Organometallic Chemistry

Regiochemistry of the addition of mercury salts to bornylene

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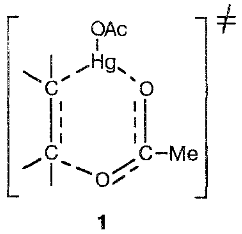
The dependence of the regiochemistry of the mercuration of bornylene on the nature of the mercurating reagent and on the solvent has been found. The structures of the intermediate and transition state in these reactions have been proposed.

Key words: mercuration; regiochemistry; regioisomers; bornylene; intermediate; transition state; reaction mechanism.

Reactions of mercury salts with strained alkenes, especially with those having a bridge-type structure, occur to afford *syn*-adducts, often in parallel with *anti*-addition.[1—4] *Syn*-addition is explained by the fact that mercury salts are able to react with a strained double bond according to a concerted scheme *via* transition states (**1** and **2**).[1,5] It has been assumed[5] that this scheme is valid not only for addition of such reagents as mercury acetate, but also for formation of solvoadducts.

In contrast to these data, evidence has been reported[2] that for strained alkenes the general reaction mechanism involving the three-membered mercurinium ion (**3**) as an intermediate remains valid. In the case of strained systems this intermediate can afford both *anti*- and *syn*-adducts through frontal attack by a nucleophile. The ratio between these adducts depends on the structure of the substrate and the reaction conditions.[2] On the basis of quantum-chemical calculations it has been suggested[6] that the *syn*-addition of mercury salts is associated with the special structure of the mercurinium



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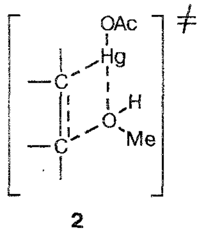

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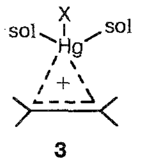

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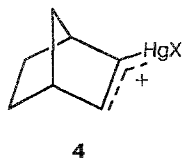

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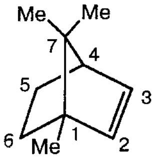
Table 1. The ratio between the products of the reaction of bornylene **5** with mercury acetate in alcohols

Alcohols	(**8a**+**9a**):(**10**+**11**)	**8a**:**9a**	**10**:**11**
MeOH	24:76	42:58	51:49 (R = Me)
EtOH	60:40	39:61	51.5:48.5 (R = Et)
Pr^nOH	90:10	34:66	not determined

intermediate (**4**) rather than with the strained character of the system. When steric restrictions prevent the conversion of intermediate **4** into the *anti*-adduct, for example, in bridged systems, the nucleophile adds to the *syn*-position.

The purpose of the present work has been to gain additional information on the mechanism of mercuration of strained alkenes using the reaction between mercury salts and bornylene (**5**) and its tendency to give reaction products as mixtures of regioisomers as an example.[7,8] $(MeCO_2)_2Hg$, $(EtCO_2)_2Hg$, and $Hg(N_3)_2$ were used as reagents. The latter was prepared from $(MeCO_2)_2Hg$ and NaN_3 in a 1:3 ratio in MeOH (see Ref. 9). $MeCO_2H$, $EtCO_2H$, MeOH, EtOH, Pr^nOH, and Pr^iOH were used as solvents. The products were isolated after treating the reaction mixtures with an aqueous solution of NaCl.

The reaction of compound **5** with $Hg(N_3)_2$ in MeOH affords a mixture of *exo*-*syn*-adducts (**6**, **7**) in the ratio of 3:2 (according to NMR), and the reaction of **5** with $(MeCO_2)_2Hg$ in Pr^iOH and $MeCO_2H$ yields *exo*-*syn*-adducts (**8a** and **9a**) in the ratio of 35:65 (the average value between those obtained by NMR and GLC). Adducts **8b** and **9b** in nearly the same ratio (38:62) are formed in the reaction of **5** with $(EtCO_2)_2Hg$ in $EtCO_2H$. The reaction of **5** with $(MeCO_2)_2Hg$ in alcohols gives a mixture of adducts **8a** and **9a** and solvoadducts (**10**, **11**). The compositions of the mixtures are presented in Table 1.



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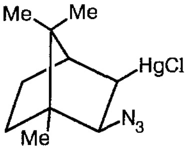

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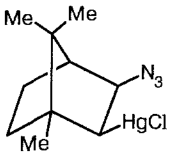

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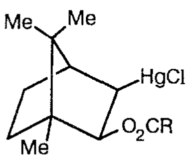
Adducts **6**, **9a**, and **8b** were isolated in the individual state. Their structures, as those of compounds **7**, **8a**, and **9b** in mixtures with their regioisomers, were confirmed by ^1H and ^{13}C NMR spectroscopy. The products formed in the reaction of **5** with mercury acetate in alcohols were identified by GLC after demercuration. The spectroscopic data for compounds **6—9** are given in Tables 2, 3.



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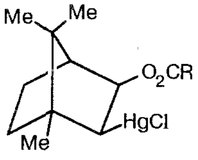

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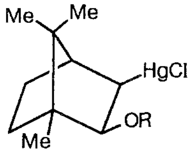

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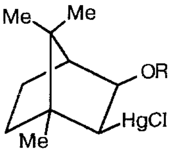
a: R = Me
b: R = Et



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The NMR signals were assigned by a two-dimensional correlation of the ^1H and ^{13}C chemical shifts (see Ref. 10), differential nuclear Overhauser effect (NOE) spectroscopy,[11] and on the basis of the characteristic

Table 2. ^1H NMR spectra of compounds **6—9** ($CDCl_3$)

Compound	δ (J_{HgH}/Hz)								
	H(2)	H(3)	H(4)	H(5)	H(6)	CH_2	CH_3	$CH_3(1)$	$CH_3(7)$
6	3.741 (120.9)	2.767 (208.4)	2.003 (122.0)	1.896 *exo* 1.131 *endo*	1.662 *exo* 1.184 *endo*	—	—	1.075	0.875 *anti* 1.288 *syn*
7	2.916 (221.0)	3.905 (129.0)	2.094	1.805 *exo* 1.084 *endo*	1.660 *exo* 1.176 *endo*			0.952	0.811 *anti* 1.239 *syn*
8a	5.043 (114.9)	2.787 (232.5)	2.105 (134.0)	1.873 *exo* 1.041 *endo*	1.546 *exo* 1.134 *endo*		2.028	0.835	0.835 *anti* 1.29 *syn*
9a	3.009 (229.7)	4.881 (108.4)	2.062	1.783 *exo* 1.183 *endo*	1.790 *exo* 1.204 *endo*		2.043	1.044	0.872 *anti* 1.289 *syn*
8b	5.056 (112.6)	2.784 (227.8)	2.080 *	1.878 *exo* 1.055 *endo*	1.548 *exo* 1.128 *endo*	2.304	1.133	0.829	0.839 *anti* 1.294 *syn*
9b	2.934 (238.7)	4.791 (107.6)	1.995	1.681 *exo* 1.080 *endo*	1.588 *exo* 1.071 *endo*	1.041		0.960	0.775 *anti* 1.202 *syn*

* Not measured.

Table 3. ^{13}C NMR spectra of compounds **6—9** ($CDCl_3$)

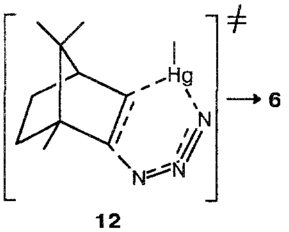
Com- pound	δ (J_{HgC}/Hz)										
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	$CH_3(7)$	$CH_3(1)$	CO	CH_2,CH_3
6	51.88	75.73 (124.8)	57.45 (1586.4)	50.38 (46.6)	30.72 (260.4)	34.56 (14.6)	46.79	21.85 *anti* 20.99 *syn*	11.57 (15.4)		
7	51.20	70.35 (1695.7)	69.63 (123.8)	50.27	25.55	37.65 (239.0)	46.44	20.96 20.63	19.19 (96.0)		
8a	49.75	83.39 (136.3)	60.08 (1664.4)	49.95 (58.0)	30.39 (271.0)	32.66	46.82	21.67 20.85	11.66	169.86	21.75
9a	50.93 (58.0)	69.38 (1630.0)	81.25 (135.3)	51.18	24.02 (17.0)	37.53 (234.7)	46.60		19.44 (97.4)	170.01	21.88
8b	49.88	83.23 (137.0)	60.16 (1643.0)	50.07 (55.0)	30.47 (272.7)	32.72 (10.0)	46.91	21.75	11.72 (20.6)	173.22	9.34;28.44
9b	50.58 (57.7)	68.00 *	80.77 (139.8)	50.99	23.81 (8.0)	37.25 (238.8)	46.21 (13.0)	21.55	19.18 (96.0)	173.11	8.98;28.13

* Not measured.

$^1H—^1H$, $^{199}Hg—^1H$, and $^{199}Hg—^{13}C$ spin-spin coupling constants of bicyclic compounds of the heptane series. The *syn*-orientations of the substituents in compounds **6—9** are confirmed by the values of $^3J_{H(2)—H(3)}$ (8.0—8.5 Hz) typical of bicyclic compounds of this kind.[12,13] This is also supported by the values of the vicinal $^3J_{Hg—H(2)}$ constants (compounds **6**, **8a**, and **8b**) and $^3J_{Hg—H(3)}$ constants (compounds **7**, **9a**, **9b**), which amount to 108—129 Hz. These $^3J_{HgH}$ values correspond to a *gauche*-orientation of the interacting nuclei in bicyclooctanes,[14] while in the case of the *syn*-interaction $^3J_{HgH}$ is higher than 250 Hz. The $^2J_{Hg—C}$ constants in the Hg—C—C—X fragment are known to be strongly dependent on the orientation of the electronegative substituent.[15] The high absolute values of $^2J_{Hg—C}$ in compounds **6—9** (124—140 Hz) close to those in bicyclooctane derivatives[14] correspond to the *syn*-orientation of the HgCl and X groups (X = N_3, OCOR, OR). The *exo*-orientation of the HgCl and X groups is also determined unambiguously. $^3J_{H(4)—endo\text{-}H(5)}$ are close to zero, while $^3J_{H(4)—exo\text{-}H(5)}$ = 3.9—4.4 Hz, which is characteristic of compounds of this sort.[12,13] Second, the $^3J_{Hg—C(5)}$ constants in compounds **6**, **8a**, and **8b** and $^3J_{Hg—C(6)}$ in **7**, **9a**, and **9b** are high (260—273 and 235—239 Hz), in accordance with the Carplus dependence on Hg—C—C—C dihedral angles, while $^3J_{Hg—C(7)}$ are low and are comparable to line widths. Finally, a pronounced positive NOE is observed for the Me-group protons of the bridges, which are in the *anti*-position with respect to the substituents upon saturation of the transitions of the *exo*-H(5) and *exo*-H(6) protons. At the same time, NOE for the *syn*-Me groups of the bridges is not observed upon excitation of transitions of the H(2) and H(3) protons, but occurs for the *endo*-H(5) and *endo*-H(6) protons, which attests to the *endo*-orientation of the former.

The regiochemistry of the addition with respect to the Me group at C(1) can be readily determined from the J_{HgC} constants. The $^3J_{HgC}$ value (96—97 Hz) for the carbon atom of this group in compounds **7**, **9a**, and **9b** is normal for a vicinal constant, and the $^4J_{HgC}$ long-range constant for the methyl group in compounds **6**, **8a**, and **8b** is 15—21 Hz. The substantial difference between $^3J_{Hg—C(4)}$ or $^3J_{Hg—C(1)}$, which are close to zero, and $^2J_{Hg—C(1)}$ (58 Hz) or $^2J_{Hg—C(4)}$ (47—58 Hz) is specific. The regiochemistry is indicated as well by the results of NOE which provide information on the dipole-dipole interaction of the H(2) protons with the Me(1) group and make it possible to assign the signals for H(2) and H(3). The position of the HgCl group may be inferred from the typical values of the $^2J_{HgH}$ and $^1J_{HgC}$ constants and ^1H and ^{13}C chemical shifts (see Tables 2, 3).

As the data obtained indicate, the regiochemistry of the mercuration of bornylene **5** can be substantially different depending on the nature of the reagent and properties of the medium. It is significant that the ratios between the regioisomeric adducts formed in the reaction of **5** with mercury azide and those formed in the reaction with mercury acetate are inverse. In our opinion, this is due to the fact that these reactions occur according to different mechanisms. Regiochemical data suggest that mercury azide adds to compound **5** by a concerted scheme *via* transition states (**12**, **13**). Transition state **12** is preferred due to less steric hindrances.



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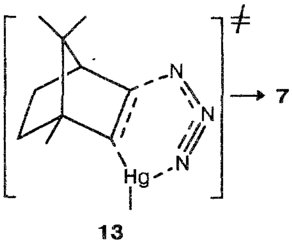

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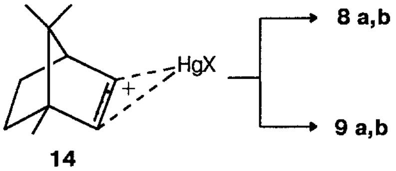
Compared with other salts, mercury azide possesses a pronounced ability to undergo *syn*-addition in reactions with strained alkenes. This stereochemistry has been observed for bicycloheptene systems[16] and framework compounds containing a cyclobutene moiety.[3,17] Mercury azide reacts to give predominantly the *syn*-adduct even with cyclobutene,[18] however, with cyclohexene the normal *anti*-adduct is formed.[3] The reaction of mercury azide with cyclopropenes is *syn*-stereoselective.[4,19] Other salts, specifically mercury acetate, react with cyclopropenes to give mixtures of stereoisomers.[4,19] These data imply that concerted addition is the general mechanism for the reaction of mercury azide with strained alkenes, which is apparently due to its high nucleophilicity.

In the reaction of compound **5** with mercury acetate in alcohols or acetic acid, other regiochemical regularities have been observed. This allows one to assume that reactions with mercury acetate and propionate involve the formation of the mercurinium intermediate (**14**), which may be converted into products **8a**, **8b**, **9a**, and **9b** as a result of frontal attack by a nucleophile. It is this mechanism that provides the predominant formation of regioisomers **9a** and **9b**, since for the nucleophilic attack at position 3 the steric factor is less important.



14

The regiochemistry observed in the mercuration of **5** in acetic acid and alcohols does not agree with the assumption[6] that the reaction occurs *via* intermediate **4**. In that case the methyl group at the head of the bridge would have exerted a stabilizing action on the intermediate and, therefore, regioisomer **8a,b** would have predominantly formed.

As the data obtained indicate, when the reaction is carried out in alcohols, the ratio between adducts **8a** and **9a** is nearly the same as in acetic acid. Obviously, in alcohols compound **14** also forms as an intermediate. Solvoadducts are likely to be formed in a similar way too. Thus, on the basis of the investigations carried out, one may conclude that mercuration of strained alkenes occurs according to a stepwise mechanism involving a cyclic mercurinium intermediate. On the other hand, those mercury salts in which the ligand is a strong nucleophile most likely react with strained systems according to a concerted mechanism.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrophotometer ($CDCl_3$). Chemical shifts are given in the δ scale and referred to TMS (internal standard). GLC analysis was carried out on a Chrom-5 instrument (10 % Carbowax) on Chromaton N-AW-DMCS (0.2-0.25), a 3.7 m column, the temperature was programmed from 130 to 170 °C, nitrogen was used as the carrier gas. TLC was carried out on LSL 5/40 μ silica gel.

Mercuration of bornylene 5. General procedure. A mercury salt (14.7 mmol) in 75 mL of a solvent was added to compound **5** (14.7 mmol) in 75 mL of a solvent. After completion of the reaction the mixture was poured into a 1 % aqueous solution of NaCl (300 mL) and extracted with $CHCl_3$; the extract was washed with H_2O until it became neutral and dried with $MgSO_4$, and the solvent was evaporated under reduced pressure.

The composition of the reaction mixture was determined after demercuration[20] by GLC using authentic samples prepared by the previously described procedures.[21]

2-Chloromercuro-1,7,7-trimethylbicyclo[2.2.1]hept-3-yl acetate (9a) was prepared from **5** (2 g, 14.7 mmol) and $(MeCO_2)_2Hg$ (4.7 g, 14.7 mmol) in $MeCO_2H$ and isolated by TLC as a viscous oil (a 11:5:2:2 C_6H_{14}—C_6H_6—EtAc—$CHCl_3$ mixture was used as the eluent).

3-Chloromercuro-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl propionate (8b). The reaction mixture prepared from **5** (1g, 7.35 mmol) and $(EtCO_2)_2Hg$ (2.8 g, 7.35 mmol) in $EtCO_2H$ was dissolved in a 9:1 C_6H_{14}—$CHCl_3$ mixture (30 mL). Cooling to −5 °C afforded 1.0 g of crystals of **8b**. M.p. 141—143 °C after the second crystallization.

2-Azido-3-chloromercuro-1,7,7-trimethylbicyclo[2.2.1]heptane (6). Compound **5** (0.20 g, 1.45 mmol) in 7 mL of MeOH was quickly added to a mixture of $(MeCO_2)_2Hg$ (0.46 g, 1.44 mmol) and NaN_3 (0.28 g, 4.3 mmol) in 10 mL of MeOH (conducting the reaction at concentrations above 0.1 *M* may lead to an explosion). After 2 h the reaction mixture was treated according to the general procedure. The resulting viscous oil was dissolved in 10 mL of MeOH. Cooling afforded 0.20 g of compound **6**, m.p. 131—132 °C.

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