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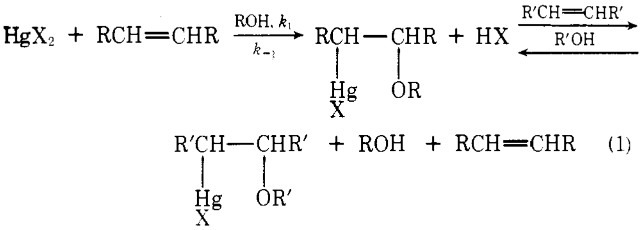
Mechanism of Alkene Exchange Reactions with Oxymercurials

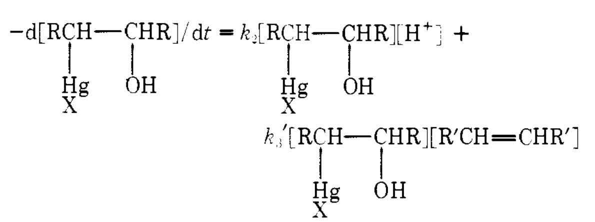
Sir:

The reaction of a mercuric salt in a protic solvent with an alkene affords an oxymercurial. It has recently been shown that oxymercurials with ionic ligands undergo facile exchange reactions with alkenes and alkoxy and hydroxy



$$\mathrm{HgX_2 + RCH{=}CHR \underset{k_{-1}}{\xrightarrow{ROH,\,k_1}} \underset{\underset{X}{Hg}}{RCH}{-}\underset{OR}{CHR} + HX \underset{R'OH}{\overset{R'CH=CHR'}{\rightleftarrows}} \underset{\underset{X}{Hg}}{R'CH}{-}\underset{OR'}{CHR'} + ROH + RCH{=}CHR} \qquad (1)$$

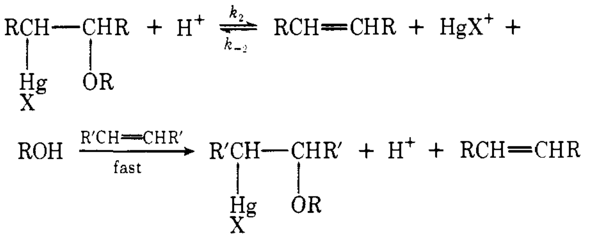
groups in protic solvents[1-3] (eq 1). The alkoxy exchange has been shown[2] to exhibit pseudo-first-order kinetics while the alkene exchange reaction of hydroxymercurials in aqueous medium has been established by Halpern[1] to accurately obey the rate law described in eq 2. The two terms in the



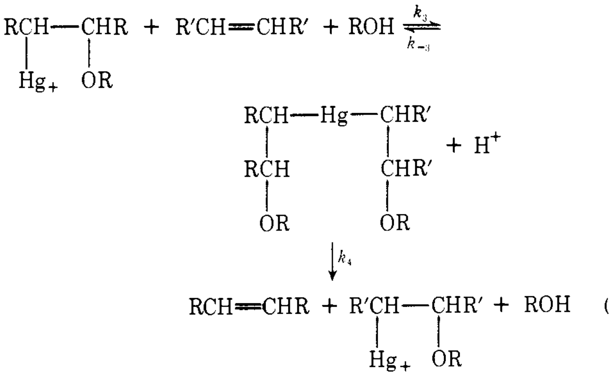
$$-d[\underset{\underset{X}{Hg}}{\mathrm{RCH}}{-}\underset{OH}{\mathrm{CHR}}]/dt = k_2[\underset{\underset{X}{Hg}}{\mathrm{RCH}}{-}\underset{OH}{\mathrm{CHR}}][\mathrm{H^+}] + k_3'[\underset{\underset{X}{Hg}}{\mathrm{RCH}}{-}\underset{OH}{\mathrm{CHR}}][\mathrm{R'CH{=}CHR'}] \qquad (2)$$

rate law were ascribed to a reversible deoxymercuration reaction (eq 3, OR = OH) and the formation of a covalently bonded transient bisoxymercurial intermediate (eq 4, OR = OH). A similar mechanism for alkene exchange was considered by Pritzkow[3] in an extensive kinetic investigation that also was unable to distinguish between a bimolecular exchange mechanism or one that involved a bisoxymercurial intermediate as in eq 4.

Our previous study showed that alkoxy exchange was facilitated by both protic acid and an excess of alkene in solution. To explain the rate enhancement due to the presence of an alkene, we postulated a mechanism involving nucleophilic attack by the exchanging alkene on the mercury atom of the oxymercurial. However, our data could not exclude the mechanism given in eq 4. We therefore elected to use an optically active oxymercurial in an exchange reaction with a racemic alkene. The resulting diastereomeric transition states involved in this exchange have afforded unequivocal evidence that *both* the optically active oxymercurial and the exchanging alkene are coordinated to the mercury in the rate limiting step. Our experiments provide a unique mechanistic probe that supplements the existing kinetic data on exchange reactions with both hydroxy-[1] and alkoxymercurials.[3] We also report evidence that precludes the formation of a bisoxymercurial (eq 4) as a major pathway in the exchange reaction of an alkoxymercurial.



$$\mathrm{\underset{\underset{X}{Hg}}{RCH}{-}\underset{OR}{CHR} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} RCH{=}CHR + HgX^+ + ROH \underset{fast}{\xrightarrow{R'CH=CHR'}} \underset{\underset{X}{Hg}}{R'CH}{-}\underset{OR}{CHR'} + H^+ + RCH{=}CHR} \qquad (3)$$



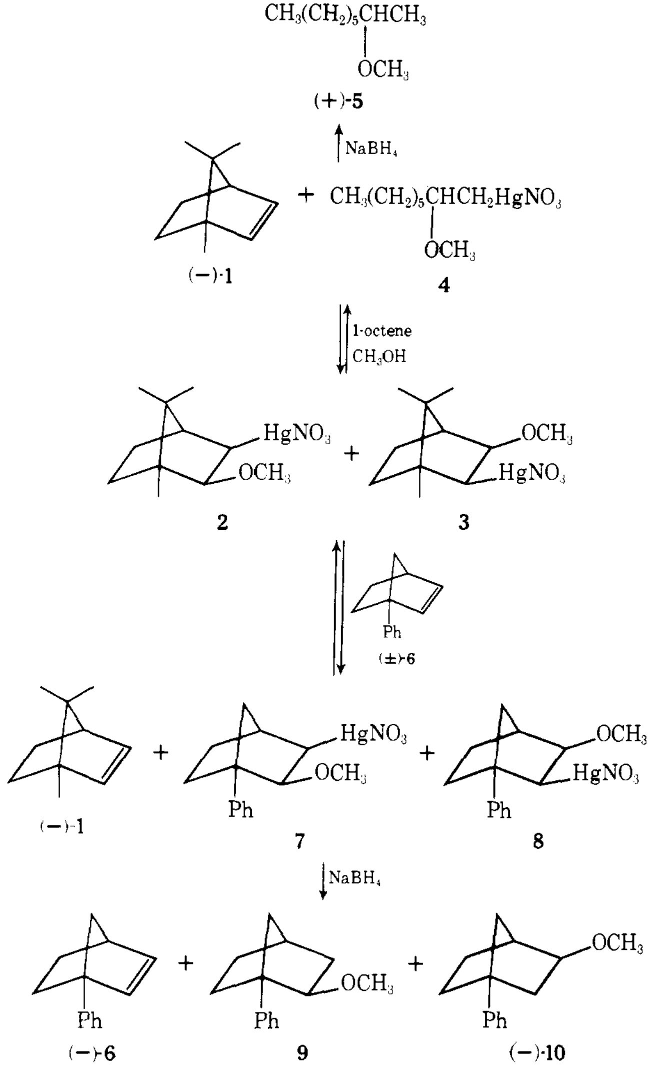
$$\mathrm{\underset{Hg_+}{RCH}{-}\underset{OR}{CHR} + R'CH{=}CHR' + ROH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \underset{\underset{OR}{RCH}}{RCH}{-}Hg{-}\underset{\underset{OR}{CHR'}}{CHR'} + H^+ \xrightarrow{k_4} RCH{=}CHR + \underset{Hg_+}{R'CH}{-}\underset{OR}{CHR'} + ROH} \qquad (4)$$

The methoxymercuration of optically active bornylene (**1**), $[\alpha]_D$ −24°, with $Hg(NO_3)_2$ and HgO (1:1) in methanol (16 hr) afforded the methoxymercurials **2** and **3** in a ratio of 2 to 1.[4] One equivalent of 1-octene was added and after 1 hr at 25° 7% exchange (eq 1) had occurred affording **1** and **4** (Scheme I). The reaction was quenched by the addition of basic $NaBH_4$. Optically active **1** was recovered from the reaction mixture and the isolated 2-methoxyoctane (**5**) had $[\alpha]_D$ +2.0°.[5] A repeat of this experiment employing **1** and $Hg(NO_3)_2$ in CH_3OH (2 hr) afforded **2** and **3** in the presence of 1 eqiv of HNO_3.[4] Exchange with 1-octene (0.8 equiv) was 5-6% complete after 10 min and the resulting methyl ether **5** had $[\alpha]_D$ +4.2°. The optical purity of **4**[6] was dependent upon the reaction time since the degenerate exchange of 1-octene with **4** resulted in loss of optical activity. However, optical yields of **5** as high as 36%[6] were observed when the exchange reaction was not allowed to go to completion.

Induced asymmetry was also observed when 1 equiv of racemic 1-phenylnorbornene (**6**) was added to a mixture of **2** and **3** in CH_3OH. Analysis by glpc indicated that about 8% exchange has occurred in 5 min when 1 equivalent of HNO_3 was present. The methoxy ethers **9** and **10** ($[\alpha]_D$ −0.6°) were produced in a ratio of 1 to 9.6.[8] Recovery of the unreacted alkene **6** showed that it was also optically active and had $[\alpha]_D$ −1.1°.

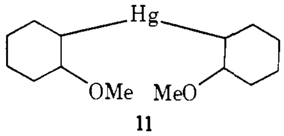
The observation of enantiomeric enrichment of the oxymercurials resulting from exchange of an alkene with optically active **2** and **3** precludes the reversible oxymercuration-deoxymercuration pathway (eq 3) as being the dominant exchange mechanism in good agreement with the ki-

Scheme I

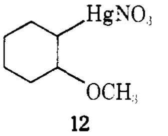


netic data.[1] More significantly, however, our results provide compelling evidence that the optically active oxymercurial and the exchanging alkene are in very close proximity in the transition state. The steric bulk of the exchanging alkene is also of obvious importance since exchange reactions of **2** and **3** with norbornene and *trans*-cyclooctene did not result in significant asymmetric induction.

The above results, however, do not necessarily exclude a transient dialkoxymercurial intermediate (eq 4). Consequently, we synthesized[10] the dialkoxymercurial **11** and examined its reactivity under typical exchange conditions. Treatment of **11** with 1 equiv of $Hg(NO_3)_2$ in CH_3OH afforded the methoxymercurial **12**[11] as determined by nmr analysis ($\delta(OCH_3)$ 3.345 ppm, analyzed as the mercurichloride). However, treatment of **11** with 1 equiv of **12** in CH_3OH resulted in >90% decomposition of **11** (135 min) with formation of **12**, elemental mercury, cyclohexene, and an unidentified methoxymercurial. Compound **11** is stable in neutral CH_3OH,[11] but it does not exchange with 1-octene.[11] More significantly, **11** is *not* stable in the presence of protic acid in methanolic solution. One equivalent of nitric acid in CH_3OH solution effected complete cleavage[11] of the carbon-mercury bond in **11** affording **12** and cyclohexyl methyl ether. However, a stirring solution of **12** in the presence of 1 equiv of cyclohexene and HNO_3 (*i.e.*, degenerate exchange conditions) failed to produce a detectable amount of cyclohexyl methyl ether or other side products even after 5 days. These results are, therefore, not consistent with eq 4 where acid cleavage (k_4) would afford an alkene and an alkoxymercurial.



11



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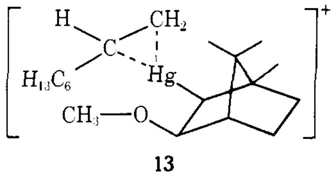

13

The above observations support our earlier suggestion that alkene exchange proceeded by electrophilic addition of the mercury of the oxymercurial to the exchanging alkene affording a bisalkene mercury cation such as **13**. A more precise assignment of the mechanism must await detailed kinetic studies of this alkoxy-exchange reaction. The involvement of **13** is consistent with the rate law given in eq 2[1] for exchange of hydroxymercurials where $k_3' \gg k_2$ and is supported by the unusually high optical yields obtained in the present work.

Acknowledgment. Acknowledgment is made to the National Institutes of Health (ES 00761-03) for support of this work.

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(4) The use of equimolar amounts of HgX_2 and HgO affords the oxymercurial in the absence of the mole of HX usually produced.
(5) The per cent exchange was kept at a minimum since the degenerate exchange of **4** with 1-octene resulted in a loss of optical activity.
(6) Optically pure (*S*)-(+)-2-methoxyoctane (**5**) having $[\alpha]_D$ +10.7° was prepared from 2-octanol $[\alpha]$ +11.2°, CCl_4 (92% optically pure)[7] by the action of NaH and CH_3I in ether.
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The Three-Phase Test for Reaction Intermediates. Nucleophilic Catalysis and Elimination Reactions

Sir:

In a recent communication[1] we introduced a technique for the detection of reaction intermediates which promises to be of complementary value to direct observation and kinetic methods. The technique involves the generation of a reaction intermediate from an insoluble polymeric precursor, and its detection by trapping on a second solid phase suspended in the same solvent (Scheme I).

Unlike classical trapping experiments, the direct reaction of precursor and trapping agent is physically prohibited in