Organometallic Chemistry

Salt effects and the mechanism of electrophilic mercuration of unsaturated compounds

3.* The reaction of mercury acetate with bornylene in the presence of sodium acetate in water-organic media

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The reaction of $Hg(OAc)_2$ with bornylene in THF—H_2O and CH_3CN—H_2O mixed solvents (75 : 25, v/v) was studied. The effects of the addition of NaOAc on the reaction rate and the composition of products were investigated. In the CH_3CN—H_2O mixture, the addition of NaOAc decreases the amount of the rearranged product, fundamentally changes the ratio between the regioisomeric solvoadducts, and promotes the formation of products of $Hg(OAc)_2$ addition. The reaction proceeds *via* an ion pair and free mercurinium ion; the cation of the ion pair and the free mercurinium ion have dissimilar structures.

Key words: mercury acetate, bornylene, ion pair, mercurinium ion, solvomercuration, salt effect, regioisomers, reaction mechanism.

In our recent works[2,3] we have shown that in the solvomercuration of unstrained alkenes by mercury acetate in methanol, the Hg^+OAc ion formed upon dissociation of $Hg(OAc)_2$ acts as a reagent. Strained alkenes are less selective in the reactions with mercury-containing electrophiles, therefore, in this case, the reaction involves mostly $Hg(OAc)_2$ due to the low concentration of Hg^+OAc. This conclusion is confirmed by the essentially dissimilar dependence of the reciprocal of the second-order rate constant on the NaOAc concentration. For unstrained alkenes, this dependence is linear at low concentrations of NaOAc. In the reactions of strained alkenes, the linear part of the dependence is missing, and the kinetic data can be adequately interpreted assuming that $Hg(OAc)_2$ is the reagent.

Decreasing the dissociating and solvating properties of the medium changes the character of the effect of a salt additive on the kinetics of the reactions involving unstrained alkenes and brings it closer to the kinetic regularities established for strained alkenes. The inverse suggestion is also obvious: *i.e.*, increasing the dissociating and solvating properties of the medium may result in

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* For the previous communication and Parts 1—2, see Refs 1—3.

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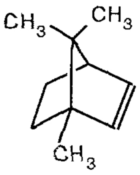
reactions with strained alkenes in which the Hg^+OAc ion also acts as the electrophilic agent. On this basis, in the present work we studied the effect of the addition of NaOAc on the kinetics and distribution of products of the reaction of bornylene (**1**) with $Hg(OAc)_2$ in water-organic media, $THF—H_2O$ and $CH_3CN—H_2O$ in a 75 : 25 v/v ratio.

Solvomercuration of **1** in various solvents has been studied previously. It was found[4] that in a $THF—H_2O$ (50 : 50) solvent mixture, the reaction yields regioisomeric alcohols **2a** and **3a** and the rearranged alcohol **4** (~6 %).

The reaction mixture also contains small amounts of acetates **2b** and **3b**.



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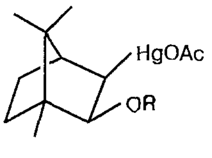

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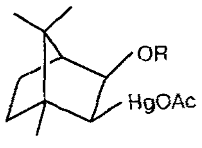

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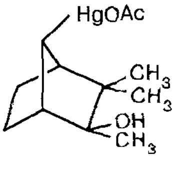


4

R = H(**a**), Ac(**b**)

Increasing the polar properties of the medium (acetone—H_2O, $CH_3CN—H_2O$) resulted in a substantial increase in the amount of **4**.[5] The use of a wide range of solvents and mercury salts showed that the bridgehead methyl group in compound **1**, contrary to the previously stated opinion,[4] possesses a clear-cut orienting action.[5,6] The structural features of bornylene **1** that determine the formation of regioisomers **2a,b** and **3a,b** and the possibility of the rearrangement could provide additional data on the role of NaOAc in solvomercuration.

Experimental

The rate of the reaction was determined as described previously.[2] Since $Hg(OAc)_2$ is hydrolyzed in water-organic media, the reaction was carried out with the addition of $7.5 \cdot 10^{-3}$ mol L^{-1} of AcOH.

When the reaction was carried out in the presence of NaOAc, acetates **2b** and **3b** were formed in addition to compounds **2a**, **3a**, and **4**. The method for identification of these acetates was described previously.[6] The ratios between the products were determined by GLC after reductive demercuration.[4]

GLC analysis was carried out on a Khrom-5 instrument using Carbowax (10%) on Chromaton N-AW-DMCS (0.2—0.25 mm) as the stationary phase and a 3.7 m column 3 mm in diameter. The temperature in the evaporating chamber on analyses of the products formed in a $THF—H_2O$ mixture was 190 °C, that for a $CH_3CN—H_2O$ mixture was 210 °C, the temperature of the column was 130 °C or 150 °C, respectively. Nitrogen was used as the carrier gas.

The general procedure for conducting the reaction of bornylene **1** with $Hg(OAc)_2$ was described in Ref. 6.

We did not manage to completely separate the reaction mixture by GLC. The products of the reduction of **3b** and **4** had identical retention times. To determine the amounts of **3b** and **4** the reaction mixture was reduced in two ways: with $NaBH_4$ and with sodium amalgam.[4] In the latter case, the reduction yields only alcohols, and the amount of **4** can be unambiguously determined. The proportion of **3b** was found from the analyses of the reaction mixtures reduced by the two methods.

The kinetic studies were carried out at the following concentrations of the reactants: $Hg(OAc)_2$ 0.01 mol L^{-1}, bornylene 0.01—0.02 mol L^{-1}, NaOAc 0.001—0.1 mol L^{-1} or $(2.5—6.25) \cdot 10^{-4}$ mol L^{-1}.

Results and Discussion

In water-organic media, as well as in CH_3OH,[2] the reaction is described by second-order kinetics. Analogous regularities hold when the reaction is carried out with the addition of NaOAc (Table 1). The introduction of NaOAc results not only in the deceleration of the reaction, but also in a substantial change in the composition of the products (Table 2). In fact, when the reaction is carried out in a $THF—H_2O$ mixture at a NaOAc concentration of $1.0 \cdot 10^{-3}$ mol L^{-1} the formation of solvoadducts is essentially suppressed, and compounds **2b** and **3b** are formed as the main products (up to ~64 %). A similar effect, though less pronounced, is observed when the reaction is carried out in a $CH_3CN—H_2O$ mixture (the proportion of **2b** and **3b** at the same concentration of NaOAc is 25 %).

Two peculiarities of the effect of NaOAc on the distribution of products in the latter reaction should be emphasized. First, in the presence of NaOAc, the amount

Table 1. Rate constants of the reaction of $Hg(OAc)_2$ with bornylene **1** in water-organic media

Solvent	NaOAc / mol L^{-1}	k / L mol^{-1} s^{-1}
$CH_3CN—H_2O$	—	$(3.64\pm0.15) \cdot 10^{-2}$
	$2.5 \cdot 10^{-4}$	$(2.03\pm0.10) \cdot 10^{-2}$
	$6.25 \cdot 10^{-4}$	$(1.21\pm0.07) \cdot 10^{-2}$
	$1.0 \cdot 10^{-3}$	$(9.52\pm0.50) \cdot 10^{-3}$
	$1.5 \cdot 10^{-3}$	$(7.27\pm0.26) \cdot 10^{-3}$
	$2.0 \cdot 10^{-3}$	$(6.53\pm0.24) \cdot 10^{-3}$
	$5.0 \cdot 10^{-3}$	$(5.35\pm0.35) \cdot 10^{-3}$
	$1.0 \cdot 10^{-2}$	$(4.05\pm0.12) \cdot 10^{-3}$
	$1.5 \cdot 10^{-2}$	$(3.35\pm0.10) \cdot 10^{-3}$
$THF—H_2O$	—	$(6.92\pm0.35) \cdot 10^{-4}$

Table 2. The effect of NaOAc on the composition of the products of the reaction of $Hg(OAc)_2$ with bornylene **1** in water-organic media

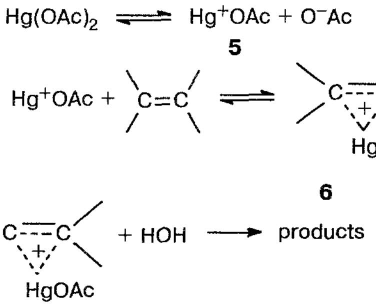
Solvent	NaOAc mol L^{-1}	(**2a**+**3a**):**4**:(**2b**+**3b**) (mol. %)	**2a**:**3a** (mol.%)	**2b**:**3b** (mol.%)
$CH_3CN—H_2O$	—	83:17[a]	61:39	
	0.001	65:10:25[b]	55:45	65:35
	0.005	50:7:43[b]	48:52	59:41
	0.01	47:5:48[b]	41:59	56:44
	0.015	43:7:50[b]	37:63	57:43
	0.1	39:4:57[b]	33:67	55:45
$THF—H_2O$	—	88:6:6	48:62	
	0.001	36:64[c]	46:54	71:29
	0.005	31:69[c]	45:55	70:30
	0.01	29:71[c]	42:58	68:32

[a] From the results of the reduction with $NaBH_4$. [b] From the results of the reduction with $NaBH_4$ and with sodium amalgam. [c] The amount of alcohol **4** was not determined.

of the rearranged alcohol **4** decreases. A similar effect was observed in Ref. 4. Second, the addition of the salt results in an inversion of the regioselectivity of solvomercuration. Without NaOAc solvoadduct **2a** is formed predominantly, while at a concentration of NaOAc of 0.01—0.015 mol L^{-1}, isomer **3a** with the opposite regiochemistry prevails. The ratio between the acetates **2b** and **3b**, whose formation is promoted by NaOAc, depends insignificantly on the salt concentration (Table 2).

The nature of the decelerating effect of NaOAc in the reaction under study was analyzed as described in the previous communications.[2,3] Figure 1 indicates that the dependence of the reciprocal of the rate constant of the reaction on the concentration of NaOAc in a $CH_3CN—H_2O$ mixture is substantially different from that observed in methanol. In general, it is similar to the dependence observed in the reactions of $Hg(OAc)_2$ with unstrained alkenes.[3] On this basis one may assume that the Hg^+OAc ion resulting from dissociation of $Hg(OAc)_2$ is the main reactant in the $CH_3CN—H_2O$ mixed solvent (Scheme 1).

Scheme 1



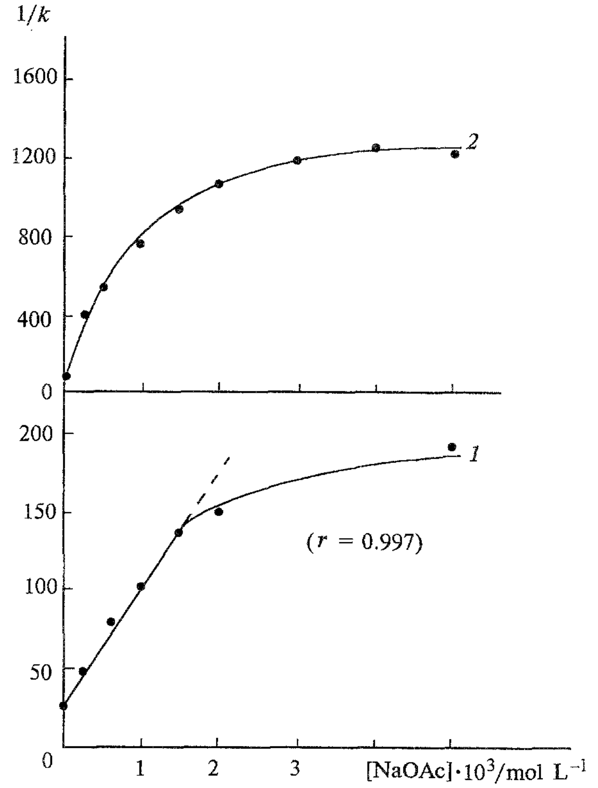
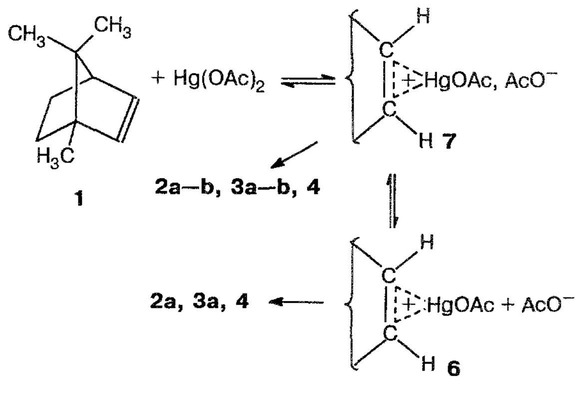


Fig. 1. The dependence of $1/k$ on the NaOAc concentration in the reaction of $Hg(OAc)_2$ with bornylene **1** in a $CH_3CN—H_2O$ mixture (the correlation coefficient for the linear section is given in parentheses) (*1*); in CH_3OH (the data were taken from Ref. 2) (*2*).

This assumption is also confirmed by the fact that when the process is carried out in $CH_3CN—H_2O$ without NaOAc, the reaction mixture contains no acetates **2b** and **3b**.

The addition of the salt significantly suppresses the reaction in which Hg^+OAc acts as the electrophile. The reaction involving $Hg(OAc)_2$ as the reactant proceeds in parallel, obviously, according to Scheme 2, which was considered previously.[3]

Scheme 2

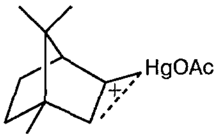


Thus, in the general case, deceleration of the reaction in the presence of NaOAc is determined by the decrease in the degree of $Hg(OAc)_2$ dissociation and the common ion effect.

When the concentration of the salt is ~0.010—0.015 mol L^{-1}, the retarding effect of NaOAc reaches its maximum value (Table 1). In this region of NaOAc concentrations the ratio between the solvoadducts becomes constant, and it may be assumed that the products are formed from ion pair **7**.

It is likely that the reaction in other mixed solvents also occurs according to the above-considered schemes. The rate of the reaction in a $THF-H_2O$ mixture is substantially lower due to the lower polarity of the solvent. For the same reason, the degree of $Hg(OAc)_2$ dissociation should also decrease. Therefore, even small amounts of salt added can suppress the reaction involving $Hg^{+}OAc$. The reaction of $Hg(OAc)_2$ with **1** occurs predominantly according to Scheme 2. Owing to the weakly polar properties of the medium, the conversion of ion pair **7** into free ion **6** probably occurs to only a small extent, and the products are mostly formed from this intermediate. In this case, one should expect that adducts **2b** and **3b** would prevail and that the ratio between solvoadducts **2a** and **3a** would vary insignificantly with the variation of NaOAc concentration, which is the case.

It has been discussed above that in CH_3CN-H_2O, the reaction occurs *via* free mercurinium ion **6** in the absence of NaOAc or *via* ion pair **7** at limiting concentrations of the salt. As follows from the data of Table 2, under these conditions, the compositions of the products and the regioselectivities of the reactions are essentially different. A comparison suggests that free ion **6** and the mercurinium cation of ion pair **7** have dissimilar structures. The substantial amount of the rearranged product **4** and the predominant formation of solvoadduct **2a** give evidence that mercurinium ion **6** has an asymmetrical structure (**8**).



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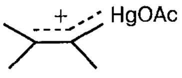

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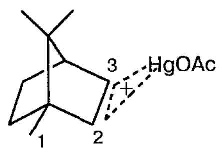

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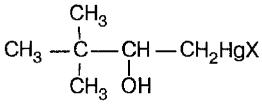
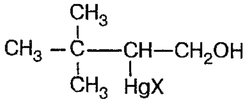
This assumption is in agreement with the results of quantum-chemical calculations, on the basis of which an asymmetrical structure (**9**) was assigned to ion **6**.[7] The formation of the mercurinium ion with structure **8** or **9** is also confirmed by the high regioselectivity of the solvomercuration of alkenes with terminal double bonds.[8] Even in the case of *tert*-butylethylene as the alkene, the ratio between regioisomers **11** and **12** is 97 : 3.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_2HgX$

11



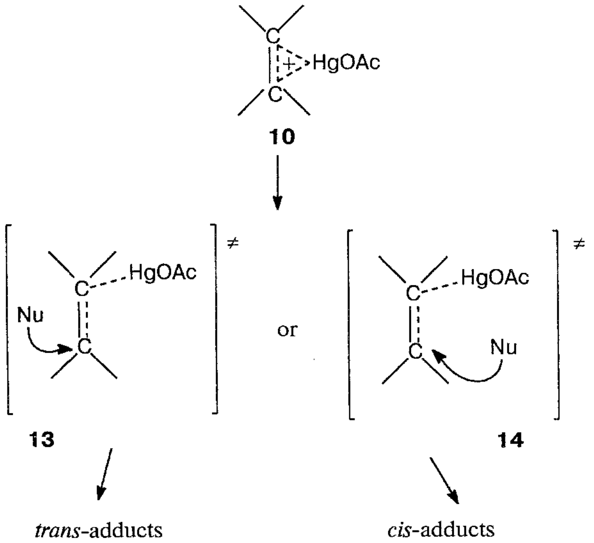
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{HgX}{CH}-CH_2OH$

12

If the ion had a symmetrical structure (**10**), an inverse ratio would have been expected, in analogy with the data on other Ad_E reactions.

Under conditions where the reaction occurs *via* the formation of ion pair **7**, solvoadduct **3a** is formed as the major product and the Wagner—Meerwein rearrangement is considerably suppressed. Therefore, one may assume that in the presence of a counter-ion, the mercurinium cation of ion pair **7** has a more symmetrical structure than the free ion. With this structure of the intermediate, the steric obstacles to the approach of the nucleophile created by the 1-methyl group, would favor the addition of the nucleophile to the less sterically hindered C(3) atom.

The stepwise mechanism of the solvomercuration of strained alkylenes leads to the inference that, unlike other cyclic species formed in electrophilic reactions, the mercurinium cation can be converted into both *trans*- and *cis*-adducts. Although for the asymmetrical cation structure **8** this transformation seems quite plausible, in the case of the symmetrical structure **10** this feature is rather unusual. What are possible causes for this reactivity of the symmetrical mercurinium ion? In our opinion, it is caused by the asymmetrical structure of transition states **13** or **14**.



With this structure of the transition state, ion **10** can be converted into products *via* attack by a nucleophile from both the back and the front.

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