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OXYMERCURATION AND DEMERCURATION OF CYCLIC ALLENES

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We have previously reported[1] the oxymercuration of some cyclic allenes in ethanol. The only product from the reaction was proposed as 2-chloromercury-3-ethoxy cyclic olefin. The structure was assigned on the basis of elemental analyses, spectral properties and chemical evidence. At that time we did not establish the stereochemistry of the vinylic organomercurials. The present communication describes the stereochemistry of the vinylic organomercurials and also the study of the stereochemistry of the chemical reduction of vinylic carbon-mercury bond with sodium borohydride which will throw some light on the behaviour of the intermediate vinylic radical in medium and large rings.

Methoxymercuration of cyclic allenes (1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-cycloundecadiene and 1,2-cyclotridecadiene) with mercuric chloride gave solid mono adducts whose NMR data are recorded in Table 1. The Hg^{199}-H^1 coupling could be traced only in the low field region and it was completely masked by side bands of methyl group in the high field. The coupling constants indicate that mercuric chloride addition to C-9 and C-10 allenes gives rise to cis-adduct whereas addition to C-11 and C-13 allenes provides trans-product.[2] The genuinity of the satellites was further confirmed by the conversion of the organomercurial into an iodo compound which did not exhibit any line in the low field region. Furthermore, the geometry of the double bond was derived from the chemical shifts of the vinylic and methine protons, which are considerably different for cis and trans compounds.

The three possible reaction intermediates in the electrophilic addition of mercuric chloride to cyclic allenes are a bridge ion (1), a non-planar allylic cation (2) and a planar

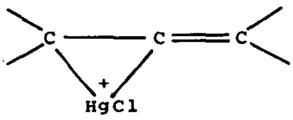
TABLE 1

NMR Data of Cyclic Vinylic Organomercurials

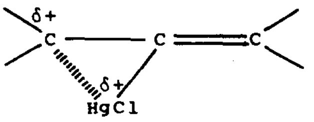
Compound	=CH- (δ)	-CH-O- (δ)	-O-CH$_3$ (δ)	Allylic -CH$_2$- (δ)	Ring -CH$_2$- (δ)	J(HgC=CH) (Hz)
$C_{10}H_{17}OHgCl$	5.80 (t,1)	4.30 (bd,1)	3.25 (s,3)	2.20 (bm,2)	1.40 (m,10)	330
$C_{11}H_{19}OHgCl$	5.80 (q,1)	4.60 (bd,1)	3.25 (s,3)	2.20 (bm,2)	1.40 (m,12)	334
$C_{12}H_{21}OHgCl$	6.50 (q,1)	3.80 (bd,1)	3.30 (s,3)	2.00 (bm,2)	1.40 (m,14)	530
$C_{14}H_{25}OHgCl$	6.30 (q,1)	3.80 (bd,1)	3.30 (s,3)	2.10 (bm,2)	1.30 (m,18)	550

The numbers in parentheses give the number of protons; (t) = triplet; (q) = quartet, (bd) = broad doublet, (s) = singlet and (m) = multiplet.

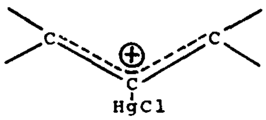
allylic cation (3). Conversion of 2 to 3 cannot be ruled out. Bach[3] has recently investigated the oxymercuration of optically active 1,2-cyclononadiene and has shown that the amount of recemization depends on the mercuric salt used. Further, Linn and others[4] have found out that mercuric chloride addition to optically active 2,3-pentadiene leads to the formation of racemic products through the intermediate 3, while mercuric acetate addition is stereospecific as it goes through 1.



1



2



3

When an allenic bond is incorporated in a carbocyclic ring, there are two modes of attack of the electrophile ($\overset{+}{Hg}Cl$), one from the hydrogen side and the other from the ring side. The former eventually gives rise to a cis double bond and the latter trans. Mercury(II) addition from the ring side is more hindered than the hydrogen side due to the presence of methylene hydrogens. The immediate change from *cis* to *trans* configuration as one ascends the series from C-10 to C-11 is difficult to conceive. If a planar allylic cation (3) is assumed to be the potential intermediate in this reaction, one would expect C-9 and C-10 allenes should favour the *cis* organomercurial and C-11 and C-13 allenes the *trans* compound on the basis of the stability of the allylic intermediate (3) in these rings.

The results on the stereochemical fate of the carbon-mercury cleavage from the stereochemically pure organomercurials with sodium borohydride are shown in Table 2. The identity and estimation of the isomeric allylic ethers have been established by NMR. Pasto and Gontarz[5] have shown that the reduction of alkyl and allylic organomercurials with sodium borohydride goes through radical intermediate. If such a mechanism is assumed to operate in the reduction of vinylic organomercurials also, only the *cis*-vinylic radical generated from *cis*-$C_{10}H_{17}OHgCl$ retains its configuration. The most probable reason is that the rehybridisation process of *cis*-vinylic radical in C-9 ring needed to achieve equilibration with its configurational isomer is prevented as it makes two collinear bonds which introduces more strain in the ring. Moreover, the *cis*-isomer is much more stable than the *trans* in a nine-membered ring,[6] and hence the product stability may dictate the stereochemical course of the reduction. Our results with organomercurials from C-10, C-11 and C-13 allenes point out that the thermodynamically more

TABLE 2

Sodium Borohydride Reduction of Cyclic Vinylic Organomercurials

Compound	Product(s)	Yield (%)
cis-$C_{10}H_{17}OHgCl$	3-methoxycyclononene (*cis*, 100%)	72
cis-$C_{11}H_{19}OHgCl$	3-methoxycyclodecene (*cis*, 78%; *trans*, 22%)	54
trans-$C_{12}H_{21}OHgCl$	3-methoxycycloundecene (*cis*, 15%; *trans*, 85%)	80
trans-$C_{14}H_{25}OHgCl$	3-methoxycyclotridecene (*cis*, 15%; *trans*, 85%)	76

stable isomer predominates in the isomeric mixture.[6] So we conclude that the vinylic radical (*cis* or *trans*) generated in these cases is capable of achieving partial equilibration with its configurational isomer, but the radical is trapped before complete equilibration as the results are the same in organomercurials from C-11 and C-13 allenes. Similar results have been obtained in the reduction of isomeric 2-bromo-2-butenes with tri-*n*-butyltin hydride[7] and also from the reduction of isomeric 3-chloro-3-hexenes with sodium naphthalenide.[8]

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