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THE CIS-ALKOXYMERCURATION OF STRAINED OLEFINS

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Alkoxymercuration reactions with olefins usually proceed by a trans-addition involving alcohol solvent; however, in those cases where the olefin is bicyclic or strained, cis-addition usually prevails.[2] cis-Alkoxymercuration with mercuric acetate has also been accompanied by the formation of 2-acetoxymercurials in addition to 2-alkoxymercurials.[2] The inclusion of sodium acetate in the reaction mixture, which has no noticeable effect when trans-oxymercuration is involved, markedly increases the amount of cis-acetoxyalkylmercury salts formed with bicyclic olefins.[2] Four-center and six-center transition states have been suggested to account for the two products observed.[2]

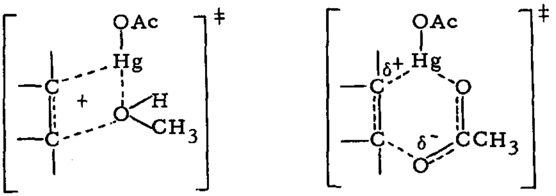
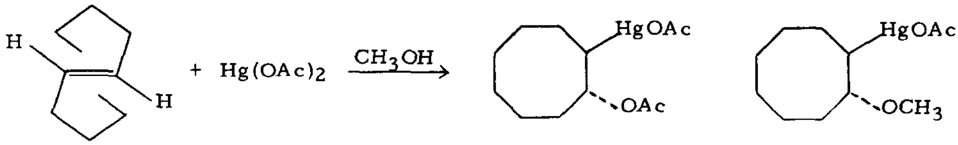


Figure 1

The highly strained olefin, trans-cyclooctene (1), is uniquely suited for a study of cis-electrophilic addition since the molecule is only accessible to attack from one side of the double bond. Examination of molecular models indicates that trans attack by solvent on a mercurinium ion intermediate would be precluded by steric exclusion, due to the methylene groups that comprise the ring. The cis-methoxymercuration of trans-cyclooctene with $Hg(OAc)_2$ in methanol has been reported[3] to afford an undisclosed amount of trans-2-acetoxycyclooctylmercuric acetate (2) in addition to the expected trans-2-methoxy compound 3. We wish to report our results on the effect of added salts on the cis-oxymercuration of trans-cyclooctene and norbornene. This data provides evidence against a four-center mechanism and for the intermediacy of a mercurinium ion.



(1)

1 2 3

Oxymercuration of cis-cyclooctene, with an equimolar quantity of mercuric acetate in methanol at 25°, afforded **3** by the usual trans-addition. Reaction with **1** under the same conditions results in cis-addition, affording a mixture of **2** (46%) and **3** (54%). The product ratios were determined by nmr analysis where the ratio of acetate bonded to carbon (CH_3, 2.07 δ, s) to free acetate (CH_3, 2.02 δ, s) was measured.[4]

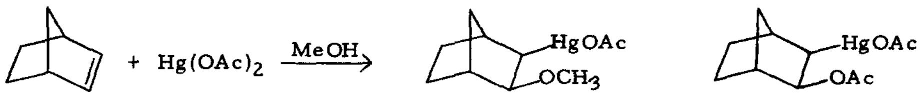
It had been previously reported that the thermodynamic product of methoxymercuration of **1** was the methoxymercurial **3** if the reaction was allowed to stir for three days.[3] We have found the half-life of interconversion of **2** to **3** to be 2.0 hr at 37° in methanol. The exchange reaction was shown to be catalyzed by the addition of one molar equivalent of sodium acetate ($t_{1/2} = 0.5$ hr).

The addition of sodium acetate to the oxymercuration reaction mixture of **1** with $Hg(OAc)_2$ in CH_3OH resulted in a pronounced increase in the ratio of **2** to **3** (Table 1). More importantly, the inclusion of anions other than acetate also resulted in the formation of up to 94% of the 2-acetoxymercurial **2**. Therefore, the previously reported[2] effects of added sodium acetate affording **6** is not necessarily decisive evidence for a six-center mechanism. The general trend observed is that addition of ligands that form covalent bonds with mercury afford an increase in the percentage of **2**, while relatively weak ligands, such as perchlorate ion, result in a decrease in **2**. Nucleophilic anions in the reaction mixture should increase the concentration of free acetate in solution by displacement of acetate from mercury and decrease the concentration of ^{+}HgX by decreasing the ionization of the mercuric salt. A substantial increase in the percentage of **2** upon addition of methoxide ion strongly argues against a four-center mechanism.[2, 3] The equilibrium described by equation 2 would predict the opposite result if a mechanism involving $CH_3O\text{-}HgX$ were operating. Furthermore, orbital symmetry considerations suggest that concerted four-center nonidentical addenda of X-Y to an olefin

$$Hg(OAc)_2 + {}^{-}OCH_3 \rightleftarrows CH_3OHg(OAc)_2^{-} \rightleftarrows CH_3OHgOAc + OAc^{-} \qquad (2)$$

would be partly forbidden although the net bonding in such a transition state is probably not zero. We are, therefore, suggesting that a six-center transition state (Figure 1) cannot by itself afford both **2** and **3** and the suggested[2] mechanism for cis-oxymercuration must be modified to explain the effect of added X^{-} (Table 1).

Oxymercuration of norbornene (**4**) with $Hg(OAc)_2$ in methanol afforded 94% of the methoxymercurial **5** (eq. 3). The effect of added chloride ion on the ratio of **5** to **6** is



(3)

4 **5**, 94% **6**, 6%

TABLE 1

Effect of added NaX on the products of cis-addition to 1 with $\mathrm{Hg(OAc)_2}$[a]

X^-	molar equivalents of X^- per mole of $\mathrm{Hg(OAc)_2}$	2, %	3, %
		46	54^b
AcO^-	0.10	79	21^c
AcO^-	0.15	87	13
AcO^-	1.0	90	10
AcO^-	2.0^d	94	6
ClO_4^-	1.0	27	73
NO_3^-	0.33^e	58	42
F^-	1.0	63	37
CH_3O^-	1.0	81	19
Cl^-	0.1	75	25
Cl^-	1.0	94^f	6
I^-	1.0	90	10

a) Reaction times were 5 min. in anh. methanol with olefin and $\mathrm{Hg(OAc)_2}$ concentrations 0.33M.
b) Product ratio obtained in the absence of added salts.
c) All results are an average of at least two experiments that agree within ±2% as determined by $NaBH_4$ reduction and GC analysis.
d) Addition of 3.0 and 4.0 equivalents of acetate ion resulted in the same product ratio as 2.0 equivalents.
e) A solution saturated with nitrate ion gave identical results.
f) The yield of acetate was shown to be 96% by nmr; the isolated acetate 2 (as HgCl) had mp 103-105° (lit[3] 93-94°).

comparable to or greater than that of acetate ion [2] (Table 2). An identical ratio of 5 to 6 (16/84) was obtained when $HgCl_2$ was utilized with two equivalents of acetate ion in solution. Since chloride ion has a much greater affinity for mercury than acetate ion, the concentration of AcO-Hg-X in solution should be extremely low.

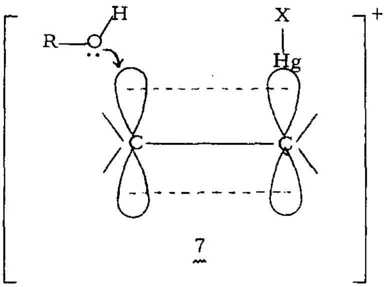
TABLE 2

Effect of added NaX on the cis-addition to norbornene[a]

X^-	molar equivalents of X^- per mole of $\mathrm{Hg(OAc)_2}$	5, %	6, %
		94^b	6
OAc^-	1.0	21	79
Cl^-	1.0	19	81
Cl^-	2.0	19	81
OAc^-	2.0^c	16	84

a) Reaction times were 30 min. at 25° with olefin and $\mathrm{Hg(OAc)_2}$ concentrations 0.1M.
b) Product ratio obtained in the absence of added salts.
c) 1 equivalent of $HgCl_2$ was employed instead of $\mathrm{Hg(OAc)_2}$.

The recent theoretical[5] and experimental evidence[6] for mercurinium ions strongly supports a mechanism wherein 3 and 5 are derived from attack of solvent methanol on an unsymmetrical mercurinium ion[5] intermediate 7, formed by attack of the nucleophilic olefi 1 and 4 on mercuric acetate. However, at this time we cannot discern whether the 2-acetoxymercurials 2 and 6 arise by attack of free acetate ion in solution on 7, where formation of an unsymmetrical cation must precede bond formation of acetate to carbon, or by a tight ion pair between 7 and acetate ion which closely resembles a six-center mechanis It is quite plausible that both mechanisms are operating. Additional work to clarify this poin is in progress.



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4. The nmr results were in excellent agreement with product ratios determined by reduction of the mercurials with $NaBH_4$ followed by GC analysis.

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