Organometallic Chemistry

Kinetics and mechanism of azidomercuration of alkenes, cycloalkenes, and their derivatives with a mercuric acetate—sodium azide system

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The kinetics of azidomercuration of alkenes, cycloalkenes, and their derivatives with a $Hg(OAc)_2$ —NaN₃ system (1 : 1, 1 : 2, and 1 : 3) was studied. Based on the data on the product structure and kinetic results, it was concluded that $HgOAcN_3$ and $Hg(N_3)_2$ play the role of azidomercuration reagents. The reactions with alkenes having a strained double bond occur by a concerted scheme. With nonstrained alkenes, a multistep mechanism is realized, its first reversible step involving the formation of a mercurinium intermediate with an ion pair structure.

Key words: azidomercuration, alkenes, cycloalkenes, strained double bond, kinetics, reaction mechanism.

The Hg(OAc)₂—NaN₃ system is a convenient reagent for the azidomercuration of alkenes.¹⁻⁹ In some cases,^{2,10,11} this reaction can be used for preparative syntheses of organic azides by performing consecutive azidomercuration—demercuration steps. A considerable number of works deal with the stereochemistry of these reactions.²⁻⁸ The data obtained suggest that the azidomercuration of strained alkenes generally occurs *cis*-stereoselectively, while nonstrained alkenes react by the usual *trans*-scheme, as exemplified by the reaction with cyclohexene.⁴

In the present work we studied the kinetics of the azidomercuration of compounds (1-6) with $Hg(OAc)_2$: NaN₃ taken in various ratios, such as 1 : 1, 1 : 2, and 1 : 3 (henceforth named reagents 1 : 1, 1 : 2, and 1 : 3, respectively), using MeOH as the solvent. For 2-bornene 1, we studied the kinetics of its azidomercuration and solvomercuration in EtOH and



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EtOH $-H_2O$, as well as in MeOH in the presence of NaOAc as a salt additive.

The products of the azidomercuration of compounds 1-4 have been described previously.^{4,6,9} When the 1 : 3 Hg(OAc)₂—NaN₃ system is used, the reactions with 1-4 give a mixture of regioisomers 7 and 8 in a 1.5 : 1 ratio and compounds 9-11, respectively.



When the $Hg(OAc)_2$: NaN₃ ratio is 1 : 1, the reaction with compound 2 gives a mixture of adducts 9 and 12 (7 : 3).

The reaction of alkenes 5 and 6 with the reagent 1:3 gave products 13 and 14. The use of the reagent 1:1 gave products of coupled solvoaddition along with azido adducts 13 and 14.

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Experimental

NMR spectra were recorded on a Varian VXR-400 spectrometer. The chemical shifts are reported on the δ scale relative to SiMe₄ (internal standard). Kinetic studies were carried out using an SF-46 spectrophotometer. TLC was performed on LSL 5/40 μ silica gel.

Azidomercuration of alkenes 5, 6. General procedure. To a solution of $Hg(OAc)_2$ and NaN_3 (component ratio 1 : 3) in MeOH an equimolar amount of an alkene in MeOH was

quickly added at ~20 °C. The concentration of $Hg(OAc)_2$ did not exceed 0.1 mol L⁻¹. After the reaction was completed, the mixture was poured into 100 mL of 1 % aqueous NaCl and extracted with chloroform. The organic layer was washed with water and dried with MgSO₄. The solvent was removed under reduced pressure.

2-Azido-1-chloromercurio-3-methoxypropane (13) was obtained as a viscous transparent oil by treatment of allyl methyl ether **5** (0.2 g, 2.8 mmol) with Hg(OAc)₂ (0.8 g, 2.5 mmol) and NaN₃ (0.49 g, 7.5 mmol) in MeOH (25 mL) for 20 h. The yield of compound **13** was 0.7 g (80 %). ¹H NMR (CD₂Cl₂), δ : 1.8–2.1 (m, 2 H, CH₂HgCl); 3.35 (s, 3 H, OMe); 3.36 (m, 2 H, CH₂OMe); 4.0 (s, 1 H, CHN₃). ¹³C NMR (CD₂Cl₂), δ : 30.72 (CH₂HgCl); 59.66 (OMe); 61.11 (CHN₃); 75.77 (<u>CH₂OMe</u>).

2-Azido-1-chloromercurio-5-methylhexane (14) was obtained as a viscous transparent oil by treatment of 5-methylhex-1-ene (6) (0.25 g, 2.5 mmol) with Hg(OAc)₂ (0.8 g, 2.5 mmol) and NaN₃ (0.49 g, 7.5 mmol) in MeOH (25 mL). After 20 h, compound **14** (0.58 g) was obtained, yield 65 %. ¹H NMR (CD₂Cl₂), δ : 0.85–1.55 (m, 11 H, (CH₂)₂CHMe₂); 2.1–2.3 (m, 2 H, CH₂HgCl); 3.8 (s, 1 H, CHN₃). ¹³C NMR (CD₂Cl₂), δ : 23.01, 23.08 (2 Me); 28.61 (CH₂HgCl); 36.02, 37.23, 37.92 ((CH₂)₂CH); 63.52 (CHN₃).

Reaction of cyclohexene with the Hg(OAc)₂—NaN₃ system (1 : 1). Cyclohexene 4 (0.5 g, 6 mmol) in MeOH (10 mL) was added to a mixture of Hg(OAc)₂ (1.94 g, 6 mmol) and NaN₃ (0.39 g, 6 mmol) in MeOH (30 mL). After the reaction ceased, the usual work-up gave 2.2 g of a crystalline product. TLC on silica gel with ethyl acetate—benzene (1 : 1) as the eluent gave 0.64 g of *trans*-1-azido-2-chloromercuriocyclohexane (11), m.p. 88—89 °C (MeOH), and 0.49 g of *trans*-1-methoxy-2-chloromercuriocyclohexane, m.p. 109—110 °C (MeOH).

The reactions with alkenes 5 and 6 were carried out in a similar way. The products were analyzed by TLC using the corresponding pure adducts.

The kinetics of the mercuration of compounds 1, 2, and 4-6 were studied by the known procedure.¹²

For dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate 3, an aliquot of the reaction mixture was added to a solution of KI ($2.5 \cdot 10^{-3}$ mol L⁻¹) in MeOH-H₂O (0.91 : 0.09), the total volume being 25 mL. The optical density due to the absorption of the HgI₃⁻ complex¹³ was determined at $\lambda = 300.5$ nm.

Kinetic experiments were carried out at 25 ± 0.1 °C until the conversion of the reagent was 65-80 % (or 55-60 % in the case of ester 3). The initial concentrations of Hg(OAc)₂ (mol L⁻¹) were 0.01 in reactions with 1, 3, 5, 6, (0.8– $1.5)\cdot10^{-3}$ with 2, and 0.001 with 4. The initial concentrations of unsaturated compounds 1-6 were $(2.0-7.5)\cdot10^{-2}$, $1.0\cdot10^{-3}-1\cdot10^{-2}$, $(1.9-8.2)\cdot10^{-2}$, 0.08-0.1, 0.08-0.46, and 0.18-0.34 mol L⁻¹, respectively.

Results and Discussion

As follows from the data obtained, the reactions of compounds 1-6 with reagents 1: 3 and 1: 2 in MeOH give azido adducts 15, irrespective of the structure of the substrate.

$$C = C \left(\begin{array}{c} 1. \text{ Hg(OAc)}_2 - \text{NaN}_3, \text{ MeOH} \\ \hline 2. \text{ Aqueous NaCl} \end{array} \right) C = C \left(\begin{array}{c} N_3 \\ \hline N_3 \end{array} \right)$$



Fig. 1. Anamorphosis of Eq. (1) for the azidomercuration of compounds 1, 5, and 6 in MeOH: *1*, $[Hg(OAc)_2] = 1.0 \cdot 10^{-2}$, $[NaN_3] = 2.91 \cdot 10^{-2}$, [6] = 0.34 mol L⁻¹; 2, $[Hg(OAc)_2] = 1.0 \cdot 10^{-3}$, $[NaN_3] = 3.0 \cdot 10^{-3}$, [1] = $5.52 \cdot 10^{-2}$ mol L⁻¹; 3, $[Hg(OAc)_2] = 1.0 \cdot 10^{-2}$, $[NaN_3] = 3.0 \cdot 10^{-3}$, [5] = 0.47 mol L⁻¹.

This is one of the interesting features of the reaction. The reactions with other mercury salts in nucleophilically active media (lowest alcohols, aqueous-organic media) occur as coupled solvomercuration.^{14,15}

When the $Hg(OAc)_2$: NaN₃ ratio is 1 : 1, the composition of the products depends on the structure of the alkene. Unsaturated compounds 1 and 2 give azido adducts 15, while the other substrates give mixtures of 15 and solvoadducts 16, as shown by TLC analysis.

$$>C=C < \frac{1. Hg(OAC)_2 - NaN_3, MeOH}{2. Aqueous NaCl}$$

$$---- 15 + CIHg - C - C - OMe$$
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As exemplified by the reaction with cyclohexene 4, solvoadduct 16 is formed initially, while compounds 15 are formed at higher degrees of conversion.

The features noted above are reflected in the kinetic regularities of this reaction. Under the conditions when only azidoadducts 15 are formed (reagents 1 : 2, 1 : 3), the rate of the process is described by a second-order reaction kinetics (1)* (Figs. 1 and 2, Table 1).

$$-\frac{d[HgX_2]}{dt} = k[HgX_2] \quad [>C=C] \tag{1}$$

In the case of the reagent 1 : 1, Eq. (1) is fulfilled for reactions with compounds 1 and 2. The k values calculated by Eq. (1) for other unsaturated substrates decrease by a factor of 3-4 in the course of the reac-





Fig. 2. Anamorphosis of Eq. (1) for the azidomercuration of compounds 2-4 in MeOH:

- *I*, $[Hg(OAc)_2] = 1.0 \cdot 10^{-3}$, $[NaN_3] = 3.0 \cdot 10^{-3}$, [3] = 8.15 \cdot 10^{-2} mol L⁻¹;
- 2, $[Hg(OAc)_2] = 1.0 \cdot 10^{-3}$, $[NaN_3] = 1.0 \cdot 10^{-3}$, [2] = $1.0 \cdot 10^{-2}$ mol L⁻¹;
- 3, $[Hg(OAc)_2] = 1.0 \cdot 10^{-3}$, $[NaN_3] = 3.0 \cdot 10^{-3}$, [4] = 0.1 mol L⁻¹.

Table 1. Mercuration rate constants for compounds 1-6 (MeOH)

Sub- strate	Reagent	Component $k/L \mod^{-1} s^{-1}$ ratio		
1	Hg(OAc) ₂ * Hg(OAc) ₂ —NaN ₃	$(1.15\pm0.05)\cdot10^{-2}$ 1:1 (2.16\pm0.13)\cdot10^{-2} 1:2 (2.45±0.24) · 10^{-3} 1:3 (1.68±0.08) · 10^{-3}		
2	Hg(OAc) ₂ ** Hg(OAc) ₂ —NaN ₃	$(7.98\pm0.26)\cdot10^{-3}$ 1:1 (1.44±0.07) $\cdot10^{-3}$ 1:2 (3.01±0.18) $\cdot10^{-4}$ 1:3 (2.93±0.23) $\cdot10^{-4}$		
3	Hg(OAc) ₂ Hg(OAc) ₂ -NaN ₃	$(1.55\pm0.05)\cdot10^{-4}$ 1:2 (3.79\pm0.09)\cdot10^{-4} 1:3 (3.08\pm0.28)\cdot10^{-4}		
4	Hg(OAc) ₂ * Hg(OAc) ₂ —NaN ₃	$\begin{array}{rrr} 1.23 \pm 0.07 \\ 1:2 & (8.32 \pm 0.77) \cdot 10^{-5} \\ 1:3 & (7.38 \pm 0.44) \cdot 10^{-5} \end{array}$		
5	Hg(OAc) ₂ ** Hg(OAc) ₂ —NaN ₃	$\begin{array}{rrr} (9.25\pm0.35)\cdot10^{-1}\\ 1.2 & (4.04\pm0.17)\cdot10^{-5}\\ 1.3 & (5.00\pm0.46)\cdot10^{-5} \end{array}$		
6	$Hg(OAc)_2$ $Hg(OAc)_2$ -NaN ₃	5.0 ± 0.6 1:3 (4.91±0.38) · 10 ⁻⁴		

* See Ref. 12. ** See Ref. 17; for compound 2a, one should read X = OMe.

tion. It should be noted that the rate of the azidomercuration of strained bicyclic compounds 1-3 differs insignificantly from the rate of the reaction with $Hg(OAc)_2$ in MeOH (see Table 1). Conversely, the rates of the azido- and methoxymercuration of non-strained compounds 4-6 differ by a factor of $(1.0-1.8) \cdot 10^4$.

These data can be explained by assuming that reversible reactions of ligand exchange occur in the $Hg(OAc)_2$ — NaN₃ system.

$$Hg(OAc)_2 + NaN_3 \implies HgOAcN_3 + NaOAc$$

 $HgOAcN_3 + NaN_3 \implies Hg(N_3)_2 + NaOAc$

One should expect that the former equilibrium is most probably observed for the reagent 1 : 1. Let us consider its role in the formation of products and in the kinetics of the azidomercuration of alkenes. Assuming that the equilibrium is established more quickly than Hg(OAc)₂ and HgOAcN₃ enter the reaction, in the general case we have Eq. (2).

$$w = k_1[\text{HgOAcN}_3] \left[\ge C = C \le \right] + k_2[\text{Hg(OAc)}_2] \left[\ge C = C \le \right], \quad (2)$$

where $[HgOAcN_3]$ and $[Hg(OAc)_2]$ are the equilibrium concentrations of the reagents.

Based on the structure of the products and the type of the kinetic equation of the reaction of bridged compounds 1 and 2 with the reagent 1 : 1, it can be concluded that the equilibrium is strongly shifted to the right, and it is the mixed salt HgOAcN₃ that serves as the azidomercurating reagent. As noted above, the rates of reactions of alkenes 1 and 2 with Hg(OAc)₂ and the reagent 1 : 1 differ insignificantly (see Table 1), so the general Eq. (2) should coincide with that established experimentally, if [HgOAcN₃] \gg [Hg(OAc)₂], and the second term in Eq. (2) can be neglected. In this case, the equilibrium concentration of the mixed salt is almost equal to the overall concentration of mercury salts.

$$-\frac{\mathrm{d}[\mathrm{HgOAcN}_3]}{\mathrm{d}t} = k_1[\mathrm{HgOAcN}_3] \left[\mathbf{C} = \mathbf{C} \mathbf{C} \right]$$
(3)

In the case of compounds **4**-**6**, Eq. (3) is not fulfilled. The nature of the alkene should not affect the equilibrium, hence HgOAcN₃ is much less reactive in these reactions than Hg(OAc)₂. This assumption was confirmed by the fact that a solvoadduct is initially formed in the reaction of cyclohexene with the 1 : 1 reagent. If $k_2 \gg k_1$, the second term in Eq. (2) can be significant, and the reaction obeys a more complex kinetic law.

Similarly, it can be considered that $Hg(N_3)_2$ serves as a reagent in the $Hg(OAc)_2$ —NaN₃ (1 : 2, 1 : 3) system. It is seen from Table 1 that the constants of the reactions of compounds **1**—**6** with the reagent 1 : 3 are somewhat smaller than those with the reagent 1 : 2. This is probably due to the formation of a nonreactive $Hg(N_3)_3^-$ complex in the former case.

To determine the reaction mechanism more reliably, we studied the effect of the ionizing strength of the solvent, Y,¹⁶ on the azidomercuration rate, using bornylene 1 as the substrate. For comparison, we also determined the effect of Y on the rate of reaction of compound 1 with Hg(OAc)₂. In all of the solvents studied, the rate is satisfactorily described by a secondorder kinetics, *i.e.*, first-order with respect to each of the reagents. The kinetic data are presented in Table 2.

Each of the reactions obeys the Grünwald—Winstein Eq. (4) (Fig. 3).

$$\lg k = \lg k_0 + mY \tag{4}$$

The *m* values were found to be 0.45 (r = 0.997), 0.47 (r = 0.985), and 0.74 (r = 0.999) for the mercuration of compound 1 with Hg(OAc)₂—NaN₃ (1 : 1, 1 : 2) and Hg(OAc)₂, respectively. The azidomercuration reactions have almost equal *m* values, which are much lower than those in the reaction with Hg(OAc)₂.

Let us consider the possible schemes of the azidomercuration of alkenes. In one of the schemes, NaN_3 acts as an external nucleophile, while $Hg(OAc)_2$ or the Hg^+OAc ion is a reagent. In this case, according to the literature data,^{12,17,18} the addition of NaOAc should decrease the reaction rate, despite the formation of azido adduct 15. As follows from Table 3, the addition of salts does not noticeably affect the reaction rate.

Table 2. Mercuration rate constants for bornylene 1 in EtOH and in an EtOH- H_2O mixture

EtOH : H_2O	Reagent				
ratio in	Hg(OAc) ₂ -	$Hg(OAc)_2$			
the solvent	1:1	1:2			
100:0	$(1.29\pm0.09)\cdot10^{-2}$	$(2.90\pm0.19)\cdot10^{-3}$	$(1.26\pm0.08)\cdot10^{-3}$		
98:2	$(2.24\pm0.12)\cdot10^{-2}$	$(6.26\pm0.40)\cdot10^{-3}$	$(2.51\pm0.16)\cdot10^{-3}$		
95:5	$(3.26\pm0.18)\cdot10^{-2}$	$(1.01\pm0.06)\cdot10^{-2}$	$(4.09\pm0.26)\cdot10^{-3}$		
90:10	$(6.21\pm0.31)\cdot10^{-2}$	$(1.72\pm0.12)\cdot10^{-2}$	$(1.08\pm0.07)\cdot10^{-2}$		
80:20	$(1.10\pm0.07)\cdot10^{-1}$	$(2.74 \pm 0.17) \cdot 10^{-2}$	$(3.85 \pm 0.18) \cdot 10^{-2}$		
70:30	$(2.21\pm0.08)\cdot10^{-1}$	$(6.74 \pm 0.49) \cdot 10^{-2}$	$(1.22\pm0.06)\cdot10^{-1}$		

This result allows us to consider that the above scheme is in fact not realized.

It is seen from the data in Table 4 that the $Hg(OAc)_2$ —NaN₃ system has much higher capability of *cis*-addition than $Hg(OAc)_2$. This is particularly evident in reactions involving bridged compound 2, for which the stereochemistry of addition is reverted on passing from $Hg(OAc)_2$ to azidomercuration reagents. It has been shown^{12,17,18} that the reaction of $Hg(OAc)_2$ with strained alkenes in polar media occurs by a multistep mechanism with the formation of ion pairs and free mercurinium ions. Conversely, the *cis*-azidomercuration of strained alkenes probably occurs by a concerted pathway (Scheme 1) *via* transition state 17.

Scheme 1



The concerted addition is facilitated by the high nucleophilicity of the azido group. This assumption is particularly evident for bridged compounds, which possess steric hindrances for the *trans*-addition of a nucleophile completing the reaction.

The scheme of azidomercuration suggested above was confirmed by the data on the solvent effect on the reaction rate. In the concerted mechanism, the ionizing

 Table 3. Azidomercuration rate constants for bornylene 1 in the presence of NaOAc (MeOH)

Concentration of NaOAc/mol L ⁻¹	$k \cdot 10^2$ /L mol ⁻¹ s ⁻¹	
0.0025	1.95±0.09	
0.01	1.95±0.11	
0.05	2.07 ± 0.09	
0.1	2.00 ± 0.07	



Fig. 3. Dependence of log k of mercuration of bornylene 1 on Y for the reagents 1 : 1 (1), 1 : 2 (2), and $Hg(OAc)_2 (3)$.

force of a solvent should be less important than in the case when a polar intermediate is formed.^{12,16–18} The m values in Eq. (4) (see above) confirm this statement. An additional argument in favor of Scheme 1 is the regiochemistry of the azidomercuration of bornylene 1.⁹ As noted above, the azidomercuration of 1 gives a mixture of regioisomers 7 and 8 (1.5 : 1). The reaction with Hg(OAc)₂ in MeOH gives similar regioisomers but in an opposite ratio (1 : 1.4). Position 2 in bornylene 1 is more sterically hindered than position 3, hence isomer 7 should be the predominant product in the case of the concerted mechanism. For the same reasons, the isomer with opposite regiochemistry should predominate in the case of the multistep mechanism (Scheme 2).

The most probable mechanism for nonstrained alkenes involves the formation of an ion pair (18) in the first step.

HģN₃, N₃ 18

 $C = C + Hg(N_3)_2$



Starting	Reagent (solvent)	cis-Product	trans-Product	Ref.	- # 1/1 · · · · · · · · · · · · · · · · · ·
compound		(mol. %)		-	
ÇO ₂ Me					
Me	Hg(OAc) ₂ (AcOH) Hg(OAc) ₂ —NaN ₃ , 1:3 (MeOH)	40 100	60	33	
CO ₂ Me					
H	$Hg(OAc)_2$ (AcOH) $Hg(OAc)_2$ —NaN ₃ , 1:3 (MeOH)	80 100	20	3 3	
CO ₂ Me	Hg(OAc) ₂ (AcOH, MeOH) Hg(OAc) ₂ —NaN ₃ , 1:3 (MeOH)	100	100	19 4	
$\langle \rangle$	Hg(OAc) ₂ (AcOH)	100		20	
CO ₂ Me	$Hg(NO_3)_2$ (MeOH) $Hg(OAc)_2$ —NaN ₃ , 1:2 (MeOH)	100	Mainly	20 5	
CO ₂ Me	Hg(OAc) ₂ (AcOH) Hg(OAc) ₂ (MeOH)	100 34	66	6 6	
CO ₂ Me	$Hg(NO_3)_2$ (MeOH) $Hg(OAc)_2$ —NaN ₃ , 1:3 (MeOH)	23 100	77	6 6	
	Hg(OAc) ₂ (AcOH) Hg(NO ₃) ₂ (MeOH) Hg(OAc) ₂ —NaN ₃ , 1:3 (MeOH)	100 60 100	40	7 7 7	
	Hg(OAc) ₂ (MeOH) Hg(OAc) ₂ -NaN ₃ , 1:3 (MeOH)	7 60	93 40	8 8	
\bigcirc	Hg(OAc) ₂ (MeOH) Hg(OAc) ₂ —NaN ₃ , 1:3 (MeOH)		100 100	15 4	

Table 4. Effect of the nature of the reagent on the stereochemistry of mercuration of cyclic unsaturated compounds

In our opinion, the features of the azidomercuration of nonstrained alkenes are, to a considerable extent, determined by the properties of the azido group. The azido group is a reactive nucleophile and should be a weak nucleofuge, since, within a certain range, the nucleofugicity of leaving groups changes oppositely to their nucleophilicity.²¹ For this reason, loosening a Hg-N₃ bond involved in the formation of an ion pair requires a considerable activation energy, the value of which evidently determines the low overall rate of the azidomercuration of alkenes by a multistep mechanism. On the other hand, the nucleophilic properties of N₃⁻ favor quicker transformation of ion pair **18** into azido adducts than into free ions. Otherwise, one would expect that solvoadducts form along with compound **15**.

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