Salt effects and the mechanism of electrophilic mercuration of unsaturated compounds

4.* The composition of products, stereochemistry, and kinetics of the reaction of mercury acetate with arylphenyl-substituted acetylenes

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The structures of the products of the reaction of arylphenyl-substituted alkynes with mercury acetate in methanol and acetic acid as well as the stereo- and regiochemistry of the reaction were determined. The reaction in methanol has an unusual regiochemistry, *viz.*, the electrophilic fragment of $Hg(OAc)_2$ adds to the carbon atom bearing the aryl substituent. The reaction in acetic acid yields *trans*-products. The kinetics of these reactions were investigated, and a correlation analysis of the kinetic data was carried out. For the reaction in CH_3OH, the effects of the addition of NaOAc on the reaction rate and on the ratio between the products were determined. Mechanisms for the reactions were suggested and discussed.

Key words: mercury acetate, arylphenylacetylenes, stereochemistry, regiochemistry, intermediate, salt effect, reaction mechanism.

The kinetic regularities and the mechanism of solvomercuration of alkenes depend on the properties and the nature of the substrate.[1–3] It has been expedient to carry out a similar study using disubstituted acetylenes as unsaturated systems. The kinetic data on the electrophilic mercuration of alkynes are scarce[4,5] and do not allow one to identify many important features of this reaction. The stereochemistry of the addition of mercury salts to disubstituted alkynes has also been poorly investigated.[6–11]

In the present work we studied the kinetics and stereo- and regiochemical regularities of the reaction of mercury acetate with arylphenyl-substituted alkynes (**1a—c**).

$$RC_6H_4C{\equiv}CC_6H_5$$
1a—c

R = H (**a**), *p*-CH_3 (**b**), *p*-OCH_3 (**c**).

CH_3OH and CH_3COOH were used as solvents.

* For Parts 1—3, see Refs 1—3.

Results and Discussion

The reaction of $Hg(OAc)_2$ with diphenylacetylene **1a** in CH_3OH has been studied previously.[12] It was found that the reaction yields a saturated compound (**2a**).

$$RC_6H_4C{\equiv}CC_6H_5 \;(\mathbf{1a\text{—}c}) + 2Hg(OAc)_2 \xrightarrow[NaCl]{CH_3OH} RC_6H_4C(HgCl)(OCH_3)C(HgCl)(OCH_3)C_6H_5 \;(\mathbf{2a\text{—}c})$$

In the present work we showed that alkynes **1b** and **1c** react in a similar way. An interesting peculiarity of the latter reactions is that the reagent adds against the electronic effects of the substituents at the triple bond. The reaction gives compounds **2b** and **2c** in which the chloromercuro groups are bound to the carbon atom that bears the aryl substituent. According to the NMR spectral data, the reaction mixture contains one more compound (8—10 %), which is probably the isomer with the opposite regiochemistry.

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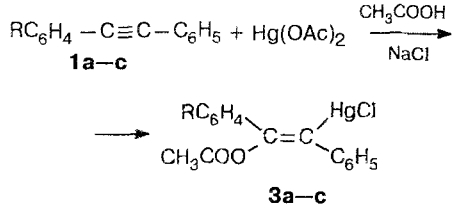
Table 1. The ^{13}C NMR spectra, δ (J_{HgC}/Hz), $CDCl_3$

Compound	C(1)*	C(2)	CH_3	$CH_3(OCOCH_3)$	$CO(OCOCH_3)$	Other			
						C_{ipso}	C_o	C_m	C_p
3b	142.44 (2295)	151.04 (267.9)	21.38	20.78	168.94 (17.2)	Ar 135.66 (60.9)	128.68 (13.0)	126.92	140.18
						Ph 138.75 (54.1)	128.32 (90.6)	130.01	127.42 (24.5)
3c	141.91 (2310)	150.53 (269.2)	55.47	20.83	169.02 (20.9)	Ar 130.86 (62.3)	128.55	114.66	160.62
						Ph 138.89 (55.3)	128.47 (90.5)	128.53	127.35 (25.0)
2b	97.01	107.73 (69.5)	21.10 51.68 51.68			Ar 139.05 (63.0)	134.13 (176.6)	130.12	133.12
						Ph 140.85 (87.2)	128.57	128.29	128.08
2b	97.59 (1736)	107.58 (70.8)	55.32 51.57 51.57			Ar 133.16 (62.5)	133.46 (174.8)	113.81 (70.8)	159.42
						Ph 140.19 (85.3)	128.97	127.73	127.21

* C(1) is the carbon atom bound to the chloromercuro group.

The reaction of diphenylacetylene **1a** with $Hg(OAc)_2$ in CH_3COOH has been studied several times.[11,13] It has been believed for a long time that this reaction yields the *cis*-adduct. We showed unambiguously[7,8] that the reaction product, **3a**, has the *trans*-configuration.



1a—c **3a—c**

The introduction of donor substituents into the benzene ring does not change the stereochemistry of the process. Mercury acetate reacts with compounds **1b** and **1c** *trans*-stereoselectively, as it reacts with **1a**. It should be noted that acetoxymercuration of **1b** and **1c** occurs with the expected regiochemistry, *i.e.*, the nucleophile, which completes the reaction, adds to the carbon atom bound to the aryl group.

The structures of the products **2b—c**, and **3b—c** were determined by ^1H and ^{13}C NMR spectroscopy (Table 1). The procedure for the structural and stereochemical identification of the compounds has been reported previously.[6,7] The most comprehensive information on the arrangement of the functional groups with respect to the HgCl substituent is provided by the $^1H—^{199}Hg$ (for the CH_3 group) and $^{13}C—^{199}Hg$ spin coupling constants. In particular, the magnitudes of the $^2J_{HgC}$ constants are a strict criterion for the stereochemical assignment. The regiochemistry of the reactions with alkynes **1b** and **1c** was determined from the long-range J_{HgC} constants for the carbon atoms of the aromatic ring, which are only observed for the substituents located in the geminal position with respect to the HgCl group.

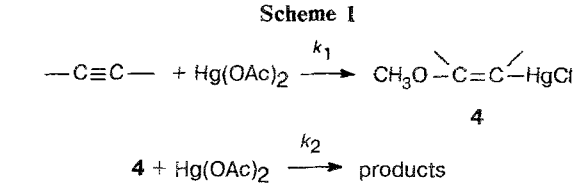
The interaction of **1a—c** with $Hg(OAc)_2$ in CH_3OH and CH_3COOH is described by a second-order kinetic equation:

$$-\frac{d[-C\equiv C-]}{dt} = k[Hg(OAc)_2][-C\equiv C-] \qquad (1)$$

Similar results were obtained[5] for the reactions of a wide range of acetylene compounds in CH_3COOH.

The stoichiometry of the reaction in CH_3OH can be adjusted to kinetic equation (1) by assuming that the methoxymercuration product (**4**) formed initially reacts with $Hg(OAc)_2$. In conformity with this assumption, the formal kinetic scheme of the process in methanol can be presented as follows:

Scheme 1



At $k_2 \gg k_1$ we have

$$-\frac{d[-C\equiv C-]}{dt} = k_1[-C\equiv C-][Hg(OAc)_2],$$

where k_1 is equal to k in Eq. (1).

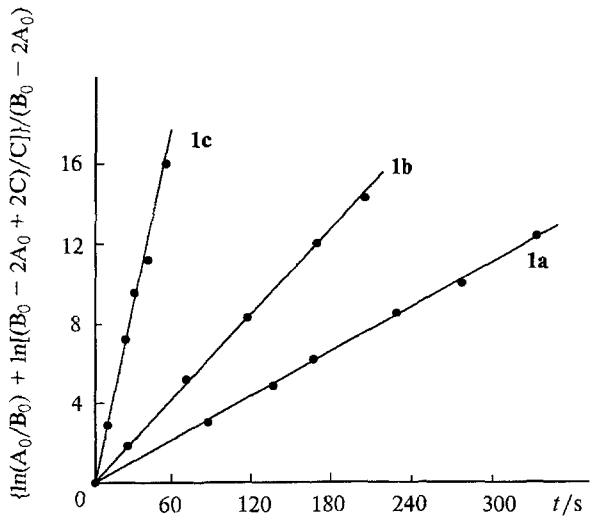


Fig. 1. The anamorphosis of Eq. (2) for methoxymercuration of alkynes **1a**, **1b**, and **1c** in CH_3OH.

By integrating Eq. (1) taking into account the stoichiometry of the reaction in CH_3OH we obtain relationship (2).

$$k = \frac{\ln\frac{A_0}{B_0} + \ln\frac{B_0 - 2A_0 + 2C}{C}}{(B_0 - 2A_0)\cdot t}. \qquad (2)$$

where A_0 and B_0 are the initial concentrations of the alkyne and $Hg(OAc)_2$, respectively (mol L^{-1}), C is the current concentration of the alkyne (mol L^{-1}). The plots presented in Fig. 1 indicate that Eq. (2) really holds. The kinetic data for the reactions in CH_3OH and CH_3COOH are listed in Table 2.

The rate constants of the reactions studied correlate with the σ^+ constants; the corresponding ρ values are: −1.11 ($r = 0.999$) for the reaction in CH_3OH and −1.41 ($r = 0.999$) for the reaction in CH_3COOH. These values are 2—4 times smaller than those in other typical reactions of electrophilic addition to unsaturated systems.[14]

The addition of sodium acetate decreases the reaction rate in CH_3OH, though the retardation effect is relatively small (Table 2). When the concentration of NaOAc is $3.0\cdot10^{-3}$ mol L^{-1}, the retardation of the reaction reaches its maximum value (Fig. 2). For the reaction in CH_3COOH, no retardation is observed at the same concentration of NaOAc. The dependence of the reciprocal of the second-order rate constant on the NaOAc concentration on CH_3OH is curvilinear (Fig. 3).

Using the reactions of $Hg(OAc)_2$ with alkynes **1a** and **1b** as examples, it has been shown that in the presence of NaOAc, the corresponding unsaturated compounds, **3a** and **3b**, are formed. According to the NMR data, the amount of the latter is as high as 20 % at a salt concentration of 0.1 mol L^{-1}. Thus, acetoxymercuration of alkynes in CH_3OH also occurs *trans*-stereoselectively. In our opinion, the presence of **3a** and **3b** in the reaction mixture is additional evidence for the stepwise formation of bis-adducts **2**.

Table 2. The rate constants of the reaction of $Hg(OAc)_2$ with alkynes **1a—c**

Alkyne	Solvent	NaOAc / mol L^{-1}	$k\cdot10^{-4}$ / L (mol s)$^{-1}$
1a	CH_3OH	—	7.10±1.14
		$2.5\cdot10^{-4}$	4.60±0.28
		$5.0\cdot10^{-4}$	4.00±0.24
		$1.0\cdot10^{-3}$	3.07±0.18
		$2.0\cdot10^{-3}$	2.40±0.16
		$3.0\cdot10^{-3}$	2.22±0.12
1b	CH_3OH	—	15.9±2.0
		$2.5\cdot10^{-4}$	7.65±0.45
		$5.0\cdot10^{-4}$	5.89±0.41
		$1.0\cdot10^{-3}$	5.01±0.32
		$2.0\cdot10^{-3}$	4.10±0.25
		$3.0\cdot10^{-3}$	3.71±0.19
1c	CH_3OH	—	55.1±3.3
1a	CH_3COOH*	—	7.34±0.48**
		$3.0\cdot10^{-3}$	7.54±0.52
1b	CH_3COOH*		18.1±2.0
1c	CH_3COOH*	—	86.8±5.0

* The temperature was 64.5 °C. ** Lit. data:[5] $7.7\cdot10^{-4}$ at 68.1 °C.

The above-noted characteristic features of methoxymercuration in the presence of NaOAc are similar to those observed in the reactions with alkenes having a strained double bond.[1—3] It has been speculated in the literature that some properties of the triple bond are similar to those of the —C=C— bond in cyclopropene compounds, and, therefore, the triple bond should possess a certain strain energy.[15,16] This suggestion has

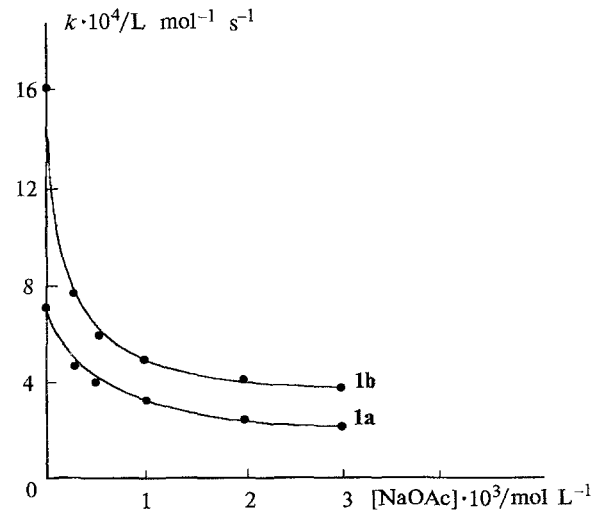


Fig. 2. The dependence of the rate constant of the reaction of $Hg(OAc)_2$ with alkynes **1a** and **1b** in CH_3OH on the concentration of NaOAc.

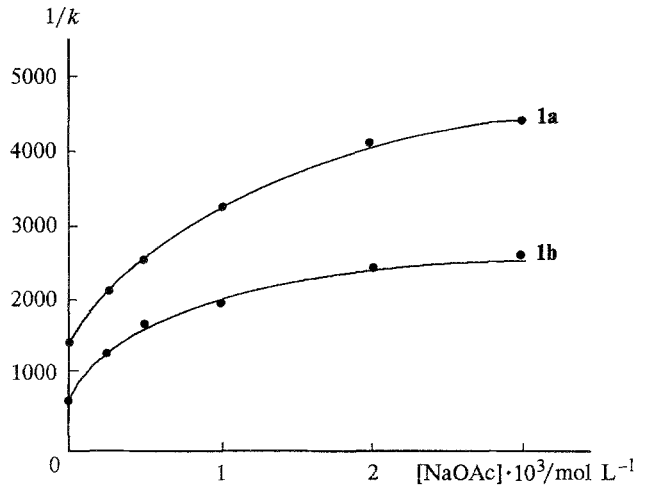


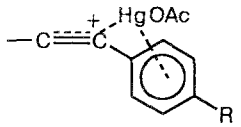
Fig. 3. The dependence of $1/k$ for the reaction of $Hg(OAc)_2$ with alkynes **1a** and **1b** in CH_3OH on the concentration of NaOAc.

been confirmed by a calculation,[17] according to which acetylene is 9.1 kcal mol^{-1} more strained than ethylene.

The results obtained imply that the general scheme, which was considered in detail in our previous publications,[1–3] is valid for the reactions of $Hg(OAc)_2$ with acetylene compounds.

In acetic acid, the reaction involves the intermediate formation of ion pair (**5**), which dissociates into ions in CH_3OH. As follows from the correlation data, the triple bond is loosened only slightly as the ion pair forms, and the positive charge is mostly located at the metal atom. In methanol, the ion pair transforms into free ion (**6**) more quickly than it is converted into products. At limiting concentrations of NaOAc the reaction mostly occurs *via* ion pair **5**, which is converted both into products and into solvoadducts.

The unusual regiochemistry of adducts **2b,c** can be explained by assuming that free mercurinium ion **6**, as in the reactions with alkenes,[3] has an asymmetrical structure. In this case, interaction is possible between the electrophilic fragment of the reagent and the benzene ring to give a π-complex structure (**7**). This type of complex formation was established for γ-arylpropylmercury chlorides.[18] In the same work, it has been found that the energy of interaction increases as the donating ability of the substituent in the benzene ring increases.



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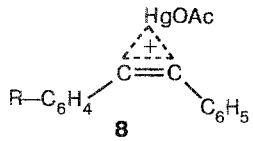

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If the stabilization of the intermediate by the formation of a type **7** complex is sufficiently effective, it can counterbalance the difference in the stabilizing abilities of the aryl and phenyl substituents provided that the electron requirements of the electron-deficient center of the intermediate are relatively low. As the data of correlation analysis imply, this situation can occur in the reaction in question.

The structure of the cation of ion pair (**8**) is apparently more symmetrical, and the conversion of this ion pair into the products is governed by the electron-releasing properties of the aryl substituent.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a VXR-400 Varian spectrometer in $CDCl_3$. The chemical shifts of the ^1H and ^{13}C nuclei were referred to the internal TMS and are presented in the δ scale.

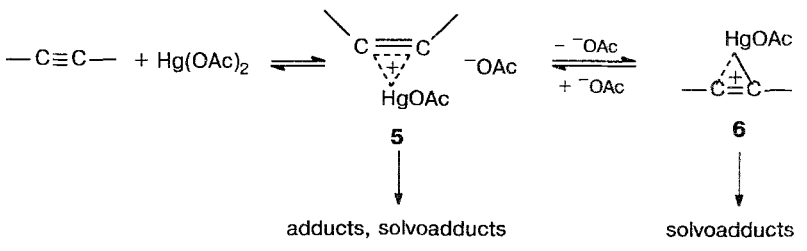
The kinetic measurements were carried out on a SF-46 spectrophotometer.

The solvents were purified by the standard procedures.[19]

The general procedure for the reaction of $Hg(OAc)_2$ with alkynes. A solution of $Hg(OAc)_2$ and a solution of alkyne were mixed at ambient temperature. The ratio between the reactants was 2 : 1 in CH_3OH or 1 : 1 in CH_3COOH. The concentrations of alkynes used in the experiments were 0.1—0.15 mol L^{-1}. When the reaction was completed, the reaction mixture was poured into a 1% aqueous solution of NaCl. The resulting precipitate was filtered off, washed with H_2O and with hexane, and dried in air at ~20 °C.

1,1-Bis(chloromercuro)-2,2-dimethoxy-1-(*p*-methylphenyl)-2-phenylethane (2b) was prepared by the reaction of 1.66 g of $Hg(OAc)_2$ and 0.5 g of compound **1b** in 40 mL of CH_3OH. The duration of the reaction was 12 h. Yield 82%. M.p. 113—115 °C with decomp. (hexane : chloroform, 1 : 4). ^1H NMR, δ: 2.305 s (3 H, CH_3), 3.452 s (6 H, 2 OCH_3), 7.05—7.15 m (9 H, C_6H_4, C_6H_5).

Scheme 2



1,1-Bis(chloromercuro)-2,2-dimethoxy-1-(*p*-methoxyphenyl)-2-phenylethane (2c) was prepared by the reaction of 1.53 g of $Hg(OAc)_2$ and 0.5 g of compound **1c** in 40 mL of CH_3OH. The duration of the reaction was 12 h. Yield 84%. M.p. 133—135 °C with decomp. (hexane : chloroform, 1 : 1). ^1H NMR, δ: 3.439 s (6 H, 2 OCH_3), 3.770 s (3 H, OCH_3), 6.73 m and 7.05—7.13 m (2 H, 7 H, C_6H_4, C_6H_5).

***E*-2-Chloromercuro-1-(*p*-methylphenyl)-2-phenylethene acetate (3b)** was prepared by the reaction of 1.16 g of $Hg(OAc)_2$ and 0.7 g of compound **1b** in 40 mL of CH_3COOH. The duration of the reaction was 48 h. Yield 78%. M.p. 183—185 °C (hexane : chloroform, 7 : 3). ^1H NMR, δ: 1.985 s (3 H, CH_3), 2.395 s (3 H, CH_3OCO), 7.58 m and 7.25 m (2 H, C_6H_4), 7.26 m and 7.35 m (3 H, 2 H, C_6H_5).

***E*-2-Chloromercuro-1-(*p*-methoxylphenyl)-2-phenylethene acetate (3c)** was prepared by the reaction of 1.0 g of $Hg(OAc)_2$ and 0.66 g of compound **1c** in 35 mL of CH_3COOH. The duration of the reaction was 48 h. Yield 88%. M.p. 170—171 °C (hexane : chloroform, 7 : 3). ^1H NMR, δ: 1.973 s (3 H, CH_3OCO), 3.830 s (3 H, OCH_3), 7.58 m and 6.93 m (2 H, 2 H, C_6H_4), 7.26 m and 7.34 m (3 H, 2 H, C_6H_5).

The reaction of $Hg(OAc)_2$ with alkyne 1b in the presence of NaOAc. Alkyne **1b** (1.5 g) in 30 mL of a solvent was added to a solution of $Hg(OAc)_2$ (3.7 g) and NaOAc (0.7 g) in 48 mL of CH_3OH. After 48 h the reaction mixture was poured into a 1% aqueous solution of NaCl and extracted with chloroform. The organic fraction was washed with H_2O and dried with $MgSO_4$. Removal of the solvent gave 3.6 g of an oily residue. Recrystallization of the residue from a hexane—chloroform mixture, 1 : 4, afforded compound **2b.** M.p. 114—115 °C (decomp.). From the mother liquor, 0.65 g of compound **3b** was isolated by preparative TLC on LSL 5/40 silica gel (using a hexane—benzene—ethyl acetate—chloroform mixture, 5 : 3 : 1 : 1, as the eluent). M.p. 182—184 °C (CH_3OH). The ^1H and ^{13}C NMR spectra of this compound are identical to those of the compound obtained directly in the reaction of $Hg(OAc)_2$ with **1b** in CH_3COOH.

The reaction of $Hg(OAc)_2$ in alkyne **1a** in the presence of NaOAc was carried out in a similar way. Product **3a** was identified in the reaction mixture by ^1H and ^{13}C NMR spectroscopy.

The rate of the reaction was measured on the basis of the change in the concentration of the alkyne. Current concentrations of alkynes were determined by spectrophotometry using calibration curves at $\lambda = 295$ nm for compound **1a**, 299 nm for **1b**, 304 nm for **1c**. The calibration curves were constructed using solutions (in CH_3OH or CH_3COOH) of alkynes, the reaction products, and their mixtures in various proportions. During the construction of the calibration plot the maximum concentration of an alkyne in the cell in the absence of the products was $4.0 \cdot 10^{-5}$ mol L^{-1}. To determine the current concentration of an alkyne, an aliquot part of the reaction mixture was poured into 25 mL of a solution of NaCl in aqueous 2-propanol (the molar fraction of *i*-C_3H_7OH was 0.91) with a concentration of $2.5 \cdot 10^{-3}$ mol L^{-1}. The volume of the aliquot portion or its dilution were adjusted in such a way that the alkyne concentration in the cell at the zero degree of conversion was $4.0 \cdot 10^{-5}$ mol L^{-1} within the limits of experimental error. Provided the conditions of the construction of the calibration curves and of the kinetic analysis are identical, the current concentration of an alkyne can be determined with an accuracy of 8—10% up to a degree of conversion of ~60%.

The reaction in CH_3OH was carried out at 25±0.1 °C. The concentrations of the starting reactants were the following: $Hg(OAc)_2$ $(7.5—9.5) \cdot 10^{-2}$ mol L^{-1}, alkynes **1a—c** $(4.5—5.0) \cdot 10^{-2}$ mol L^{-1}, NaOAc $2.5 \cdot 10^{-4}—3.0 \cdot 10^{-3}$ mol L^{-1}.

The reaction in CH_3COOH was carried out at 64.5±0.1 °C. The concentrations of the starting reactants were the following: $Hg(OAc)_2$ $(6.5—7.5) \cdot 10^{-2}$ mol L^{-1}, **1a**, **1c** 0.05 mol L^{-1}, **1b** 0.005 mol L^{-1}.

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