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THE ADDITION OF WATER AND ALCOHOLS TO ALLENES CATALYZED BY MERCURIC SALTS

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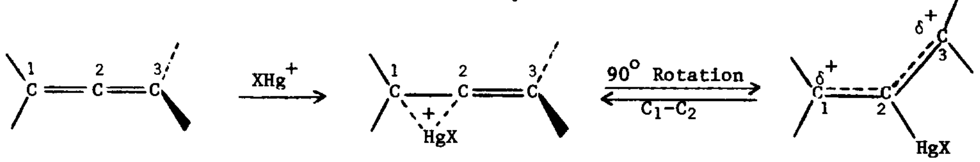
The preferred mechanism for the oxymercuration of olefins involves a bridged or π-complexed mercurinium ion intermediate.[2] Several investigators have recently suggested that mercurinium ion intermediates are involved in the alkoxymercuration of allenes.[3,4] Waters and Caserio[5] have also reported the addition of mercuric acetate to optically active 2,3-pentadiene in methanol to proceed by a trans addition affording an optically active product.

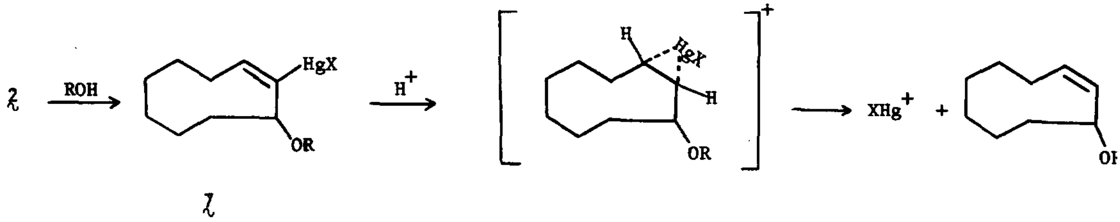
We wish to report our results on the hydration and alkoxymercuration of optically active 1,2-cyclononadiene (1) and to suggest mercuric oxide and boron trifluoride etherate as an effective catalyst for the addition of alcohols to substituted allenes. Since the p-orbitals involved in the formation of the mercurinium ion 2 are orthogonal to the p-orbitals of the adjacent double bond, the oxymercuration of an optically active allene is of particular interest. If 2 is of sufficient stability to overcome the considerable allylic resonance energy to be gained by a 90° C_1-C_2 bond rotation, an optically active product will result. Alternatively, if the reaction proceeds through a planar allylic carbonium ion 3, the resulting products should be racemic.



2 3

The mercuric oxide - boron trifluoride etherate catalyzed addition of ethanol to optically active 1,2-cyclononadiene[6] afforded 3-ethoxy-cis-cyclononene (4)[3] that had $[\alpha]^{25}_{D}$ + 17.7° (C 1.21 CH_2Cl_2). Similarily, the addition of methanol to 1 catalyzed by $HgO{\cdot}BF_3$ afforded optically active 3-methoxy-cis-cyclononene (5) $[\alpha]^{25}_{D}$ + 7.3 (C 3.11 CH_2Cl_2). The hydration of optically active 1 with mercuric sulfate and sulfuric acid[3] in water-dioxane solvent gave 3-hydroxy-*cis*-cyclononene (6) that had $[\alpha]^{25}_{D}$ + 8.3° (*C* 6.00 CH_2Cl_2). Compound 6 was converted by the Williamson ether synthesis to 5 that had $[\alpha]^{25}_{D}$ + 5.3° (*C* 4.40 CH_2Cl_2).

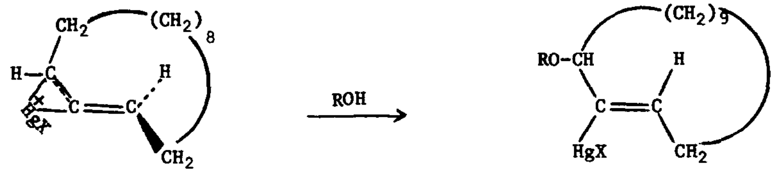
The formation of optically active products in the above reactions provides convincing evidence for the intermediacy of the mercurinium ion 2. The formation of the *cis*-product from 1 requires attack of XHg^+ *cis* to the hydrogen on the adjacent double bond, i.e., from the "outside" of the ring. Although we have not yet established whether the solvent is attacking 2 by *trans* addition or by front side displacement of HgX, the direction of solvolysis is the same for both hydration and addition of alcohols to 1. The direction of attack by solvent on 2 determines the absolute configuration at C_1, but has no effect on the stereochemistry of the double bond in the product. The intermediate organomercury derivative 7 is not isolated under these conditions, but acid catalyzed cleavage of the carbon-mercury bond[7] results as outlined below. Solvolysis of 2



occurred almost exclusively at C_1 affording allylic products with only trace quantities of cyclononanone being observed by vpc.[3] The structure of 6 was confirmed by spectral and chemical means. The position of the double bond was established by Jones oxidation of the allylic alcohol to afford the conjugated ketone, 2-cyclononenone.[10] Catalytic hydrogenation of 5 gave methoxycyclononane which was identical in all respects to an authentic sample synthesized from cyclononanone.

The carbon atom attacked by solvent observed here and previously[3-5] is in disagreement with a report by Petrov and Fedorova[8] which states that ketones are the only products formed by the addition of water and alcohols to allenes irrespective of the structure of the diene. Terminal allenes, however, do afford ketones under the above reaction conditions.[9]

The addition of water and alcohols to racemic 1,2-cyclotridecadiene (8) yielded products with the same orientation of addition to the allene, but with a *trans*-double bond. Thus, treatment of 8 with $HgSO_4 \cdot H_2SO_4$ in methanol gave a 65% yield of 3-methoxy-*trans*-cyclotridecene. Similarly, the catalytic action of $HgO \cdot BF_3$ on 8 in ethanol afforded 3-ethoxy-*trans*-cyclotridecene in 78% yield. The structure of the addition products to 8 was established in a similar manner to that used for 4. The assignment of a *trans*-double bond is based on a strong infrared absorption in the 975 cm^{-1} region. In order to obtain the *trans*-adduct the mercurinium ion 9 must be formed by addition of XHg^+ *cis* to the methylene group on the adjacent double bond. Stereospecific acidolysis of the solvolysis product 10 would then afford the observed products with a *trans*-double bond. Since the thermodynamic stability of the products seems to be important in these reactions, it may be suggested that the transition states for solvolysis of the mercurinium ions in the above reactions, as well as with linear allenes,[4] should more closely resemble the products[11] than the starting dienes. The stereochemistry of the products should then be determined to a large extent by the



9 10

difference in free energy between the cisoid and transoid transition states leading to the cis and trans allylic products. This argument is consistent with the exclusive formation of the thermodynamically more stable cis isomer from 1. If the above argument is correct it is quite likely that the mercurinium ions involved in these reactions are not linear π-complexes, but that considerable rehybridization at C_1 and C_2 has occurred. Waters and Kiefer[4] have previously invoked a σ-bonded mercurinium ion to explain their results employing a steric argument.

The reaction of 1,2-disubstituted allenes with $HgO \cdot BF_3$ in alcohol solvents should prove to be a general method for the synthesis of allylic alcohols and ethers. The *in situ* acidolysis reaction has the advantage of not having to reduce an organomercurial to the alcohol addition product. In addition, only catalytic quantities (approximately 5 mole percent) of mercuric salt are required. In a typical experiment 0.4 g of 1 in 0.5 ml of ethanol was added dropwise to 0.06 g of red mercuric oxide and 40 μl of boron trifluoride etherate in 0.5 ml of ethanol. The reaction mixture stirred for 1-5 hr at room temperature and after extraction the product was isolated by distillation or by vpc. Although mercuric sulfate has traditionally been used with conc. sulfuric acid for the hydration of acetylenes and allenes, boron trifluoride etherate has proven to be an equally effective acid catalyst. Our results are summarized in Table 1.

TABLE 1

Additions to 1,2-Cyclononadiene

ROH	Catalyst	Product	Yield[b] %
CH_3-	$HgO \cdot BF_3$	3-methoxycyclononene	69
C_2H_5-	$HgO \cdot BF_3$	3-ethoxycyclononene	80
C_2H_5-	$HgSO_4 \cdot BF_3$	3-ethoxycyclononene	74
$(CH_3)_2CH$-	$HgO \cdot BF_3$	3-isopropoxycyclononene	81
$(CH_3)_3C$-	$HgO \cdot BF_3$	3-t-butoxycyclononene	63
$C_6H_5CH_2$-	$HgO \cdot BF_3$	3-benzyloxycyclononene	85
CH_3-	$HgSO_4 \cdot H_2SO_4$	3-methoxycyclononene	75
H-	$HgSO_4 \cdot H_2SO_4$[a]	3-hydroxycyclononene	78

[a] A co-solvent must be used to achieve a homogenous reaction mixture. Best results were obtained by using acetone-water (10:1).

[b] All yields are based on isolated material. Satisfactory elemental analyses were obtained for all new compounds. The nmr spectra were in accord with the proposed structures.

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