METALLATION OF ALKYNES. PART 8.[1] SUBSTITUENT EFFECTS IN THE ACETOXYMERCURATION OF DIARYLETHYNES

Enrico Ballico[1], Giorgio Cerichelli[2*], Simona Fossa[1],
Barbara Floris[1*] and Federico Giordano[3*]

[1] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata",
Via della Ricerca Scientifica, I-00133 Roma, Italy
[2] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Coppito Due,
Via Vetoio, I-67010, L'Aquila, Italy
[3] Dipartimento di Chimica, Università di Napoli "Federico II",
Via Mezzocannone 4, I-80341, Napoli, Italy

Summary. *Meta*- and *para*-substituted diphenylethynes were reacted with mercuric acetate in acetic acid. The mercurated addition compounds were isolated and identified. The stereochemistry of the reaction, elucidated by X-ray analysis, is consistent with an *anti* addition. Substituent effects are in agreement with an electrophilic reaction and rate constants are best related by σ^+.

Organomercurio compounds have been used in organic synthesis, especially in solvomercuration-demercuration reactions[2]. The reaction of Hg(II) species with carbon-carbon double bonds is an electrophilic addition, that proceeds *via* a cationic intermediate, the nature of which has been interpreted either as a carbocation (on the basis of regiochemistry) or as a bridged mercurinium ion (on the basis of stereochemistry). The intermediate is now better considered as a non symmetrical mercurinium ion[3,4]. There is still interest in the mechanism of this reaction[5], that is generally compared with bromination[5-7].

Much less investigated has been the corresponding reaction of alkynes, although its use in organic synthesis has been quite important[2]. Studies on regiochemistry[8,9] and stereochemistry[8,10,11] gave results depending on the alkyne. Kinetic experiments confirmed that acetoxymercuration of alkynes is an electrophilic reaction[12], but electronic substituent effects could be separated from steric effects only recently, when acetoxymercuration of substituted 1-arylpropynes was investigated[1]. However, the experimental picture resulting from 1-arylpropynes was complicated by the occurrence of regioisomers, beside the possibility of stereoisomers. Moreover, stereochemistry could be assigned only indirectly, because the acetoxymercurio derivatives of 1-arylpropynes were not suitable for X-ray analysis.

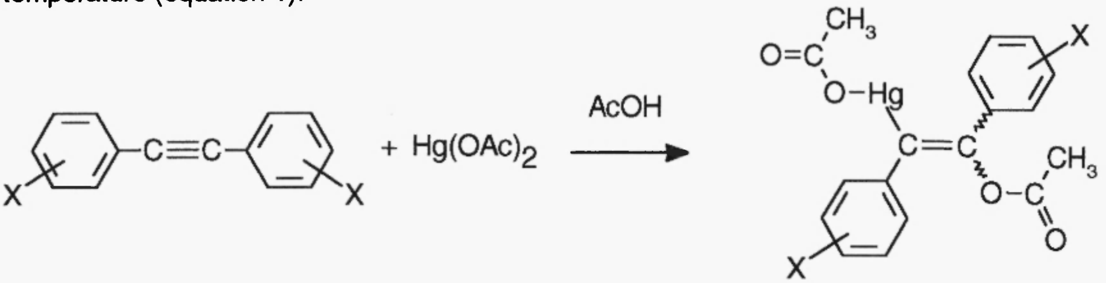
We report here a kinetic investigation on the acetoxymercuration of diarylethynes with the same substituent on both rings. The choice of substrates was made in order to overcome the complication of regioisomers, stereoisomers being the only possible isomers resulting from addition reactions.

Results and Discussion

Preparation of Substrates. A number of diarylethynes, bearing the same substituent in the same position of the two rings, were prepared by reacting the copper acetylide, ArCCCu, with the corresponding aryl iodide, ArI.[13,14] Alternative methods recently reported in the literature[15] were also attempted, but they did not give good results with our substrates. Copper acetylides were obtained from the corresponding arylethynes[14] that, in turn, were mostly prepared by double dehydrochlorination under basic conditions of *gem*-dichloro compounds, obtained from substituted acetophenones and PCl_5[16]. Other synthetic strategies to arylethynes were used, such as Pd(II)-catalysed reaction of aryl iodides with 3-methyl-1-butyn-3-ol[17] or with trimethylsilylethyne[18] and bromination-debromination of substituted cinnamic acids[19].

A major problem has been separation of diarylethynes from unreacted iodobenzenes, that were eluted almost simultaneously by column chromatography with hexane as eluent. Diarylethynes pure enough for kinetic measurements (> 98% by GC) were obtained only by careful fractional distillation under vacuum of the crude reaction mixture, pre-purified by column chromatography.

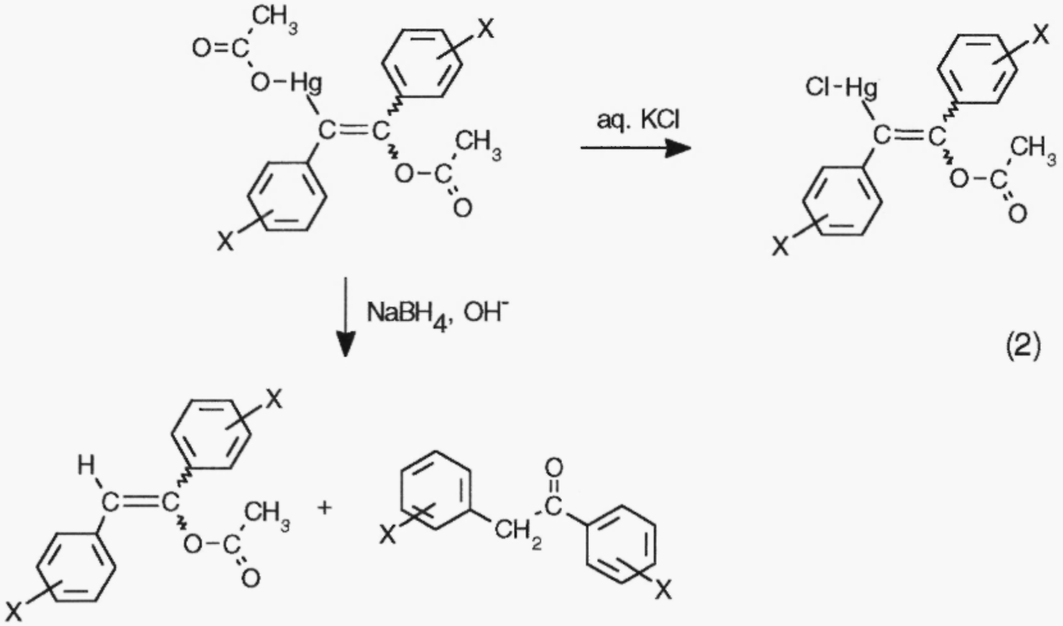
Product Analysis. Diarylethynes were reacted with mercuric acetate in acetic acid at room temperature (equation 1).



(1)

The reaction was monitored by GC analysis, following the disappearance of alkyne, mercurated species being not detectable. With less reactive substrates, the reaction was interrupted before completion, to avoid solvodemercuration.

Products from acetoxymercuration reaction were isolated and identified by mass and ^1H NMR spectra, and subsequently transformed into chloromercurio derivatives. Reductive demercuration of acetoxymercurio species, a well-established method[20], also contributed to product analysis (equation 2):



(2)

Particular care is necessary during isolation and purification of mercurated compounds, especially in the presence of electron-withdrawing substituents. Acetic acid must be removed without heating and heating over room temperature has to be avoided in all subsequent operations. If this were not the case, loss of HgX_2 occurred and R_2Hg species were isolated, as indicated by X-ray diffraction analysis[21].

Stereochemistry. No evidence for the presence of two stereoisomers has been found. The reaction appears to be stereospecific and a *trans* arrangement of aryl groups around the carbon-

carbon double bond was observed in the X-ray structure of 1-acetoxy-2-chloromercurio-1,2-di(4-methylphenyl)ethene (Figure 1).

A similar *trans* disposition was found in 1-acetoxy-2-chloromercurio-1-(4-fluorophenyl)-phenylethene (from acetoxymercuration of (4-fluorophenyl)phenylethyne[22]) and 1-acetoxy-2-chloromercurio-1,2-bisdiphenylethene (from acetoxymercuration of diphenylethyne)[11]. Interestingly, products from alkoxymercuration of diphenylethyne showed a *cis* disposition[23]. The different solvent system must be the responsible for the different stereochemistries, but no rationale can be offered at present.

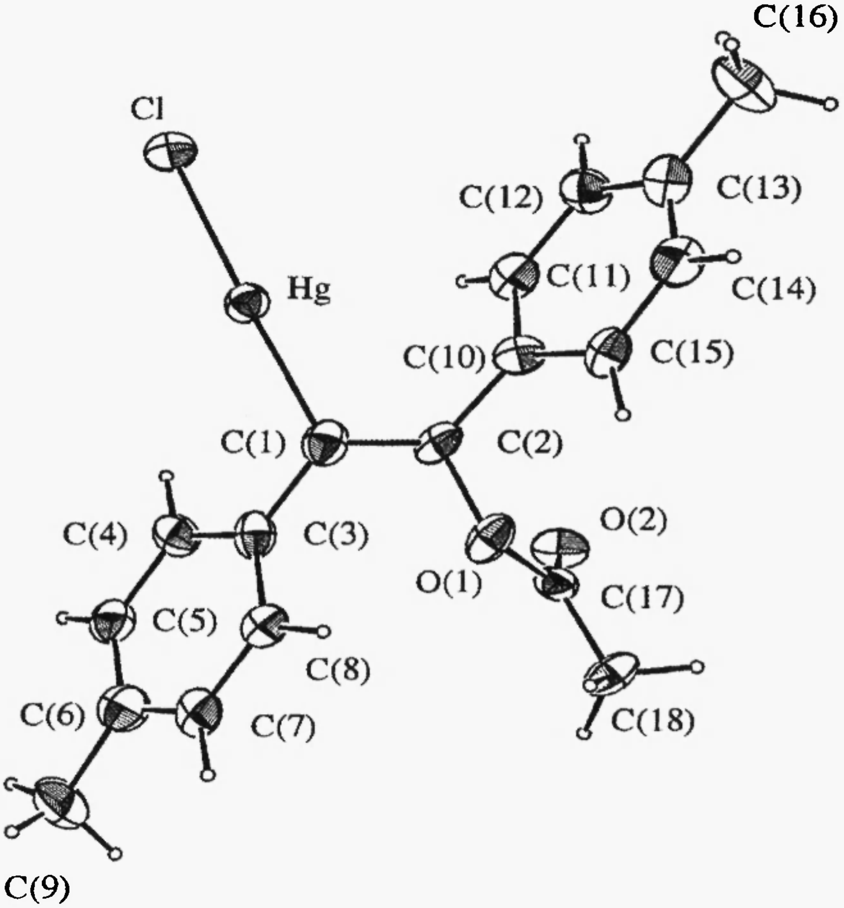


Figure 1. ORTEP view of (*E*)-1-chloro-2-acetoxymercurio-1,1-di(4-methylphenyl)ethene. Selected bond lengths (Å) and angles (°): Hg-Cl 2.276(4), Hg-C(1) 2.07(2), C(1)-C(2) 1.34(2), C(1)-C(3) 1.48(2), C(2)-C(10) 1.48(2), O(1)-C(2) 1.43(2), O(1)-C(17) 1.39(2); Cl-Hg-C(1) 173.4(5), Hg-C(1)-C(2) 117(1), Hg-C(1)-C(3) 118(1), C(2)-C(1)-C(3) 125(1), O(1)-C(2)-C(1) 117(1), O(1)-C(2)-C(10) 112(1), C(1)-C(2)-C(10) 129(1).

The molecular structure shown in Fgure 1 exhibits the same features observed in the homologous molecule 4-$FC_6H_4C(OAc)=C(HgCl)Ph$[22]. The planes through the C(3)/C(9) and C(10)/C(16) phenyl groups and the acetoxy group form with the planar olefinic fragment, defined by C(1), C(2), C(3), C(10), and O(1), the following dihedral angles: 33(1), 39(1) and 81(1)°, respectively. The olefinic plane is somewhat distorted (χ^2= 45) and Hg and Cl are at a distance of 0.370(1) and 0.455(5) Å away from it. These effects, as well as the deviation from linearity of the bond angle Cl-Hg-C(1), are probably the result of packing requirements. As in the cognate molecules[22,23], the valence angles C(3)-C(1)-C(2) and C(10)-C(2)-C(1), formed by the double bond and the C_{sp^2}-C(phenyl) bonds, display significantly higher values [125(1) and 129(1)°, respectively] than the adjacent angles. These features cannot be ascribed to steric contacts, but rather should be taken as the result of an electronic effect.

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, with the exception of nitro-substituted compounds. The acetoxymercuration of diarylethynes followed a second-order rate law, first order in substrate and first order in $Hg(OAc)_2$, as already found with other alkynes[1,12]. The results are summarised in Table 1.

Table 1. Second-order Rate Constants for the acetoxymercuration of diarylethynes, $X\text{-}C_6H_4C{\equiv}CC_6H_4X$, at 25°C.

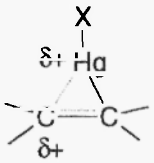
Entry	X	k_2, $M^{-1}s^{-1}$	$[Hg(OAc)_2]$/ [alkyne]	Method[a]
1	4-OMe	$(3.4\pm0.5) \times 10^{-3}$	280-2000	B
2	4-Me	$(2.3\pm0.3) \times 10^{-4}$	10-700	A,B
3	3-Me	$(5.5\pm0.3) \times 10^{-5}$	160-2000	B
4	2-Me	$(1.4\pm0.2) \times 10^{-4}$	100	B
5	4-Cl	$(2.5\pm0.4) \times 10^{-5}$	170-1000	A,B
6	3-Cl	$(1.6\pm0.3) \times 10^{-5}$	10-900	B
7	4-Br	$(2.5\pm0.6) \times 10^{-5}$	10-1500	A,B
8	3-Br	$(1.5\pm0.3) \times 10^{-5}$	10-2800	A,B
9	$4\text{-}NO_2$	$(3.4\pm0.6) \times 10^{-6}$	90-900	B
10	$3\text{-}NO_2$	$(5.1\pm0.5) \times 10^{-6}$	90-100	B

[a] See Experimental

The acetoxymercuration reaction is favoured by electron-donating substituents, as expected for an electrophilic attack in the rate-determining step and in agreement with previously reported data[1,12].

Linear Free Energy Relationship. In order to evaluate substituent effects quantitatively, empirical linear free energy relationships were considered. With 1-arylpropynes, the best correlation was obtained with Hammett σ values[24] for most substituents, apart from strongly electron releasing ones[1]. Diarylethynes, however, gave a very poor correlation with Hammett σ values. An attempt to correlate reactivities with σ^+ values[24] eventually resulted in two different straight lines, as shown in Figure 2. Slopes gave $\rho = -2.61$ and -1.12, respectively.

Although Hammett-type plots concave upwards are considered as diagnostic for a change in the reaction mechanism[25], we think that our result may be explained if we consider the cationic intermediate as having a partial positive charge on the carbon atom, favoured by the extended conjugation:



The partial positive charge is stabilized more effectively in the presence of electron-releasing substituents than with electron withdrawing ones. As a consequence, the sensitivity of the reaction to electronic substituent effects is larger with the former than with the latter substituents. However, in both cases it is low, when compared with bromination in acetic acid of substrates that react *via* a carbocation intermediate (*e.g.*, ρ = - 4.87 with substituted styrenes[26]), thus indicating that the amount of positive charge on sp^2 carbon atom of the intermediate is less than unity, accordingly with the structure proposed above.

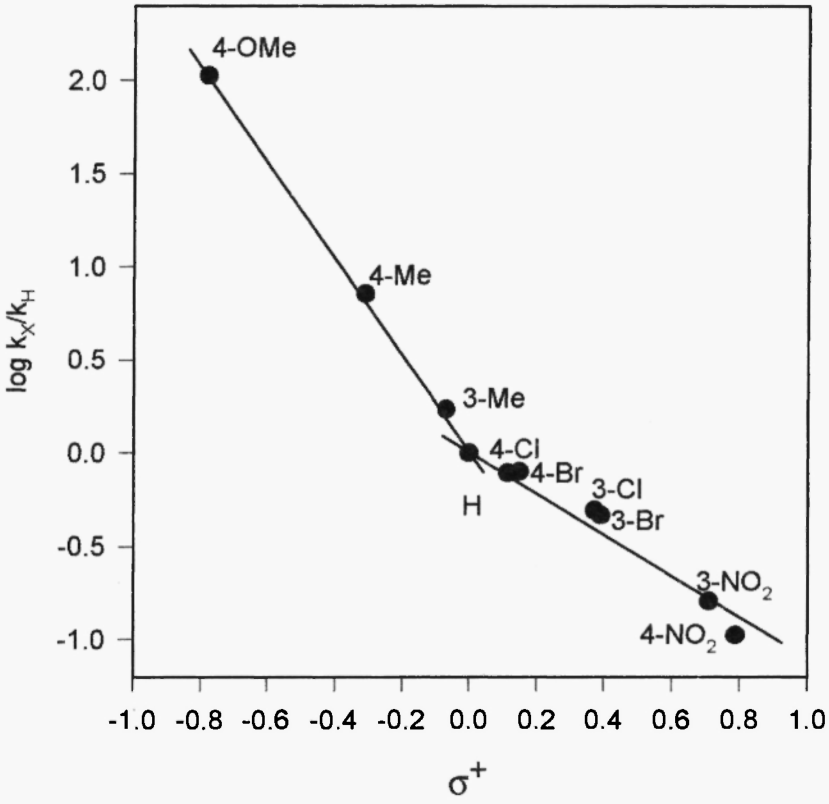


Figure 2. Linear free-energy relationship of rate constants with σ^+.

If one considers the electron density of sp C atoms of alkynes, as it results from ^{13}C chemical shifts, which are known to be charge-controlled, the pattern is quite complicated (Figure 3). There is not a single relationship with σ nor with σ^+ values. ^{13}C C≡C resonances of *meta*-substituted alkynes are practically independent of substituents. On the other hand, chemical shifts of sp carbon atoms in *para*-substituted compounds are linearly related either with σ or with σ^+ values only if *p*-OMe (in the former case) or *p*-NO_2 (in the latter one) are left out of the straight line. Moreover, the overall variation of chemical shifts is quite small ($\Delta\delta$ = 4.1 ppm) and lower than that of aromatic carbon atoms attached to the triple bond ($\Delta\delta$ = 13.2 ppm[27]). Apparently, the electronic density on sp C atoms is mostly determined by π bonds and is little affected by substituents.

Therefore the importance of electronic substituent effects on ^{13}C chemical shifts of triple bond carbon atoms is different from that on their reactivity with mercuric acetate. Such a difference suggests that acetoxymercuration is an orbital controlled reaction rather than a charge-controlled one, in agreement with the soft character of Hg(II) as a Lewis acid[28].

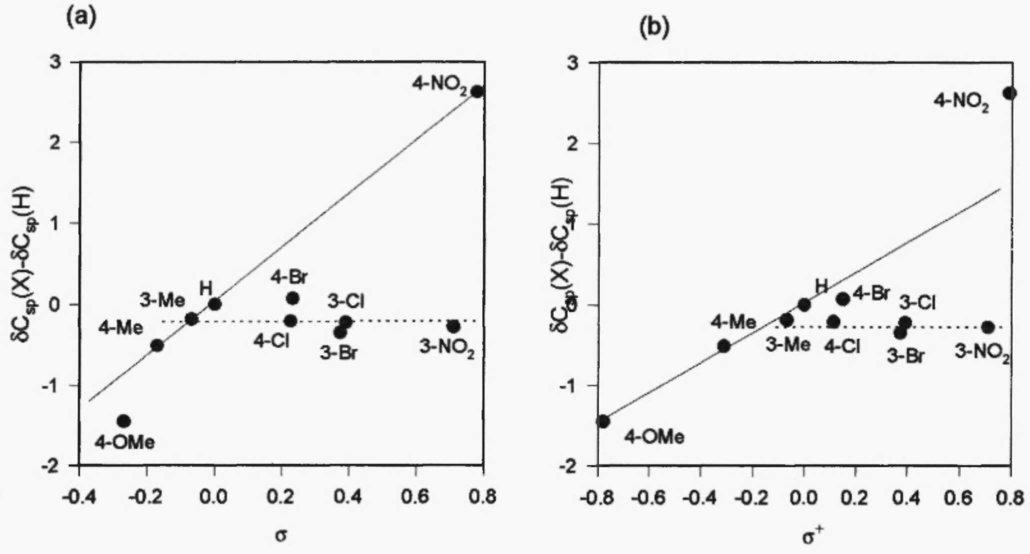


Figure 3. Linear free-energy relationship of ^{13}C chemical shifts (C sp) with (a) Hammett σ and (b) σ$^+$.

Experimental

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 x 0.25 mm capillary column.
Bruker WP-80, AM400, and AC-300P spectrometers were used to obtain ^1H and ^{13}C NMR spectra as $CDCl_3$ solutions with tetramethylsilane as the internal standard.
Direct inlet (electronic impact, E.I., 50 eV) and F.A.B. 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 Jasco 7850 spectrophotometers.

Materials. Mercuric acetate (Merck) was a commercially available grade reagent. Ultapure acetic acid (Erba RSE) was used in kinetic experiments. Arylethynes were prepared as described previously[1]. Arylethynes were transformed into copper(I) derivatives with aqueous solutions of cuprous iodide[14], in yields ranging from 21 to 75%, depending on the substituent.
Substituted diarylethynes were obtained by refluxing equimolar amounts of ArC≡CCu and ArI in anhydrous pyridine, under nitrogen atmosphere[14]. After usual workup, the following diarylethynes were obtained, gas chromatographically pure, after distillation in a Kugelrohr apparatus (under reduced pressure, 1 mm Hg), of the solid material from column chromatography (silica gel, hexane as the eluant). Mass spectra fragmentations were found in agreement with those reported for similar compounds[29].
bis(2-Methylphenyl)ethyne. Yield: 33%; mp 28-30°C. ^1H NMR, δ (ppm): 2.52 (6H, s, CH_3), 7.2-7.5 (8H, complex, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 206 (M^+; MF, 206.16), 176 (M^+-2CH_3), 103 ($M^+/2$).

bis(3-Methylphenyl)ethyne. Yield: 57%; mp 58-61°C. ^{1}H NMR, δ (ppm): 2.33 (6H, s, CH_3), 7.1-7.4 (8H, complex, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 206 (M^+; MF, 206.16), 176 (M^+-2CH_3), 103 (M^+/2).

bis(4-Methylphenyl)ethyne. Yield: 46%; mp 122-123°C. ^{1}H NMR, δ (ppm): 2.35 (6H, s, CH_3), 7.13, 7.41, *J*=8.0 Hz (8H, AB *para* pattern, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 206 (M^+; MF, 206.16), 176 (M^+-2CH_3), 103 (M^+/2).

bis(4-Methoxyphenyl)ethyne. Yield: 20%; mp 137-139°C. ^{1}H NMR, δ (ppm): 3.81 (6H, s, OCH_3), 6.86, 7.45, *J*=11.8 Hz (8H, AB *para* pattern, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 238 (M^+; MF, 238.14), 223 (M^+-CH_3), 119 (M^+/2).

bis(3-Chlorophenyl)ethyne. Yield: 51%; mp 71-73°C. ^{1}H NMR, δ (ppm): 7.2-7.5 (complex, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 246, 248, 250 (M^+, Cl isotopes; MF, 247.04), 176 (M^+-2Cl), 123 (M^+/2).

bis(4-Chlorophenyl)ethyne. Yield: 43%; mp 177-178°C. ^{1}H NMR, δ (ppm): 7.33, 7.44, *J*=8.8 Hz (AB *para* pattern, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 246, 248, 250 (M^+, Cl isotopes; MF, 247.04), 176 (M^+-2Cl), 123 (M^+/2).

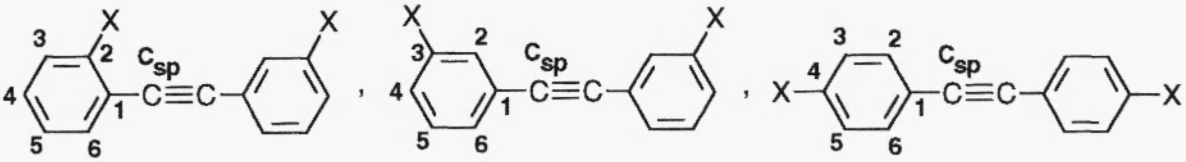
bis(3-Bromophenyl)ethyne. Yield: 90%; mp 94-96°C. ^{1}H NMR, δ (ppm): 7.2-7.7 (complex, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 334, 336, 338 (M^+, Br isotopes; MF, 336.02), 176 (M^+-2Br).

bis(4-Bromophenyl)ethyne. Yield: 24%; mp 180-181°C. The yield was lowered by the concurrent formation of 1-(4-bromophenyl)-2-(4-iodophenyl)ethyne, and the consequent difficult separation. ^{1}H NMR, δ (ppm): 7.35, 7.47, *J*=8.8 Hz (AB *para* pattern, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 334, 336, 338 (M^+, Br isotopes; MF, 336.02), 176 (M^+-2Br).

bis(3-Nitrophenyl)ethyne. Yield: 12%; mp 144-145°C. ^{1}H NMR, δ (ppm): 7.2-8.5 (complex, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 268 (M^+; MF, 268.21), 176 (M^+-2NO_2).

bis(4-Nitrophenyl)ethyne. Yield: 65%; mp 142-143°C. ^{1}H NMR, δ (ppm): 7.72,8.27, *J*=9.0 Hz (AB *para* pattern, aromatic); ^{13}C NMR in Table 2. GC/MS (*m/z*): 268 (M^+; MF, 268.21), 176 (M^+-2NO_2).

Table 2. ^{13}C NMR Spectra of Diarylethynes in $CDCl_3$.



Substituent	Chemical shift, δ (ppm)[a]							
	C1	C2	C3	C4	C5	C6	C_{sp}	X
H	123.25	131.58	128.22	128.31	128.22	131.58	89.36	
2-Me	123.31	139.93	129.45	128.19	125.57	131.85	92.29	20.92
3-Me	123.15	132.16	137.94	128.65	128.18	129.05	89.18	21.19
4-Me	120.36	131.40	129.05	138.13	129.05	131.40	88.86	21.46
4-OMe	115.67	132.83	113.92	159.35	113.92	132.83	87.91	55.24
3-Cl	124.46	131.48	134.22	128.83	129.58	129.74	89.01	
4-Cl	121.41	132.78	128.74	134.50	128.74	132.78	89.16	
3-Br	124.79	134.51	121.42	133.68	128.74	132.78	89.14	
4-Br	121.94	132.99	131.69	122.80	131.69	132.99	89.44	
3-NO_2	123.66	126.58	148.16	124.00	129.60	137.33	89.09	
4-NO_2	128.86	132.63	123.80	147.72	123.80	132.63	91.99	

[a] Assigned from comparison with calculated chemical shifts[30].

Product Analysis. In a typical experiment, 1 mmol of alkyne was reacted with 1.5 mmol of $\mathrm{Hg(OAc)_2}$ in 20 ml 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 $\mathrm{CH_2Cl_2}$, washed with water to remove unreacted mercuric acetate, and dried over anhydrous $\mathrm{Na_2SO_4}$. The acetoxymercurio derivative obtained after evaporation of dichloromethane, as a very viscous liquid, was characterised by mass and NMR spectra.

In selected cases, an aliquot of the acetoxymercurio species was transformed into the chloromercurio derivative, by adding 10% aqueous KCl to a dichloromethane solution of it. The solid precipitate was recrystallized with EtOH-$\mathrm{CH_2Cl_2}$-hexane and characterised.

Reductive demercuration was also performed on a portion of the acetoxymercurio compound, dissolved in $\mathrm{CH_2Cl_2}$. An aqueous basic (NaOH) solution of $\mathrm{NaBH_4}$ was added dropwise, under stirring, at 0°C. Metallic mercury separated almost immediately. The organic layer was washed with water to neutrality, dried over anhydrous $\mathrm{Na_2SO_4}$, and examined by GC/MS. A single vinyl ester was obtained in all cases, accompanied by various amounts of ketone (equation 2). For example, reductive demercuration of acetoxymercurio derivative from bis(4-methylphenyl)ethyne gave 100% 1-acetoxy-1,2-di(4-methylphenyl)ethene and traces (not integrated) of 1,2-di(4-methylphenyl)ethanone, whereas 62% 1-acetoxy-1,2-di(3-methylphenyl)ethene and 36% 1,2-di(3-methylphenyl)ethanone were the result of the same reaction performed with the acetoxymercurio derivative from bis(3-methylphenyl)ethyne. The following compounds were obtained.

1-Acetoxy-2-acetoxymercurio-1,2-di(2-methylphenyl)ethene.

$o\text{-}\mathrm{MeC_6H_4C(HgOAc){=}C(OAc)C_6H_4}o\text{-}\mathrm{Me}$. Yield: 50%. ^{1}H NMR, δ (ppm): 1.76 (3H, s) and 1.91 (3H, s), $\mathrm{HgOCOC}H_3$ and $\mathrm{OCOC}H_3$; 2.43 (3H, s) and 2.48 (3H, s), Ar-CH_3; 7.1-7.5 (8H, complex), aromatic. ^{13}C NMR, δ (ppm): 177.0, $\mathrm{HgO}C\mathrm{OCH_3}$, 168.1, $\mathrm{O}C\mathrm{OCH_3}$. MS (E.I., 50eV), *m/z*: cluster around 525 (M$^+$, Hg isotopes; MF, 524.95), cluster around 482 (M$^+$-$\mathrm{COCH_3}$, Hg isotopes), cluster around 465 (M$^+$-$\mathrm{OCOCH_3}$, Hg isotopes), 265 (M$^+$-$\mathrm{HgOCOCH_3}$), and fragments from the organic moiety.

1-Acetoxy-2-acetoxymercurio-1,2-di(3-methylphenyl)ethene.

$m\text{-}\mathrm{MeC_6H_4C(HgOAc){=}C(OAc)C_6H_4}m\text{-}\mathrm{Me}$. Yield: 78%. ^{1}H NMR, δ (ppm): 1.93 (3H, s) and 1.95 (3H, s), $\mathrm{HgOCOC}H_3$ and $\mathrm{OCOC}H_3$; 2.32 (3H, s) and 2.36 (3H, s), Ar-CH_3; 7.1-7.5 (8H, complex), aromatic. ^{13}C NMR, δ (ppm): 176.7, $\mathrm{HgO}C\mathrm{OCH_3}$, 168.8, $\mathrm{O}C\mathrm{OCH_3}$. MS (E.I., 50eV), *m/z*: cluster around 525 (M$^+$, Hg isotopes; MF, 524.95), cluster around 482 (M$^+$-$\mathrm{COCH_3}$, Hg isotopes), cluster around 465 (M$^+$-$\mathrm{OCOCH_3}$, Hg isotopes), 265 (M$^+$-$\mathrm{HgOCOCH_3}$), and fragments from the organic moiety.

1-Acetoxy-2-acetoxymercurio-1,2-di(4-methylphenyl)ethene.

$p\text{-}\mathrm{MeC_6H_4C(HgOAc){=}C(OAc)C_6H_4}p\text{-}\mathrm{Me}$. Yield: 73%. ^{1}H NMR, δ (ppm): 1.99 (6H, s), $\mathrm{HgOCOC}H_3$ and $\mathrm{OCOC}H_3$; 2.34 (3H, s) and 2.36 (3H, broad s), Ar-CH_3; 7.20, 7.54, J=8.0 Hz (8H, AB *para* pattern), aromatic. ^{13}C NMR, δ (ppm): 177.1, $\mathrm{HgO}C\mathrm{OCH_3}$, 169.0, $\mathrm{O}C\mathrm{OCH_3}$. MS (E.I., 50eV), *m/z*: cluster around 525 (M$^+$, Hg isotopes; MF, 524.95), cluster around 482 (M$^+$-$\mathrm{COCH_3}$, Hg isotopes), cluster around 465 (M$^+$-$\mathrm{OCOCH_3}$, Hg isotopes), 265 (M$^+$-$\mathrm{HgOCOCH_3}$), and fragments from the organic moiety. From treatment with KCl, $p\text{-}\mathrm{MeC_6H_4C(HgCl){=}C(OAc)C_6H_4}p\text{-}\mathrm{Me}$; mp 195-196°C. MS (E.I., 50eV), *m/z*: cluster around 500 (M$^+$, Cl and Hg isotopes; MF, 501.37), cluster around 465 (M$^+$-$\mathrm{OCOCH_3}$, Cl and Hg isotopes).

1-Acetoxy-2-acetoxymercurio-1,2-di(4-methoxyphenyl)ethene.

$p\text{-}\mathrm{MeOC_6H_4C(HgOAc){=}C(OAc)C_6H_4}p\text{-}\mathrm{OMe}$. Yield: 80%. ^{1}H NMR, δ (ppm): 1.98 (6H, s), $\mathrm{HgOCOC}H_3$ and $\mathrm{OCOC}H_3$; 3.72 (6H, s) OCH_3; 6.89, 7.5, J=8.1 Hz (8H, AB *para* pattern), aromatic. MS (E.I., 50eV), *m/z*: cluster around 556 (M$^+$, Hg isotopes; MF, 556.95), cluster around 497 (M$^+$-$\mathrm{COCH_3}$, Hg isotopes), and fragments from the organic moiety.

1-Acetoxy-2-acetoxymercurio-1,2-di(3-chlorophenyl)ethene.

$m\text{-}\mathrm{ClC_6H_4C(HgOAc){=}C(OAc)C_6H_4}m\text{-}\mathrm{Cl}$. Yield: 47%. ^{1}H NMR, δ (ppm): 1.98 (6H, s), COCH_3; 7.2-7.6 (8H, complex), aromatic. MS (E.I., 50eV), *m/z*: cluster around 566 (M$^+$, Cl and Hg isotopes; MF, 565.80), cluster around 524 (M$^+$-$\mathrm{COCH_3}$, Cl and Hg isotopes), cluster around 503 (M$^+$-

$OCOCH_3$, Cl and Hg isotopes), 304, 306, 308 (M^+-HgOAc, Cl isotopes), 246, 248, 250 (M^+-HgOAc-OAc, Cl isotopes), and fragments from the organic moiety. MS/MS (daughters of 566), *m/z*: 524, 505, 304. FAB (matrix: di(2-hydroxyethyl) sulphide, MF 122.18), *m/z*: cluster around 687 (M^+ + matrix, Cl and Hg isotopes), 628 (M^+ + matrix -OAc, Cl and Hg isotopes).

1-Acetoxy-2-acetoxymercurio-1,2-di(4-chlorophenyl)ethene.
p-$ClC_6H_4C(HgOAc)=C(OAc)C_6H_4$*p*-Cl. Yield: 28%. ^1H NMR, δ (ppm): 2.00 (6H, s), $COCH_3$; 7.51-7.68, *J*=8.0 Hz (8H, AB *para* pattern), aromatic. MS (E.I., 50eV), *m/z*: cluster around 566 (M^+, Cl and Hg isotopes; MF, 565.80), cluster around 524 (M^+-$COCH_3$, Cl and Hg isotopes), cluster around 503 (M^+-$OCOCH_3$, Cl and Hg isotopes), 305, 307, (M^+-HgOAc, Cl isotopes), and fragments from the organic moiety. MS/MS (daughters of 565), *m/z*: 526, 504. From treatment with KCl, *p*-$ClC_6H_4C(HgCl)=C(OAc)C_6H_4$*p*-Cl; mp 177-178°C

1-Acetoxy-2-acetoxymercurio-1,2-di(3-bromophenyl)ethene.
m-$BrC_6H_4C(HgOAc)=C(OAc)C_6H_4$*m*-Br. Yield: 40%. ^1H NMR, δ (ppm): 2.18 (6H, s), $COCH_3$; 7.3-7.8 (8H, complex), aromatic. MS (E.I., 50eV), *m/z*: cluster around 655 (M^+, Br and Hg isotopes; MF, 654.70), cluster around 396 (M^+-HgOAc, Br isotopes), and fragments from the organic moiety. MS/MS (daughters of 655), *m/z*: 398. FAB (matrix: di(2-hydroxyethyl) sulphide, MF 122.18), *m/z*: cluster around 776 (M^+ + matrix, Br and Hg isotopes), 717 (M^+ + matrix -OAc, Br and Hg isotopes).

1-Acetoxy-2-acetoxymercurio-1,2-di(4-bromophenyl)ethene.
p-$BrC_6H_4C(HgOAc)=C(OAc)C_6H_4$*p*-Br. Yield: 28%. ^1H NMR, δ (ppm): 2.15 (6H, s), $COCH_3$; 7.36-7.47, *J*=8.8 Hz (8H, AB *para*-pattern), aromatic. MS (FAB, matrix: di(2-hydroxyethyl) sulphide, MF 122.18), *m/z*: cluster around 776 (M^+ + matrix, Br and Hg isotopes), 717 (M^+ + matrix -OAc, Br and Hg isotopes). From treatment with KCl, *p*-$BrC_6H_4C(HgCl)=C(OAc)C_6H_4$*p*-Br; mp 186-187°C. MS (E.I., 50eV), *m/z*: cluster around 630 (M^+, Br, Cl and Hg isotopes; MF, 631.10), cluster around 590 (M^+-$COCH_3$, Br, Cl and Hg isotopes); 334, 336, 338 (M^+-HgCl-OAc, Br isotopes), and fragments from the organic moiety. MS/MS (daughters of 632), *m/z*: 350 (M^+-HgCl-$COCH_3$).

1-Acetoxy-2-acetoxymercurio-1,2-di(3-nitrophenyl)ethene.
m-$NO_2C_6H_4C(HgOAc)=C(OAc)C_6H_4$*m*-$NO_2$. Yield: 33%. ^1H NMR, δ (ppm): 2.18 (6H, s), $COCH_3$; 7.3-8.4 (8H, complex), aromatic. MS (FAB, matrix: di(2-hydroxyethyl) sulphide, MF 122.18), *m/z*: cluster around 586 (M^+, Hg isotopes, MF 586.89). MS/MS (E.I., 50eV, daughters of 587), *m/z*: 330 (M^+-HgOAc), 270 (M^+-HgOAc-OAc).

1-Acetoxy-2-acetoxymercurio-1,2-di(4-nitrophenyl)ethene.
p-$NO_2C_6H_4C(HgOAc)=C(OAc)C_6H_4$*p*-$NO_2$. Yield: 50%. ^1H NMR, δ (ppm): 2.10 (6H, s), $COCH_3$; 7.69, 8.23, *J*=9.0 Hz (8H, AB *para*-pattern), aromatic. MS (E.I., 50eV), *m/z*: cluster around 587 (M^+, Hg isotopes; MF, 586.89), cluster around 544 (M^+-$COCH_3$, Hg isotopes); cluster around 527 (M^+-OAc, Hg isotopes), and fragments from the organic moiety. MS/MS (daughters of 587), *m/z*: 544 (M^+-$COCH_3$). MS (FAB, matrix: di(2-hydroxyethyl) sulphide), *m/z*: cluster around 708 (M^+ + matrix, Hg isotopes).

X-Ray Crystallography. Crystal data and relevant details of the structure analysis of 1-acetoxy-2-chloromercurio-1,2-di(4-methylphenyl)ethene are listed in Table 3. The compound was recrystallized from ethanol-dichloromethane.

X-ray data were collected at room temperature on an Enraf-Nonius CAD4-F automatic diffractometer, using Mo-Kα graphite-monochromated radiation, operating in the ω/θ scan mode. The unit cell parameters were obtained by a least squares fitting of the setting values of 25 strong reflections in the θ range $11 < \theta < 13°$. Three monitoring reflections, measured after every 500 data acquisitions, showed insignificant intensity fluctuations. The structure was solved by routine application of the Patterson and Fourier techniques and the non-hydrogen atoms were refined anisotropically. The full matrix least-squares refinement minimised the quantity $\Sigma w(DF)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02\ F_o)^2 + 0.1]$, where σ is derived from counting statistics. The H-atoms were placed in calculated positions with isotropic thermal parameters 1.2 times larger than the B_{eq} of the carrier atoms at the beginning of each least-square cycle and not refined. At the end of the isotropic refinement, a

Table 3. Summary of Crystallographic Data and Refinement Conditions.

Formula	$HgClO_2C_{18}H_{17}$	Crystal size /mm	0.1 x 0.1 x 0.3
M	501.4	λ (Mo Kα) /Å	0.7093
Crystal system	orthorhombic	θ_{max} (°)	26
Space group	$P\,ca2_1$	μ /cm^{-1}	90.9
a /Å	18.729(2)	No. of indep. refl.	1799
b /Å	11.681(1)	No. of refl. above 3σ(I)	1222
c /Å	7.876(2)	No. of refined parameters	198
U /Å^3	1723(2)	R^a	0.030
Z	4	R$_w$^{b}	0.035
F (000) /e	952	Goodness of fit^c	0.944
D$_c$ /g cm^{-3}	1.93	Final Δ/σ (max.)	0.03

[a] $R = \Sigma(|F_o-K|F_c||)/\Sigma F_o$

[b] $R = [\Sigma w(F_o-K|F_c|^2/\Sigma wF_o^2]$

[c] Goodness of fit = $[\Sigma w(F_o-K|F_c|)^2/(N_o-N_v)]$, where N_o and N_v are the number of observations and refined parameters, respectively.

Table 4. Final Fractional Atomic Coordinates and Displacement Parameters (Å^{2}x10^3) of the non-hydrogen Atoms with their e.s.d.s in parentheses.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	X	*Y*	*Z*	U_{eq}
Hg	0.53268(2)	0.15158(4)	0.0	52.5(1)
Cl	0.6148(2)	0.2930(3)	-0.0376(7)	76(2)
O(1)	0.3377(5)	-0.0225(9)	0.105(1)	62(3)
O(2)	0.3356(6)	-0.0049(8)	0.388(1)	61(3)
C(1)	0.4585(7)	0.028(1)	0.064(2)	62(5)
C(2)	0.3922(7)	0.063(1)	0.098(2)	52(4)
C(3)	0.4827(7)	-0.092(1)	0.070(2)	56(5)
C(4)	0.5486(8)	-0.117(1)	0.141(2)	59(5)
C(5)	0.5733(8)	-0.232(1)	0.161(2)	68(6)
C(6)	0.5327(9)	-0.320(2)	0.106(3)	81(7)
C(7)	0.4685(7)	-0.297(1)	0.035(2)	63(5)
C(8)	0.4449(6)	-0.185(1)	0.022(3)	53(4)
C(9)	0.5561(9)	-0.444(2)	0.135(4)	113(9)
C(10)	0.3624(8)	0.180(1)	0.099(2)	53(5)
C(11)	0.3983(8)	0.269(1)	0.178(2)	63(5)
C(12)	0.3719(8)	0.382(1)	0.167(2)	67(6)
C(13)	0.3094(8)	0.405(2)	0.077(3)	84(7)
C(14)	0.2724(7)	0.315(1)	0.003(4)	77(5)
C(15)	0.2968(6)	0.203(1)	0.025(3)	58(4)
C(16)	0.2825(9)	0.527(1)	0.062(3)	112(11)
C(17)	0.3109(7)	-0.047(1)	0.266(2)	48(4)
C(18)	0.2535(9)	-0.126(1)	0.249(4)	65(4)

correction for absorption effects was applied, according to Walker and Stuart[31], by using the computer program DIFABS (Max. and min. values of the absorption correction were 1.56 and 0.61). The final Fourier difference map showed no peak grater than 0.76 e Å^{-3}.
All calculations, carried out on a Vax 750 at the Centro Interdipartimentale di Metodologie Chimico-fisiche of the University of Naples "Federico II", were performed by using the Enraf-Nonius (SDP) set of programs[32]. Final atomic parameters are presented in Table 4.

Kinetic Measurements. Kinetic experiments have been carried out under pseudo-first order conditions, with different techniques, *i.e.* gas chromatographic and spectrophotometric measurement. The former method (Method A) allows to follow the disappearance of alkyne in function of time, mercurated species being not detectable by gas chromatography. With the latter method (Method B), the absorbance variation, associated with the formation of product, was followed in function of time. Rate constants obtained with the two methods are in excellent agreement.
(A). Known quantities in acetic acid of excess Hg(OAc)$_2$, the alkyne, and the appropriate internal standard, were mixed in a thermostatted reaction vessel and kept stirred. 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$_2$SO$_4$. Blank experiments confirmed the reliability of the method. Diphenylmethane as used as the internal standard.
(B). Solutions of known concentrations of the reactants were separately put in a silica cell with septum, allowed to reach 25°C in the thermostatted cell compartment of the spectrophotometer, and mixed. The absorbance variation with time was followed at the appropriate wavelength, chosen by recording preliminary spectra in the range 280-340 nm. For low reacting alkynes, solutions containing known concentrations of both reactants were prepared and kept in a thermostat at 25°C. Aliquots of each solution were taken at known times and the absorbance was read at the appropriate wavelength. All the runs were followed up to 80-90% conversion, except those with nitro-substituted alkynes (60-75%). Pseudo-first order rate constants were calculated using Sigma-Plot[33].
The data are reported in Table 1, as overall second-order constants. They are mean values of several runs, carried out under conditions specified as follows (wavelengths in parentheses).
bis(4-Methoxyphenyl)ethyne: *p*-MeOC$_6$H$_4$C≡CC$_6$H$_4$*p*-OMe, 3.05 x 10^{-5} to 2.50 x 10^{-4} M; Hg(OAc)$_2$, 7.12 x 10^{-2} to 1.07 x 10^{-1} M (293 nm).
bis(4-Methylphenyl)ethyne: *p*-MeC$_6$H$_4$C=CC$_6$H$_4$*p*-Me, 8.34 x 10^{-6} to 1.02 x 10^{-2} M; Hg(OAc)$_2$, 3.34 x 10^{-2} to 1.00 x 10^{-1} M (270, 310 nm).
bis(3-Methylphenyl)ethyne: *m*-MeC$_6$H$_4$C≡CC$_6$H$_4$*m*-Me, 2.50 x 10^{-5} to 2.04 x 10^{-4} M; Hg(OAc)$_2$, 3.34 x 10^{-2} to 8.00 x 10^{-2}M (274, 310 nm).
bis(2-Methylphenyl)ethyne: *o*-MeC$_6$H$_4$C=CC$_6$H$_4$*o*-OMe, 3.18 x 10^{-4} M; Hg(OAc)$_2$, 3.34 x 10^{-2} M (284 nm).
bis(4-Chlorophenyl)ethyne: *p*-ClC$_6$H$_4$C≡CC$_6$H$_4$*p*-Cl, 2.99 x 10^{-5} to 1.03 x 10^{-2} M; Hg(OAc)$_2$, 3.34 x 10^{-2} to 1.00 x 10^{-1} M (288 nm).
bis(3-Chlorophenyl)ethyne: *m*-ClC$_6$H$_4$C=CC$_6$H*m*-Cl, 3.82 x 10^{-5} to 1.94 x 10^{-4} M; Hg(OAc)$_2$, 3.34 x 10^{-2} to 8.00 x 10^{-2} M (282, 310 nm).
bis(4-Bromophenyl)ethyne: *p*-BrC$_6$H$_4$C≡CC$_6$H$_4$*p*-Br, 2.11 x 10^{-5} to 9.89 x 10^{-3} M; Hg(OAc)$_2$, 3.36 x 10^{-2} to 1.00 x 10^{-1} M (291 nm).
bis(3-Bromophenyl)ethyne: *m*-BrC$_6$H$_4$C=CC$_6$H*m*-Br, 2.38 x 10^{-5} to 1.22 x 10^{-2} M; Hg(OAc)$_2$, 3.34 x 10^{-2} to 1.00 x 10^{-1} M (283 nm).
bis(4-Nitrophenyl)ethyne: *p*-NO$_2$C$_6$H$_4$C≡CC$_6$H$_4$*p*-NO$_2$, 3.08 x 10^{-5} to 3.80 x 10^{-4} M; Hg(OAc)$_2$, 3.36 x 10^{-2} to 1.03 x 10^{-1} M (328 nm).
bis(3-Nitrophenyl)ethyne: *m*-NO$_2$C$_6$H$_4$C=CC$_6$H$_4$*m*-NO$_2$, 1.46 x 10^{-5} to 3.80 x 10^{-4} M; Hg(OAc)$_2$, 3.36 x 10^{-2} to 1.03 x 10^{-1} M (292 nm).

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References

1. Part 7, B. Floris and E. Tassoni, *Organometallics*, 1994, **13**, 4746.
2. R. C. Larock, *Solvomercuration/Demercuration Reactions in Organic Synthesis*, Springer-Verlag, Berlin, 1986 and references therein.
3. M. Bassetti, B. Floris and G. Illuminati, *J. Organomet. Chem.*, 1980, **202**, 351.
4. M. J. S. Dewar and K. M. Merz jr., *Organometallics*, 1985, **4**, 1967.
5. J. B. Lambert, E. C. Chelius, R. H. Bible jr. and E. Hajdn, *J. Am. Chem. Soc.*, 1991, **113**, 1331.
6. H. B. Vardhan and R. D. Bach, *J. Org. Chem.*, 1992, **57**, 4948.
7. S. Yamabe and T. Minato, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3339.
8. S. Uemura, H. Miyoshi and M. Okano, *J. Chem. Soc. Perkin 1*, 1980. 1098.
9. R. J. Spear and W. A. Jensen, *Tetrahedron Lett.*, 1977, 4535.
10. R. D. Bach, R. A. Woodard, T. J. Anderson and M. D. Glick, *J. Org. Chem.*, 1982, **47**, 3707.
11. V. R. Kartashov, T. N. Sokolova, E. V. Skorobogatova, A. N. Chernov, D. V. Bazhenov, Yu. K. Grishin, Yu. A. Ustynyuk and N. S. Zefirov, *Zh. Org. Khim.*, 1989, **25**, 1846; Engl. trans., Plenum Publ., 1990, 1668.
12. M. Bassetti and B. Floris, *J. Org. Chem.*, 1986, **51**, 4140.
13. C. E. Castro and R. D. Stephens, *J. Org. Chem.*, 1963, **28**, 2163.
14. R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, **28**, 3313.
15. A. Carpita, A. Lessi and R. Rossi, *Synthesis*, 1984, 571.
16. A. D. Allen and C. D. Cook, *Can. J. Chem.*, 1963, **41**, 1085.
17. D. E. Ames, D. Bull and C. Takundwa, *Synthesis*, 1981, 364.
18. a) S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627; b) W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280.
19. S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, *J. Am. Chem. Soc.*, 1954, **76**, 4558.
20. F. G. Bordwell and M. I. Douglass, *J. Am. Chem. Soc.*, 1966, **88**, 993.
21. B. Floris and F. Giordano, manuscript in preparation.
22. E. Ballico, B. Floris and F. Giordano, *J. Chem. Res. (M)*, 1966, 0689; *J. Chem Res. (S)*, 1996, 86. 23. M. Bassetti, M. P. Trovato and G. Bocelli, *Organometallics*, 1990, **9**, 2292.
24. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1970, p.356.
25. F. Ruff and I. G. Csizmadia, *Organic Reactions. Equilibria, Kinetics and Mechanism*, Elsevier, Amsterdam, 1994, p.177.
26. G. H. Schmid, A. Modro and K. Yates, *J. Org. Chem.*, 1980, **45**, 665.
27. F. D. Ewing in N. B. Chapman and J. Shorter Eds., *Correlation Analysis in Chemistry*, Plenum Press, New York and London, 1978, and references therein.
28. T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., Harper Collins Publ., New York, 1987, p.319.
29. D. V. Ramana and N. V. S. Rama Krishna, *Org. Mass Spctrom.*, 1989, **24**, 903.
30. Softshell International (1994) *C-13 NMR Module*, Softshell International, Ltd., Grand Junction, U.S.A.
31. N. Walker and D. Stuart, *Acta Crystallogr., Sect A*, 1983, **39**, 158.
32. Enraf-Nonius (1989) *CAD-4 Software*, Version 5.0, Enraf-Nonius, Delft, The Netherlands.
33. Jandel Scientific (1994) *SigmaPlot*, Version for Windows, Jandel Scientific GmbH, Erkrath, Germany.

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