain length of the alkyl groups may increase the steric interaction even in the unbranched alkyl groups. Formation of only one isomer (2) when R = Pr^i can be easily understood by this assumption. The t-butyl group is sterically too large to be attacked by the acetate anion. Thus, the isomer ratio may be determined in the last step. In acetoxythallation, on the other hand, the step involving Tl(OAc)$_2^+$ attack on acetylenes seems to play an important role in determining the isomer ratio. It has been known that the intermediate in oxythallation of olefins has more carbocation character compared to that in oxymercuration.[17] Thus, acetoxythallation of acetylenes seems to proceed

$$(1) \xrightarrow[\text{AcOH}]{\text{Tl(OAc)}_3} \left[\begin{array}{c} \text{OAc}^- \\ \text{Ph—C=C—R} \\ \text{O} \quad \text{Tl—OAc} \\ \text{C—O} \\ \text{Me} \\ \text{(B)} \end{array} \right] + \left[\begin{array}{c} \text{OAc}^- \\ \text{Ph—C=C—R} \\ \text{AcO—Tl} \quad \text{O} \\ \text{O—C} \\ \text{Me} \\ \text{(C)} \end{array} \right] \longrightarrow (9) + (10)$$
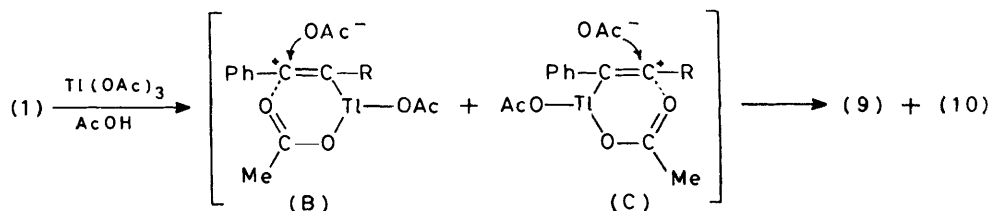
ively (Table 1)] is 2.8—1.9 : 1 for the n-alkyl groups R = Me—Bu^n,[6] the isomer ratio (2) : (3) increased markedly on increasing the carbon chain length in the alkyl group in acetoxymercuration. Although alkyl groups having unbranched chains would not normally be expected to produce such steric differences at the site of

$$\begin{array}{c} \text{HgZ} \\ \text{C=C} \\ \text{Ph} \quad \text{CH}_2 \\ \text{OAc}^- \quad \text{R} \\ \text{(A)} \end{array}$$
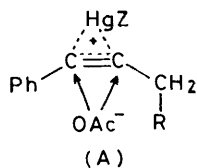
reaction, this finding may be explained by assuming a bridged mercurinium ion intermediate in which phenyl and alkyl groups are not on a straight line, but are bent toward the attacking side of acetate anion as shown in the structure (A), in which the two alternative sites of

via open vinyl cation intermediates like (B) and (C) rather than a bridged species. Here the cations may be with oxygen from an acetate of the thallium moiety, preventing the attack of acetate anion from the same side leading to the cis-adduct. Intermediate (B) is surely more stable than (C) because of the stabilization of the cationic centre by the phenyl group and this may result in a preferable formation of (9), as found experimentally. In this case the steric effect of linear alkyl groups is not important, because the attack of Tl(OAc)$_2^+$ occurs on linear acetylenes. The fact that no acetoxythallation occurred in the case of R = Pr^i may also support this supposition, because Tl(OAc)$_2^+$ is much larger than the Hg(OAc)$^+$ species in oxymercuration, and the Pr^i group is sterically large enough to prevent the initial step of the reaction.

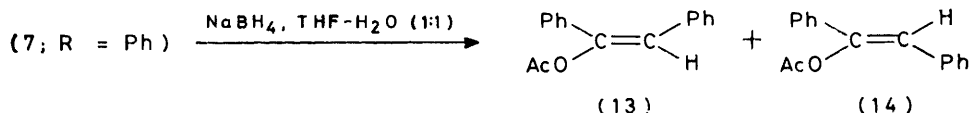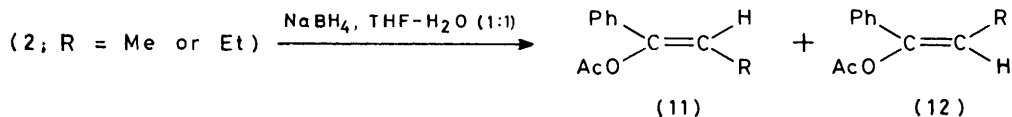It has been reported that solvo-mercuration of acetylenes with mercury(II) acetate and subsequent in

TABLE 2

The NaBH$_4$ or NaBD$_4$ reduction of acetoxymercurials

Acetoxymercurial (2 mmol)	NaBH$_4$ or NaBD$_4$ (1 mmol)	Solvent (20 ml)	Temp. (°C)	Time (h)	Products and yields (%) [a]						
					(11)	(11-D)	(12)	(12-D)	PhCOCH$_2$R	(1)	PhCH$_2$COMe
(2; R = Me) + (3; R = Me) [b]	NaBH$_4$	MeOH–1N NaOH	0	0.5	0		0		72	0	27
(2; R = Et)	NaBH$_4$	MeOH–1N NaOH	0	0.5	0		0		66 [c]	0	
(2; R = Me)	NaBH$_4$	H$_2$O–THF (1 : 1)	20	1	63		21		6	5	
(2; R = Me)	NaBH$_4$	H$_2$O–THF (1 : 1)	0	1	67		14		5	5	
(2; R = Et)	NaBH$_4$	H$_2$O–THF (1 : 1)	0	1	74		11		trace	6	
(7; R = Ph)	NaBH$_4$	H$_2$O–THF (1 : 1)	0	1	(13) 30		(14) 15				
(2; R = Me)	NaBD$_4$	H$_2$O–THF (1 : 1)	0	1	14	69	5	11	0	0	
(2; R = Me)	NaBH$_4$	MeOD	0	2	67	9	11 [d]		5	8	
(2; R = Me)	NaBH$_4$	THF–D$_2$O	0	1	71	12	17 [d]		0	0	

[a] Based on acetoxymercurial consumed; determined by g.l.c. [b] (2) : (3) = 2.7 : 1. [c] Other product, 1-phenylbutan-1-ol 5%. [d] The ratio (12) : (12-D) was not determined.
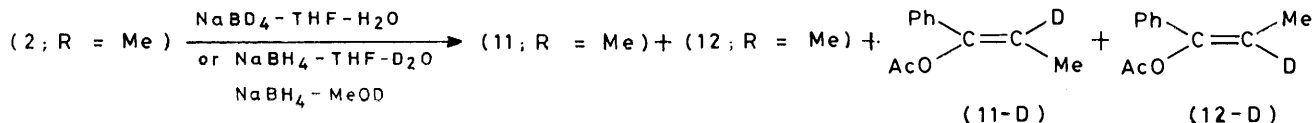
situ demercuration by $NaBH_4$ in alkaline conditions gave ketones,[18] enol ethers,[19] and amines.[19] When we treated a 2.7 : 1 mixture of (2; R = Me) and (3; R = Me) or (2; R = Et) with $NaBH_4$ in alkaline methanol

$$(2; R = Me \text{ or } Et) \xrightarrow{NaBH_4, THF-H_2O \ (1:1)}$$

Ph C=C H / AcO R (11)   +   Ph C=C R / AcO H (12)

$$(7; R = Ph) \xrightarrow{NaBH_4, THF-H_2O \ (1:1)}$$

Ph C=C Ph / AcO H (13)   +   Ph C=C H / AcO Ph (14)

(pH 12) at 0 °C for 1 h, a mixture of propiophenone (72%) and benzyl methyl ketone (27%), or butyrophenone (66%) was produced, respectively, together with a small amount

$$(2; R = Me) \xrightarrow[\text{or } NaBH_4-THF-D_2O]{NaBD_4-THF-H_2O} (11; R = Me) + (12; R = Me) +$$
$$NaBH_4 - MeOD$$

Ph C=C D / AcO Me (11-D)   +   Ph C=C Me / AcO D (12-D)

of the corresponding alcohol in the latter case. On the other hand, a similar treatment of (2; R = Me or Et) or (7; R = Ph) under neutral condition (pH 6—7) produced two stereoisomeric vinyl acetates in each case. The isomer ratios depended on the reaction conditions, but the protodemercuration product with retention of configuration was favoured in all cases. Typical results are shown in Table 2. The result is in contrast to that of the $NaBH_4$ reduction of the thallium(III) analogue, which proceeded with complete retention of configuration; for example, only (11) was obtained from (9), almost quantitatively.[6] From a mechanistic point of view the following results should also be noteworthy. (*i*) The reduction of (2; R = Me) with $NaBD_4$ in aqueous THF afforded (11; R = Me) and (12; R = Me) together with deuteriodemercuration products, (11-D) and (12-D), the ratios (11-D) : (11) and (12-D) : (12) being 4.9 and 2.3 : 1, respectively; (*ii*) the reaction of (2; R = Me) with $NaBH_4$ in McOD or THF–D_2O gave (11) and (12) as main products, but (11-D) and (12-D) were also formed. The results shown in Table 2 clearly show that *ca.* 10—20% of hydrogen for demercuration comes from solvent. Although the radical scheme through an alkylmercury hydride has been proposed for $NaBH_4$ reduction of alkylmercury(II) compounds in aqueous THF,[20,21] the mechanism for reduction of vinylmercury(II) compounds has not yet been studied. Whitesides and San Filippo [21] have pointed out very briefly that the reduction of vinylmercury(II) compounds may follow mechanisms different in at least certain major details from those involved in reduction of alkylmercury(II) halides. Our findings described here might show the possibility of the

partial presence of a vinyl anion intermediate which may pick up deuterium from solvent, because it seems to be difficult for a vinyl radical intermediate to pick up deuterium from solvent. Thus, both radical and ionic mechanisms may occur concurrently in the $NaBH_4$ reduction of vinylmercury(II) compounds, although more work is necessary to verify this.

EXPERIMENTAL

Alkylphenylacetylenes were prepared as previously described. Other organic and inorganic materials were commercial products and used without further purification. I.r. spectra (KBr disc and paraffin and hexachlorobutadiene mulls) were recorded with a Hitachi EPI-S2 spectrometer. ^1H n.m.r. spectra were taken with a Varian A-60 and a Varian EM-360 instruments for solutions in $CDCl_3$, CCl_4, CD_3OD, or C_5D_5N with $SiMe_4$ as internal standard. G.l.c. analyses were carried out with Shimadzu 5APTF and 4BMPF apparatus [PEG 6000 (25%)–Chromosorb W (3 m), Apiezon-L(30%)–Celite (1 m), and EGSS-X(30%)–Chromosorb W (1 m) columns: N_2 as carrier gas]. Authentic samples of (4 and 5; X = H, Br, or I),[6] (11; R = Me),[*,6] (12; R = Me),[22] (11-D),[6] and (13)[9] were prepared by the reported methods.

Acetoxymercuration of (1) *or* (6).—A typical procedure was as follows. Methylphenylacetylene (1; R = Me) (1.16 g, 10 mmol) was added to acetic acid (10 ml) containing mercury(II) acetate (1.59 g, 5 mmol) at 60 °C; the mixture was then stirred for 5 h. After cooling, 10% aqueous potassium chloride was added to give a white precipitate which was collected by filtration and washed with n-hexane. This was purified further by dissolution into chloroform to remove the insoluble small amount of unreacted mercury(II) acetate, and then by evaporation of $CHCl_3$ to give a crude mixture of (2; R = Me) and (3; R = Me) [1.96 g, 96% yield based on $Hg(OAc)_2$ reacted]; (2)/(3) = 3.0 (by comparing the intensities of methyl protons of the acetoxy-group in ^1H n.m.r.), m.p. 104—108 °C. The mixture was separated by recrystallization twice from ethanol: (2; R = Me), m.p. 120 °C; $\nu_{max.}$ 1 740 ($\nu_{C=O}$), 1 640 ($\nu_{C=C}$), and 1 210 ($\nu_{=C-O}$) cm^{-1}; δ ($CDCl_3$) 2.01 [3 H, s, MeC=, $J(^{199}Hg-Me)$ 190 Hz], 2.19 (3 H, s, AcO), and 7.2—7.6 (5 H, m, Ph):

* (11; R = Me) ≡ (4; R = Me, X = H).

(3; R = Me), m.p. 155—157 °C; i.r. almost the same as that of (2; R = Me); δ (CDCl₃) 1.88 (3 H, s, AcO), 2.24 [3 H, s, MeC=, $J(^{199}Hg-Me)$ 26 Hz], and 7.1—7.5 (5 H, m, Ph).

Reaction conditions and yields, isomer ratio, and characterization of the products are summarized in Table 1. Isolation of (3; R = Et, Prⁿ, and Buⁿ) and (7; R = Et) was unsuccessful. ¹H N.m.r. data for other acetoxymercurials are as follows [the isomer ratio (2) : (3) was determined by comparing the intensities of methyl protons of the acetoxy-group]: δ (CDCl₃) (2; R = Et) 1.13 (3 H, t, Me), 2.15 (3 H, s, OAc), 2.40 [2 H, q, $J(^{199}H-CH_2)$ 229 Hz], and 7.2—7.7 (5 H, m, Ph): (3; R = Et): 1.87 (3 H, s, OAc): (2; R = Prⁿ); 0.98 (3 H, t, Me), 1.55 (2 H, qt, CH₂), 2.16 (3 H, s, OAc), 2.38 [2 H, t, =CCH₂, $J(^{199}Hg-CH_2)$ 221 Hz], and 7.2—7.6 (5 H, m, Ph): (3; R = Prⁿ); 2.01 (3 H, s, OAc): (2; R = Buⁿ); 0.93 (3 H, t, Me), 1.2—1.7 (4 H, m, methylenes), 2.17 (3 H, s, OAc), 2.40 [2 H, t, =CCH₂⁻ $J(^{199}Hg-CH_2)$ 219 Hz], and 7.25—7.65 (5 H, m, Ph): (3; R = Buⁿ); 1.88 (3 H, s, OAc): (2; R = Prⁱ); 1.01 (6 H, d, CHMe₂), 2.18 (3 H, s, OAc), 3.17 (1 H, m, CHMe₂), and 7.25—7.7 (5 H, m, Ph): (7; R = Ph); 1.98 (3 H, s, OAc), and 7.3—7.9 (10 H, m, Ph): (8; R = Et); 1.00 (3 H, t, Me), 1.07 (3 H, t, Me), 2.2—2.7 [4 H, m, =CCH₂⁻, $J(^{199}Hg-CH_2)$ 216 Hz], and 2.25 (3 H, s, OAc): (7; R = Et); 1.95 (3 H, s, OAc).

An acetoxymercurial with acetate attached to mercury instead of chlorine was also obtained as a white solid in the case of (6; R = Et) by evaporation of acetic acid below 40 °C from the reaction mixture before addition of aqueous KCl and by addition of n-hexane to the residue: (8; R = Et, Cl replaced by OAc), m.p. 85—87 °C; δ (CDCl₃) of methyl protons of acetate ligand is 2.00 (3 H, s).

Reaction of (1; R = Me) *with Mercury*(II) *Acetate at higher Temperature.*—To an acetic acid (10 ml) solution of mercury(II) acetate (1.59 g, 5 mmol) was added (1; R = Me) (1.16 g, 10 mmol) at reflux temperature and the resulting yellow-orange solution was refluxed for 3 h with stirring. After cooling, aqueous NaCl was added to the solution and the precipitated white solids were filtered off. The filtrate was extracted with benzene, and the extract was then washed with aqueous NaHCO₃ and dried over Na₂SO₄. This was concentrated to *ca.* 5 ml and analysed by g.l.c. with ethyl cinnamate as internal standard. The products were propiophenone (75% yield, based on Hg²⁺ consumed) and benzyl methyl ketone (25% yield).

Protodemercuration of a Mixture of (2; R = Me) *and* (3; R = Me).—An acetate acid (10 ml) solution of a mixture of (2; R = Me) and (3; R = Me) (3 : 1, 0.82 g, 2 mmol) was refluxed for 1 h. After the work-up procedure as described above, the g.l.c. analysis revealed the presence of (4; X = H) (41%), (5; X = H) (14%), propiophenone (23%), benzyl methyl ketone (7%), and (1; R = Me) 5%).

A similar reaction in the presence of mercury(II) acetate (0.636 g, 2 mmol) at reflux for 2 h afforded a mixture of propiophenone (75%) and benzyl methyl ketone (25%).

Halogenodemercuration of (2; R = Me).—To a pyridine (10 ml) solution of (2; R = Me) (0.82 g, 2 mmol) was added a pyridine solution (10 ml) of bromine (0.32 g, 2 mmol) at room temperature during 5 min and the resulting solution was stirred for 3 h. After treating with dilute aqueous HCl to remove pyridine, the solution was extracted with benzene. The extract was treated as above and g.l.c. analysis using diphenylmethane as internal standard revealed the presence of (4; X = Br) (100% yield). Distillation afforded pure (4; X = Br) (0.2 g) (b.p. 86 °C at 6 mmHg), the retention

time on g.l.c. and the n.m.r. spectrum being the same as those of an authentic sample.

To a methanol (20 ml) solution of (2; R = Me) (0.41 g, 1 mmol) was added solid iodine (0.25 g, 1 mmol) in small portions at room temperature with stirring. After being kept for 2 h the solution was added to saturated aqueous NaCl (150 ml) and then extracted with benzene (3 × 50 ml). The extract was washed with aqueous Na₂S₂O₃ (*ca.* 1M) and water, dried over Na₂SO₄, and then concentrated to *ca.* 5 ml. G.l.c. analysis using ethyl cinnamate as internal standard showed the presence of (4; X = I) (100%). Distillation afforded pure (4; X = I) (0.1 g) (b.p. 110 °C at 10 mmHg), the retention time on g.l.c., and the n.m.r. spectrum being the same as those of an authentic sample.

When a mixture of (2; R = Me) and (3; R = Me) (2 mmol) was treated with iodine–methanol or bromine–pyridine as above, the products were a mixture of (4; X = I) and (5; X = I) and a mixture of (4; X = Br) and (5; X = Br), respectively, in almost quantitative yield.

Reaction of (2; R = Me), (2; R = Et), *and* (7; R = Ph) *with* NaBH₄ *or* NaBD₄ *in a Protic Solvent.*—To a 50% aqueous tetrahydrofuran (20 ml) solution containing (2; R = Me) (0.82 g, 2 mmol) was added solid sodium borohydride (0.04 g, 1 mmol) in small portions at 0—4 °C with stirring. After being kept for 1 h at 0 °C, aqueous NaCl was added and the solution was extracted with benzene. G.l.c. analysis of the extract showed the presence of (11; R = Me) (67.2%), (12; R = Me) (14.4%), propiophenone (5.0%), and (1; R = Me) (5.4%). The retention times on g.l.c. and n.m.r. spectra of (11; R = Me) and (12; R = Me), which were isolated by distillation, were consistent with those of authentic samples.

In the case of reduction of (7; R = Ph) benzene was evaporated from the extract to leave a pale yellow solid, the n.m.r. of which revealed the presence of two vinyl acetates; δ (CDCl₃), 2.10 (3 H, s, OAc) and 6.43 (1 H, s, =CH) for (13), 2.30 (3 H, s, OAc) and 6.63 (1 H, s, =CH) for (14). The retention time on g.l.c. and n.m.r. spectrum of (13) were consistent with those of an authentic sample obtained by protolysis of (7; R = Ph) with aqueous HCL or by heating (6; R = Ph) with Hg (OAc)₂ in refluxing acetic acid for 2 h.

The isomer ratio of (11-D) : (11) and (12-D) : (12) was obtained by comparing the intensities of methyl protons of the acetoxy-group with those of the vinyl proton, and also by comparing those of the methyl protons [doublet for (11) and singlet for (11-D)].

Reaction of Terminal Acetylenes with Mercury(II) *Acetate.*— A mixture of (1; R = H) (1.02 g, 10 mmol) and mercury(II) acetate (1.59 g, 5 mmol) in acetic acid (10 ml) was stirred at 20 °C for 1 h. The precipitated white solid was collected and washed with n-hexane. It was revealed to be almost pure bis(phenylethynyl)mercury (1.35 g, 64%), m.p. 124—125 °C (lit.,[23] m.p. 124.5—125 °C). Similar treatment in chloroform afforded a clear homogeneous solution from which chloroform was evaporated to leave a 94% yield of the same white solid as above. The same scale reaction of oct-1-yne with mercury(II) acetate in chloroform at 20 °C for 0.5 h gave 1.88 g (90% yield) of bis(oct-1-ynyl)mercury-(II), m.p. 76—78 °C (lit.,[24] m.p. 80.4—80.7 °C).

To a methanol (20 ml) solution of mercury(II) acetate (5 mmol) was added (1; R = H) (10 mmol) at 20 °C with stirring and the mixture was kept for 1 h. The white precipitate formed was filtered off [0.45 g (22% yield), m.p. 161—164 °C] and was bis(benzoylmethyl)mercury(II), lit.,[25] m.p. 168—170 °C; the filtrate was added to saturated

aqueous NaCl (150 ml) and extracted with benzene. G.l.c. analysis of the extract showed the presence of α-methoxy-styrene (55% yield) and acetophenone dimethyl acetal (10%).

Bis(phenylethynyl)mercury (0.403 g, 1 mmol) or bis(oct-1-ynyl)mercury (0.42 g, 1 mmol) were converted into acetophenone (80%) or octan-2-one (70%) respectively by heating in acetic acid (20 ml) at reflux for 2 h.

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