Organometallic Chemistry

Reaction of mercury salts with dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*cis-endo*-9,10-dicarboxylate in acetic acid

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The reaction of dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*cis-endo*-9,10-dicarboxylate with mercury salts $Hg(OCOR)_2$ (R = CCl_3, CF_3, CH_2Cl) in acetic acid yields a mixture of solvoadducts and products of addition of the anionic moiety of the reagent having the *trans*-configuration. In the case of $Hg(OCOCCl_3)_2$, *cis*-solvoadduct was detected along with the *trans*-isomer. The amount of the addition products is determined by the nature of the mercury salt and increases in the order $Hg(OCOCH_2Cl)_2 < Hg(OCOCCl_3)_2 \approx Hg(OCOCF_3)_2$. The reaction is assumed to involve contact and solvent-separated ion pairs.

Key words: mercury salts, solvoadduct, adduct, stereoisomers, reaction mechanism, intermediate, contact ion pair, solvent-separated ion pair.

Previously,[1,2] it was concluded based on kinetic data that free solvated mercurinium ions are formed as intermediates in the reactions of mercury(II) salts with nonstrained alkenes in alcoholic and aqueous solutions and then they are converted into solvoadducts. Conversely, the reactions with strained alkenes afford contact ion pairs, whose transformation into the reaction products depends on the properties of the medium and reaction conditions.[1,3,4]

A typical feature of Ad_E reactions occurring *via* an ion-pair mechanism is the formation of the addition products of the reagents from the ion pair.[1,3–7] Evidently, the lower the polarity and the solvating properties of the solvent, the higher the probability of the transformation of the ion pair into the addition products in relation to the probability of its transformation into free solvated mercurinium ion followed by the formation of solvoadducts. Therefore, in this work, we studied the composition of the products of reactions of mercury salts $Hg(OCOR)_2$ (R = CH_2Cl, CCl_3, CF_3) with highly strained dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*cis-endo*-9,10-dicarboxylate (**1**) in acetic acid, considered the structural features of the substrate, and determined the stereochemistry of these reactions.

Results and Discussion

It was shown previously[8] that the reaction of **1** with mercury acetate in acetic acid occurs smoothly to give one product (**2**), having the *trans*-configuration. In a

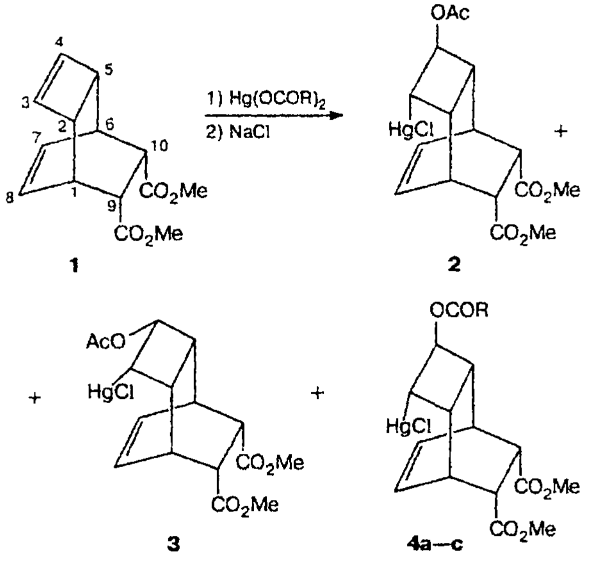
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2173—2176, November, 1999.

1066-5285/99/4811-2149 $22.00

mixed solvent ($CH_3COOH-THF$), *cis*-isomer **3** is formed in a yield of up to 15% besides **2**.[9,10]

Here we found that the reactions of mercury salts $Hg(OCOR)_2$ (R = CH_2Cl, CCl_3, CF_3) with *cis*-diester **1** follow a more complex pathway. Thus when $Hg(OCOCCl_3)_2$ is used as the reagent, together with the expected *trans*-compound **2**, compounds **3** and **4a** are also formed, the latter being the major product. The **2** : **3** : **4a** ratio in the reaction mixture amounts to 1 : 2 : 7 (NMR data).

The *anti*-addition of the reagent is also the major pathway in the reaction with $Hg(OCOCF_3)_2$. In this case, only traces of product **3** were found (TLC data). Apart from **4b**, solvoadduct **2** is formed. The **2** : **4b** ratio is 1 : 9.



R = CCl_3 (**a**), CF_3 (**b**), CH_2Cl (**c**)

The reaction of **1** with $Hg(OCOCH_2Cl)_2$ yields products **2** and **4c**; however, acetoxymercuration is the predominant reaction route. The **2** : **4c** ratio in the reaction mixture is 7 : 3.

The structure of **2** was established by comparing its melting point and the IR spectrum with those of an authentic sample.[8] Compound **3** was not isolated in a pure state. The product isolated from the reaction mixture by TLC contained admixtures (10—15%) of compounds **2** and **4a**. The product was analyzed by NMR spectroscopy. The ^1H and ^{13}C NMR spectral parameters (Tables 1 and 2) of compound **3** isolated in this study were identical to those of a pure sample.[9,10] The structure of adduct **4b** was proved by its hydrolysis giving a known compound (**5**), whose physicochemical parameters coincided with those of the product **5** prepared by an alternative synthesis[11] (Scheme 1).

The structures of products **4a** and **4c** were established by NMR spectroscopy (Tables 1 and 2). The

Table 1. δ ^{13}C chemical shifts and J_{Hg-C} spin-spin coupling constants ($CDCl_3$) in the NMR spectra of compounds **3**, **4a**, and **4c**

Atom	δ ^{13}C (J_{Hg-C}/Hz)		
	3	**4a**	**4c**
C(1)	37.47 (175.8)	38.20 (154.6)	38.35 (155.3)
C(2)	38.70 (−109.2)	40.69 (−53.5)	40.81 (−52.0)
C(3)	51.95 (1672.7)	50.31 (1665.4)	51.39 (1616.3)
C(4)	73.45 (−145.7)	81.23 (−27.8)	77.05 (−32.0)
C(5)	45.52 (77.7)	46.51 (237.0)	46.60 (238.0)
C(6)	34.31 (22.0)	35.51 (38.1)	35.60 (37.4)
C(7)	138.27	135.84	136.08
C(8)	128.82 (21.98)	131.28 (11.7)	131.08 (11.7)
C(9)	46.69	46.28	46.39
C(10)	46.22	44.96	45.08
CO(CO_2Me)	172.29 172.41 (17.6)	172.41 172.12	173.53 172.18
CH_3(CO_2Me)	51.89 51.89	51.89 51.89	51.98 51.98
CO(OCOR)	170.07 (8.8)	161.15	166.68
R(OCOR)	21.15 (13.2)	89.42	40.66

Scheme 1

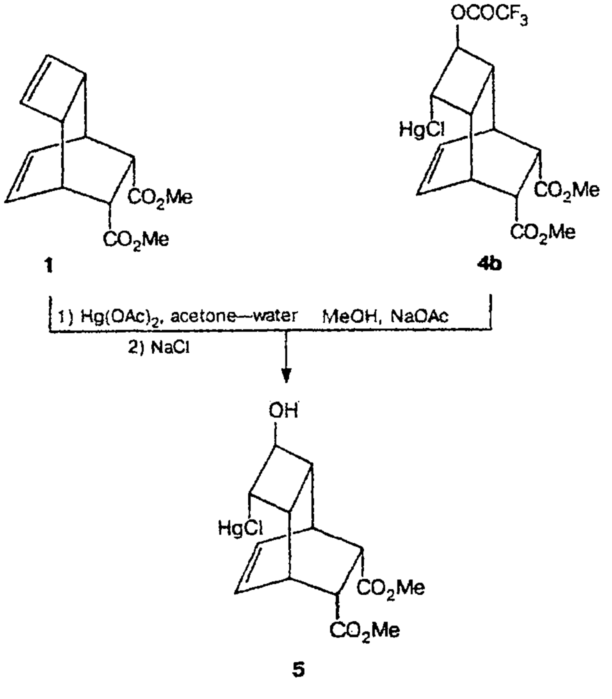


Table 2. δ ^{1}H and δ ^{199}Hg* chemical shifts and $J_{\mathrm{Hg-H}}$ spin-spin coupling constants ($CDCl_3$) in the NMR spectra of compounds **3**, **4a**, and **4c**

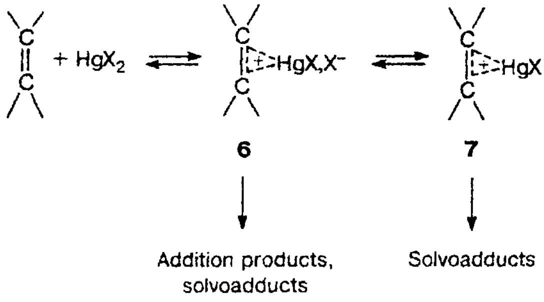
Atom	δ ^{1}H ($J_{\mathrm{Hg-H}}$/Hz)		
	3	**4a**	**4c**
H(1)	2.93	3.02	2.96
H(2)	2.80 (187.8)	2.88 (150.0)	2.80
H(3)	3.52 (237.6)	3.30	3.20
H(4)	5.27 (175.4)	4.74 (216.0)	4.59
H(5)	3.11	2.96	2.80
H(6)	3.00	3.30	3.24
H(7)	6.62	6.69	6.67
H(8)	6.50	6.71	6.67
H(9)	2.89	2.97	2.94
H(10)	2.97	2.88	2.80
$CH_3(CO_2CH_3)$	3.60 3.60	3.62 3.62	
$CH_3(OCOCH_3)$	2.06		

* δ ^{199}Hg: −989.63 (**3**), −1039.46 (**4a**), −1029.15 (**4c**).

criteria for structural identification of the products of mercuration of ester **1** based on NMR data have been described in detail.[10] The stereochemistry of the addition of the reagent is indicated unambiguously by the magnitudes of the geminal $^2J_{\mathrm{HgC}}$ constants. The spin—spin coupling constants $^2J_{\mathrm{HgC}}$ for *trans*-isomers **4a** and **4c** are substantially smaller in magnitude than those for isomer **3** with *syn*-arrangement of the HgCl and OCOR groups. Thus the $^2J_{\mathrm{HgC(2)}}$ value for compounds **4a** and **4c** is one half of and $^2J_{\mathrm{HgC(4)}}$ is one fifth of the corresponding constants for *cis*-isomer **3** (see Table 1). The $^3J_{\mathrm{HgC(5)}}$ constants for the stereoisomers are also substantially different. For *trans*-adducts **4a** and **4c**, this constant is 237—238 Hz, whereas for *cis*-isomer **3** it is 77.7 Hz. The site of attachment of the HgCl group is determined based on the $^3J_{\mathrm{HgC(1)}}$ value. For products **3**, **4a**, and **4c** with *endo*-arranged HgCl groups (torsional angle ≈10°), this constant is 155—176 Hz. It is known[10,12] that the *exo*-arrangement of the HgCl group (torsional angle ~110°) results in much smaller $^3J_{\mathrm{HgC(1)}}$ values (~113 Hz).

The $^3J_{\mathrm{HgH}}$ constants also exhibit a clear-cut dependence on the torsional angle, which permits configuration assignment of the pair of stereoisomeric *cis*- and *trans*-adducts **3** and **4**. Thus, the $^3J^{cis}_{\mathrm{HgH(4)}}$ constant for H(4) in compound **4a** is substantially greater than $^3J^{trans}_{\mathrm{HgH(4)}}$ for compound **3** (216.0 Hz and 175.4 Hz, respectively, see Table 2).

A typical feature of the reactions studied is the formation of large quantities of addition products. The proportion of this reaction pathway is determined by the nature of the mercury salt and increases in the sequence $Hg(OCOCH_2Cl)_2 < Hg(OCOCCl_3)_2 \sim Hg(OCOCF_3)_2$. In our opinion, these data are in good agreement with the scheme according to which the reaction involves ion pairs, a contact (**6**) and a solvent-separated (**7**) ion pair, which occur in equilibrium with each other.



X = $OCOCH_3$, $OCOCF_3$, $OCOCCl_3$, $OCOCH_2Cl$

Previously it has been noted[13] that in media with dielectric constants of up to 20, charged species exist mainly as ion pairs. Therefore, in CH_3COOH ($\varepsilon = 6.2$), the probability of dissociation of **7** into free solvated ions can apparently be neglected. The position of the **6** $\rightleftharpoons$ **7** equilibrium depends on the stability of the cationic fragment and nucleophilicity of the anion. Evidently, ion pair **6** is destabilized in the reaction of **1** with $Hg(OCOCCl_3)_2$ and $Hg(OCOCF_3)_2$ by the strong electron-withdrawing groups, $OCOCCl_3$ and $OCOCF_3$, present in the cationic part of the intermediate. This is why it is converted into adducts **4a** and **4b** more rapidly than into solvent-separated ion pair **7** upon the addition of the anionic part of the reagents. The $OCOCH_2Cl$ group in $Hg(OCOCH_2Cl)_2$ is less electronegative; hence, contact ion pair **6** can pass into the solvent-separated ion pair to a noticeable extent. This results in a substantially lower amount of **4c** and the predominant formation of solvoadduct **2**.

The formation of *cis*-solvoadduct **3** in the case where $Hg(OCOCCl_3)_2$ is used is apparently due to the reaction of the cation of contact ion pair **6** with the solvent contained in the solvation shell of the intermediate. In a previous study,[4] this route in the mercuration of alkenes is considered in more detail.

Experimental

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian VXR-400 spectrometer and ^{199}Hg NMR spectra (17.8 MHz) were run on a Jeol FX-100 spectrometer.

Dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-*cis*-*endo*-9,10-dicarboxylate (**1**) was prepared by a known procedure,[14] m.p. 54—56 °C (from C_6H_{14}; *cf.* Ref. 14: m.p. 55 °C).

Mercury trifluoroacetate was synthesized by a previously described procedure,[15] m.p. 167—168 °C (from TFA; *cf.*

Ref. 15: m.p. 167—168 °C); mercury monochloro- and trichloroacetates were synthesized directly from HgO and the corresponding acid in an AcOH solution. To bind the water evolved, the appropriate amount of Ac_2O was added.

TLC isolation of products was performed using silica gel LSL 5/40 and an Et_2O—hexane—AcOEt—$CHCl_3$ mixture (6 : 2 : 1 : 1) as the eluent.

Dimethyl *trans-endo*-4-trichloroacetoxy-3-chloromercuriotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis-endo*-9,10-dicarboxylate (4a) and dimethyl *cis-endo*-4-acetoxy-3-chloromercuriotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis-endo*-9,10-dicarboxylate (3). Freshly prepared yellow HgO (1.8 g, 8 mmol) and Ac_2O (1.0 mL) were added to CCl_3COOH (2.6 g, 16 mmol) in 45 mL of AcOH. The mixture was stirred until the color entirely vanished. Diene **1** (2.0 g, 8.0 mmol) in 45 mL of AcOH was added to the resulting solution of $Hg(OCOCCl_3)_2$. After 16 h, the reaction mixture was poured into 200 mL of a 1% aqueous solution of NaCl. The precipitate was filtered off, washed with water, and dried in air to give 5.1 g of a crystalline product, yield 75%. Preparative TLC yielded 1.8 g of compound **4a**, m.p. 136—137 °C (from AcOEt), IR, v/cm^{-1}: 1762 ($OCOCCl_3$); 0.25 g of compound **2**, m.p. 180—181 °C (from AcOEt; *cf.* Ref. 8: 182 °C); 0.5 g of compound **3** mixed with **2** and **4a** (proportion of impurities <10—15%).

Dimethyl *trans-endo*-4-trifluoroacetoxy-3-chloromercuriotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis-endo*-9,10-dicarboxylate (4b). Diene **1** (1.0 g, 4 mmol) in 10 mL of a solvent was added to $Hg(OCOCF_3)_2$ (1.73 g, 4 mmol) in 15 mL of AcOH. After 6 h, the reaction mixture was treated with brine, extracted with $CHCl_3$, washed with water, and dried with $MgSO_4$. The solvent was evaporated under reduced pressure to give 2.0 g of a product as an oil, yield 73%. Preparative TLC yielded 0.6 g of **4b** as an oil, IR, v/cm^{-1}: 1790 ($OCOCF_3$); 0.1 g **2**, m.p. 181—182 °C (from AcOEt; *cf.* Ref. 8: 182 °C). The reaction mixture also contained a substance whose R_f corresponded to adduct **3** but its amount was too low for isolation.

Dimethyl *trans-endo*-4-monochloroacetoxy-3-chloromercuriotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis-endo*-9,10-dicarboxylate (4c). A mixture of $CH_2ClCOOH$ (1.5 g, 16 mmol), freshly precipitated yellow HgO (1.8 g, 8 mmol), 70 mL of AcOH, and 1.0 mL of Ac_2O was stirred until the HgO completely dissolved. Diene **1** (2.0 g, 8 mmol) in 20 mL of AcOH was added to 40 mL of a solution of $Hg(OCOCH_2Cl)_2$. After 16 h, the reaction mixture was treated with brine. The precipitate was filtered off, washed with water, and dried in air to give 4.4 g of a product in 80% yield. Preparative TLC gave 0.64 g of **4c**, m.p. 168—170 °C (from AcOEt), IR, v/cm^{-1}: 1755 ($OCOCH_2Cl$); 1.41 g of **2**, m.p. 181—181.5 °C (from AcOEt; *cf.* Ref. 8: 182 °C).

Hydrolysis of adduct 4b. Compound **4b** (0.4 g, 6.7 mmol) in 3 mL of MeOH was refluxed for 2 h in the presence of 0.1 g of NaOAc. The usual workup gave 0.35 g of dimethyl *trans-endo*-4-hydroxy-3-chloromercuriotricyclo[4.2.2.$0^{2,5}$]dec-7-ene-*cis-endo*-9,10-dicarboxylate (**5**), m.p. 154—156 °C (from MeOH; *cf.* Ref. 11: 154—156 °C). The melting point of its mixture with adduct **5** prepared by an alternative synthesis[11] showed no depression.

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Received February 17, 1999;
in revised form May 25, 1999