# **Organometallic Chemistry**

## Stereochemistry of addition of mercury salts to alkynes

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Reactions of  $Hg(OOCR)_2$  (R = Et,  $Pr^n$ ,  $Pr^i$ , and  $Bu^n$ ) with methylphenylacetylene (with the corresponding acids as solvents) give mixtures of *cis*- and *trans*-adducts. The quantity of the *cis*-adduct increases with increase in the length of the acyl substituent. *syn*-Addition also occurs in the acetoxymercuration of *m*-chlorophenyl(methyl)acetylene and 1-methoxybut-2-yne; in the latter case, this route predominates. The stereochemistry of the reaction can also depend on the ratio of the reactants. It is proposed that the reaction occurs by several schemes in which these factors manifest themselves in different degrees.

Key words: mercury salts, acetoxymercuration, alkynes, stereoisomers, regioisomers, intermediate, reaction mechanism.

The stereochemistry of the addition of mercury salts to acetylene derivatives has been studied previously.<sup>1-9</sup> Primary attention was devoted to the reactions with mercuric acetate in acetic acid. It was found<sup>2,3</sup> that the reaction of dimethylacetylene and diethylacetylene with Hg(OAc)<sub>2</sub> at room temperature is *trans*-stereoselective. Methylphenylacetylene reacts with Hg(OAc)<sub>2</sub> in a more complicated way. This reaction yields<sup>3</sup> two regioisomeric *trans*-adducts. A more detailed study that we carried out showed that together with the above-mentioned compounds, the reaction yields a small amount of the *cis*isomer.<sup>4</sup> This compound was obtained in a pure state, and its structure was unambiguously proved by NMR spectroscopy and X-ray diffraction analysis.<sup>4,5</sup>

It has been believed for a long period<sup>3</sup> that the reaction with diphenylacetylene affords the *cis*-adduct.

However, it has been found<sup>6,7</sup> that this reaction gives the *trans*-isomer.

In the present work, we continued the study of the stereochemistry of addition of mercury salts to methylphenylacetylene (1). We used  $Hg(OOCR)_2$  (R = Et, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>) as the reagents and the corresponding acids as solvents. In addition, we studied the stereochemistry of acetoxymercuration of alkynes (2-6) with substituents possessing different abilities to stabilize the transition state.

Reaction products were isolated as chloromercurio derivatives after treatment of the reaction mixture with an aqueous solution of NaCl. The experiments were carried out at room temperature. The structures of the products and their proportions were determined using <sup>1</sup>H, <sup>13</sup>C, and <sup>199</sup>Hg NMR spectroscopy.

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#### **Results and Discussion**

The reaction of alkyne 1 with  $Hg(OOCEt)_2$  in propionic acid at a reactant ratio of 1 : 1 gives two *trans*isomers (7a and 8a) and a *cis*-adduct (9a) (60 : 15 : 25). In this case, the amount of the *cis*-isomer is much greater than that formed in the reaction of alkyne 1 with  $Hg(OAc)_2$  in AcOH, where the ratio of the corresponding adducts is<sup>4</sup> 86 : 8 : 6, and the proportion of the *cis*-isomer does not increase when the temperature is raised from 25 to 65 °C. When the reaction with  $Hg(OOCEt)_2$  is carried out at 65–70 °C, the amount of 9a does not increase but, instead, it markedly decreases (from 25% to 17–20%).



In a similar reaction with  $Hg(OOCPr^n)_2$  in butyric acid, syn-addition becomes the predominant reaction pathway, and the ratio of the yields of products 7b, 8b, and 9b is 40 : 6 : 54.

The amount of the *cis*-isomer depends on the ratio of the reactants and decreases as the alkyne : mercury salt ratio increases (the concentration of the mercury salt remaining constant). When a fivefold excess of alkyne 1 is made to react with  $Hg(OOCEt)_2$  in propionic acid, only compounds 7a and 8a are formed (68 : 32). Similar regularity has been observed<sup>4</sup> in the reaction of alkyne 1 with  $Hg(OAc)_2$  in AcOH. In this case, the *cis*isomer is not formed at a twofold excess of the alkyne.

Special experiments showed that the *cis*-adduct does not result from isomerization of the *trans*-isomer 8. Thus, when after completion of the reaction with mercuric acetate or propionate the reaction mixture is kept for a period 3-4 times longer than the reaction time, the proportions of 7, 8, and 9 do not change. At 65-70 °C, isomerization does not occur either. These results imply that cis-adducts 9 are primary reaction products.

When alkyne 1 reacts with Hg(OOCBu<sup>n</sup>)<sub>2</sub>, cis-adduct 9d is the major product after 15 days. According to TLC, the reaction gives one more compound (10---20%), whose  $R_f$  value is close to that of adduct 7a. Presumably, this is *trans*-adduct 7d. The reaction mixture contains also substantial amounts of the alkyne. When duration of the reaction is increased to 30 days, compound 9d is also the major product. In this case, the reaction mixture contains organomercury compounds of unknown structures, which obviously result from decomposition of 7d.

The reaction of alkyne 1 with  $Hg(OOCPr^{i})_{2}$  in isobutyric acid follows a somewhat different pathway. In this case, compound 7c is the main reaction product (yield 40%).

In a study<sup>1</sup> of the reaction of alkyne 2 with  $Hg(OAc)_2$ in AcOH, by analogy with earlier results,<sup>9</sup> it was concluded that the reaction gives two *trans*-compounds (10 and 11) in a ratio of 55 : 45.



The product formed in a smaller amount was not isolated in a pure state.<sup>1</sup>

In the present study, we showed that the conclusion made in the study cited<sup>1</sup> was erroneous. In reality, this reaction gives *trans*- and *cis*-isomers (10 and 12) as the main products (55 : 45). According to TLC, the reaction mixture contains a small amount of one more compound, which is apparently *trans*-adduct 11.

The reaction of alkyne 2 with  $Hg(OOCCCl_3)_2$  in AcOH gives regioisomers (13 and 14) in a ratio of 67 : 33. Both products result from the *trans*-addition of the reagent rather than from the conjugated solvomercuration.



We showed that the reaction of  $Hg(OAc)_2$  in AcOH with alkynes 3 and 4 is as *trans*stereoselective as the reaction with diphenylacetylene and yields products 15 and 16.



Comparison of the results of acetoxymercuration of alkynes 1

R = Me (15); OMe (16)

and 2 demonstrates that the introduction of an electron-withdrawing substituent in the benzene ring favors the formation of the *cis*-isomer. Therefore, it was especially interesting to study acetoxymercuration of acetylene derivatives 5 and 6 containing electron-withdrawing substituents structurally differing from aryl groups and incapable of  $\pi$ -- $\pi$ -conjugation with the multiple bond.

It was found that acetoxymercuration of alkyne 5 yields stereoisomers 17 and 18 in a ratio of 66 : 34.



This reaction is the first example in which acetoxymercuration of alkynes occurs predominantly as *syn*addition. However, with a 10-fold excess of the alkyne, the reaction yields mainly *trans*-adduct 18. According to NMR spectroscopy, the amount of compound 17 does not exceed 10%.

The reaction of  $Hg(OAc)_2$  with alkyne 6 in AcOH gives two regioisomeric *trans*-adducts (19 and 20) in a ratio of 31 : 69.



The structure of compound 20 is quite unusual, because the reaction ends in the addition of the OAc group to the carbon atom bearing the more electronegative substituent, viz,  $-CH_2OAc$ .

The parameters of the NMR spectra of adducts 7-20 are listed in Tables 1-4. The signals were assigned based on the previously discovered criteria.<sup>4,6,7</sup>

The resonance frequency of the alkyl groups in the <sup>1</sup>H NMR spectra of compounds 7–14 (see Table 1) depends on the stereochemistry of the molecule. As in the case of acetoxymercuration products,<sup>4</sup> in the pair of stereoisomers 8 and 9, the methyl group protons are more shielded (by ~0.2 ppm) in the case of the *trans*-isomer. For both groups in the ethyl radical, the opposite situation is observed. The  $J_{Hg,H}$  constants can be used to determine the mutual arrangement of this group and HgCl, because the following inequality holds:<sup>4,10</sup>

Table 1. Data of the <sup>1</sup>H NMR spectra of compounds 7-16 (CDCl<sub>3</sub>)

Com-					
pound	СН3	F	R		
	$(J_{\rm Hg,H}/\rm Hz)$	CH3	CH <sub>2</sub>		
72	2.003 s (190.4)	1.179 t <sup>a</sup>	2.487 qª	7.3—7.5 m	
8a	2.262 s (25.8)	0.942 t <sup>a</sup>	2.187 qª	7.17.3 m	
9a	2.038 s (13.6)	1.240 t <sup>a</sup>	2.483 qª	7.1–7.3 m	
7b	1.914 s (190.0)	0.868 m	1.615 m; 2.351 m	7.2—7.4 m	
9b	1.922 s (13.0)	0.923 m	1.640 m; 2.319 m	7.1—7.3 m	
7 <b>c</b>	1.977 s (190.3)	1.220 dª	2.705 sept <sup>a</sup> (CH)	7.3—7.5 m	
9d	1.954 s (12.5)	0.891 m	1.347 m; 1.624 m; 2.367 m	7.1—7.3 m	
10	2.027 s (188.5)	2.211 s	·	7.37.5 m	
12	2.023 s (13.6)	2.201 s		7.1-7.3 m	
13	2.161 s (188.2)			7.37.5 m	
14	2.347 s (24.5)			7.1-7.5 m	
15	1.985 s	2.395 s	7.26 (m 7.37 (m 7.23 (m 7.58 (m	a, 3 H, Ph); a, 2 H, Ph); a, 2 H, Ar); a, 2 H, Ar)	
16	i.973 s	3.830 s	7.26 (m 7.34 (m 6.93 (m 7.59 (m	n, 3 H, Ph); n, 2 H, Ph); n, 2 H, Ar); n, 2 H, Ar)	

<sup>a</sup> The  ${}^{3}J_{\text{H,H}}$  values are 7.2-7.5 Hz.

Table 2. Data of the <sup>1</sup>H NMR spectra of compounds 17-20 (CDCl<sub>3</sub>)

Com-	δ (J <sub>Hg,H</sub> /Hz)					
pound	СН3	CH <sub>2</sub>	CH3CO	CH <sub>3</sub> O		
17	1.947 t (11.0)	4.036 q (164.5)	2.080 s	3.297 s		
18	2.001 t (20.0)	3.901 q (142.6)	2.074 s	3.247 s		
19	2.060 t ()	4.621 q (176.7)	2.001; 2.108			
20	1.876 t (197.6)	4.599 q (18.5)	2.105; 2.176			

These data on the spin-spin coupling constants are readily available, since the  ${}^{1}H - {}^{199}Hg$  satellites in the spectra of the Me groups manifested as singlets are

				δ <sub>C</sub> (J <sub>HR</sub>	<sub>C</sub> /Hz)				δ <sub>Hg</sub>
C(1) <sup>a</sup>	C(2)	CH3	R(CO)	Cipso	Co	C <sub>m</sub>	C <sub>p</sub>	CO	8
138.58 (2298)	151.42 (308.8)	19.56 (108.0)	27.46 (CH <sub>2</sub> , J = 11.0); 9.11 (CH <sub>3</sub> )	138.94 (64.1)	126.88 (13.4)	129.05	129.27	171.87 (24.2)	-1097.9
140.06 (2244)	149.15 (300.3)	23.58 (94.6)	27.46 (CH <sub>2</sub> , J = 9.8); 8.87 (CH <sub>3</sub> )	138.40 (52.5)	128.08 (82.4)	128.50 <sup>5</sup>	127.10 (30.4)	172.18 (22.0)	-1150.8
139.50 (2214)	151.59 (88.5)	17.40 (127.6)	27.37 (CH <sub>2</sub> , J = 9.8); 9.11 (CH <sub>3</sub> )	138.46 (55.5)	128.86 (85.0)	128.76 (22.0)	127.18 (32.0)	172.77 (22.6)	-1185.3
139.904	151.20 (314.9)	19.65 (104.0)	36.51, 18.55 (CH <sub>2</sub> ); 13.77 (CH <sub>2</sub> )	138.81	127.00	129.03	129.21	171.07	
140.12 <sup>d</sup>	148.82 <sup>d</sup>	23.80 (90.0)	35.94, 18.15 (CH <sub>2</sub> ); 13.71 (CH <sub>3</sub> )	138.90	128.45	128.30	126.90	171.30	
139.19 <sup>d</sup>	151.20 (88.1)	17.51 (130.0)	36.01, 18.51 (CH <sub>2</sub> ); 13.89 (CH <sub>3</sub> )	138.81 (55.0)	129.07 (86.0)	128.71 (20.2)	127.12 (32.0)	172.06 (21.6)	
139.78 <sup>d</sup>	151.52 (-87.9)	17.46 (128.6)	36.36, 22.42, 27.11 (CH <sub>2</sub> ); 13.74 (CH <sub>3</sub> )	138.62 (55.2)	128.94 (84.2)	128.77 (20.5)	127.18 (32.0)	172.21 (21.0)	
138.63 <sup>d</sup>	151.28 (309.0)	19.57 (106.0)	34.10 (CH); 18.89 (CH <sub>3</sub> )	138.63	126.87	129.09	129.25	174.47	
139.99 (2293)	15.015 (303.6)	19.62 (103.8)	20.65	140.64 (64.0)	127.23; 129.19	135.0; 129.45	130.41	168.36	-1106.2
138.56 (2229)	152.50 (88.4)	17.49 (126.0)	21.32 (10.0)	140.41 (58.9)	128.74 (84.6); 126.98 (81.8)	134.56 (22.4); 129.99 (33.6)	127.33 (33.6)	169.19 (22.0)	-1198.0
141.64 (2282)	149.40 (332.1)	19.39 (85.9)	89.50	138.28 (60.1)	125.25; 127.27	135.40; 130.69	130.21	159.29 (19.1)	
140.20 <sup>d</sup>	148.77 <sup>d</sup>	22.14d	89.45	138.79	126.32;	134.55;	128.28	159.25 <sup>d</sup>	

Table 3. Data of the <sup>13</sup>C and <sup>199</sup>Hg NMR spectra of compounds 7-16

<sup>a</sup> The designation C(1) is used for the carbon atom linked to the HgCl group.

20.78

20.83

<sup>b</sup> Were not measured.

142.44

(2295)

141.90

(2310)

Compound 72

82

92

7b<sup>c</sup>

86°

9bc

9d

7c

10

12

13

14d

15

16

<sup>c</sup> Parameters of 7b-9b were determined for the reaction mixture.

21.38

55.49

(OMe)

<sup>d</sup> Determined in a mixture with compound 13.

151.04

(267.9)

150.53

(269.2)

clearly difined, despite the scalar relaxation occurring even in an intense magnetic field, and the magnitude of the smaller constant, J<sup>trans</sup>Hg,Me, is more than 10 Hz. The introduction of an electronegative substituent into the aromatic ring (compounds 10, 12-14) has almost no effect on the  $J_{Hg,Me}$  constants.

The above-considered relationship between the magnitude of  $J_{Hg,H}$  and the regio- and stereochemical structure of the molecules is also observed in compounds

17-20 for the methyl and methylene groups located at the double bond (see Table). However, it is noteworthy that, in contrast to what was to be expected, the  $J_{HR,H}$ constants for this group are somewhat smaller than those for the methyl group, in spite of the presence of the electron-withdrawing oxygen atom at the CH<sub>2</sub> group, This points to a noticeable interaction between the electronic systems of the double bond and the CH2OAc substituent. In the series of these compounds, a long-

129.95

126.92;

130.014

114.66;

128.534

168.94

(17.2)

169.02

(20.9)

140.18;

127.42

(24.5)

160.62;

127.35

(25.0)

127.75 128.69

(13.0);

128.32

(90.6)

128.55;

128.47

(90.5)

135.66 (Ar,

J = 60.9);

138.75 (Ph,

J = 54.1)

130.86 (Ar,

J = 62.3);

138.89 (Ph,

J = 55.3)

Table 4. Data of the  ${}^{13}C$  NMR spectra of compounds 17-20 (CDCl<sub>3</sub>)

Com	-	δ (J <sub>Hg,C</sub> /Hz)						
po- und	C(1) <sup>a</sup>	C(2)	CH3	CH <sub>2</sub>	CH3(0	) CH <sub>3</sub> (C	0) CO	
17	138.96 (2307)	149.17 (83)	17.37 (142)	71.22 (<5)	58.03	21.29	169.49 (20)	
186	140.36 (2352)	147.65 (305)	22.82 (94)	70.54 (<5)	58.07	20.75	168.24 (16)	
19	135.73 (2410)	151.41 (306)	23.39 (89)	63.31 (21)		20.77; 21.15	171.08; 168.41	
20¢	140.01 (2356)	146.21 (306)	18.76 (98)	64.85 (80)		21.06; 20.45	170.73; 168.53	

<sup>n</sup> The designation C(1) is used for the carbon atom linked to the HgCl group.

<sup>b</sup> Determined in a mixture with compound 17.

<sup>c</sup> Determined in a mixture with compound 19.

range coupling between the protons of the Me and  $CH_2$  groups with  $J_{H,H}$  values of 1.1-1.7 Hz is typically manifested.

As follows from measurements for compounds 7a -9a, 10, and 12 in chloroform, shielding of the <sup>199</sup>Hg nuclei displays a noticeable dependence on the structure of the adduct. Since the <sup>199</sup>Hg chemical shifts depend only slightly on substituents R remote from the HgCl group or on substituents in the aromatic ring, there is an analogy with the data on acetoxymercuration products.<sup>4</sup> The  $\delta_{Hg}$  values for isomers 7a, 8a, and 9a are equal to -1097.9, -1150.8, and -1185.3 ppm, and those for isomers 10 and 12 are -1106.2 and -1198.0 ppm, respectively. Each structural type has its own characteristic range of shielding. The difference between the  $\delta_{Hg}$ values for stereoisomers 8 and 9 is ~35 ppm, and interchanging of the methyl and aryl groups at the doublebond carbon atoms, C(1) and C(2), changes the <sup>199</sup>Hg chemical shift more significantly.

The assignment of the resonance lines in the <sup>13</sup>C NMR spectrum (see Tables 3 and 4) is substantially facilitated by the presence of the <sup>13</sup>C-<sup>199</sup>Hg satellites. In particular, owing to the presence of the long-range  $J_{Hg,C}$ constants, it becomes possible to assign the signals of the aryl groups located in the geminal position in relation to HgCl. The long-range <sup>199</sup>Hg-<sup>13</sup>C spin-spin coupling in the compounds under consideration can be efficiently used even for the OOCR groups, both for the carbonyl carbon atom and for the substituent R. In some cases, the determination of the  $J_{Hg,C}$  constants for mixtures was difficult due to the low concentrations of the required compounds. For the direct 1/Hg,C constant, whose magnitude exceeds 2200 Hz, the measurements under these conditions were even more hampered due to broadening of the satellite lines caused by scalar relaxation.

It has been established previously<sup>11</sup> that the  ${}^{2}J_{Hg,C}$  constants provide information on the stereochemistry of addition of mercury salts, because they are strongly

dependent on the mutual orientation of the electronegative substituent and the Hg atom at the double bond. The positive values of the  ${}^{2}J_{\text{Hg,C}}$  constant for *trans*adducts 15 and 16 are 267.9 and 269.2 Hz, while those for all the other *trans*-isomers studied are greater than 300 Hz. Conversely, for *cis*-isomers 9a, 9b, 9d, 12, and 17, this constant is negative and relatively small in magnitude (-83 to -88 Hz). Thus, this spectral parameter permits an unambiguous conclusion on the configurational position of the OOCR group in the molecule.

The magnitudes of the  ${}^{i}J_{Hg,C}$  constants of stereoisomers are also different: they are larger for the *trans*isomer than for the corresponding *cis*-isomer. However, this criterion, unlike the previous one, cannot be used to determine the geometry in the case where only one stereoisomer is formed, because the range of variation of  ${}^{i}J_{Hg,C}$  over the whole series of compounds is fairly broad and exceeds the difference between the constants for two diastereomers.

The  ${}^{3}J_{\text{Hg,C}}$  constants of the methyl group in compounds 8, 9, 12, and 17–19 obey a Karplus type dependence on the dihedral angle, *i.e.*, the inequality  ${}^{3}J^{reas}_{\text{Hg,C}} > {}^{3}J^{cis}_{\text{Hg,C}}$  holds. This assignment criterion is quite reliable, because the  ${}^{3}J_{\text{Hg,C}}$  values for stereoisomers are substantially dissimilar. The change in the constants on going from the *cis*-position of the Me group to its *trans*-position is 30–48 Hz (35–51%). The ranges of variation of the constants in the series of individual conformers are relatively small, about 5 and 16 Hz, respectively, and the ranges of the  ${}^{3}J^{reans}_{\text{Hg,C}}$ and  ${}^{3}J^{cis}_{\text{Hg,C}}$  constants do not overlap. The magnitudes of the geminal  ${}^{2}J_{\text{Hg,C}}$  constants in this series of compounds are intermediate between those of the  ${}^{3}J^{reans}_{\text{Hg,C}}$ and  ${}^{3}J^{cis}_{\text{Hg,C}}$  constants.

Due to intramolecular steric interactions between the substituents at the double bond, the <sup>13</sup>C chemical shifts of the methyl groups experience a typical stereospecific dependence, the range of their variation being more than 6 ppm. The largest difference in shielding is observed for the C atoms of these groups located in the trans- and cis-positions with respect to the Hg atom. The greater shielding characterizes the trans-C atoms. Attention is attracted by the fact that, despite different substituents in compounds 8, 9, 12, 14, and 17–19, the  $\delta_{\rm C}$  values for this group in compounds of the same configuration vary only slightly: in the case of cis-orientation, shielding remains virtually constant  $(\delta \ (7.4-17.5))$ , and in the case of *trans*-orientation, it changes by less than 2 ppm ( $\delta$  22.1–23.8). The position of the signals of the Me group occupying a gem-position with respect to the Hg atom also remains virtually constant over the series of compounds 7, 10, 13, and 20. For the former three compounds, this signal is manifested at 8 19.4-19.7, while for compound 20, it occurs at  $\delta$  18.8. Thus, the ranges of  $\delta_{\mathbf{C}}$  of the Me groups in stereoisomers do not overlap and are characteristic.

Previously, it was known<sup>1-3,9</sup> that mercury salts add to acetylenes *trans*-stereospecifically. The results of the

present study indicate that under certain conditions, the formation of *cis*-adducts can become the predominant reaction pathway. This reaction route is facilitated by electronegative substituents at the double bond. However, the absence of *cis*-adducts in the reaction of  $Hg(OAc)_2$  with alkyne 6 in AcOH indicates that the influence of the substituent electronegativity on the *syn*-addition is ambiguous. Among the factors that determine *syn*-addition, the ratio of the reactants seems especially unusual.

On the whole, the results of this study demonstrate, in our opinion, that the reaction of mercury salts with disubstituted acetylenes can occur by several mechanisms in which the above-considered factors are manifested in different ways.

We believe that the dependence of the composition of the reaction products on the ratio of the reactants is due to the formation of complex 21, which is converted into intermediate 22.



Another argument supporting the hypothesized structure of intermediate 22 is provided by the data<sup>12</sup> on hydration of acetylene derivatives by the Hg(ClO<sub>4</sub>)<sub>2</sub>— HClO<sub>4</sub> system. The yield of the reaction products, ketones, increases with an increase in the substrate : Hg<sup>2+</sup> ion ratio and decreases with a decrease in this ratio. This finding was explained in terms of formation of the complex  $(-C \equiv C-)_2 Hg^{2+}$ , which was identified by UV spectroscopy. In addition to intermediate 22, formation of the mercurinium ion (23) is also possible. This assumption was made<sup>1-3.9</sup> to rationalize the *trans*stereoselective addition of mercury salts to alkynes.



By analogy with the concept of ion-pair mechanism in  $Ad_E$  reactions,<sup>13,14</sup> it can be assumed that intermediates 22 and 23 exist as ion pairs (contact and solventseparated). In low-polarity media and with a relatively low electronegativity of the ligand, the formation of a contact ion pair is more likely. Apparently, this situation is realized in the reaction of alkyne 2 with  $Hg(OOCCCl_3)_2$  in AcOH, in which regioisomeric products 13 and 14 are formed upon addition of the reagent rather than upon conjugated solvomercuration.

Now we consider the possible schemes for the formation of the *cis*-adducts. It has been found that mercurinium ions 23, arising in the reactions with strained alkenes, can be converted not only into *trans*-, but also into *cis*-adducts.<sup>15,16</sup> According to published data,<sup>17</sup> alkynes can be regarded as strained systems. In view of this analogy, the possibility of formation of *cis*adducts from intermediate 23 cannot be ruled out completely. It should be borne in mind that the mercurinium ion can be appreciably asymmetrical, which favors the possibility of *syn*-addition.<sup>18</sup> However, in our opinion, the formation of *cis*-adducts in the reactions in question occurs most likely by the concerted scheme.



Thus, we believe that the reaction of mercury salts with alkynes occurs by several mechanisms in which the factors considered above exert different effects. Consequently, the effect of a particular factor on the stereoand regiochemistry of the reactions is determined by the contribution of one or another mechanism to the overall yields of the reaction products.

When the alkyne possesses substantial electron-donating capacity and its relative concentration is high, complex 21 and, hence, intermediate 22, play the predominant role in the formation of the reaction products.

When the concentration of the alkyne diminishes and it contains electron-withdrawing substituents, which decrease the electron-donating capacity of the triple bond, the formation of complex 21 and intermediate 22 can become less probable. In this case, the reaction would occur via intermediate 23 and by the concerted scheme, and the product ratio would be determined by other factors. It seems obvious that the transition state in the concerted mechanism should be less polar than the transition state on the way to intermediate 23; therefore, a decrease in the polar properties of the solvent and an increase in the electronegativity of the substituent at the triple bond should hamper the reaction involving intermediate 23 and facilitate the concerted reaction. In terms of this interpretation, an increase in the nucleophilic properties of the ligand (OOCMe < OOCEt  $\approx$  OOCPr<sup>n</sup>) should also facilitate the *syn*-addition.

Apparently, the low nucleophilicity of the ligand accounts for the fact that no *cis*-adducts are formed in the reaction of alkyne 2 with  $Hg(OOCCCl_3)_2$  in AcOH.

The specific course of the reaction of alkyne 1 with  $Hg(OOCPr^i)_2$  might be due to the larger radius of the ligand. In all probability, steric effects are more significant in the concerted reaction than in the reaction occurring *via* intermediate 23; for this reason, this reaction gives *trans*-compound 7c as the major product.

When  $Hg(OOCR)_2$  reacts with alkyne 1, the *cis*adducts are formed in such a way that the nucleophile that completes the reaction adds to the carbon atom bearing the Me group. This result is in good agreement with the scheme proposed for the formation of *cis*adducts.

It has been reported<sup>19</sup> that alkyl groups stabilize a low-polarity transition state more efficiently than the phenyl group. Therefore, the *cis*-adducts should arise predominantly *via* transition state A.



It can be seen from the results obtained that the ratio of the reactants has an effect not only on the stereochemistry of the addition of mercury salts to methylphenylacetylene 1 but also on the ratio of *trans*-adducts 7 and 8. Thus in the reaction of 1 with Hg(OAc)<sub>2</sub>, this ratio is<sup>4</sup> 75 : 25 for an alkyne : mercury salt ratio, equal to 2 : 1, and 86 : 8 for 1 :, 1 ratio of the reactants. In the reaction with Hg(OOCEt)<sub>2</sub>, the *trans*isomers 7a and 8a are formed in a ratio of 68 : 32, when the ratio of the reactants is 5 : 1, or 60 : 15 when the ratio of the reactants is 1 : 1. In our opinion, these results provide additional evidence supporting the assumption that this reaction involves more than one intermediate. In fact, if this reaction occurred only *via*  intermediate 23, the competing pathway involving transition state 25 would result in lower yields of the *trans*adducts and an invariable ratio of the regioisomers. However, the reaction schemes proposed here are able to explain this feature, because the reactions of 22 and 23 with nucleophiles may differ in regiochemistry.

The unusual route of the reaction of alkyne 6 with  $Hg(OAc)_2$  in AcOH is apparently due to the effect of the neighboring acetoxy group, which results in the formation of intermediate 26.



The subsequent attack on the methylene group by the acetate anion leads to compound 20.

### Experimental

<sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), and <sup>199</sup>Hg (71.3 MHz) NMR spectra were recorded on a Varian VXR-400 spectrometer. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were referred to tetramethylsilane, and the <sup>199</sup>Hg chemical shifts were referred to external dimethylmercury. TLC analysis and isolation of products were carried out on silica gel LSL 5/40 using a hexane-benzene-ethyl acetate-chloroform mixture (5 : 3 : 1 : 1) as the eluent and iodine for visualization. Under the chosen conditions, the reaction mixture of alkynes and mercury salts could be completely separated. For all reaction mixtures,  $R_f^{cis}(9) > R_f^{trans}(8) > R_f^{trans}(7)$ .

Mercury salts were prepared from yellow mercury oxide and the corresponding acid at a temperature not exceeding 70 °C. After cooling, the crystals were filtered off and recrystallized from the corresponding acid.

Reaction of alkyne 1 with Hg(OOCEt)2. Alkyne 1 (1.16 g, 10 mmol) in 20 mL of propionic acid was added to a solution of Hg(OOCEt)<sub>2</sub> (3.5 g, 10 mmol) in 40 mL of the same solvent. After 2 days, the reaction mixture was poured into 300 mL of a 1% aqueous solution of NaCl. The resulting precipitate was washed with water and hexane. Yield 4 g (94%). The precipitate was dissolved in CHCl<sub>3</sub>. The insoluble mercury compounds were filtered off (10-15%), CHCl<sub>3</sub> was removed at a reduced pressure, and the residue was analyzed by TLC and NMR. Recrystallization from a C<sub>6</sub>H<sub>14</sub>--CHCl<sub>3</sub> mixture (7:3) gave 1 g of (E)-2-chloromercurio-1-phenylprop-1-enyl propionate (7a), m.p. 110-111 °C. Preparative TLC of the mother liquor obtained after separation of 7a gave 0.3 g of (E)-2-chloromercurio-1-methyl-2-phenylvinyl propionate (8a), m.p. 121-123 °C (C<sub>6</sub>H<sub>14</sub>-CHCl<sub>3</sub>, 7 : 3), and 0.5 g of (Z)-2-chloromercurio-1-methyl-2-phenylvinyl propionate (9a), m.p. 107-108 °C (C<sub>6</sub>H<sub>14</sub>-CHCl<sub>3</sub>, 7 : 3).

The reactions with  $Hg(OAc)_2$  and  $Hg(OOCEt)_2$  were carried out in a similar way at 65-70 °C (the concentration of the mercury salt was 0.1-0.2 mol L<sup>-1</sup>). The usual workup gave reaction mixtures (yield 75-80%), which were then analyzed by TLC and NMR.

**Reaction of alkyne I with Hg(OOCEI)\_2 with a fivefold** excess of the alkyne was carried out at a concentration of the

mercury salt of 0.1-0.15 mol L<sup>-1</sup>. After completion of the reaction and treatment with NaCl, the reaction mixture was stirred with 20 mL of hexane for 30 min; this operation was repeated three times. After removal of C<sub>6</sub>H<sub>14</sub>, the mixture was analyzed by NMR.

Reaction of alkyne 1 with Hg(OOCPr<sup>a</sup>)<sub>2</sub>. Compound 1 (1.1 g, 9.4 mmol) in 35 mL of butyric acid was added to a solution of the mercury salt (3.5 g, 9.3 mmol) in 60 mL of the same solvent. The reaction mixture was kept in the dark for 9 days, then 4 g of NaCl was added, and the mixture was stirred for 3 h. The main bulk of the solvent was removed at a reduced pressure at a temperature not higher that 70 °C. The residue was mixed with CHCl3, washed with an aqueous solution of NaHCO<sub>3</sub> and with H<sub>2</sub>O to neutral reaction, and dried with MgSO<sub>4</sub>. Removal of CHCl<sub>3</sub> gave 3.2 g (77%) of a mixture of products 7b, 8b, and 9b as an oil. The composition of the mixture was determined by NMR without isolation of individual compounds; for this purpose, the reaction mixture was purified by TLC from minor impurities (5-10%), whose  $R_{\rm f}$  values were much smaller than those of the main reaction products.

(E)-2-Chloromercurio-1-phenylprop-1-enyl isobutyrate (7c). Alkyne 1 (1.0 g, 8.6 mmol) in 10 mL of isobutyric acid was added to a solution of Hg(OOCPri)<sub>2</sub> (3.2 g, 8.5 mmol) in 20 mL of the same solvent. After 3 weeks, the reaction mixture was worked up as described above to give 1.5 g (40%) of compound 7c, m.p. 115-118 °C ( $C_6H_{14}$ ).

(Z)-2-Chloromercurio-1-methyl-2-pheaylvinyl pentanoate (9b). Alkyne 1 (0.3 g, 2.7 mmol) in 3 mL of pentanoic acid was added to a solution of Hg(OOCBu<sup>n</sup>)<sub>2</sub> (1.1 g, 2.7 mmol) in 10 mL of the same solvent. After 14 days, NaCl was added to the reaction mixture, and the mixture was stirred for 3 h and mixed with CHCl<sub>3</sub>. The acid was removed by repeated treatment with an aqueous solution of NaHCO<sub>3</sub>, and the solution was dried with MgSO<sub>4</sub>. Removal of CHCl<sub>3</sub> gave 0.6 g of compound 9d, m.p. 46---47 °C (MeOH).

According to TLC, the reaction mixture contained one more compound (~10%) and unreacted alkyne. When the reaction time was increased to 30 days, the total yield of the product increased to 57-60%.

2-Chloromercurio-1-(*m*-chlorophenyl)prop-1-enyl trichloroacetate (13). Alkyne 2 (0.5 g) in 5 mL of AcOH was added to a solution of Hg(OOCCCl<sub>3</sub>)<sub>2</sub>, prepared from CCl<sub>3</sub>COOH (1.11 g) and freshly precipitated yellow HgO (0.75 g) in a mixture of 18 mL of AcOH and 0.34 mL of Ac<sub>2</sub>O. After 4 h, the reaction mixture was treated with an aqueous solution of NaCl to give 1.03 g of a crystalline precipitate (yield 60%). Crystallization of the precipitate gave product 13, m.p. 157– 159 °C (C<sub>6</sub>H<sub>14</sub>-CHCl<sub>3</sub>, 7 : 3).

(E)-2-Chloromercurio-2-(m-chlorophenyl)-1-methylvinyl trichloroacetate (14) was identified by NMR spectroscopy in a mixture with 13, after substracting the signals due to 13.

Reaction of Hg(OAc)<sub>2</sub> with alkynes 2-6 in AcOH. Solutions of Hg(OAc)<sub>2</sub> and an alkyne were mixed at room temperature. The concentrations of the reagents were 0.1-0.25 mol L<sup>-1</sup>. After completion of the reaction, the reaction mixture was poured into a 1% aqueous solution of NaCl. If a precipitate was formed, it was filtered off and washed with H<sub>2</sub>O and C<sub>6</sub>H<sub>14</sub>. If the products were oily, they were extracted with CHCl<sub>3</sub>, the organic fraction was washed with water to a neutral reaction and dried with MgSO<sub>4</sub>, and the solvent was removed at a reduced pressure.

(E)-2-Chloromercurio-1-(*m*-chlorophenyl)prop-1-enyl acetate (10) and (Z)-2-chloromercurio-2-(*m*-chlorophenyl)-1-methylvinyl acetate (12) were prepared from Hg(OAc)<sub>2</sub> (1.59 g, 5 mmol) and compound 2 (0.8 g, 5 mmol) in 40 mL of AcOH. After 48 h, 1.8 g of an oil was formed, yield 70%. Preparative TLC gave 10, m.p. 119–120 °C ( $C_6H_{14}$ -CHCl<sub>3</sub>, 7 : 3) (cf. Ref. 1: 116–117 °C) and 12, m.p. 113–114 °C ( $C_6H_{14}$ -CHCl<sub>3</sub>, 7 : 3).

(E)-2-Chloromercuriobut-2-ene-1,3-diol diacetate (19) was prepared from Hg(OAc)<sub>2</sub> (2.01 g, 6.3 mmol) and compound 6 (2.12 g, 18.9 mmol) in 30 mL of AcOH. After 10 days, 1.64 g of an oily reaction mixture was obtained, yield 60%. Double recrystallization gave product 19, m.p. 82.5-83 °C (MeOH).

(E)-3-Chloromercuriobut-2-ene-1,2-diol diacetate (20) was identified by NMR spectroscopy in a mixture with 19, after substracting the signals due to 19.

(Z)-2-Chloromercurio-3-methoxy-1-methylprop-1-enyl acetate (17) and (E)-2-chloromercurio-3-methoxy-1-methylprop-1-enyl acetate (18) were prepared from Hg(OAc)<sub>2</sub> (2.2 g, 6.9 mmol) and compound 5 (0.58 g, 6.9 mmol) in 30 mL of AcOH. After 20 h, 1.64 g of a crystalline residue was obtained, yield 63%. The resulting mixture was dissolved in boiling MeOH, and insoluble mercury compounds were filtered off. Evaporation of the solvent gave 1.15 g of a crystalline product; the ratio of the components was determined by NMR. Recrystallization from MeOH (4 times) gave 17, m.p. 114-115 °C. The crystalls obtained from mother liquors were combined and recrystallized twice from MeOH, m.p. 84-86 °C. According to NMR, the content of the main substance 18 was ~90%.

(E)-2-Chloromercurio-2-phenyl-1-(p-tolyl)vinyl acetate (15) was obtained from Hg(OAc)<sub>2</sub> (1.16 g, 3.6 mmol) and compound 3 (0.7 g, 3.6 mmol) in 40 mL of AcOH. The reaction time was 48 h, yield 78%, m.p. 183-185 °C (C<sub>6</sub>H<sub>14</sub>--CHCl<sub>3</sub>, 7 : 3).

(E)-2-Chloromercurio-1-(p-methoxyphenyl)-2-phenylvinyl acetate (16) was obtained from Hg(OAc)<sub>2</sub> (1.0 g, 3.1 mmol) and compound 4 (0.66 g, 3.2 mmol) in 35 mL of AcOH. The reaction duration was 48 h, yield 88%, m.p. 170-171 °C (C<sub>6</sub>H<sub>14</sub>-CHCl<sub>3</sub>, 7 : 3).

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