Metalation of Alkynes. 7. Substituent Effects in Acetoxymercuration of 1-Arylpropynes[1]

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1-Arylpropynes were added to mercuric acetate in acetic acid, with the regiochemistry depending on the substituent. Kinetics of acetoxymercuration were investigated. Second-order rate constants are best related by the Hammett σ.

Introduction

Oxymetalation reactions have been extensively investigated with alkenes, allowing applications in organic synthesis.[2] The mechanism of alkene oxymercuration is still under discussion, especially in comparison with bromination.[3,4] Much less investigated was the corresponding reaction of alkynes. Regiochemistry[5,6] and stereochemistry[5,7,8] of acetoxymercuration were studied, with results depending on the alkyne. Kinetics indicated that acetoxymercuration of alkynes is an electrophilic reaction.[9] However, electronic substituent effects could not be separated from steric effects, because the investigated alkynes were too different structurally (dialkyl-, arylalkyl-, and diarylalkynes). We report here a kinetic investigation on acetoxymercuration of 1-arylpropynes, in order to assess the relevance of electronic substituent effects.

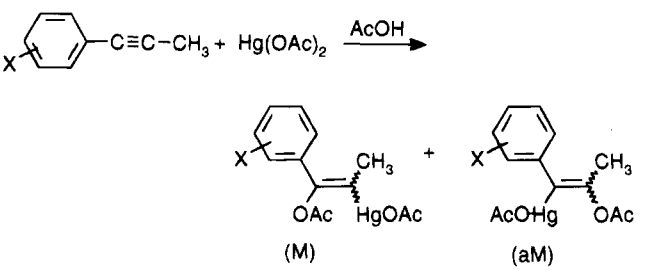
Results and Discussion

A number of substituted 1-phenylpropynes were prepared. The synthesis was not a trivial step, with problems arising in the presence of some substituents. Generally, the procedure involved the formation of arylethynes, which were transformed into acetylides and then alkylated with methyl iodide.[10] Problems have been encountered with *m*-bromophenylethyne, because of competitive lithiodebromination on the aromatic ring, with subsequent formation of methyl-substituted 1-phenylpropyne. Moreover, *m*-nitro- and *p*-nitro-substituted phenylethynes gave extensive polymerization, with the formation of a viscous red material, from which it was not possible to recover the desired arylpropyne. Attempts to remove the acetylene hydrogen with bases different from BuLi (*e.g.*, lithium diisopropylamide in THF or Na in toluene) also failed.

Arylethynes were prepared by a double dehydrochlorination under basic conditions of *gem*-dichloro compounds obtained from substituted acetophenones and PCl_5.[11] Attempts to obtain 1-arylpropynes directly, applying the same reactions to substituted propiophenones[12] gave no satisfactory results. Other synthetic strategies to arylethynes were used, such as Pd(II)-catalyzed reaction of aryl iodides with 3-methyl-1-butyn-3-ol[13] or with (trimethylsilyl)ethyne[14] and bromination–dehydrobromination of substituted cinnamic acids.[15]

Product Analysis. 1-Arylpropynes were reacted with $Hg(OAc)_2$ in acetic acid at room temperature. The reaction was already reported for some 1-arylpropynes under analogous conditions.[6] However, acetoxymercuration products were not isolated as such, but directly transformed into chloromercurio derivatives. We isolated addition products which were identified by mass and ^1H NMR spectra and subsequently transformed into chloromercurio derivatives. Reductive demercuration of acetoxymercurio species contributed also to product analysis (see Experimental Section).

Regiochemistry. Only a Markovnikov-type addition product (M, see equation) was found with electron-donating substituents, *i.e.*, *p*-OMe (as already reported),[6] *p*-Me (differently from previous report[6]), and *m*-Me and



o-Me (which are newly reported here); 20–30% of anti-Markovnikov (aM) products were found with electron-withdrawing substituents, in agreement with Spear's data,[6] although in somewhat lower amounts.

Stereochemistry. Stereochemical assignment to these compounds is not an easy task, because of the absence of protons on the double bond. Thus, an indirect assignment was made in the literature, on the

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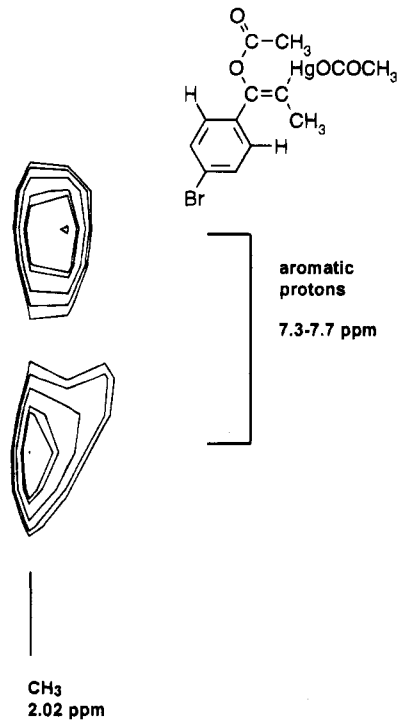

Figure 1. NOE crosspeak between the resonance due to aromatic protons and that due to CH_3, obtained with ROESY on 1-acetoxy-1-(4-bromophenyl)-2-(acetoxymercurio)propene, as reported in the Experimental Section. A mixing time of 300 ms was applied.

basis of protodemercurated compounds PhCH=C(OAc)-CH_3 and PhC(OAc)=$CHCH_3$,[16-18] which both had methyl and phenyl groups in trans positions. Bromodemercurated products also resulted in a trans arrangement.[19] It was assumed that "since these demetallations are known to proceed generally with retention of configuration",[19] mercurated species had to be trans. However, it was demonstrated that halodemetalation of vinyl mercurials occurs with retention or inversion of configuration, depending on experimental conditions.[20] The same might happen with protodemercuration, especially considering that retention of configuration was demonstrated only for the protodethallation reaction.[16]

Recently, an attempt was made to assess the stereochemistry directly, using mainly the NMR criterion that $^2J_{H_gC}{}^1$ has a large positive spin–spin coupling constant or a negative value, when the adduct is trans or cis, respectively.[8] On this basis, to the Markovnikov adduct from 1-(3-chlorophenyl)propyne was assigned the trans structure, while the cis stereochemistry was attributed to the anti-Markovnikov adduct from the same alkyne.

We tried a different approach, using a NOE experiment with a ROESY pulse sequence for p-BrC_6H_4C-(OAc)=C(HgCl)CH_3. The result appears quite conclusive (Figure 1). A NOE crosspeak was found between the resonance due to the aromatic protons and that of CH_3, thus indicating that the proton–proton proximity ranges from 2.5 to 3.5 Å. This distance can be reached only if aryl and methyl groups are in a cis arrangement. The lack of NOE between acetoxy and methyl groups confirms the result. Thus, the major addition product from 1-(4-bromophenyl)propyne can be regarded as (*Z*)-1-acetoxy-1-(4-bromophenyl)-2-(chloromercurio)-propene.

Table 1. Overall Second-Order Rate Constants for the Acetoxymercuration of 1-Arylpropynes, X–C_6H_4–C≡CCH_3, at 25 °C

entry	X	k_2, M^{-1} s^{-1}	$[Hg(OAc)_2]/[alkyne]$	method
1	*p*-OMe	0.13 ± 0.01	10–170	B
2	*p*-Me	$(1.1 \pm 0.1) \times 10^{-2}$	0.1–67	A, B
3	*m*-Me	$(3.2 \pm 0.2) \times 10^{-3}$	10–36	A, B
4	*o*-Me	$(4.1 \pm 0.2) \times 10^{-3}$	10–106	A, B
5	*m*-Cl	$(1.1 \pm 0.2) \times 10^{-3}$	10	A
6	*p*-Cl	$(1.5 \pm 0.3) \times 10^{-3}$	10–128	A, B
7	*p*-Br	$(1.6 \pm 0.1) \times 10^{-3}$	10–187	A, B

Kinetics. Kinetic experiments were performed under pseudo-first-order conditions, by spectrophotometry and by gas chromatography, following the formation of the addition product and the disappearance of the substrate, respectively. Results in excellent agreement were obtained with the two methods. The reaction was generally followed up to 80–90% conversion. The acetoxymercuration of 1-arylpropynes follows a second-order rate law, first order in substrate and first order in $Hg(OAc)_2$, as already found for other alkynes.[9]

The results are summarized in Table 1. Apparently, the acetoxymercuration reaction is favored by electron-donating substituents, as expected for an electrophilic attack in the rate-determining step and in agreement with previously reported data.[9] Unfortunately, 1-(4-nitrophenyl)propyne could not be prepared in an amount sufficient for complete kinetic investigation. From preliminary data it seems more reactive than expected and therefore must be investigated carefully. 1-(4-Chlorophenyl)propyne showed a very good linear relationship between k_{obs} and $[Hg(OAc)_2]$ for concentrations up to 9×10^{-2} M of the excess reagent. Scattered but reproducible results were obtained with $[Hg(OAc)_2]$ higher than 1×10^{-1} M.

Linear Free Energy Relationship. In order to evaluate substituent effects quantitatively, empirical linear free energy relationships were considered. The choice of parameters for the correlation is a problem, when alkynes are involved. It is known that σ_R^0 is the best scale to account for substituent effects in alkenes, especially for substituents directly on the double bond,[21] but no indication is available for alkynes.

Our attention was directed mainly to Hammett σ and σ^+ values. The best correlation was obtained with Hammett σ values[22] for most of substituents, apart from strongly electron-releasing ones (Figure 2, value for the unsubstituted 1-phenylpropyne was taken from ref 9).

1-(2-Methylphenyl)propyne falls on the straight line, if the σ_p value of the methyl group is used. This finding is not surprising, because the ortho-substituted arylpropiolic acids are aligned with meta and para derivatives.[23] By the way, we could not check the relationship

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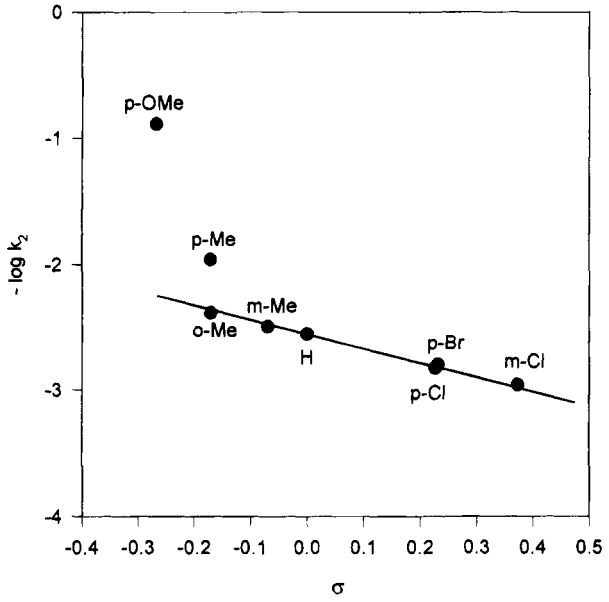

Figure 2. Linear free-energy relationship of rate constants with Hammett σ.

with the alkyne σ values calculated from arylpropiolic acids, because two substituents only are in common with our series.

p-Methyl- and, even more clearly, *p*-methoxy-substituted compounds do not follow the linear correlation with Hammett σ values, but fall above the straight line; *i.e.*, they are faster than expected from the correlation.

This behavior may be explained in terms of a variation of the nature of the cationic intermediate: the intermediate might have a pronounced mercurinium ion character within the series and a large carbocation character when electron-donating substituents can stabilize the positive charge on the carbon atom. This hypothesis is supported by the observed regiochemistry, carbocation-type intermediates leading to a single addition product, whereas mercurinium-type intermediates yielded two regioisomers.

The reaction sensitivity to electronic substituent effects is low, with a slope −1.08. The ϱ value (negative, as expected in a reaction where the rate-determining step is electrophilic) is also consistent with the hypothesis of a mercurinium ion intermediate. As a matter of fact, halogenation of substituted styrenes in AcOH—a reaction demonstrated to occur *via* carbocationic intermediates—has high ϱ values, *i.e.*, −3.22 and −4.87 with chlorine[24] and bromine,[25] respectively. Unfortunately, data are not available for acetoxymercuration of substituted styrenes.

In conclusion, acetoxymercuration of substituted 1-phenylpropynes confirmed that the reaction occurs *via* electrophilic attack in the rate-determining step and indicated that the cationic intermediate can shift in the same series from a bridged mercurinium species to a carbocation. These structures must be considered as limit cases, between which the actual intermediate falls, as already suggested for methoxymercuration of alkynes.[26]

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Experimental Section

Gas chromatographic analyses have been carried out with a Carlo Erba HRGC 5300 Mega Series instrument, equipped with a 2 m 3% OV-17 or a 30 m × 0.25 mm capillary column.

Bruker WP-80 and AM 400 spectrometers were used to obtain ^{1}H NMR spectra as $CDCl_3$ solutions. All chemical shifts are given in ppm from tetramethylsilane. NOE experiments were performed in the rotating frame mode (ROESY).[27,28] The experiment was performed three times, with mixing times of 100, 200, and 300 ms. The spectra were measured in the phase sensitive mode using TPPI.[29] A total of 512 experiments were carried out, accumulating 128 scans over 2K of memory. Processing of the data was performed on a Digital graphic workstation using the TRITON NMR processing program.[30] A real 1024 × 1024 matrix was obtained. A polynomial baseline correction was applied in both dimensions.

Direct inlet (electronic impact EI, 50 eV) mass spectra were obtained with a VG Quattro spectrometer. Gas-mass spectrometry analyses have been performed with a Hewlett-Packard 5970B system, equipped with a Hewlett-Packard gas chromatograph.

Spectrophotometric measurements were made with Philips PU 8730 UV/vis (preliminary spectra), Cary 219, and HP 8452 diode array (kinetic experiments) spectrophotometers.

Materials. Mercuric acetate (Merck) was a commercially available grade reagent. Bis(triphenylphosphino)palladium dichloride was prepared from $PdCl_2$ and triphenylphosphine in *N,N*-dimethylformamide.[31] Ultrapure acetic acid (Erba RSE) was used in kinetic experiments.

The following arylethynes were prepared according to ref 11 (yields in parentheses): (*o*-methylphenyl)ethyne (35%), (*m*-methylphenyl)ethyne (21%), (*p*-methylphenyl)ethyne (37%), (*m*-chlorophenyl)ethyne (33%), (*p*-chlorophenyl)ethyne (40%), (*m*-bromophenyl)ethyne (30%), (*p*-bromophenyl)ethyne (50%). (*p*-Methoxyphenyl)ethyne was formed in 24%[13] or 50%[15] yield, (*m*-nitrophenyl)ethyne was prepared in 15%[14] and 10%[15] yields and 36% (*p*-nitrophenyl)ethyne was obtained.[15]

Arylethynes were treated with BuLi in THF at −78 °C and then methyl iodide was added.[10] Not all the arylethynes could be transformed into 1-arylpropynes. The following alkynes were prepared (yields in parentheses): 1-(2-methylphenyl)-propyne (49%), 1-(3-methylphenyl)propyne (46%), 1-(4-methylphenyl)propyne (89%), 1-(4-methoxyphenyl)propyne (50%), 1-(3-chlorophenyl)propyne (15%), 1-(4-chlorophenyl)propyne (71%), 1-(4-bromophenyl)propyne (20%), 1-(3-bromophenyl)-propyne (2%). The last compound was a minor constituent (20%) of the reaction mixture, the main product being 1-(3-methylphenyl)propyne, as shown by gas—mass analysis. Thus, the *m*-bromo derivative could not be used for kinetic experiments.

All the compounds were distilled under vacuum (16—18 mmHg) and became gas chromatographically pure. Their identification was achieved by ^{1}H NMR and mass spectra.

Product Analysis. In a typical experiment 1 mmol of alkyne was reacted with 1.5 mmol of $Hg(OAc)_2$ in 50 mL of AcOH at room temperature, monitoring the disappearance of substrate by GC. Acetic acid was removed under vacuum, without heating, and the residue was dissolved in CH_2Cl_2, washed with water to remove unreacted mercuric acetate, and dried over anhydrous Na_2SO_4. The acetoxymercurio deriva-

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tive, obtained after evaporation of dichloromethane as a viscous pale yellow liquid, was characterized by direct inlet (EI) mass spectrometry and ^{1}H NMR.

In selected cases, an aliquot of the acetoxymercurio species was quantitatively transformed into the chloromercurio derivative, by adding 10% aqueous KCl to a dichloromethane solution of it. The solid precipitate was recrystallized with EtOH/hexane and characterized by EI mass spectrometry and ^{1}H NMR. Melting points were in agreement with available literature data.[6]

Reductive demercuration was performed on a portion of the acetoxymercurio compound dissolved in CH_2Cl_2. An aqueous basic (NaOH) solution of $NaBH_4$ was added under stirring at 0 °C. Metallic mercury separated almost immediately. The organic layer was washed with water to neutrality, dried over anhydrous Na_2SO_4, and examined by GC/MS. The following results were obtained.

From 1-(4-Methoxyphenyl)propyne. Yield: 16%, 4-$CH_3OC_6H_4C(OAc)$=$C(HgOAc)CH_3$. ^{1}H NMR, δ (ppm): 2.00, s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 196 Hz); 2.20, s, 3H, $OCOCH_3$; 3.80, s, 3H, OCH_3; 6.9–7.4, complex, 4H, aromatic protons. MS (EI, 50 eV), *m/z*: cluster around 400 ($M^+ - OCOCH_3$, Hg isotopes; MF, 464.87). From treatment with KCl, 4-$CH_3OC_6H_4C(OAc)$=$C(HgCl)CH_3$, MS (EI, 50 eV), *m/z*: cluster around 402 ($M^+ - OCOCH_3$, Hg and Cl isotopes). From reductive demercuration, GC/MS (*m/z*): 25% *p*-$OCH_3C_6H_4C$≡CCH_3 (146, M^+; MF, 146.19), 21% $ArCOCH_2CH_3$ (164, M^+; 135, $ArCO^+$; 107, Ar^+; MF, 164.20), 54% *p*-$CH_3OC_6H_4C(OAc)$=$CHCH_3$ (206, M^+; 164, $M^+ - COCH_2$; 135, $ArCO^+$; 43, CH_3CO^+; MF, 206.24).

From 1-(4-Methylphenyl)propyne. Yield: 97%, 4-$CH_3C_6H_4C(OAc)$=$C(HgOAc)CH_3$. ^{1}H NMR, δ (ppm): 1.99, s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 192 Hz); 2.19, s, 3H, $OCOCH_3$; 2.33, s, 3H, $ArCH_3$; 7.14–7.44, dd, 4H, aromatic protons (J = 23 Hz, 8Hz). MS (EI, 50 eV), *m/z*: cluster around 449 (M^+; MF, 448.87, Hg isotopes). From treatment with KCl, 4-$CH_3C_6H_4C(OAc)$=$C(HgCl)CH_3$, MS (EI, 50 eV), *m/z*: cluster around 425 (M^+, Hg, and Cl isotopes; MF, 424.70). Anal. Calcd for $C_{12}H_{13}O_2HgCl$: C, 33.89; H, 3.08. Found: C, 31.34; H, 2.70. From reductive demercuration, GC/MS (*m/z*): 100% *p*-$CH_3C_6H_4C$≡CCH_3 (130, M^+; MF, 130.19); not integrated, $ArCOCH_2CH_3$ (148, M^+; 119, base peak, $ArCO^+$; 91, Ar^+; MF, 148.04); not integrated, *p*-$CH_3C_6H_4C(OAc)$=$CHCH_3$ (190, M^+; 148, $M^+ - COCH_3 - H$; 133, $M^+ - OCOCH_3$; 119, $ArCO^+$; 91, Ar^+; MF, 190.08); not integrated, $ArCOCOCH_3$ (162, M^+; 119, $ArCO^+$; 91, Ar^+; MF, 162.19); not integrated, $ArCOCH(OH)CH_3$ (164, M^+; 147, $M^+ - H_2O + H^+$; 119, $ArCO^+$; 91, Ar^+; MF, 164.21).

From 1-(3-Methylphenyl)propyne. Yield: 70%, 3-$CH_3C_6H_4C(OAc)$=$C(HgOAc)CH_3$. ^{1}H NMR, δ (ppm): 1.98, s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 192 Hz); 2.19, s, 3H, $OCOCH_3$; 2.34, s, 3H, $ArCH_3$; 7.1–7.4, complex, 4H, aromatic protons. MS (EI, 50 eV), *m/z*: cluster around 447 (M^+, Hg isotopes; MF, 448.87). Anal. Calcd for 3-$CH_3C_6H_4C(OAc)$=$C(HgCl)CH_3$ (from treatment with KCl, $C_{12}H_{13}O_2HgCl$): C, 33.89; H, 3.08. Found: C, 31.22; H, 2.80. From reductive demercuration, GC/MS (*m/z*): 35% *m*-$CH_3C_6H_4C$≡CCH_3 (130, M^+, MF, 130.19), 30% $ArCOCOCH_3$ (162, M^+; 119, $ArCO^+$; 91, Ar^+; MF, 162.19), 35% *m*-$CH_3C_6H_4C(OAc)$=$CHCH_3$ (190, M^+; 148, M^+ $COCH_3$ – H; 119, $ArCO^+$; 91, Ar^+; 43, CH_3CO^+; MF, 190.08).

From 1-(2-Methylphenyl)propyne. Yield: 80%, 2-$CH_3C_6H_4C(OAc)$=$C(HgOAc)CH_3$. ^{1}H NMR, δ (ppm): 1.91, s, 3H, =CCH_3 (J_{Hg-H} = 192 Hz); 1.99, s, 3H, $HgOCOCH_3$; 2.09, s, 3H, $OCOCH_3$; 2.36, s, 3H, $ArCH_3$; 7.2–7.5, complex, 4H, aromatic protons. MS (EI, 50 eV), *m/z*: cluster around 406 ($M^+ - COCH_3$, Hg isotopes; MF, 448.87). Anal. Calcd for 2-$CH_3C_6H_4C(OAc)$=$C(HgCl)CH_3$ from treatment with KCl, $C_{12}H_{13}O_2HgCl$): C, 33.89; H, 3.08. Found: C, 33.04; H, 2.90. From reductive demercuration, GC/MS (*m/z*): 10% *o*-$CH_3C_6H_4CH$=$C(OAc)CH_3$ (190, M^+; MF, 190.08; 148, $M^+ - COCH_3$ – H; 119, $ArCO^+$); 90% $ArCOCOCH_3$ (162, M^+; 118, $M^+ - COCH_3$ – H; 107, Ar^+; MF, 162.19); not integrated, $ArCOCH(OH)CH_3$ (163, M^+ – H; 146, $M^+ - H_2O$; 118, $ArCO^+$ – H; 91, Ar^+H; MF, 164.21).

From 1-(4-Bromophenyl)propyne. Overall yield: 86%. 61% 4-$BrC_6H_4C(OAc)$=$C(HgOAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.01 [s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 189 Hz)], 2.19 [s, 3H, $OCOCH_3$], 7.4–7.6 [complex, 4H, aromatic protons]. 25% 4-$BrC_6H_4C(HgOAc)$=$C(OAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.25 [s, =CCH_3], 1.90 [s, $OCOCH_3$]. MS (EI, 50 eV), *m/z*: 514 (cluster, M^+, Br and Hg isotopes; MF, 513.73). From treatment with KCl: 4-$BrC_6H_4C(OAc)$=$C(HgCl)CH_3$ ^{1}H NMR [δ (ppm)] 2.02 [s, 3H, =CCH_3 (J_{Hg-H} = 186 Hz)], 2.20 [s, 3H, $OCOCH_3$], 7.3–7.7 [complex, 4H, aromatic protons]; 29% 4-$BrC_6H_4C(HgCl)$=$C(OAc)CH_3$ ^{1}H NMR [δ (ppm)] 1.90 [s, $OCOCH_3$]. MS (EI, 50 eV), *m/z*: 490 (cluster, M^+; Br, Cl, and Hg isotopes; MF, 490.18). Anal. Calcd for $C_{11}H_{10}O_2BrHgCl$: C, 26.95; H, 2.06. Found: C, 28.11; H, 2.10. From reductive demercuration, GC/MS (*m/z*): 64% *p*-BrC_6H_4C≡CCH_3 (194, 196, M^+; MF, 195.06); 36% $ArCOCH_2CH_3$ (212, 214, M^+; 183, 185, $ArCO^+$; 155, 157, Ar^+; MF, 213.07); not integrated, $ArCH_2COCH_3$ (212, 214, M^+; 169, 171, $ArCH_2^+$); not integrated, *p*-$BrC_6H_4C(OAc)$=$CHCH_3$ (254, 256, M^+; 212, 214, $M^+ - COCH_3$ – H; 183, 185, $ArCO^+$; 155, 157, Ar^+; MF, 255.11).

From 1-(4-Chlorophenyl)propyne. Overall yield: 98%. 69% 4-$ClC_6H_4C(OAc)$=$C(HgOAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.00 [s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 192 Hz)], 2.20 [s, 3H, $OCOCH_3$], 7.2–7.5 [complex, 4H, aromatic protons]. 29% 4-$ClC_6H_4C(HgOAc)$=$C(OAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.25 [s, =C-CH_3], 1.93 [s, $OCOCH_3$]. MS (EI, 50 eV), *m/z*: cluster around 470 (M^+, Cl and Hg isotopes; MF, 468.68). From treatment with KCl: 70% 4-$ClC_6H_4C(OAc)$=$C(HgCl)CH_3$ ^{1}H NMR [δ (ppm)] 2.02 [s, 3H, =CCH_3], 2.20 [s, 3H, $OCOCH_3$] 7.2–7.5 [complex, 4H, aromatic protons] 30% 4-$ClC_6H_4C(HgCl)$=$C(OAc)CH_3$ ^{1}H NMR [δ (ppm)] 2.25 [s, =CCH_3], 1.94 [s, $OCOCH_3$]. MS (EI, 50 eV), *m/z*: cluster around 446 (M^+; MF, 445.15, Cl and Hg isotopes). Anal. Calcd for $C_{11}H_{10}O_2HgCl_2$: C, 29.64; H, 2.26. Found: C, 28.84; H, 2.06. From reductive demercuration, GC/MS (*m/z*): 100% *p*-ClC_6H_4C≡CCH_3 (150, 152, M^+, MF, 150.61); not integrated, $ArCOCH_2CH_3$ (168, 170, M^+; 139, 141, $ArCO^+$; MF, 168.62); not integrated, *p*-$ClC_6H_4C(OAc)$=$CHCH_3$ (210, 212, M^+; MF, 210.66).

From 1-(3-Chlorophenyl)propyne. Overall yield: 24%. 19% 3-$ClC_6H_4C(OAc)$=$C(HgOAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.03 [s, 6H, $HgOCOCH_3$ + =CCH_3 (J_{Hg-H} = 194 Hz)], 2.23 [s, 3H, $OCOCH_3$], 7.2–7.5 [complex, 4H, aromatic protons]. 5% 3-$ClC_6H_4C(HgOAc)$=$C(OAc)CH_3$: ^{1}H NMR [δ (ppm)] 2.25 [s, =CCH_3], 1.93 [s, $OCOCH_3$]. MS (EI, 50 eV), *m/z*: cluster around 470 (M^+, Cl and Hg isotopes; MF, 468.68). From reductive demercuration, GC/MS (*m/z*): 5% *m*-ClC_6H_4C≡CCH_3 (150, 152, M^+; MF, 150.61), 61% $ArCOCH_2CH_3$ (168, 170, M^+; 139, 141, $ArCO^+$; 111, 113, Ar^+; MF, 168.62), 6% *m*-$ClC_6H_4CH_2COCH_3$ (168, 170, M^+; 125, 127, $ArCH_2^+$; 43, $COCH_3^+$; MF, 168.62), 25% *m*-$ClC_6H_4COCOCH_3$ (182, 184 M^+; 147, $M^+ - Cl$; 139, 141, $ArCO^+$; 111, 113, Ar^+; MF, 182.61), *m*-$ClC_6H_4COCH(OH)CH_3$ (183, 185, $M^+ - H$; 125, 127, $ArCH_2^+$; MF, 184.63). GC/MS analysis of the same sample, performed immediately after reductive demercuration, showed also two not integrated peaks, that disappeared after 1 day, *m*-ClC_6H_4CH=$C(OAc)CH_3$ and *m*-$ClC_6H_4C(OAc)$=$CHCH_3$ (210, 212, M^+; MF, 210.66).

Kinetic Measurements. Kinetic experiments have been carried out under pseudo-first order conditions, with different techniques.

A. Known quantities in acetic acid of excess $Hg(OAc)_2$, the alkyne, and the appropriate internal standard were mixed in a thermostated reaction vessel. Samples (0.5 mL) of the reaction mixture were taken at known times and added with 5 mL of water and 1 mL of hexane in a separatory funnel. The organic phase was examined at the gas chromatograph immediately after separating and drying with anhydrous Na_2SO_4. Blank experiments confirmed the reliability of the method. Diphenylmethane was used as the internal standard.

The disappearance of the substrate was followed with time, mercurated species not being detectable by gas chromatography.

B. Solutions at known concentrations of the reactants were separately put in a silica cell with a septum, allowed to reach 25 °C in the thermostated cell compartment of the spectrophotometer, and mixed. The absorbance variation, due to the formation of the product, was followed with time, at the appropriate wavelength, chosen by recording preliminary spectra in the range 280−340 nm. When infinity time absorbance was not available, the value was extrapolated according to Mangeldorf's method.[32] When available, experimental and extrapolated values were in excellent agreement.

The data are reported in Table 1 as overall second-order rate constants. They are mean values of several runs carried out under conditions specified as follows (wavelengths and fractions of the reaction followed are given in parentheses).

1-(4-Methoxyphenyl)propyne: *p*-$MeOC_6H_4C{\equiv}CMe$, 3.25×10^{-4} to 3.25×10^{-3} M; $Hg(OAc)_2$, 2.02×10^{-3} to 1.01×10^{-2} M (284 nm, 76−98%).

1-(4-Methylphenyl)propyne: *p*-$MeC_6H_4C{\equiv}CMe$, 1.48×10^{-3} to 1.53×10^{-2} M; $Hg(OAc)_2$, 1.16×10^{-3} to 1.01×10^{-1} M (300 nm, 64−97%).

(32) Bamford, C. H.; Tipper, C. F. H. *Comprehensive Chemical Kinetics*; Elsevier: Amsterdam, 1969; Vol. 1.

1-(3-Methylphenyl)propyne: *m*-$MeC_6H_4C{\equiv}CMe$, 2.30×10^{-3} to 3.80×10^{-3} M; $Hg(OAc)_2$, 1.10×10^{-2} to 1.00×10^{-1} M (295, 300 nm, 64−89%).

1-(2-Methylphenyl)propyne: *o*-$MeC_6H_4C{\equiv}CMe$, 7.93×10^{-4} to 1.77×10^{-3} M; $Hg(OAc)_2$, 1.00×10^{-2} to 1.63×10^{-1} M (280, 290, 298, 300 nm, 68−99%); isosbestic point at 293 nm.

1-(4-Bromophenyl)propyne: *p*-$BrC_6H_4C{\equiv}CMe$, 6.71×10^{-4} to 4.10×10^{-3} M; $Hg(OAc)_2$, 2.00×10^{-2} to 1.67×10^{-1} M (298, 300 nm, 65−74%).

1-(4-Chlorophenyl)propyne: *p*-$ClC_6H_4C{\equiv}CMe$, 1.17×10^{-3} to 6.30×10^{-3} M; $Hg(OAc)_2$, 2.00×10^{-2} to 1.67×10^{-1} M (300 nm, 72−93%).

1-(3-Chlorophenyl)propyne: *m*-$ClC_6H_4{\equiv}CMe$, 4.23×10^{-3} M; $Hg(OAc)_2$, 3.97×10^{-2} M (64%).

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