

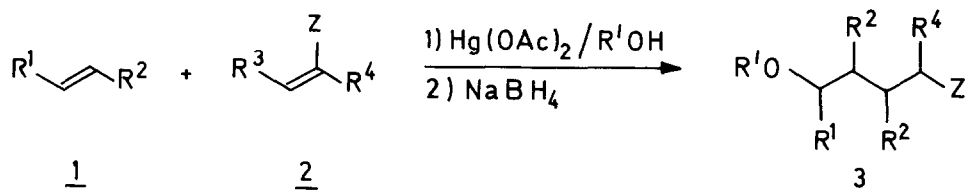
DIASTEREOSELECTIVITY OF THE MERCURATION
OF ACYCLIC ALLYLIC ALCOHOLS

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Summary: The diastereoselectivity of the mercuration of acyclic alkenes 4 can be reversed by changing the substituent in the allylic position; with alcohols the erythro isomers 5 and with esters or hemiacetals the threo isomers 6 and 8 are formed predominantly (Table I).

The solvomercuration of electron-rich alkenes 1 followed by reductive coupling with electron-poor alkenes 2 offers a versatile method for the synthesis of carbon-carbon chains.¹⁾ In the formation of products 3, up to four chiral C-atoms are generated depending on the number of prochiral vinylic C-atoms at alkenes 1 and 2. The first chiral center results from the ionic solvomercuration of alkene 1 whereas the other chiral centers in the product 3 are formed during radical addition²⁾ and radical abstraction reactions.³⁾ In this communication we describe the diastereoselectivity of the solvomercuration reaction of allylic alcohols and their derivatives.



It is well known that in cyclic alkenes the diastereoselectivity of the mercuration reaction can be reversed by changing the neighboring group.⁴⁾ Less is known about this effect in the solvomercuration of acyclic alkenes.⁵⁾

We have now shown that reactions of open chain allylic alcohols 4 (X=H) with equimolar amounts of $\text{Hg}(\text{OAc})_2$ in $\text{H}_2\text{O}/\text{THF}$ (1:1) and reduction with a two-fold excess of an alkaline solution of NaBH_4 give predominantly the erythro diols 5 ($\text{R}'=\text{H}$).⁶⁾ Under the same conditions allylic esters 4 (X= $\text{R}''\text{CO}$) yield, after solvolysis, the threo isomers 6 ($\text{R}'=\text{H}$) as main products. The formation of threo isomers dominates also in the reactions of hemiacetals 4 (X= Cl_3CCHOH) with $\text{Hg}(\text{CF}_3\text{CO}_2)_2$ in THF as solvent and reduction with NaBH_4 (Table I).

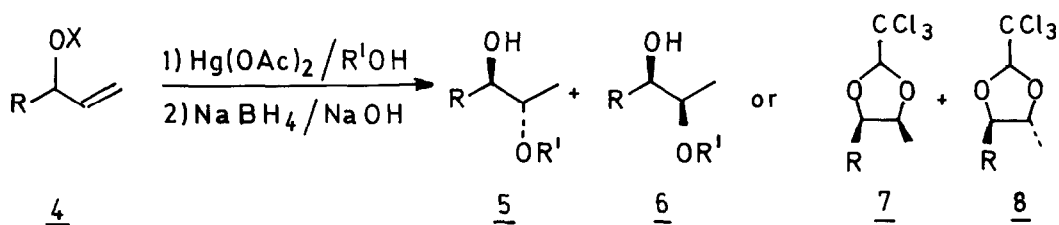


Table I

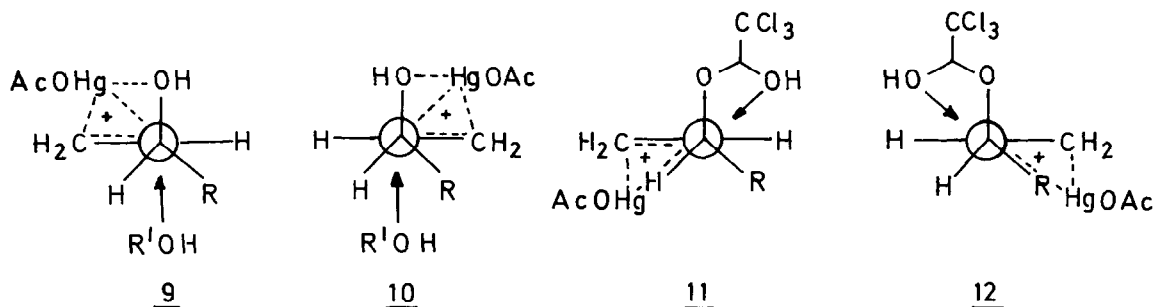
Diastereoselectivity of the mercuration of alkenes 4 (20°C)

R	R'	X	<u>5</u> : <u>6</u>	<u>7</u> : <u>8</u>	Yields (%)
C_2H_5	H	H	76:24		65
C_2H_5	CH_3	H	93:7		72
<i>i</i> - C_3H_7	H	H	80:20		67
C_6H_5	H	H	88:12		66
<i>t</i> - C_4H_9	H	H	98:2		70
C_2H_5	H	CH_3CO	39:61		63
C_2H_5	H	<i>t</i> - $\text{C}_4\text{H}_9\text{CO}$	35:65		60 ^{a)}
C_2H_5	H	$\text{C}_6\text{H}_5\text{CO}$	23:77		64
C_2H_5	H	Cl_3CCHOH		19:81	80
<i>t</i> - C_4H_9	H	CH_3CO	13:87		65
<i>t</i> - C_4H_9	H	Cl_3CCHOH		9:91	72

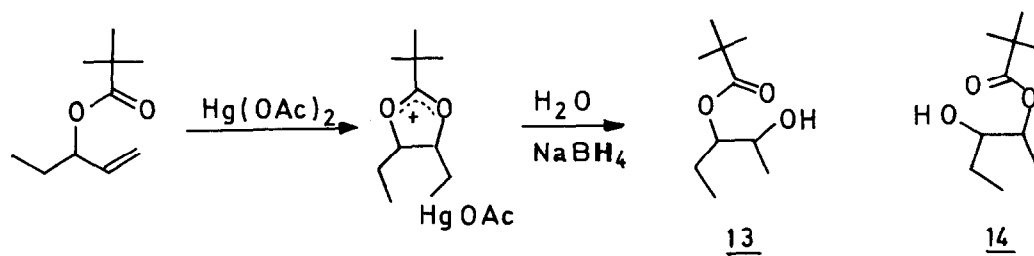
a) After reductive cleavage with LiAlH_4 .

The preferred formation of the erythro isomer 5 ($\text{R}'=\text{H}$) in the solvomercuration of allylic alcohols 4 (X=H) can be compared with the stereochemistry of peracid epoxidation⁷⁾ of similar alkenes in which the OH-group acts as a directing substituent for the electrophile. The formation of 5 ($\text{R}'=\text{H}$) proceeds faster because transition state 9 is less crowded than 10. That the

external nucleophile plays a role in these reactions is shown by the solvomercuration of 4 ($R=C_2H_5$, $X=H$) with CH_3OH in which the diastereoselectivity increases from 76:24 (H_2O) to 93:7 (Table I).



The formation of the threo product 8 occurs via intramolecular cyclization of the mercurated intermediate 11, which is less crowded than intermediate 12. The same reasoning can explain the preferred formation of the threo isomers 6 ($R'=H$) in reactions of allylic esters 4 ($X=R''CO$) if cyclic acyloxonium ions are formed which are attacked by water at the cationic C-atom⁸⁾ to give a mixture of regioisomers. This reaction sequence is proved by the pivalic ester 4 ($R=C_2H_5$, $X=t-C_4H_9CO$) in which the isomers 13 and 14 are formed in about equimolar amounts.



These mercuration studies show that the diastereoselectivity of two step reactions can be inverted if by variation of the neighboring group its stereodirecting effect acts either in the first step or in the second step.

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