Organometallic Chemistry

Reactions of mercury salts with benzo- and tetrafluorobenzobarrelenes

T. N. Sokolova,[a] Yu. K. Grishin,[b] I. V. Timofeev,[a] and V. R. Kartashov,[a]*

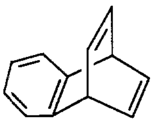
[a]Nizhnii Novgorod Technical State University,
24 ul. Minina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831) 236 9475
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0126

Regiochemistry and stereochemistry of the addition of mercury salts to benzobarrelene and tetrafluorobenzobarrelene have been studied in acetic acid and methanol. The effect of the substrate structure on the regiochemistry of the reaction is discussed.

Key words: benzobarrelenes, solvo- and azidomercuration; regiochemistry; regioisomers, structure; Hg—double bond coordination, effect on the ratio of isomeric products.

It is known that the reactions of mercury salts with diene and polyene bridged compounds are characterized by a variety of regiochemical results.[1—8] We,[4—8] as well as other researches,[9,10] have suggested that this arises mainly from the reaction of the mercury salt with two spatially close double bonds or with a double bond and a functional group.[3,11,12] These interactions can occur both in the ground and transition states. Our study of the $HgCl_2$—bicyclo[2.2.2]octa-2,5-diene system using ^{199}Hg NMR spectroscopy has confirmed that this interaction does actually take place.[13] The tendency of the mercury ion or HgCl groups to undergo intramolecular and intermolecular coordination with electron-donating sites (*e.g.*, unsaturated and aromatic systems or halogen atoms) has been demonstrated by various methods.[14,15]

We have studied the reactions of mercury salts with benzobarrelene (**1**) and tetrafluorobenzobarrelene (**2**) with the aim of extending the knowledge of the effect of coordination on the regiochemistry of the mercuration of polyenic bridged systems.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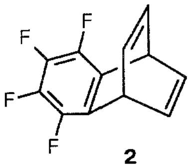

2

$Hg(OAc)_2$ in CH_3COOH and $Hg(NO_3)_2$ and $Hg(N_3)_2$ in CH_3OH* were used as reagents. The reactions were performed at room temperature and at reagent concentrations 0.1—0.15 *M*.

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* Mercury azide was prepared by mixing $Hg(OAc)_2$ and NaN_3 in a ratio of 1 : 3 in CH_3OH; the concentration of the reagent did not exceed 0.1 *M*

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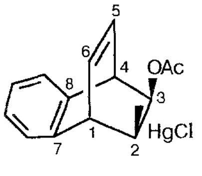
We found that the reaction of **1** with $Hg(OAc)_2$ in CH_3COOH affords a 4:1 mixture of (**3**) and (**4**).



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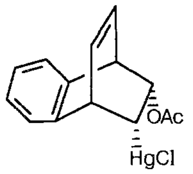
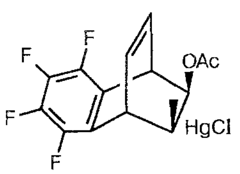


4

The same reaction with **2** is known to give rise to compounds (**5**) and (**6**) with similar structures.[16] However, the ratio of regioisomers **5** and **6** (2:3) differs from that observed in the case of **1**.



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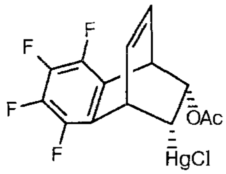

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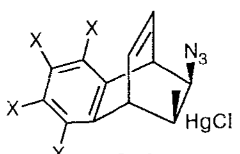
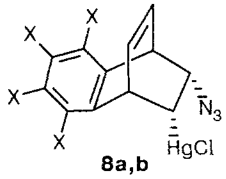
The reaction of compound **1** with mercury azide in CH_3OH affords two isomers (**7a**) and (**8a**) in a ratio of 17 : 3.



7a,b

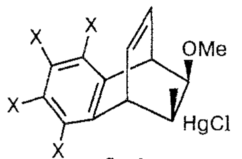


8a,b

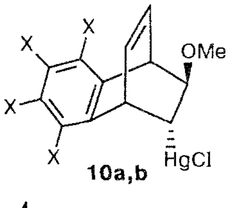
X = H(**a**), F(**b**)

Azidomercuration of **2** yields mainly adduct **7b** (up to 90 %). Compounds **4** and **8** were separated in a pure form by preparative TLC on silica gel.

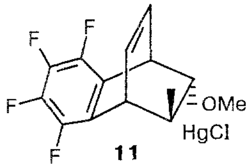
The reactions of **1** and **2** with $Hg(NO_3)_2$ in CH_3OH are more complicated; however, the regiochemical results are similar. Preparative TLC data show that the reaction mixtures contain five products. We failed to isolate compounds whose concentrations in the reaction mixture were low (*ca.* 5—10 %). The reaction with **1** affords compounds **9a** and **10a**; the reaction with **2** yields adducts **9b**, **10b**, and **11**. The concentration of each adduct in the reaction mixtures did not exceed 40 %.



9a,b



10a,b



11

X = H(**a**), F(**b**)

The structures of products **3**—**4** and **7**—**11** were determined by ^1H, ^{13}C, and ^{199}Hg NMR spectroscopy. The spectral parameters are given in Tables 1 and 2. In establishing the structures of these products on the basis of their NMR parameters, we used criteria discussed earlier[5] for the mercuration products of bicyclo[2.2.2]octa-2,5-diene.

The $^1H—^1H$, $^{199}Hg—^1H$, and $^{199}Hg—^{13}C$ spin-spin coupling constants provide the best defined criteria for the configurational assignments of adducts **3**—**4** and **7**—**11**, which have rigid frameworks. Thus, unambiguous information on the stereochemistry of addition in

Table 1. Chemical shifts of ^1H and ^{199}Hg and the J_{Hg-H} constants (in $CDCl_3$)

Compound	δ(*J*/Hz)								
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	Me	Ar	Hg
3	4.249	3.030 (183.9)	5.225 (106.7)	4.385 (29.0)	6.519	6.909	2.090	7.25 (1H) 7.1 (3H)	−1198.9
4	4.272	3.198 (177.7)	5.321 (107.6)	4.321 (26.4)	6.478	6.646	1.933	7.15—7.30	
7a	4.168 (62.0)	2.935 (170.5)	4.079 (120.0)	4.350 (30.0)	6.558	6.864		7.21 (1H) 7.11 (3H)	
7b	4.581 (70.0)	2.872 (180.5)	4.103 (120.6)	4.731 (25.2)	6.602	6.890			−1217.2
9a	4.118 (72.4)	3.031 (176.2)	3.745 (113.0)	4.363 (29.5)	6.443	6.835		7.08; 7.08 7.06; 7.19	−1203.2
9b	4.561 (73.0)	2.999 (185.9)	3.779 (111.0)	4.833 (25.8)	6.492	6.880	3.483		−1216.2
10a	4.169 (75.4)	2.241 (163.8)	4.072	4.330	6.344	6.651		7.24; 7.15 7.12; 7.11	
10b	4.578 (74.4)	2.166 (177.6)	4.017 (222.8)	4.724	6.352	6.683	3.434		−1137.9
11	4.615 (70.0)	1.885 (180.8)	4.217 (251.2)	4.715 (30.0)	6.577	6.737	3.370		−1156.2

Table 2. Chemical shifts of ^{13}C and J_{HgC} constants (in $CDCl_3$)

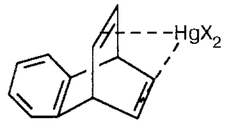
Compound	δ(*J*/Hz)											
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	CO	Me	MeO	Ar
3	44.86 (60.4)	58.59 (1769.6)	74.39 (127.0)	45.30	132.76	137.40 (60.1)	144.40 (224.4)	139.09	169.94	21.81		122.76; 124.87 125.95; 126.42
4	44.86 (59.0)	60.18 (1755.7)	74.25 (104.3)	45.35	132.77	138.65 (224.1)	144.92 (46.2)	138.93	170.10	21.70		121.73; 125.84 126.35; 127.23
7a	44.87 (54.4)	58.76 (1809.8)	63.42 (109.0)	45.10	132.09	137.52 (63.4)	144.01 (227.8)	139.35				122.89; 124.06 126.00; 126.52
7b	37.51 (60.0)	57.08 (1852.0)	62.20 (99.8)	37.24	131.99	136.85 (62.9)	126.88	122.12				138.77; 139.24 141.72; 142.53
8a	44.89 (52.3)	60.99 (1860.6)	62.50 (81.2)	44.87	132.64	138.46 (227.4)	144.60	138.34				121.64; 125.68 126.31; 127.42
9a	44.79 (40.0)	60.99 (1795.4)	81.37 (126.0)	43.47	132.03	136.85 (65.6)	145.08 (237.8)	139.76			56.06	122.63; 124.36 125.53; 126.00
9b	37.24 (39.9)	58.99 (1839.1)	80.20 (124.5)	35.81	131.84	136.45 (58.5)	127.76 (245.1)	122.53			56.37	138.48; 138.83 141.50; 142.80
10a	44.88 (79.0)	59.33 (1674.6)	82.48 (62.5)	45.53 (33.1)	130.85	135.58 (218.3)	144.82 (49.9)	139.96			56.72	121.97; 124.88 126.04; 127.04
10b	36.94 (76.9)	56.46 (1689.0)	81.29 (69.5)	38.33 (28.3)	130.45	135.66 (207.7)	126.47 (50.0)	122.98			57.03	139.01; 139.25 141.08; 143.07
11	36.94 (91.9)	54.88 (1763.7)	80.98	37.12	133.18	137.78 (50.0)	125.89 (236.3)	121.04			56.61	139.10; 141.25 141.28; 144.90

the case of **10a** and **10b** is obtained from the values of $^3J_{H(2)-H(3)}$ (3.3 and 3.6 Hz, respectively), whereas for the *cis* adducts, $^3J_{H(2)-H(3)}$ is 7.7—8.4 Hz. This is consistent with the knowledge about the relation between the constants of vicinal spin-spin coupling and the dihedral angles. The values of $^3J_{Hg-H(3)}$ for the stereoisomers differ accordingly: they are 107—121 Hz and > 220 Hz for the *cis* and *trans* adducts, respectively.

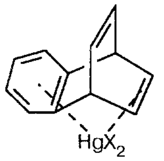
Previously it was found[17] that the $^2J_{Hg-C(3)}$ constants depend strongly on the mutual spatial orientation of the Hg atom and the substituent at C(3). High absolute values of this constant (because $^2J_{Hg-C(3)} < 0$) are observed for the *cis* isomers (≥ 100 Hz), whereas in the *trans* isomers they are equal to or below 70 Hz.

The vicinal constants $^3J_{Hg-C(6)}$ and $^3J_{Hg-C(7)}$ make it possible to locate the mercury atom with respect to the double bond and the aromatic ring. These constants have substantially different values because the Hg—C(2)—C(1)—C(6) and Hg—C(2)—C(1)—C97) dihedral angles are 60 and 180° in compounds **3**, **7**, **9**, and **11**, whereas these angles are 180 and 60° in compounds **4**, **8**, and **10**.

The data thus obtained show that the reaction products result from the attack of the mercury salt at the double bond of the cyclohexadiene moiety of compounds **1** and **2** both from the side of the aryl ring (**4**, **8**, and **10**) and from the side of the bridging —CH=CH— group (**3**, **7**, **9**, and **11**). It is believed that these results and the regiochemistry of mercuration of other related bicyclic systems[4—8] are determined by a coordinative interaction between the reagent and the substrate. This interaction, as applied to dienes **1** and **2**, can be achieved in two ways: reagent—two double bonds (**12**) and reagent—double bond—benzene ring (**13**).



12



13

Except the data on the reaction of **2** with $Hg(OAc)_2$ in CH_3COOH,[16] the studied reactions are characterized by the predominant formation of products through intermediate **12**. This suggests that a system consisting of two framework double bonds exerts a higher chelating effect on the mercury ion than one involving a double bond and an aryl group.

The acetoxymercuration of **2** affords predominantly **6**. This is difficult to explain from the known facts. It can only be noted that the reaction through intermediate **13** does not determine the regiochemistry of reaction, because it is known that the donor ability of an aromatic system toward the mercury ion decreases as the H atoms are replaced by F (*cf.* Ref. 18). Apparently, the coordinative interactions between the benzene fluorine atoms and the mercury atom of the reagent shown in intermediate **13** play no substantial role because the fluorine atoms and the π-system of the double bond are far apart (≥ 4 Å).

Experimental

The ^1H, ^{13}C, and ^{199}Hg NMR spectra were recorded on a Varian VXR-400 spectrometer, in $CDCl_3$ as the solvent. Chemical shifts of ^1H and ^{13}C were recorded relative to TMS, and those for ^{199}Hg, to Me_2Hg, and correspond to the δ scale. The spectra were analyzed by two-dimensional homonuclear and heteronuclear (^{13}C and ^{1}H) correlation spectroscopy.[19]

Benzobarrelene **1** and tetrafluorobarrelene **2** were prepared according to methods reported previously (*cf.* Refs. 20 and 21, respectively).

Reaction of 1 with $Hg(OAc)_2$ in CH_3COOH. 1.0 g (6.5 mmol) of **1** in 20 mL of CH_3COOH was added to 2.0 g (6.3 mmol) of $Hg(OAc)_2$ in 40 mL of CH_3COOH. The reaction mixture was allowed to stand in the dark for a day, and was then poured into a 1 % aqueous solution of NaCl (240 mL) and extracted with $CHCl_3$. The organic phase was washed with water until the reaction was neutral and dried with $MgSO_4$. After the removal of the solvent under reduced pressure, 2.5 g (yield 90 %) of a crystalline compound was obtained. From there, *cis-exo*-2-chloromercuro-3-acetoxybenzo-7,8-bicyclo[2.2.2]oct-5-ene (**3**), m.p. 163—164 °C, was isolated by recrystallization from CH_3OH. The mother liquor was evaporated and the residue (1 g) was subjected to preparative TLC on Silica gel LSL 5/40 (5 : 3 : 1 : 1 hexane—Et_2O—AcOEt—chloroform was used as the eluent) to afford *cis-endo*-2-chloromercuro-3-acetoxybenzo-7,8-bicyclo[2.2.2]oct-5-ene (**4**), m. p. 151—152.5 °C (from CH_3OH).

Reaction of 1 with mercury azide in CH_3COOH. 0.3 g (1.95 mmol) of **1** in 5 mL of CH_3OH was added quickly to a mixture of $Hg(OAc)_2$ (0.62 g, 1.95 mmol) and NaN_3 (0.38 g, 5.85 mmol) in 16 mL of CH_3OH. After 2.5 h, the reaction mixture was worked up as described above. After the removal of the solvent, 2.5 g of a crystalline compound was obtained from three simultaneous runs. *Cis-exo*-2-chloromercuro-3-azidobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**7a**), m.p. 135—137 °C (with decomposition), was obtained (1.2 g) by recrystallization from AcOEt. From the mother liquor, 0.14 g of *cis-endo*-2-chloromercuro-3-azidobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**8a**), m.p. 112—114 °C (from CH_3OH), was obtained by preparative TLC on silica gel.

The reaction of **2** with mercury azide in CH_3OH was performed in a similar manner. *cis-exo*–2-Chloromercuro-3-azidotetrafluorobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**7b**), m.p. 153—154 °C (with decomposition) was obtained by recrystallization from ethyl acetate.

Reaction of 1 with $Hg(NO_3)_2$ in CH_3OH. 1.0 g (6.5 mmol) of **1** in 20 mL of CH_3OH was added at −40 °C to a suspension of 1.1 g (3.2 mmol) of $Hg(NO_3)_2$ and 0.7 g (32 mmol) of freshly precipitated yellow HgO in 40 mL of the solvent. The mixture was stirred for 30 min and then worked up as above. After the removal of the solvent, 2.3 g of a crystalline compound was obtained. Preparative TLC afforded 0.97 g of *cis-exo*-2-chloromercuro-3-methoxybenzo-7,8-bicyclo[2.2.2]oct-5-ene (**9a**), m.p. 136—137 °C (from a 9 : 1 mixture of ethyl acetate and hexane), and 0.28 g of *trans-endo*-2-chloromercuro-3-methoxobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**10a**), m.p. 165—167 °C (from chloroform).

Reaction of 2 with $Hg(NO_3)_2$ in CH_3OH was performed as described above. The reaction products were separated by preparative TLC to yield 0.25 g of *cis-exo*-2-chloromercuro-3-methoxytetrafluorobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**9b**), m.p. 170—171 °C (with decomposition, from CH_3OH), 0.4 g of *trans-endo*-2-chloromercuro-3-methoxytetrafluorobenzo-7,8-bicyclo[2.2.2]oct-5-en (**10b**), m.p. 189—191 °C (with decomposition, from CH_3OH), and 0.35 g of *trans-exo*-2-chloromercuro-3-methoxytetrafluorobenzo-7,8-bicyclo[2.2.2]oct-5-ene (**11**), m.p. 180—181 °C (with decomposition, from ethyl acetate).

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