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Stereochemistry of the Acetoxymercuration of Alkynes. A Synthesis of Vinyl Acetates

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The stereochemistry of acetoxymercuration of 3-hexyne has been established as antarafacial on the basis of an X-ray crystallographic study. Acetoxymercuration of diphenylacetylene afforded (*Z*)-α-acetoxy-β-(acetoxymercuri)stilbene by a suprafacial addition of $Hg(OAc)_2$. A simple method for the in situ acetoxymercuration–demercuration of dialkyl-substituted alkynes to afford vinyl acetates is described. The sodium borohydride reduction of vinyl mercurials was shown to produce divinyl mercurials while demercuration with zinc dust in acetic acid provided a useful synthetic method for the preparation of vinyl acetates.

The mercury-catalyzed hydration of alkynes has been used industrially for the preparation of aldehydes. The synthesis of ketones from alkynes is also a useful laboratory procedure that utilizes mercuric salts.[1] The tacit assumption has been made that vinyl mercurials are intermediates in such reactions.[2] The addition product[3] of acetylene and mercuric chloride was first characterized as (*E*)-(β-chlorovinyl)mercury bromide by Russian workers[4] on the basis of $^1H-^{199}Hg$ NMR coupling constants.[4c]

The stereochemistry of electrophilic addition of HgX_2 to cyclooctyne[5] has been assigned as suprafacial while both (*Z*)- and (*E*)-vinyl mercurials were reported upon oxymercuration of diphenylacetylene[6] and 2-butyne.[7] The structural assignments were based upon dipole moment and infrared studies. In a recent report on the mercuration–carbonylation of a series of propargylic alcohols antarafacial addition of $HgCl_2$ was observed.[8a] Acetoxymercuration of 2-butyne has been reported[8b] to afford the (*E*)-β-acetoxyvinyl mercurial. Mercuration–demercuration of acetylenes has also been employed recently in the synthesis of ketones,[9] acyloins[10] and enol acetates.[11]

A number of kinetic investigations aimed at elucidating the mechanism of these reactions have been reported.[2b,12] Both π complexes[2b] and a bis(acetylene–mercuric ion) complex have been invoked. Despite these efforts and considerable mechanistic speculation, virtually no contemporary acceptable evidence is available concerning the overall reaction pathway. We now report on the basis of X-ray data that simple 1,2-dialkylalkynes undergo acetoxymercuration by an antarafacial addition. Acetoxymercuration of diphenylacetylene, however, affords only the suprafacial adduct in contrast to an earlier literature report[6] where both *syn*- and *anti*-vinyl mercurials were reported.

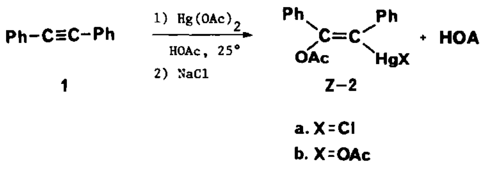
Table I. Relative Amounts of (*Z*)-2 and (*Z*)-3 Formed in Refluxing Acetic Acid

time, h	% mercurial (*Z*)-2	% (*Z*)-vinyl acetate 3
1	100	0
2	45	55
3	40	60
4	37	63
5	33	67
24	0	100

Results and Discussion

Acetoxymercuration of Diphenylacetylene. Mercuric acetate was chosen as the electrophilic salt in this study since its use would enable us to readily isolate the intermediate vinyl mercurial. The addition of HgX_2 to alkynes in protic solvents generates 1 mol of HX, and ionic salts of mercury (e.g., ClO_4, NO_3) afford a strong acid that is capable of protodemercuration of the vinylmercury adduct. We elected to study the acetoxymercuration of diphenylacetylene first since an earlier report[6] suggested that both syn and anti mercury adducts were formed while more recent investigations[8b,13] have resulted in only suprafacial addition to the carbon–carbon triple bond. In fact, Uemura[13b] noted this compound to be the exception among an entire series of alkynes where acetoxymercuration proceeded in a trans fashion.

Diphenylacetylene (1) was prepared by the reaction of the dihydrazone of benzil with mercuric oxide according to the method of Cope.[14] Treatment of 1 with $Hg(OAc)_2$ in acetic acid at room temperature for 96 h afforded (*Z*)-α-acetoxy-β-(chloromercuri)stilbene (**2a**) in 75% yield (eq 1). It was our experience that under a variety of



(1)

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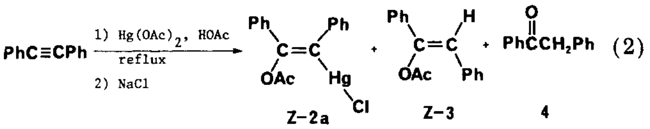
reaction conditions and concentrations of substrate (*Z*)-**2** was formed to the exclusion of the *E* stereoisomer.

Increasing the temperature, according to the procedure of Drefahl,[6] resulted in demercuration of (*Z*)-**2** to afford (*Z*)-2-acetoxystilbene (**3**) and minor amounts of deoxybenzoin (**4**, eq 2).



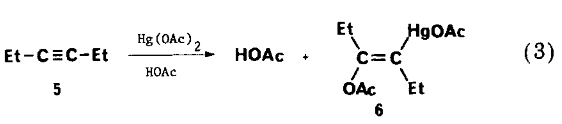
$$\text{PhC}\equiv\text{CPh} \xrightarrow[\text{2) NaCl}]{\text{1) Hg(OAc)}_2\text{, HOAc, reflux}} (\text{Ph})(\text{OAc})\text{C}{=}\text{C}(\text{Ph})(\text{HgCl}) + (\text{Ph})(\text{OAc})\text{C}{=}\text{C}(\text{H})(\text{Ph}) + \text{PhC(=O)CH}_2\text{Ph} \quad (2)$$

Z-2a Z-3 4

The structure of **3** was established by independent synthesis,[15] and the ratios of **2** to **3** as a function of reaction time are given in Table I. The product ratios were determined by integration of the respective acetoxy resonances in the ^{1}H NMR spectrum. We further note that the melting point (100 °C) and basic infrared absorptions of acetoxystilbene **3** are the same as those given[6] for the purported anti isomer of **2** which interestingly was reported to have given a correct elemental analysis. From a synthetic viewpoint the yield of vinyl mercurial (*Z*)-**2** was optimized (75%) at room temperature while refluxing overnight gave a good yield (79%) of vinyl acetate **3** that was only slightly contaminated with deoxybenzoin.

Stereochemistry of Acetoxymecuration of 3-Hexyne. The suprafacial mode of addition noted for diphenylacetylene is contrary to that typically observed for alkenes,[16] allenes,[17] and simple disubstituted alkynes.[8] The stereochemical assignment of the products of oxymercuration of disubstituted alkynes has by necessity been based upon the indirect evidence of spectroscopy or chemical derivitization.[8b] For example, Larock[8b] has transformed 3-hexyne into its corresponding trans ene diacetate via a mercuration–esterification reaction, suggesting the intermediacy of a trans acetoxymercuri chloride. We chose 3-hexyne as a typical dialkyl-substituted acetylene and decided to prepare suitable crystals of its product of oxymercuration for X-ray analysis, thereby producing unequivocal structural evidence for the resulting vinyl mercurial.

Relatively mild (12 °C) reaction conditions, with equimolar amounts of $Hg(OA_c)_2$ and 3-hexyne (**5**) in acetic acid, afforded an optimal yield (97%) of (*E*)-3-acetoxy-4-(acetoxymercuri)-3-hexene (**6**, eq 3) as a crystalline solid, mp 57 °C. Reaction of **5** at room temperature also afforded **6**, albeit in lower yield and with a small amount of demercurated vinyl acetate. An attempt to isomerize vinyl mercurial **6** at 70 °C was apparently not successful. No new acetoxy resonances appeared in the NMR spectrum although a new absorption in the infrared (1710 cm^{-1}) did indicate the formation of a ketone, presumably 3-hexanone. The isomerization of the analogous 2-butyne adduct has been reported.[18]



$$\text{Et{-}C}\equiv\text{C{-}Et} \xrightarrow[\text{HOAc}]{\text{Hg(OAc)}_2} \text{HOAc} + (\text{Et})(\text{OAc})\text{C}{=}\text{C}(\text{HgOAc})(\text{Et}) \quad (3)$$

5 6

A single crystal of (*E*)-acetoxy mercurial **6** was obtained after several recrystallizations from cyclohexane and cyclohexane–diethyl ether mixtures.[19] X-ray data on mercuri acetate **6** show the compound to exist in a trans configuration about the carbon–carbon double bond. There is some angular strain about the double bond as evidenced by the 129° C_3–C_4–C_5 bond angle (Figure 1a). Presumably this is due to repulsive ethyl group–mercury interactions.

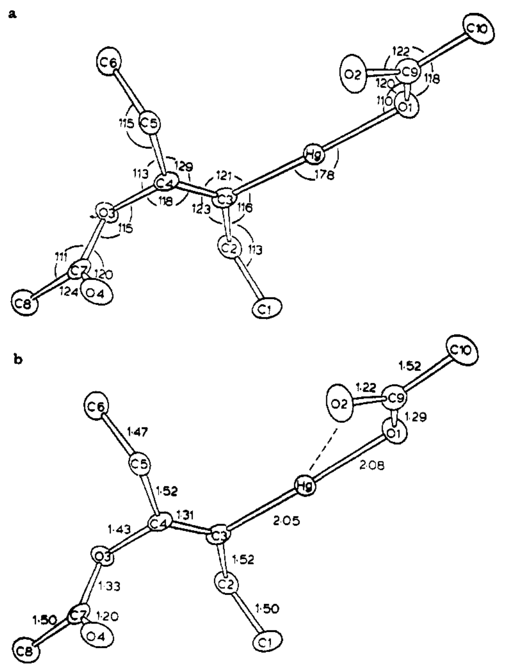


Figure 1. (b) Bond angles in (*E*)-3-acetoxy-4-(acetoxymercuri)-3-hexene (**6**). (b) Bond lengths in **6**.

Table II. Dihedral Angles in (*E*)-3-Acetoxy-4-(acetoxymercuri)-3-hexene (6)

atoms	dihedral angles, deg	atoms	dihedral angles, deg
C1, C2-C5, C6	−178	O3, C4-C3, Hg	−179
C1, C2-C3, C4	−113.8	C3, C4-O3, C7	99.8
C3, C4-C5, C6	110.9	Hg, C3-C4, C5	6.3
C2, C3-C4, C5	−175.8		

The carbonyl oxygen of the acetate bonded to the Hg also appears to interact with the Hg atom. The intramolecular distance between these atoms is 2.75 (1) Å, while this same oxygen atom has an intermolecular distance of 2.66 (1) Å to another Hg atom of an adjacent molecule. The O_1–Hg–C angle is 178° (1) while the O–Hg and Hg–C distances are 2.08 (1) and 2.05 (1) Å, respectively. Of particular interest in Figure 1b is the fact that the O_1–C_9 and O_2–C_9 bond distances for the mercury-bound acetate are at 1.29 and 1.22 Å, respectively. This is indicative of a relatively ionic mercury–acetate bond since the former C–O bond has been shortened by approximately 0.05 Å and the latter elongated by 0.02 Å.

Table II lists important dihedral angles in mercurial **6**. The dihedral angle for the plane defined by the mercury and the alkene atoms and the plane defined by the double

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[16] Kitching, W. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 61.

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[19] Mercuriacetate **6** crystallizes in the monoclinic space group $P2_1/c$ with the following lattice parameters: a = 10.082 (2) Å b = 13.315 (3) Å, c = 9.569 (2) Å, β = 97.12 (2)°, four molecules in the unit cell. Data were collected by the $\theta/2\theta$ method on a Syntex $P2_1$ four-circle diffractometer with monochromatic Mo Kα radiation. A total of 1129 reflections were considered to be observed by the criterion $I/\sigma(I)$ > 2.5. The data were corrected for absorption, Lorentz, and polarization phenomena. The structure was solved by Patterson and Fourier methods. Positional and anisotropic thermal parameters were refined by full-matrix least-squares methods to final discrepancy indices of R = 0.031 and R_w = 0.036. Contributions from hydrogen atoms were calculated and included, but their position and thermal parameters were not varied.

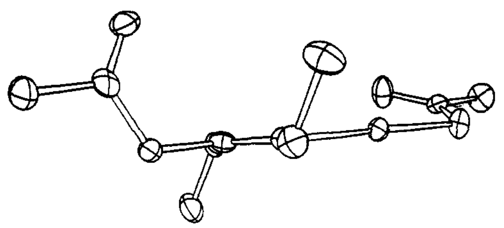
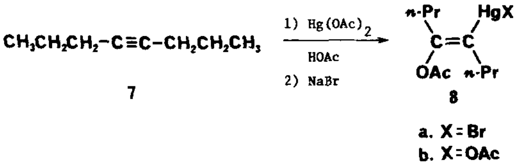


Figure 2. Perspective view of (*E*)-3-acetoxy-4-(acetoxymercuri)-3-hexene (**6**).

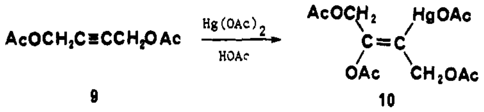
bond and the methylene carbon of the ethyl group syn to the mercury is 6.3°. This would appear to require a slight deviation from planarity of the π system. Another interesting feature of **6** is the C1, C2–C5, C6 torsion angle of 178°. Thus, the terminal methyl groups of the ethyl portions of **6** are anti. This would place the electrons of the C1–C2 and C5–C6 σ bonds in good position to overlap with the alkene π system. This could be interpreted as resulting from σ–π hyperconjugation[20] (Figure 2).

Acetoxymercuration of Selected Alkynes. We next extended our study to include a more hindered alkyne. Room-temperature reaction of 4-octyne (**7**) with a solution of $Hg(OAc)_2$ in acetic acid (eq 4) resulted in an excellent yield (92%) of (*E*)-4-acetoxy-5-(acetoxymercuri)-4-octene (**8b**) as a clear oil. The stereochemical assignment is supported by NMR chemical shift data (vide infra). The corresponding mercuri bromide **8a** was a solid (mp 61–62 °C).



(4)

Similarly, 1,4-butyndiol diacetate (**9**) afforded (*E*)-1,2,4-triacetoxy-3-(acetoxymercuri)-2-butene (**10**) in essentially quantitative yield (eq 5). Spectral data supported the structure, and the δ 2 region of its ^1H NMR spectrum exhibited four discernible acetoxy methyl resonances. The corresponding dimethyl ether of 1,4-butynediol afforded a 70% yield of (*E*)-2-acetoxy-3-(acetoxymercuri)-1,4-dimethoxy-2-butene (**11**).

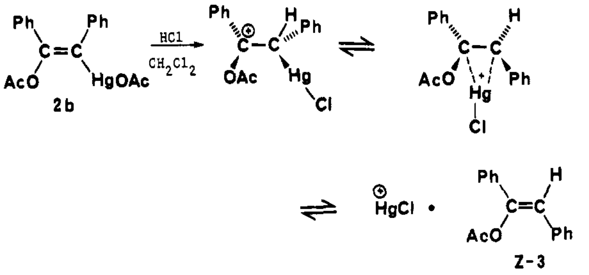


(5)

Highly hindered alkynes such as 2,2,5,5-tetramethyl-3-hexyne (**12**) are not reactive under these relatively mild reaction conditions. After 1 week at 25 °C with mercuric acetate in acetic acid, 86% of the di-*tert*-butylalkyne **12** was recovered. The sterically encumbered 2,5-dimethyl-2,5-dimethoxy-3-hexyne (**13**) was also reluctant to undergo acetoxymercuration, and 89% of alkyne **13** was recovered after being refluxed in $Hg(OAc)_2/HOAc$ for 24 h. Even 3,3-dimethyl-1-phenyl-1-butyne (**14**) returned 90% of the starting alkyne after 1 week in the comparable acetic acid media. Conceivably the steric strain which would be incurred by either suprafacial or antarafacial addition of mercuric acetate to these hindered alkynes would be prohibitive. One would incur a steric interaction of the bulky R groups with mercury as noted in the above X-ray study. In addition, deoxymercuration could occur to afford the starting alkyne.

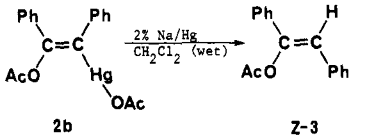
Carbon–Mercury Bond Cleavage. Acid-promoted demercuration of organomercurials has been studied extensively,[21,22] and the stereochemistry of protic acid cleavage typically occurs with retention of configuration.[21] A retention mechanism for C–Hg bond cleavage of vinyl mercurials with DCl has been also been suggested,[23] but these studies have been challenged.[24] We felt that vinyl mercurial **2a** would present a unique test of the retention mechanism since the difference in ground-state energies of the resulting (*Z*)- and (*E*)-2-acetoxystilbenes should be approximately 4.5 kcal mol.[25]

Treatment of mercuri acetate **2b** with dry HCl in methylene chloride solution afforded a high yield of the corresponding (*Z*)-acetate (eq 6). Nearly identical results were obtained with concentrated HCl. Presumably a mercurinium ion intermediate is involved,[22a] and the vicinal phenyl groups provide an ample driving force for isomerization and subsequent demercuration.



(6)

In an effort to generate a vinyl anion in the reduction of **2b**, we attempted to achieve a rapid two-electron transfer by the use of zinc metal in acetic acid solvent. However, treatment of the *Z* mercurial **2b** in acetic acid with zinc powder afforded, after 2 h, a 93% yield of the (*Z*)-vinyl acetate **3**. A discernible amount of the corresponding *E* isomer could not be detected by GLC analysis. Almost identical results were observed when a solution **2b** in wet methylene chloride was treated with 2% sodium amalgum, affording an 80% yield of (*Z*)-**3** (eq 7). In a control experiment, no appreciable isomerization of the *cis*-vinyl acetate (*E*)-**3** to the trans isomer (*Z*)-**3** was detected. It is of interest to note that the reduction of organomercurials with sodium amalgum has previously been shown to occur with complete retention of configuration with saturated substrates.[26]



(7)

The reduction of organomercurials with sodium borohydride is generally thought to proceed via a free-radical pathway.[27] The rate of inversion for vinyl radicals has

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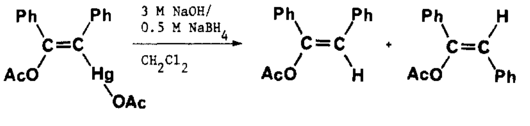
[24] (a) Banney, P. J.; Kitching, W.; Wells, P. R. *Tetrahedron Lett.* **1968**, 27. (b) Jenson, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968; p 64.

[25] The difference in ground-state energy of (*Z*) and (*E*)-stilbene has been reported to be 4.5 kcal/mol. Turner, R. B.; Nettelton, D. E., Jr.; Perleman, M. *J. Am. Chem. Soc.* **1958**, *80*, 1430.

[26] (a) Jensen, F. R.; Miller, J. J.; Cristol, S. J.; Beckley, R. S. *J. Org. Chem.* **1972**, *37*, 4341. (b) Galle, J. E.; Hassner, A. *J. Am. Chem. Soc.* **1972**, *94*, 3930.

been estimated to be on the order of 10^9. Therefore, one would anticipate that if a free-radical mechanism were operating, the thermodynamic product of the reduction of the mercurial **2b** would be the (*Z*)-vinyl acetate (*Z*)-**3**. However, reduction of **2b** afforded a mixture of (*E*)- and (*Z*)-stilbene acetates with a predominance of the thermodynamically *less stable* isomer (*E*)-**3**. Reaction of mercurial **2b** with basic sodium borohydride afford an 83% yield of stilbene acetates (eq 8) with a cis/trans ratio of 64:36

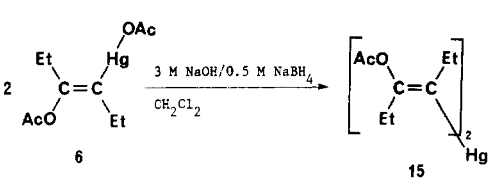


2b E-3 Z-3 (8)

(GLC). A similar reduction carried out at −80 °C gave a cis/trans ratio of 65:35 as determined by integration of the acetoxy methyl resonances in the NMR. The authenticity of these resonances was established by sidebanding techniques and comparison with authentic samples prepared by an independent synthesis.[15] Sodium borohydride in alkaline methanol has previously been used in the reduction of mercurials derived from alkylphenylacetylenes.[13b]

These data are clearly not consistent with a long-lived free-radical intermediate. More significantly, this observation provides convincing evidence that the initial product of the acetoxymercuration of diphenylacetylene (**1**) is the *Z* mercurial **2b**. On the basis of the above results, it is highly unlikely that isomerization of the *E* mercurial, irrespective of the mechanism, would occur to afford the less stable (*E*)-vinyl acetate.

To further explore the synthetic utility of the acetoxymercuration of alkynes, we studied the behavior of mercuri acetate **6** under various reduction conditions. Surprisingly, the sodium borohydride reduction (eq 9) did not afford the expected 3-acetoxy-3-hexene but rather the divinyl mercurial **15** and elemental mercury. We next subjected vinyl mercurial **6** to reduction with zinc powder in acetic acid (eq 10) and isolated (62%) isomerically pure (*Z*)-3-acetoxy-3-hexene (**16**). In a similar manner, the divinyl mercurial **15** afforded a good yield (83%) of vinyl acetate **16**. The assigned trans stereochemistry of the divinyl mercurial **15** and vinyl acetate **16** was predicated on the assumption that the geometric configuration in the acetoxy mercurial **6** was retained throughout the reduction sequence. The NMR spectrum of the crude product evidenced only one acetoxy resonance. Thus, it appears that the zinc reduction is synthetically useful for these compounds and deserves further consideration.



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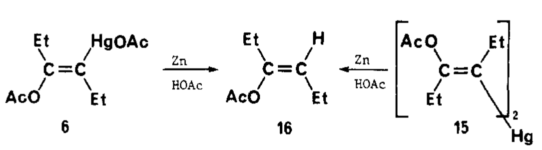
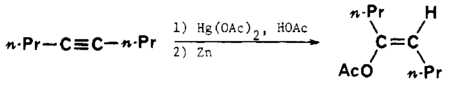


6 16 15 (10)

The sodium borohydride reduction of vinyl mercurial **8b**, derived from 4-octyne, also afforded divinyl mercurial **17** in excellent yield (96%). Subsequent reduction with zinc in acetic acid gave (*Z*)-4-acetoxy-4-octene (**18**) in 90% yield. The synthetic utility of this reaction sequence is greatly enhanced by a "one-pot" conversion of the alkyne to its corresponding vinyl acetate without isolation of the intermediate divinyl mercurial. Reaction of 4-octyne with mercuric acetate at room temperature for 2 h with subsequent addition of zinc powder afforded an excellent yield (89%) of (*Z*)-vinyl acetate **18** (eq 11). The in situ reduction procedure employing Zn powder is quite general and should prove to be a synthetically useful procedure for the stereospecific synthesis of vinyl acetates.



18 (11)

NMR Studies To Determine the Effect of Pyridine as a Chemical Shift Reagent. In the course of our research, the problem of assigning the structures of the vinyl acetoxy mercurials posed a challenging problem. Our initial ^{1}H NMR studies indicated that acetoxymercuration of symmetrically disubstituted alkynes generally proceeds to give only one diastereomer. Without the availability of the opposite isomer, there were few methods we could utilize to assign the *E* or *Z* configuration to the carbon–carbon double bond.

Since we had unequivocally established the structure of the 3-hexyne adduct **6** as having the trans configuration, we elected to study the pyridine-induced NMR shift of this isomer. This method of NMR analysis had been successfully applied to a series of oxymercurials derived from alkenes.[28] In that study we established that the alkoxy groups syn to the mercuri halide or mercuri acetate experienced chemical shifts of 5–9.5 Hz upon addition of pyridine, while the anti compounds experienced a lesser chemical shift of 4.5–6.6 Hz.

Those acetoxy mercurials (**6** and **8**) which have been assigned the trans stereochemistry exhibit only a small (0.5 Hz) downfield shift in their NMR spectra upon the addition of pyridine (see Experimental Section). However, the *cis*-stilbene acetoxy mercurial **2b** exhibited a downfield shift for the carbon-bound acetoxy methyl resonance of 7.5 Hz upon the addition of 10 equiv of pyridine. Smaller changes in this chemical shift value were observed (i.e., 3.5 Hz/2.5 equiv of added pyridine) with lesser amounts of pyridine. These data support the assigned cis and trans configurations of **2b** and **8**, respectively.

In summary, we have shown that dialkyl-substituted alkynes afford *anti*-vinyl mercurials upon acetoxymercuration, while the opposite situation obtains with diaryl-substituted alkynes. The "one-step" method for acetoxymercuration of simple dialkyl-substituted alkynes provides a useful synthesis of vinyl acetates.

Experimental Section

General Methods. NMR spectra were obtained on a Varian Associates A-60-A spectrometer. Peak positions are reported in δ units from tetramethylsilane which was used as an internal standard. All mass spectra were obtained by using an Associated Electrical Industries Model MS 902 mass spectrometer at 70 eV or lower.

Phenylacetylene was obtained from Aldrich Chemical Co. Sodium borohydride was obtained from Alfa-Ventron Chemical Co. 2,5-Dimethyl-3-hexyne-2,5-diol was obtained from Air Reduction Chemical Co. 2,2,5,5-Tetramethyl-3-hexyne was obtained from Chemical Samples Co. 3-Hexyne and 4-octyne were obtained from Columbia Organic Chemicals Co., Inc. 1,4-Butynediol was obtained from General Aniline and Film Co.

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Diphenylacetylene (1) was prepared by a modification of the method of Cope.[14] A mixture of 105.1 g (0.5 mol) benzil, 250 mL of 2-propanol, 100 mL of methanol, and 100 g of 64% hydrazine hydrate afforded 108 g (90%) of dihydrazone, mp 151–152 °C. A suspension of 108 g of the dihydrazone in 500 mL of dry benzene was treated with 5 g of yellow mercuric oxide and heated over steam until a gray color was noted. The steam was removed and 235 g of mercuric oxide, in 10-g portions, was added at such a rate as to keep the solvent refluxing. The mixture was filtered and the filtrate dried (Na_2SO_4). After removal of benzene at an aspirator, 63 g (70%) of diphenylacetylene (1) was isolated by distillation; bp 97–105 °C (0.3 mm).

(*Z*)-*α*-Acetoxy-*β*-(chloromercuri)stilbene (2a). Diphenylacetylene (5.4 g, 0.03 mol) and mercuric acetate (9.6 g, 0.03 mol) were stirred 96 h in 50 mL of acetic acid. The solvent was removed at an aspirator and the resulting viscous oil dissolved in 100 mL of chloroform. The solution was washed with 100 mL of saturated sodium chloride and 100 mL of water and dried ($MgSO_4$). The solvent was concentrated, affording 9.8 g (75%) of **2a**: mp 140–141 °C; (lit.[6b] mp 141 °C); IR (CCl_4), 1770 (s) cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 10), 1.95 (s, 3).

Attempted Preparation of (*E*)-*α*-Acetoxy-*β*-(chloromercuri)stilbene. By use of the procedure of Drefahl and Schaaf,[6] mercuric acetate (3 g, 9 mmol) and diphenylacetylene (5 g, 0.025 mol) were added to 47 mL of refluxing acetic acid. After 4 h, 30 mL of acetic acid was removed under reduced pressure, and 25 mL of chloroform was added. The organic phase was washed with 25 mL of saturated sodium chloride, dried ($MgSO_4$), and added to 50 mL of petroleum ether. Slow cooling afforded 3 g of white crystals (mp 91–98 °C). Recrystallization from ethanol afforded 2.3 g (98%) of (*Z*)-*α*-acetoxystilbene (3) identical in every respect with an authentic sample prepared by the method of House and Trost.[15]

(*E*)- and (*Z*)-*α*-Acetoxystilbenes. By use of the method of House and Trost,[15] 5 g (0.025 mol) of deoxybenzoin, 75 mL of carbon tetrachloride, and 26 g of acetic anhydride gave 2.3 g (38%) of (*Z*)-*α*-acetoxystilbene (3). Recrystallization from methanol gave white needles: mp 100–100.5 °C; IR (CCl_4) 1765 (s) cm^{-1}; NMR (CCl_4) δ 7.45 (m, 10), 6.62 (s, 1), 2.20 (s, 3). The mother liquors from crystallization of 3 were concentrated, and the *E* isomer was purified by preparative GLC (5 ft. × 1.25 in., 10% SE-30), affording a viscous yellow oil: IR (CCl_4) 1765 (s) cm^{-1}; NMR (CCl_4) δ 7.35 (s, 4), 7.15 (s, 6), 6.42 (s, 1), 2.12 (s, 3).

Acetic Acid Protolysis of 2b. A stirred solution of 0.25 g (5 mmol) of (*Z*)-*α*-acetoxy-*β*-(acetoxymercuri)stilbene in 20 mL of acetic acid was refluxed 24 h. The solution was concentrated, and the residue was dissolved in chloroform and washed with water. The dried ($MgSO_4$) solution was concentrated, affording 0.11 g (95%) of product identical in every respect with an authentic sample of (*Z*)-3.[15]

Zinc Reduction of (*Z*)-*α*-Acetoxy-*β*-(acetoxymercuri)stilbene (2b). To a stirred solution of 0.25 g (0.5 mmol) of **2b** in 20 mL of acetic acid acid was added 1 g of zinc powder. After 2 h, 20 mL of methylene chloride and 20 mL of water were added, and the methylene chloride layer was separated. The organic phase was washed twice with water and once with saturated sodium bicarbonate, dried ($MgSO_4$), and concentrated, affording 0.14 g (93%) of (*Z*)-3 that was identical in every respect with an authentic sample.[15]

Sodium Amalgum Reduction of (*Z*)-*α*-Acetoxy-*β*-(acetoxymercuri)stilbene (2b). To a stirred solution of 2.5 g (0.005 mol) of **2b** in 25 mL of methylene chloride was added 50 g of 2% sodium amalgum. After 48 h, the solvent was decanted from the metal residue, dried ($MgSO_4$), and concentrated, affording 1.0 g (80%) of (*Z*)-*α*-acetoxystilbene (3).

Sodium Borohydride Reduction of (*Z*)-*α*-Acetoxy-*β*-(acetoxymercuri)stilbene (2b). To a stirred solution of 0.23 g (0.5 mmol) of **2b** in 25 mL of methylene chloride, was added 30 mL of 0.5 M sodium borohydride/3 M sodium hydroxide solution. After 2.5 h, the organic layer was washed with water and dried ($MgSO_4$), and the solvent was concentrated, affording an oil. A cis/trans ratio of 64:36 for the two stilbene acetates was established by GLC analysis (200 °C, 2.2-m column, 10% SE-30, 2.5 mL/s He flow). Preparative GLC afforded 0.09 g (83%) of (*E*)- and (*Z*)-3, with the *E* isomer having the shorter retention time.

Sepctral data for (*E*)-3: IR (CCl_4) 1769 (s), 1205 (s) cm^{-1}; NMR (CCl_4) δ 7.35 (s, 4), 7.15 (s, 6), 6.42 (s, 1), 2.12 (s, 3).

Spectral data for (*Z*)-3: IR (CCl_4) 1770 (s), 1195 (s) cm^{-1}; NMR (CCl_4) δ 7.45 (m, 10), 6.62 (s, 1), 2.21 (s, 3). A similar reduction carried out at −80 °C gave a 65:35 cis/trans stilbenyl acetate ratio by NMR integration of the acetoxy methyl protons.

(*E*)-3-Acetoxy-4-(acetoxymercuri)-3-hexene (6). To a solution of 0.82 g (0.01 mol) of 3-hexyne in 27.5 mL of acetic acid/acetic anhydride (10:1 v/v) at 12 °C was added 3.2 g (0.01 mol) of mercuric acetate. After 72 h, the solvents were removed under reduced pressure with warming, and the residue was dissolved in 25 mL of methylene chloride. The solution was washed with water and dried ($MgSO_4$), and the solvent was removed. Recrystallization from cyclohexane afforded 4.0 g (97%) of **6**: mp 57 °C; IR (CCl_4) 1770 (s) cm^{-1}; NMR (CCl_4) δ 2.4 (m, 3), 2.15 (s, 3), 1.1 (m, 6).

Anal. Calcd for $C_{10}H_{16}HgO_4$: C, 29.96; H, 4.02. Found: C, 30.00; H, 4.46.

Symmetrization of Vinyl Mercurials. (a) (*E*)-3-Acetoxy-4-(acetoxymercuri)-3-hexene (6). To a stirred solution of 0.20 g (0.5 mmol6) of **6** in 25 mL of methylene chloride was added 20 mL of 0.5 M sodium borohydride/3.0 M sodium hydroxide solution. After 2 h, the organic layer was separated and washed with 25 mL of water, dried ($MgSO_4$), and concentrated, affording 0.11 g (92%) of the divinyl mercurial **15**: mp 63–64 °C; IR (CCl_4) 1750 (s) cm^{-1}; NMR (CCl_4) δ 2.3 (q, 8, J = 7 Hz), 2.1 (s, 6), 1.1 (m, 12).

Anal. Calcd for $C_{16}H_{26}HgO_4$: C, 39.79; H, 5.42. Found: C, 39.81; H, 5.66.

(b) (*E*)-4-Acetoxy-5-(acetoxymercuri)-4-octene (8b). In a like manner 0.25 g (0.5 mmol) of **8b** afforded 0.12 g (96%) of the corresponding dimercurial **17**: IR (CCl_4) 1750 (s) cm^{-1}; NMR (CCl_4) δ 2.35 (m, 8, J = 7.5 Hz), 2.05 (s, 6), 1.5 (m, 8), 0.95 (m, 12).

Zinc Reduction of Vinyl Mercurials. (a) (*Z*)-3-Acetoxy-3-hexene (16). To a stirred solution of 0.41 g (5 mmol) of 3-hexyne in 10 mL of acetic acid was added 1.60 g (0.005 mol) of mercuric acetate. After disappearance of the yellow color (~2 h), 50 mL of methylene chloride was added followed by 3.2 g of zinc dust. The solution was decanted and the metallic residue washed with 60 mL of methylene chloride. The acetic acid was extracted with 100 mL of water and 100 mL of saturated sodium bicarbonate. The organic phase was dried ($MgSO_4$) and concentrated, affording 0.67 g (66%) of crude **16**. The GLC yield (62%) was determined by using decane as an internal standard (2.2-m column, 10% SE-30, 65 °C); IR (neat) 1760 (s), 1220 (s) cm^{-1}; NMR (CCl_4) δ 4.95 (t, 1, J = 7 Hz), 2.1 (m, 7), 1.0 (m, 6).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 99.2. Found: C, 67.32; H, 9.84.

(b) (*Z*)-4-Acetoxy-4-octene (18). In a similar manner, 1.10 g (0.01 mol) of 4-octyne was reacted with 3.2 g (0.01 mol) of mercuric acetate, affording a quantitative yield of 1.73 g of crude **18**. The GLC yield (89%) was determined by using cyclodecane as an internal standard (2.2-m, column, 10% SE-30, 107 °C).

Spectral data for **18**: IR (neat) 2960, 2940, and 2880 (m), 1760 (s), 1215 (s) cm^{-1}; NMR (CCl_4) δ 4.95 (t, 1, J = 7 Hz), 2.08 (s, 3), 2.3–0.75 (m, 14).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.40; H, 10.84.

Reduction of Bis(*trans*-2-acetoxy-1-ethylbut-1-enyl)mercury (15). To a solution of 0.48 g (1 mmol) of the mercurial **15** in 20 mL of acetic acid was added 0.4 g of zinc powder. After 10 min, 40 mL of methylene chloride and 200 mL of water were added. The organic layer was separated, washed with a saturated sodium bicarbonate solution, and dried ($MgSO_4$). The concentrated methylene chloride solution afforded 83% of crude (*Z*)-3-acetoxy-3-hexene (3). A sample of **3** was isolated by preparative GLC (6-ft column, 10% SE-30, 80 °C) and was identical in every respect with the same sample prepared from mercurial **6**.

(*E*)-4-Acetoxy-5-(acetoxymercuri)-4-octene (8b). To a stirred solution of 1.20 g (0.01 mol) of 4-octyne in 10 mL of acetic acid was added 3.20 g (0.01 mol) of mercuric acetate. After 20 min, a yellow viscous oil was isolated by evaporation of the acetic acid. The oil was dissolved in 50 mL of methylene chloride, washed with 50 mL of water, and dried ($MgSO_4$). Removal of the solvent afforded 4.05 g (91.6%) of **8b** as a clear oil: IR 2960,

Table III

added equiv of pyridine	chemical shift, Hz	
	mercury-bound acetate	carbon-bound acetate
0	114.4	111.5
0.5	113.9	111.9
1.0	113.8	112.9
1.5	113.8	113.8
2.5	113.5	115.0
4	113.1	115.9
6	112.8	117.0
8	112.6	118.0
10	112.6	119.0

2930, and 2870 (m), 1755 (s), 1220 and 1165 (s) cm^{-1}; NMR (CCl_4) δ 2.3 (m, 4), 2.13 (s, 3) 1.97 (s, 3), 1.5 (m, 4), 0.9 (m, 6).

The compound was analyzed as its mercuri bromide **8a** which was prepared by washing a methylene chloride solution of **8b** with a saturated aqueous sodium bromide solution: mp 61–62 °C; IR (CCl_4) 2965, 2935, 1762 (s), 1215 and 1165 (s) cm^{-1}; NMR (CCl_4) δ 2.25 (q, 4, J = 7 Hz), 2.11 (s, 3), 1.5 (m, 4), 0.9 (m, 6).

Anal. Calcd for $C_{10}H_{17}BrHgO_2$: C, 26.70; H, 3.81. Found: C, 26.86; H, 3.75.

Reduction of Bis(*trans*-2-acetoxy-1-*n*-propylpent-1-enyl)mercury (17). To a solution of the mercurial **17** (0.27 g, 0.5 mmol) in 15 mL of acetic acid was added 0.2 g of zinc powder. After 15 min, 40 mL of methylene chloride and 200 mL of saturated sodium bicarbonate were added. The organic layer was dried ($MgSO_4$), and the methylene chloride solution was concentrated, affording 0.15 g (94%) of crude (*Z*)-4-acetoxy-4-octene. The major product (>95%) was isolated by preparative GLC (10% SE-30, 100 °C), affording 0.12 g (75%) of **18**.

Acetoxymercuration of 1,4-Butynediol Diacetate (9). To a stirred solution of 3.2 g (0.01 mol) of mercuric acetate in 30 mL of acetic acid and acetic anhydride (1:1 v/v) was added 1.72 g (0.01 mol) of **9**. After 72 h, the solvents were removed under reduced pressure with warming. The white crystalline residue was washed with pentane, affording 4.90 g (99%) of (*E*)-1,2,4-triacetoxy-3-(acetoxymercuri)-2-butene (**10**): mp 133–134 °C; IR (halocarbon) 2995 (m), 1750 (s) cm^{-1}; NMR (CH_2Cl_2) δ 4.7 (s, 4), 2.10 (s, 3), 2.00 (s, 3), 1.99 (s, 3), 1.92 (s, 3).

Anal. Calcd for $C_{12}H_{16}HgO_8$: C, 29.48; H, 3.29. Found: C, 29.44; H, 3.51.

(*E*)-2-Acetoxy-3-(acetoxymercuri)-1,4-dimethoxy-2-butene (11). To a stirred solution of 1.6 g (0.005 mol) of mercuric acetate in 20 mL of acetic acid was added 2 mL of acetic anhydride and 0.58 g (0.005 mol) of 1,4-butynediol dimethyl ether. After 16 h, the solvents were removed under reduced pressure. The residue was dissolved in 50 mL of methylene chloride, washed with 50 mL of water, dried ($MgSO_4$), and concentrated, affording 1.53 g (70%) of **11**: mp 79–80 °C; IR (CCl_4) 1770 cm^{-1}; NMR δ 3.95 (s, 2), 3.5 (m, 2), 3.45 (s, 3), 3.35 (s, 3), 2.15 (s, 3).

NMR Studies. To a solution of 0.25 g (0.5 mmol) of **2b** in 1 mL of methylene chloride were added increasing amounts of pyridine. Chemical shift values (in hertz) for the two acetate peaks were determined by using sidebanding techniques, and the data are summarized in the Table III. The solvents were removed at an aspirator affording 0.23 g of the original mercurial **2b**.

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Registry No. 1, 501-65-5; (*Z*)-**2a**, 75721-25-4; (*E*)-**2a**, 82352-01-0; **2b**, 82352-02-1; (*E*)-**3**, 24647-07-2; (*Z*)-**3**, 13892-81-4; **5**, 928-49-4; **6**, 82352-03-2; **7**, 1942-45-6; **8a**, 82352-04-3; **8b**, 82352-05-4; **9**, 1573-17-7; **10**, 82352-06-5; **11**, 82352-07-6; **15**, 82352-08-7; **16**, 82352-09-8; **17**, 82352-10-1; **18**, 82352-11-2; benzil, 134-81-6; benzil dihydrazone, 4702-78-7; mercuric oxide, 21908-53-2; mercuric acetate, 1600-27-7; 1,4-butynediol dimethyl ether, 16356-02-8.

Mechanistic Aspects of the Silver(I)-Promoted Rearrangement of Cyclopropene Derivatives

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The silver ion promoted isomerizations of several substituted cyclopropenes have been studied. The results of these studies have been compared to the rearrangements encountered on thermolysis and photolysis. Treatment of 1,3-diphenyl-2-methyl-3-benzylcyclopropene with silver ion afforded 1-phenyl-2-methyl-3-benzylindene as the exclusive product. In contrast, photolysis of this system gave rise to the isomeric 1-methyl-2-phenyl-3-benzylindene. The results obtained from the silver ion reduced reaction of 1-phenyl-2,3,3-trimethylcyclopropene indicates that the ring opening is not governed by the same electronic considerations that control its photochemical behavior. Placement of an allyl group on the C_3 position of the cyclopropene ring causes a different mode of behavior to occur on exposure to silver ion. These compounds give rise to bicyclo[3.1.0]hex-2-enes. The reaction proceeds with complete retention of stereochemistry about the π bond. A mechanism is proposed that involves preferential attack of the silver ion on the σ bond to give rise to an argentiocarbonium ion. Consistent with this mechanistic scheme were experiments in which the initially generated intermediate could be trapped with nucleophilic solvent. The regioselectivity of bond cleavage of an unsymmetrically substituted cyclopropene was found to be strongly dependent upon relative carbonium ion stabilities. An overall mechanistic picture is presented that provides a reasonable explanation of the processes that lead to each of the observed products.

The mechanism for the interconversion of the cyclopropene ring and the corresponding bond-cleaved species continues to be of both theoretical and experimental interest.[1-4] Recent calculations predict that the thermal ring opening of cyclopropene should proceed to a diradical planar intermediate which may subsequently decay to a vinylcarbene.[5] Despite the fact that the cyclopropene ring

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