Organometallic Chemistry

Salt effects and the mechanism of electrophilic mercuration of unsaturated compounds

2.* Salt effects and the nature of the electrophilic reagent in the solvomercuration of alkenes

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The kinetics of the addition of $Hg(OAc)_2$ to strained and unstrained alkenes was studied in MeOH solution in the presence of NaOAc. Based on salt effects, the HgOAc ion was shown to be the actual reagent in the reaction of the unstrained alkenes, whereas $Hg(OAc)_2$ was the reagent in the case of the strained alkenes. The mechanisms of the solvomercuration of alkenes of various structures were proposed.

Key words: solvomercuration, mechanism of reaction, mercury acetate, salt effect, alkenes, kinetics.

There are many reports on the stereo- and regiochemistry of the solvomercuration of alkenes,[1–4] the kinetics of this reaction,[4–6] and the use of the latter for preparative purposes.[3,7] Although this reaction is rather typical of Ad_E type reactions, some specific features are observed. First, it should be noted that the stereochemistry of the reaction is especially sensitive to the structure of the substrate.[1–4] In the case of the unstrained alkenes, this reaction is *trans*-stereoselective,[3] while the reaction with the bridged and some monocyclic systems containing a strained double bond proceeds mainly by a *cis*-scheme and is often accompanied by a parallel *trans*-addition.[1–4] In the reactions of mercury salts with cyclopropene derivatives, the stereochemistry can change from *trans*- to *cis*-stereoselective addition depending on the conditions of the process and on the structure of the cyclopropene system.[4]

The other specific feature of the mercuration is the fact that the electrophilic addition of mercury salts occurs as conjugated solvomercuration in low alcohols and mixed aqueous-organic solvents.[8] Only in the case of some bridged strained alkenes, are the products of solvomercuration accompanied by moderate amounts of the products of the addition of the reagent.[5] The reasons for these specific features are not yet clear. Some authors consider[1] the *cis*-products to be formed according

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* For the previous report see *Izv. Akad. Nauk, Ser. Khim.*, 1994, 819 [*Russ. Chem. Bull.*, 1994, **43**, 760 (Engl. Transl.)].

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 344—352, February, 1995.

to a concerted scheme. However, in another work[9] it is suggested that the reaction with the strained alkenes involves a mercurinium intermediate. For these systems, the mercurinium intermediate is capable of being converted not only to the *trans*-, but also to the *cis*-adducts as a result of a frontal attack by the counterion. Quantum-chemical calculations lead to the conclusion that the *cis*-addition of mercury salts is caused by specific structures of the substrate and the mercurinium intermediate.[10]

It is not yet clear what the nature of the electrophilic reagent is. Many researchers believe that the reagent is the HgX^+ ion that results from the dissociation of the salt.[11] Other authors[12] consider the HgX_2 salt as the electrophilic reagent. Analogous conclusions were also obtained by interpreting the kinetic data for the solvomercuration of alkenes.[6] In Ref. 13, it is proposed that the ion pair $HgOAc^+$, OAc^- is the reagent in the reactions of styrenes with mercury acetate in methanol.

Thus, although there are a great number of works that deal with investigations of the mechanism of the reaction of mercury salts with unsaturated compounds, even the principal regularities are still open to discussion. In our opinion, the main reason for this uncertainty is the absence of any facts that could unequivocally confirm or rule out one or another proposition.

We consider salt effects[5,14,15] to be a useful instrument for investigating the mechanism of the electrophilic mercuration of alkenes. In the previous work,[5] we studied the reaction of bornylene (**1**) with $Hg(OAc)_2$ in various solvents with small NaOAc additives. The data obtained indicated that the reagent is mainly the $Hg(OAc)_2$ salt. The reaction proceeds via an ion-pair mechanism involving the participation of a free mercurinium ion. In view of this conclusion, the proposition that *cis*-adducts are formed by a synchronous mechanism can be safely excluded.

$CH_2{=}CH{-}CH_2X$

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X=Me (**a**), OCOMe (**b**), Br (**c**)

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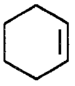

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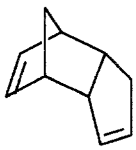

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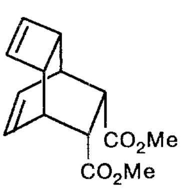

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The present work is a continuation of our investigations of the effect of NaOAc additives on the solvomercuration of unsaturated compounds (**2a—c**)—(**7**) that have either normal or strained double bonds.

Methanol and a methanol-isopropanol mixture were used as solvents.

Experimental

The ratios between the products of the reactions of $Hg(OAc)_2$ with compounds **5**—**7** were determined by GLC after their reduction as described earlier,[5] using calibration plots.

The kinetic studies were performed using a known procedure.[5] The purity of the reagents and solvents was 99.0—99.8 %.

Starting concentrations (mol L^{-1}) of the reagents for the reaction in methanol were the following: in the reaction with **2a**: $[Hg(OAc)_2]$ $5.0 \cdot 10^{-4}$; [**2a**] $5.0 \cdot 10^{-3}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction with **2b**: $[Hg(OAc)_2]$ $5.0 \cdot 10^{-4}—1.0 \cdot 10^{-3}$; [**2b**] $5.75 \cdot 10^{-3}—1.0 \cdot 10^{-2}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction with **2c**: $[Hg(OAc)_2]$ $1.0 \cdot 10^{-2}$; [**2c**] $5.0 \cdot 10^{-2}$, [NaOAc] $(1.5—5.0) \cdot 10^{-3}$; $[Hg(OAc)_2]$ $1.0 \cdot 10^{-3}$, [**2c**] $(1.0—7.4) \cdot 10^{-2}$, [NaOAc] $0—6.25 \cdot 10^{-4}$. In the reaction with compound **3**: $[Hg(OAc)_2]$ $5.0 \cdot 10^{-4}$, [**3**] $5.0 \cdot 10^{-3}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction with compound **4**: $[Hg(OAc)_2]$ $5.0 \cdot 10^{-4}$, [**4**] $5.0 \cdot 10^{-3}$, [NaOAc] $0—1.25 \cdot 10^{-3}$; $[Hg(OAc)_2]$ $2.0 \cdot 10^{-4}—2.0 \cdot 10^{-3}$, [**4**] $(2.0—6.0) \cdot 10^{-3}$, [NaOAc] $2.0 \cdot 10^{-3}—1.5 \cdot 10^{-2}$. In the reaction with compound **5**: $[Hg(OAc)_2]$ $5.0 \cdot 10^{-4}$, [**5**] $(2.0—5.0) \cdot 10^{-3}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction with compound **6**: $[Hg(OAc)_2]$ $1.0 \cdot 10^{-3}$, [**6**] $2.5 \cdot 10^{-2}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction with compound **7**: $[Hg(OAc)_2]$ $1.0 \cdot 10^{-3}$, [**7**] $(2.5—6.0) \cdot 10^{-3}$, [NaOAc] $0—5.0 \cdot 10^{-3}$. In the reaction of compound **4** in a MeOH—i-C_3H_7OH mixture: $[Hg(OAc)_2]$ $1.0 \cdot 10^{-3}$, [**4**] $(1.0—6.0) \cdot 10^{-2}$, [NaOAc] $0—2.0 \cdot 10^{-3}$.

Results and Discussion

The reaction of $Hg(OAc)_2$ with compounds **2**—**7** in methanol and in a methanol-isopropanol mixture is described by second-order Eq. (1) (first-order with respect to each reagent).

$$-\mathrm{d}\frac{[Hg(OAc)_2]}{\mathrm{d}t} = k\,[Hg(OAc)_2]\left[\gt C{=}C\lt\right] \qquad (1)$$

Kinetic Eq. (1) was found by an integration method. It is also valid in the case of the NaOAc additives. The general order of the reaction with compound **2c** was also determined by a differential method (n = 2±0.1). The log k value found by this method was −3.79, whereas $\log k_{exp} = -3.72$.

For all of the reactions investigated, a dramatic decrease in the reaction rates is observed in the presence of NaOAc, especially at low concentrations (Table 1). Thus, when the concentration of the salt additive is $6.25 \cdot 10^{-4}$ mol L, the rate constant of the reaction with compound **2c** is 66 times lower, and for the other

Table 1. Rate constants of the solvomercuration of alkenes **2a—c —7**

Alkene, solvent	NaOAc /mol L^{-1}	k/L (mol s)$^{-1}$	k_{diss} /L (mol s)$^{-1}$
2a, MeOH	—	$(9.25 \pm 0.35) \cdot 10^{-1}$	
	$5.0 \cdot 10^{-5}$	$(3.76 \pm 0.15) \cdot 10^{-1}$	
	$2.5 \cdot 10^{-4}$	$(1.43 \pm 0.06) \cdot 10^{-1}$	
	$5.0 \cdot 10^{-4}$	$(8.86 \pm 0.30) \cdot 10^{-2}$	
	$6.25 \cdot 10^{-4}$	$(6.93 \pm 0.30) \cdot 10^{-2}$	
	$1.25 \cdot 10^{-3}$	$(4.20 \pm 0.17) \cdot 10^{-2}$	
	$3.0 \cdot 10^{-3}$	$(2.21 \pm 0.10) \cdot 10^{-2}$	
	$5.0 \cdot 10^{-3}$	$(1.85 \pm 0.07) \cdot 10^{-2}$	
2b, MeOH	—	$(2.40 \pm 0.12) \cdot 10^{-1}$	
	$5.0 \cdot 10^{-5}$	$(1.29 \pm 0.06) \cdot 10^{-1}$	
	$2.5 \cdot 10^{-4}$	$(5.25 \pm 0.17) \cdot 10^{-2}$	
	$6.25 \cdot 10^{-4}$	$(2.44 \pm 0.10) \cdot 10^{-2}$	
	$1.25 \cdot 10^{-3}$	$(1.26 \pm 0.04) \cdot 10^{-2}$	
	$2.0 \cdot 10^{-3}$	$(8.58 \pm 0.35) \cdot 10^{-3}$	
	$3.5 \cdot 10^{-3}$	$(6.95 \pm 0.21) \cdot 10^{-3}$	
	$5.0 \cdot 10^{-3}$	$(5.96 \pm 0.18) \cdot 10^{-3}$	
2c, MeOH	—	$(2.43 \pm 0.06) \cdot 10^{-2}$	
	$5.0 \cdot 10^{-5}$	$(3.31 \pm 0.12) \cdot 10^{-3}$	
	$1.0 \cdot 10^{-4}$	$(2.00 \pm 0.08) \cdot 10^{-3}$	
	$2.5 \cdot 10^{-4}$	$(9.48 \pm 0.36) \cdot 10^{-4}$	
	$5.0 \cdot 10^{-4}$	$(5.06 \pm 0.15) \cdot 10^{-4}$	
	$6.25 \cdot 10^{-4}$	$(3.85 \pm 0.16) \cdot 10^{-4}$	
	$1.5 \cdot 10^{-3}$	$(1.60 \pm 0.07) \cdot 10^{-4}$	
	$3.0 \cdot 10^{-3}$	$(1.16 \pm 0.04) \cdot 10^{-4}$	
	$5.0 \cdot 10^{-3}$	$(0.97 \pm 0.06) \cdot 10^{-4}$	
3, MeOH	—	$(4.11 \pm 0.21) \cdot 10^{-1}$	
	$5.0 \cdot 10^{-5}$	$(1.78 \pm 0.07) \cdot 10^{-1}$	
	$2.5 \cdot 10^{-4}$	$(6.78 \pm 0.32) \cdot 10^{-2}$	
	$3.75 \cdot 10^{-4}$	$(4.15 \pm 0.15) \cdot 10^{-2}$	
	$6.25 \cdot 10^{-4}$	$(2.72 \pm 0.12) \cdot 10^{-2}$	
	$1.25 \cdot 10^{-3}$	$(1.47 \pm 0.08) \cdot 10^{-2}$	
	$2.0 \cdot 10^{-3}$	$(9.25 \pm 0.35) \cdot 10^{-3}$	
	$3.5 \cdot 10^{-3}$	$(7.14 \pm 0.30) \cdot 10^{-3}$	
	$5.0 \cdot 10^{-3}$	$(6.16 \pm 0.35) \cdot 10^{-3}$	
4, MeOH	—	1.23 ± 0.07	
	$5.0 \cdot 10^{-5}$	$(4.86 \pm 0.20) \cdot 10^{-1}$	
	$2.5 \cdot 10^{-4}$	$(1.55 \pm 0.07) \cdot 10^{-1}$	
	$6.25 \cdot 10^{-4}$	$(8.81 \pm 0.34) \cdot 10^{-2}$	
	$1.25 \cdot 10^{-3}$	$(4.65 \pm 0.15) \cdot 10^{-2}$	
	$2.0 \cdot 10^{-3}$	$(2.74 \pm 0.22) \cdot 10^{-2}$	
	$5.5 \cdot 10^{-3}$	$(2.10 \pm 0.05) \cdot 10^{-2}$	
4, MeOH : i-C_3H_7OH (50 : 50, vol. %)	—	$(7.52 \pm 0.30) \cdot 10^{-2}$	
	$5.0 \cdot 10^{-5}$	$(3.58 \pm 0.15) \cdot 10^{-2}$	
	$2.5 \cdot 10^{-4}$	$(1.50 \pm 0.06) \cdot 10^{-2}$	
	$6.25 \cdot 10^{-4}$	$(9.44 \pm 0.40) \cdot 10^{-3}$	
	$1.5 \cdot 10^{-3}$	$(6.81 \pm 0.31) \cdot 10^{-3}$	
	$2.0 \cdot 10^{-3}$	$(6.18 \pm 0.21) \cdot 10^{-3}$	
	$3.0 \cdot 10^{-3}$	$(5.56 \pm 0.28) \cdot 10^{-3}$	
	$5.0 \cdot 10^{-3}$	$(5.16 \pm 0.22) \cdot 10^{-3}$	
4, MeOH : i-C_3H_7OH (20 : 80, vol. %)	—	$(1.87 \pm 0.06) \cdot 10^{-2}$	
	$5.0 \cdot 10^{-5}$	$(4.39 \pm 0.20) \cdot 10^{-3}$	
	$2.5 \cdot 10^{-4}$	$(2.70 \pm 0.12) \cdot 10^{-3}$	
	$6.25 \cdot 10^{-4}$	$(2.46 \pm 0.11) \cdot 10^{-3}$	
	$1.5 \cdot 10^{-3}$	$(2.30 \pm 0.10) \cdot 10^{-3}$	
	$2.0 \cdot 10^{-3}$	$(2.20 \pm 0.12) \cdot 10^{-3}$	
5, MeOH	—	1.84 ± 0.09	
	$5.0 \cdot 10^{-5}$	$(3.30 \pm 0.10) \cdot 10^{-1}$	$4.59 \cdot 10^{-1}$
	$2.5 \cdot 10^{-4}$	$(1.79 \pm 0.06) \cdot 10^{-1}$	$1.42 \cdot 10^{-1}$
	$6.25 \cdot 10^{-4}$	$(1.10 \pm 0.05) \cdot 10^{-1}$	$1.00 \cdot 10^{-1}$
	$1.0 \cdot 10^{-3}$	$(8.19 \pm 0.45) \cdot 10^{-2}$	$9.39 \cdot 10^{-2}$
	$1.5 \cdot 10^{-3}$	$(6.28 \pm 0.28) \cdot 10^{-2}$	
	$2.25 \cdot 10^{-3}$	$(5.17 \pm 0.25) \cdot 10^{-2}$	
	$5.0 \cdot 10^{-3}$	$(3.94 \pm 0.20) \cdot 10^{-2}$	
6, MeOH	—	$(7.98 \pm 0.26) \cdot 10^{-3}$	
	$5.0 \cdot 10^{-5}$	$(3.40 \pm 0.16) \cdot 10^{-3}$	$3.27 \cdot 10^{-3}$
	$2.5 \cdot 10^{-4}$	$(2.18 \pm 0.08) \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$
	$6.25 \cdot 10^{-4}$	$(1.67 \pm 0.05) \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$
	$1.0 \cdot 10^{-3}$	$(1.42 \pm 0.06) \cdot 10^{-3}$	$1.42 \cdot 10^{-3}$
	$1.5 \cdot 10^{-3}$	$(1.25 \pm 0.05) \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$
	$3.0 \cdot 10^{-3}$	$(1.05 \pm 0.04) \cdot 10^{-3}$	
7, MeOH	—	$(8.61 \pm 0.50) \cdot 10^{-1}$	
	$2.5 \cdot 10^{-4}$	$(9.46 \pm 0.32) \cdot 10^{-2}$	
	$6.25 \cdot 10^{-4}$	$(5.53 \pm 0.19) \cdot 10^{-2}$	
	$1.0 \cdot 10^{-3}$	$(4.24 \pm 0.15) \cdot 10^{-2}$	
	$1.5 \cdot 10^{-3}$	$(3.46 \pm 0.11) \cdot 10^{-2}$	
	$2.0 \cdot 10^{-3}$	$(3.08 \pm 0.14) \cdot 10^{-2}$	
	$3.0 \cdot 10^{-3}$	$(2.84 \pm 0.12) \cdot 10^{-2}$	

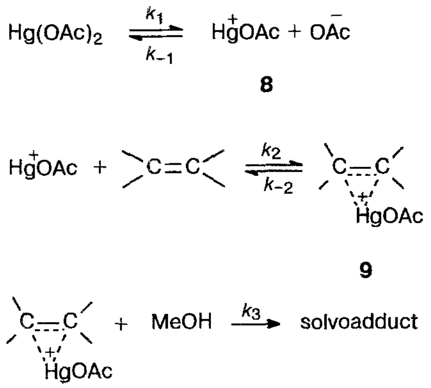
unstrained alkenes a 10—30-fold decrease in the rate constant is observed. In the case of the reaction with compound **6**, the effect of the salt additive is minimum. It should be noted that, at the NaOAc concentrations that cause the most retardation of the reaction, the effect that the additives have on the properties of the medium and on the reaction rate by changing the ionic strength of the solution can be neglected.

Let us consider the solvomercuration of unstrained alkenes **2a—c**, **3**, **4**. According to the published data[8,16] and the results of the present work, solvoadducts are formed in the reactions of $Hg(OAc)_2$ with **2a—c**, **3**, **4** in MeOH (including the reactions with the NaOAc additives). Based on the repeatedly described hypotheses,[9] one can conclude that $HgOAc^+$ is the reagent in these reactions. The dissociation constant of $Hg(OAc)_2$ in water is $1.8 \cdot 10^{-4}$.[17] In the case of a methanol solution, $Hg(OAc)_2$ should be a rather weak electrolyte, according to the analysis of the influence of the nature of the solvent on the dissociation constant.[18] Therefore, even moderate NaOAc additives can significantly decrease $[HgOAc^+]$ and, hence, the reaction rate.

The solvomercuration of alkenes **2a—c**, **3**, **4** can be described by Scheme 1 taking into account the nature of the reagent.

In principle, the reaction described by Scheme 1 may also occur under conditions of quasi-equilibrium when $[HgOAc^+]$ is determined by the dissociation constant ($k_{-1} \gg k_2$), as well as under the conditions of stationary concentrations when the $HgOAc^+$ ion, as it is formed, is involved in the subsequent conversions. In the first case, using the method of stationary concentra-

Scheme 1



tions for species (**9**), the following equation was obtained:

$$-\frac{d[\mathrm{Hg(OAc)_2}]}{dt}=\frac{k_2k_3[\overset{+}{\mathrm{H}}\mathrm{g(OAc)_2}]\left[{>}\mathrm{C{=}C}{<}\right]}{k_{-2}+k_3}. \quad (2)$$

For ion (**8**):

$$[\overset{+}{\mathrm{Hg}}\mathrm{OAc}]=\frac{K[\mathrm{Hg(OAc)_2}]}{[\overset{-}{\mathrm{OAc}}]}, \quad (3)$$

then

$$\frac{-d[\mathrm{Hg(OAc)_2}]}{dt}=\frac{k_2k_3K[\mathrm{Hg(OAc)_2}]\left[{>}\mathrm{C{=}C}{<}\right]}{k_{-2}+k_3[\overset{-}{\mathrm{OAc}}]}. \quad (4)$$

Since the degree of $\mathrm{Hg(OAc)_2}$ dissociation is low, the equilibrium concentration of the reagent can be taken as equal to its analytical concentration. Using the known equilibrium for weak electrolytes, it is easy to find that $[\mathrm{OAc^-}] = \alpha[\mathrm{Hg(OAc)_2}]$. Taking into account the degree of dissociation (α) of weak electrolytes, we obtain:

$$[\mathrm{OAc^-}] = K^{1/2}[\mathrm{Hg(OAc)_2}]^{1/2}. \quad (5)$$

Putting expression (5) in Eq. (4) results in:

$$\frac{-d[\mathrm{Hg(OAc)_2}]}{dt}=\frac{k_2k_3K^{1/2}[\mathrm{Hg(OAc)_2}]^{1/2}\left[{>}\mathrm{C{=}C}{<}\right]}{k_{-2}+k_3}. \quad (6)$$

Thus, under quasi-equilibrium conditions of the reaction, the order of the reaction with respect to the reagent should be 0.5, which does not agree with the experimental data. This is the argument that earlier[12] resulted in ruling out the "dissociative" mechanism. In fact, a fractional order disagrees not with the "dissociative" mechanism in general, but only with the variant of this mechanism, in which the concentration of ion **8** is determined by the equilibrium constant (K) of the first stage.

Based on Scheme 1, where the principle of stationary concentrations is also valid for the $\mathrm{HgOAc^+}$ ion, we can obtain Eq. (7):[5]

$$\frac{-d[\mathrm{Hg(OAc)_2}]}{dt}=\frac{k_1k_2k_3[\mathrm{Hg(OAc)_2}]\left[{>}\mathrm{C{=}C}{<}\right]}{k_2k_3\left[{>}\mathrm{C{=}C}{<}\right]+k_{-1}(k_2+k_3)[\overset{-}{\mathrm{OAc}}]}. \quad (7)$$

For the order with respect to alkene to correspond to that found experimentally, it must be accepted that

$$k_2k_3\left[{>}\mathrm{C{=}C}{<}\right] \ll k_{-1}(k_2+k_3)[\overset{-}{\mathrm{OAc}}].$$

Then

$$\frac{-d[\mathrm{Hg(OAc)_2}]}{dt}=\frac{k_1k_2k_3[\mathrm{Hg(OAc)_2}]\left[{>}\mathrm{C{=}C}{<}\right]}{k_{-1}(k_2+k_3)[\overset{-}{\mathrm{OAc}}]}, \quad (8)$$

where the experimentally found second order rate constant is equal to

$$k_{\mathrm{exp}}=\frac{k_1k_2k_3}{k_{-1}(k_2+k_3)[\overset{-}{\mathrm{OAc}}]}. \quad (9)$$

In the presence of NaOAc, the rate constant is described by expression

$$k=\frac{k_1k_2k_3}{k_{-1}(k_2+k_3)([\overset{-}{\mathrm{OAc}}]+[\overset{-}{\mathrm{OAc}}_{\mathrm{d}}])}, \quad (10)$$

where $[\mathrm{OAc_d}]$ is the concentration of $\mathrm{OAc^-}$ which equals [NaOAc]. As follows from Eq. (10), the dependence of $1/k$ on the salt concentration should be depicted by a straight line starting from the point that equals $1/k_{\mathrm{exp}}$:

$$1/k = 1/k_{\mathrm{exp}} + a[\mathrm{OAc_d}], \quad (11)$$

where

$$a=\frac{k_{-1}(k_2+k_3)}{k_1k_2k_3}.$$

The data given in Figs. 1, 2 show that, when the salt concentration is lower than $2.5 \cdot 10^{-3}$ mol $\mathrm{L^{-1}}$, this dependence is in fact linear, but at higher NaOAc concentrations it becomes curvilinear and then reaches a plateau. It should be specially noted that, regardless of the difference in the slopes of the lines, the deflection from the linear dependence occurs at the same NaOAc

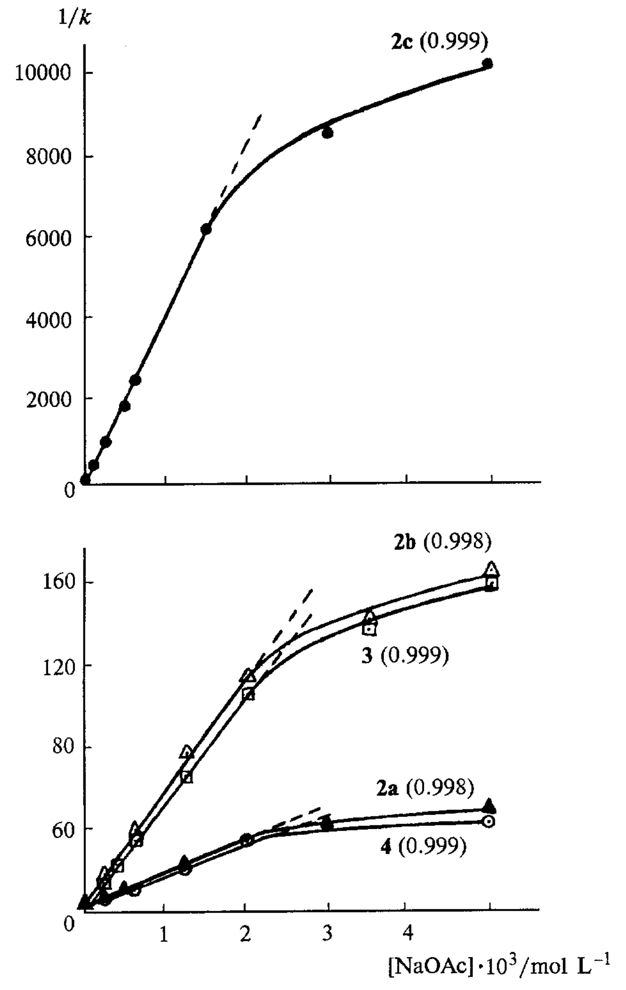


Fig. 1. Dependence of $1/k$ on [NaOAc] in the reaction of $Hg(OAc)_2$ with alkenes **2a—c**, **3**, **4** in MeOH (in brackets, the correlation coefficients r for the linear parts are given).

concentration regardless of the nature of the alkene. This fact indicates that linear dependence (11) is determined only by the nature of the reagent.

At relatively high concentrations of salt ($>2.5 \cdot 10^{-3}$ mol L^{-1}), the value of [$HgOAc^+$] decreases significantly, and a parallel route with mercury acetate as a reagent arises in the course of the reaction. As expected, in this case linear dependence (11) is not valid.

The analysis of the kinetic data obtained in the presence of the NaOAc additives allows one to conclude that, in the absence of salt or at low NaOAc concentrations, the $HgOAc^+$ ion is the actual reagent. In this case, a decrease in the ionization and dissociation properties of the medium should lead to a decrease in [$HgOAc^+$] and therefore to a change in the character of dependence (11). In this connection, we studied the kinetics of the solvomercuration of cyclohexene in MeOH—i-C_3H_7OH mixtures (50 : 50 and 20 : 80 in volume, respectively). The data obtained are shown in Fig. 2. In a mixed solvent, the $1/k$—OAc_d^- dependence differs from that in MeOH.

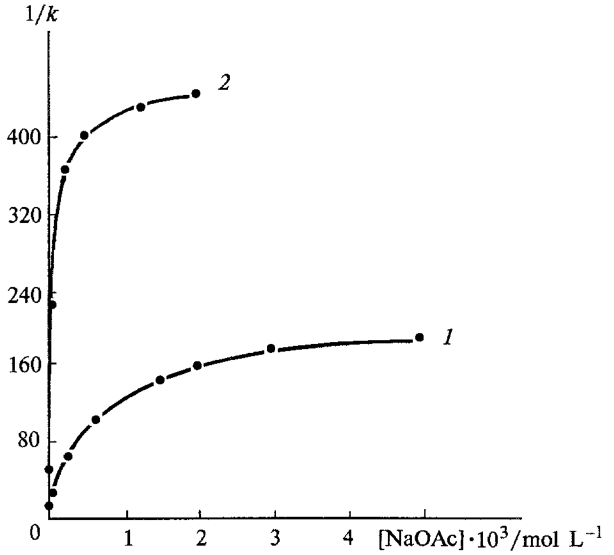


Fig. 2. Dependence of $1/k$ on [NaOAc] in the reaction of $Hg(OAc)_2$ with cyclohexene **4**: *1*, in a MeOH—i-C_3H_7OH mixture (50 : 50, vol. %); *2* , in a MeOH—i-C_3H_7OH mixture (20 : 80, vol. %).

The results obtained in the (20 : 80) MeOH—i-C_3H_7OH mixture are especially significant. Even small amounts of NaOAc additives ($5.0 \cdot 10^{-5}$ mol L^{-1}) results in a 4.3-fold decrease in the rate constant (see Table 1). An increase in the salt concentration from $5.0 \cdot 10^{-5}$ to $2.0 \cdot 10^{-3}$ mol L^{-1} results in only a 2-fold decrease in the reaction rate. The degree of $Hg(OAc)_2$ dissociation in a mixed solvent should be significantly lower than that in methanol. Therefore, even small amounts of NaOAc suppress the dissociative reaction, and the products formed involve the participation of $Hg(OAc)_2$ as a reagent.

Let us considered the kinetic data for strained alkenes **5—7**. The distinctive feature of these systems is the absence of the linear dependence $1/k$—[OAc^-] (Fig. 3). The other pecularity is the fact that added NaOAc induces the formation of adducts or increases the amount of the adducts (Table 2). The products of the reactions with compounds **5—7** have been described earlier.[2,19,20]

Based on conclusions reported previously[5] and on the above-mentioned pecularities, it is proposed that $Hg(OAc)_2$ is the reagent in the mercuration of compounds **5—7** (Scheme 2).

The addition of NaOA causes the transformation of free ion **12** to solvate-separated (**11**) and close (**10**) ion pairs. At limiting NaOAc concentrations (~0.01 mol L^{-1}), when the rate constant becomes independent of [NaOAc], the reaction proceeds via ion pairs **10**, **11**.

The analysis of Scheme 2 by the method of stationary concentrations leads to equation, which unfortunately could not be checked experimentally. In order to

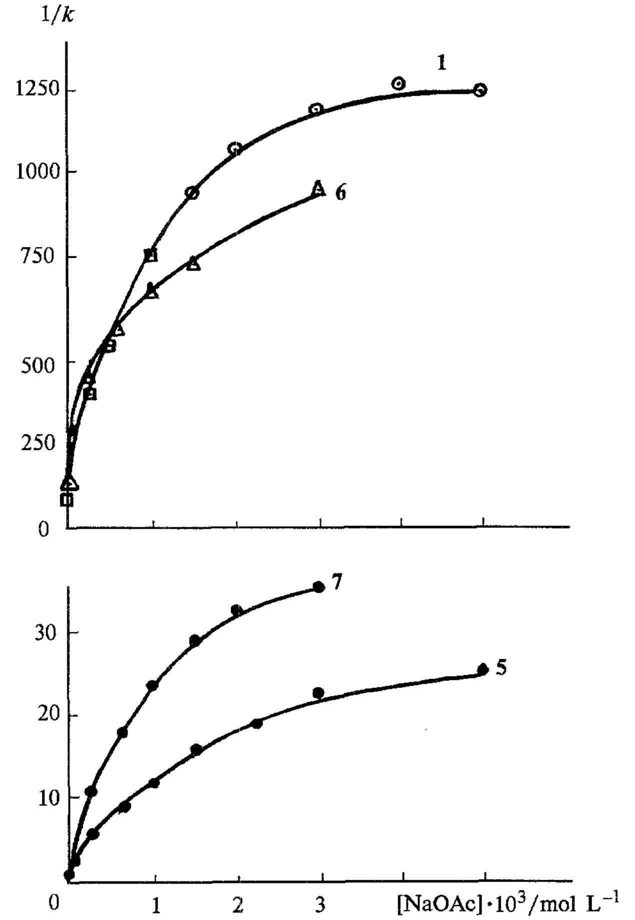


Fig. 3. Dependence of $1/k$ on [NaOAc] in the reaction of $Hg(OAc)_2$ with alkenes **1**, **5**—**7** in MeOH (the curve for compound **1** was plotted using the data reported in Ref. 5).

Table 2. Influence of NaOAc on the ratio between adducts and solvoadducts in the solvomercuration of alkenes (**2a**—**c**) — (**7**)

Alkene	NaOAc /mol L^{-1}	$P_1 : R_3$ /mol. %	$(P_1 + P_2) : P_3$ /mol. %
5	—	21 : 79	45 : 55
	$2.5 \cdot 10^{-4}$	27 : 73	58 : 42
	$6.25 \cdot 10^{-4}$	32 : 68	70 : 30
	$1.0 \cdot 10^{-3}$	38 : 62	82 : 18
	$1.5 \cdot 10^{-3}$	41 : 59	90 : 10
	$5.0 \cdot 10^{-3}$	46 : 54*	
6	—	0 : 100	
	$2.5 \cdot 10^{-4}$	7 : 93	22 : 78
	$5.0 \cdot 10^{-4}$	10 : 90	31 : 69
	$1.0 \cdot 10^{-3}$	13 : 87	43 : 57
	$2.0 \cdot 10^{-3}$	19 : 81	63 : 37
	$5.0 \cdot 10^{-3}$	30.5 : 69.5*	

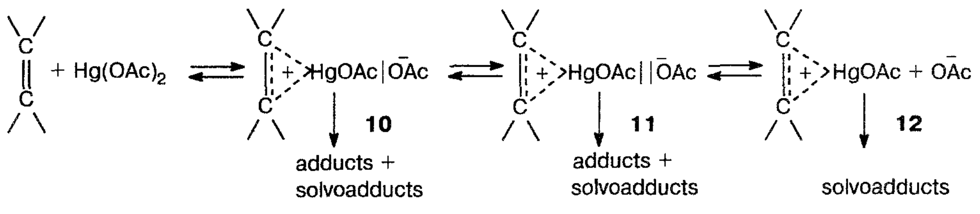
* Ratios that were used for calculation of the θ value.

confirm the proposed ion-pair mechanism involving participation of free ion **12**, we considered a simplier scheme regarding ion pairs **10**, **11** as a united pair **13**, which is converted to the adducts and solvoadducts with the effective constants k_2, k_3, respectively (Scheme 3).

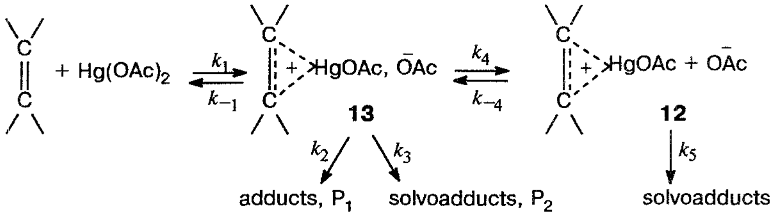
A similar approach is commonly used for the analysis of complex reactions that proceed via an ion-pair mechanism.[21] An analogous procedure was used for the interpretation of the kinetic data obtained for the reaction of $Hg(OAc)_2$ with bornylene **1**.[5] In these works, the expressions that allow one to check the agreement of a proposed scheme with the observed regularities are considered in detail.

It follows from Scheme 3 (see Ref. 5) that the ratio between the products of the conversion of ion pair **13** and the solvoadducts generated from a free mercurinium ion **12** should depend linearly on the concentration of NaOAc added. It should be stressed that in the reaction with bornylene **1** at [NaOAc] > $1.0 \cdot 10^{-2}$ mol L^{-1}, only solvoadducts are formed,[5] while the reactions with compounds **5**—**7** yield both adducts and solvoadducts even with a 10-fold excess of NaOAc with respect to the

Scheme 2



Scheme 3



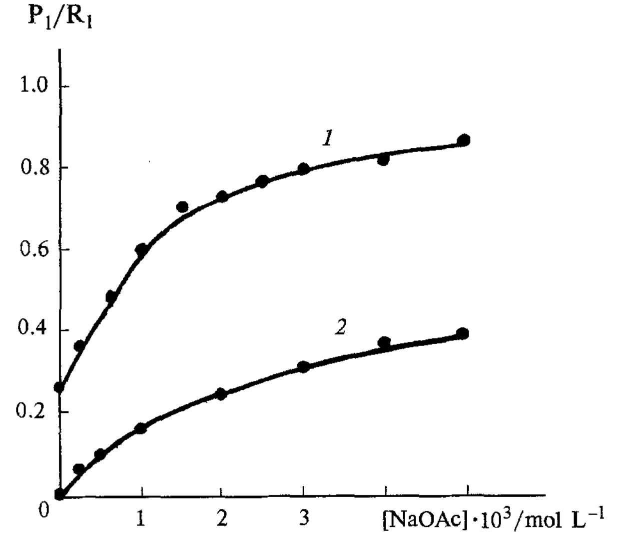


Fig. 4. Dependence of the P_1/R_3 ratio on [NaOAc]: *1*, for the reaction of $Hg(OAc)_2$ with compound **5** in MeOH; *2*, for the reaction of $Hg(OAc)_2$ with compound **6** in MeOH.

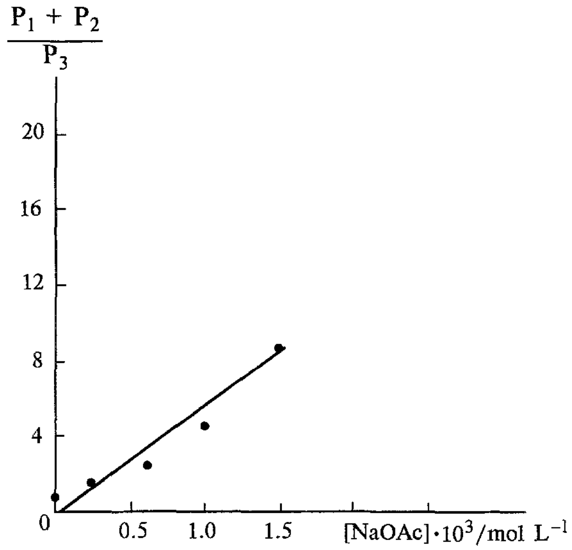


Fig. 5. Dependence of the $(P_1 + P_2)/P_3$ ratio on [NaOAc] in the reaction of $Hg(OAc)_2$ with compound **5** in MeOH (r = 0.982).

reagent. Therefore, if the adducts/solvoadducts ratio is used (see, for example, Ref. 5), a linear dependence is not valid (see Table 2, Fig. 4). This attests to the fact that solvoadducts are formed not only from ion **12**. If the ratio of adducts and solvoadducts generated from ion pair **13** at intermediate concentrations of NaOAc is believed to be the same as that at the limiting additive concentrations (the dependence $1/k$—[OAc⁻] reaches a plateau, see Fig. 3), it is possible to calculate the amount of solvoadducts generated only from ion **12**.

If the adduct/solvoadduct (P_1/P_2) ratio at the NaOAc limiting concentrations is denoted as θ, the amount of product ($P_1 + P_2$) generated from ion pair **13** at intermediate [NaOAc] is described by expression (12).

$$P_1 + P_2 = P_1 + P_1/\theta \tag{12}$$

The amount of solvoadducts that are formed from mercurinium ion **12** is expressed by Eq. (13):

$$P_3 = R_3 - P_1/\theta, \tag{13}$$

where R_3 is the total amount of solvoadducts determined experimentally, mol. %, P_1 is the amount of adducts determined experimentally, mol. %, and θ is 0.85 and 0.44 for compounds **5** and **6**, respectively.

In this case, if Scheme 3 is valid, expression (14) is obtained:

$$\frac{P_1 + P_2}{P_3} = \frac{k_2 + k_3}{k_4} + \frac{(k_2 + k_3)k_{-4}}{k_5 k_4}[\mathrm{O\overset{-}{A}c}]. \tag{14}$$

Figures 5 and 6 show that this linear dependence is valid in fact.

The analysis of the dependence of k on [NaOAc]^5 also confirms the validity of Scheme 3. For the systems studied where ion pair **13** affords solvoadducts, Eq. (15) is obtained:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}}{k_1(k_2 + k_3)} - \frac{k_{-1}}{k_1(k_2 + k_3)} \times$$
$$\times \left(\frac{1}{\dfrac{(k_2 + k_3)k_{-4}\,[\mathrm{OAc}]}{k_4 k_5} + \dfrac{k_2 + k_3}{k_4} + 1} \right). \tag{15}$$

Then we introduced a designation analogous to that reported in Ref. 5:

$$\frac{(k_2 + k_3)k_{-4}\,[\mathrm{OAc}]}{k_4 k_5} + \frac{k_2 + k_3}{k_4} = \mathrm{d}, \tag{16}$$

where the ratios between the combination of the constants are equal to the right side of Eq. (14). The graphic dependences shown in Figs. 5 and 6 are described by Eqs. (17) and (18), respectively.

$$\frac{P_1 + P_2}{P_3} = (5639 \pm 100)\,[\mathrm{O\overset{-}{A}c}] - (0.06 \pm 0.03), \tag{17}$$

$$\frac{P_1 + P_2}{P_3} = (823 \pm 29)\,[\mathrm{O\overset{-}{A}c}] - (0.016 \pm 0.006). \tag{18}$$

Eq. (15) indicates that the $1/k$ ratio should depend linearly on $1/(\mathrm{d} + 1)$, which is in fact observed (see Figs. 7, 8).

Eqs. (19) and (20), which approximate the graphic dependences (see Figs. 7 and 8, respectively), make it

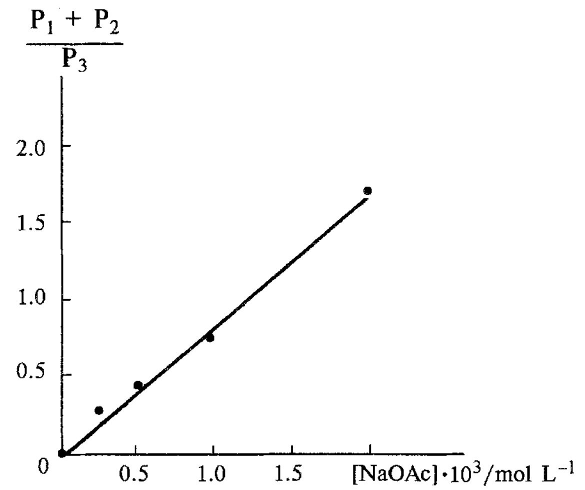


Fig. 6. Dependence of the $(P_1 + P_2)/P_3$ ratio on [NaOAc] in the reaction of $Hg(OAc)_2$ with compound **6** in MeOH (r = 0.995).

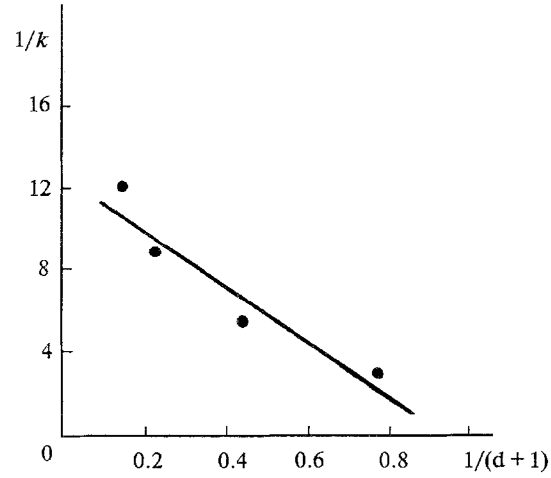


Fig. 7. Dependence of $1/k$ on the value of $1/(d + 1)$ in the reaction of $Hg(OAc)_2$ with compound **5** in MeOH (r = 0.938).

possible to calculate the rate constants for a fixed [NaOAc].

$$1/k = (13 \pm 4) - (13 \pm 1)/(5639[OAc^-] + 1.0) \quad (19)$$

$$1/k = (1225 \pm 40) - (958 \pm 25)/(823[OAc^-] + 1.0) \quad (20)$$

A comparison between k calculated with Eqs. (19), (20) and those found experimentally showed that they agree satisfactorily (see Table 1).

At limiting [NaOAc], when the stage of the conversion of ion pair **13** to free ion **12** ($k_4 = 0$) is absent, or directly using the method of stationary concentrations for Scheme 4, Eq. (21) is obtained:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}}{k_1(k_2 + k_3)} \quad (21)$$

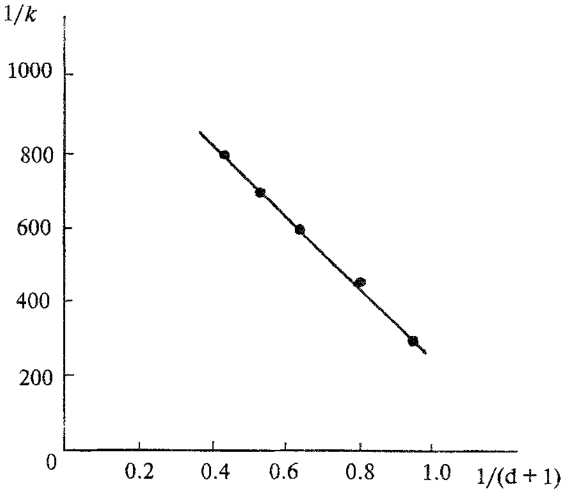
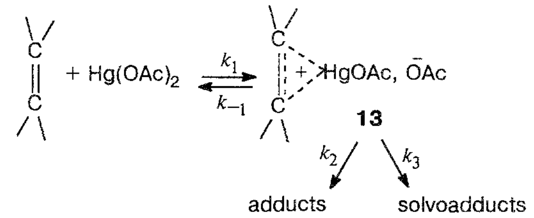


Fig. 8. Dependence of $1/k$ on the value of $1/(d + 1)$ in the reaction of $Hg(OAc)_2$ with compound **6** in MeOH (r = 0.995).

Scheme 4



Eqs. (19), (20), and (21) indicate that the segments that are cut off at the ordinates axis (see Figs. 7, 8), are 13.0 and 1225.0, respectively. Using these data, one can calculate $k_{diss} = 7.69 \cdot 10^{-2}$ L (mol s)$^{-1}$ for compound **5** and $k_{diss} = 8.16 \cdot 10^{-4}$ L (mol s)$^{-1}$ for compound **6**. In the second case, the calculated rate constant is close to the constant found experimentally ($1.05 \cdot 10^{-1}$ L (mol s)$^{-1}$), while in the first case the correlation is less satisfactory ($k_{exp} = 3.94 \cdot 10^{-2}$ L (mol s)$^{-1}$). From our point of view, however, this is not in disagreement with the proposed interpretation.

Thus, the analysis of the kinetic data and the arguments reported earlier[5] allow one to conclude that in the reaction of the strained alkenes in methanol the reagent is mainly the $Hg(OAc)_2$ salt rather than the free ion $HgOAc^+$. In the presence of the NaOAc additives, the parallel route according to Scheme 1 can be entirely neglected. It appears that the reactivity of the strained and unstrained alkenes with respect to electrophilic reagents HgOAc and $Hg(OAc)_2$ differ significantly due to the state and the properties of the strained double bond.[22]

References

1. T. G. Traylor, *Accouns. Chem. Res.*, 1969, **2**, 152.
2. V. R. Kartashov, T. N. Sokolova, E. V. Skorobogatova, Yu. K. Grishin, D. V. Bazhenov, V. A. Roz'nyatovsky,

A. C. Koz'min, and N. S. Zefirov, *Zh. Org. Khim.*, 1990, **26**, 1953 [*J. Org. Chem. USSR*, 1990, **26** (Engl. Transl.)].
3. Sh. O. Badayn, S. Zh. Dav'chan, Zh. A. Chobayan, and S. K. Vardapedyan, *Arm. Khim. Zh.*, 1984, **37**, 407 (in Russian).
4. V. R. Kartashov, E. V. Skorobogatova, and N. S. Zefirov, *Usp. Khim.*, 1993, **62**, 991 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
5. V. R. Kartashov, T. N. Sokolova, I. V. Timofeev, E. V. Skorobogatova, and N. S. Zefirov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 819 [*Russ. Chem. Bull.*, 1994, **43**, 760 (Engl. Transl.)].
6. S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 2783.
7. H. C. Brown, J. T. Kurek, Min-Hon Rei, and K. L. Thompson, *J. Org. Chem.*, 1984, **49**, 2551.
8. O. A. Reutov, I. P. Beletskaya, and V. I. Sokolov, *Mekhanizmy reaktsii metalloorganicheskikh soedinenii* [*Mechanisms of Reactions of Organometallic Compounds*], Khimiya, Moscow, 1972, 222 (in Russian).
9. R. D. Bach and R. F. Richter, *J. Am. Chem. Soc.*, 1972, **94**, 4747.
10. M. J. S. Dewor and K. M. Merz, *Organometallics*, 1985, **4**, 1967.
11. H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, 1973, **95**, 8665.
12. K. L. Mallik and M. N. Das, *J. Am. Chem. Soc.*, 1960, **82**, 4269.
13. A. Lewis, *J. Org. Chem.*, 1984, **49**, 4682.
14. A. Lupi and B. Chubar, *Solevye effekty v organicheskoi i metalloorganicheskoi khimii* [*Salt Effects in Organic and Organometallic Chemistry*], Mir, Moscow, 1991, 375 (Russ. Transl.).
15. I. C. Ambidge, S. K. Dwight, C. M. Rynard, and T. T. Tidwell, *Can. J. Chem.*, 1977, **55**, 3086.
16. T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2614.
17. D. Banerjea, I. P. Singh, *Zeitschr. Anorgan and Allgemeine Chem.*, 1964, B. 331, 225.
18. N. A. Izmailov, *Elektrokhimiya rastvorov* [*Electrochemistry of Solutions*], Khimiya, Moscow, 1976, 488 (in Russian).
19. V. R. Kartashov, T. N. Sokolova, E. V. Skorobogatova, Yu. K. Grishin, D. V. Bazhenov, and N. S. Zefirov, *Zh. Org. Khim.*, 1991, **27**, 261 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
20. J. K. Stille and S. C. Stinson, *Tetrahedron*, 1964, **20**, 1387.
21. R. V. Hoffman, *Mekhanizmy khimicheskikh reaktsii* [*Mechanisms of Chemical Reactions*], Khimiya, Moscow, 1979, 300 (in Russian).
22. N. S. Zefirov and V. I. Sokolov, *Usp. Khim.*, 1967, 263 [*Russ. Chem. Rev.*, 1967 (Engl. Transl.)].

Reseived July 20, 1994