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THE ADDITION OF HOBr TO ALLENE
SECONDARY DEUTERIUM ISOTOPE EFFECTS

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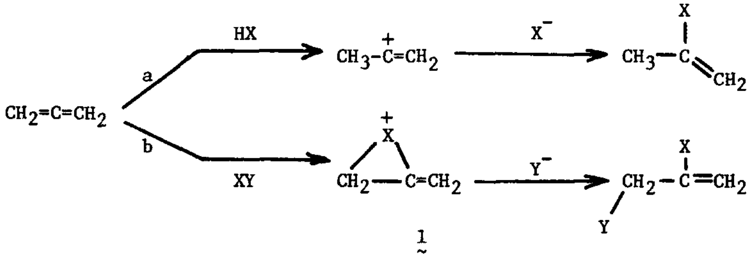
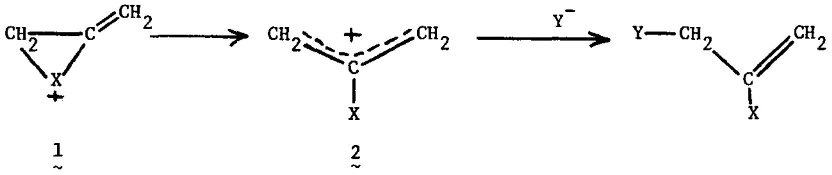
Electrophilic additions to allene interestingly proceed with orientations for addition which are very much dependent upon the nature of the electrophile.[2] Additions involving a proton as the reactive electrophile, for example, proceed with almost exclusive attack at the terminal methylene position, while additions of halogens or arene sulfenyl halides proceed with apparent initial attack at the central carbon atom. In order to rationalize these discordant results, it has been hypothesized that in cases where a stable "onium" ion (1) can be formed, the overall addition can be depicted as in path b below.[2] The case for "onium" ion intermediacy has been enhanced by the direct observation of bromonium ion 1 (X=Br) in $SbF_5 \cdot SO_2$ solution at -80°.[3]



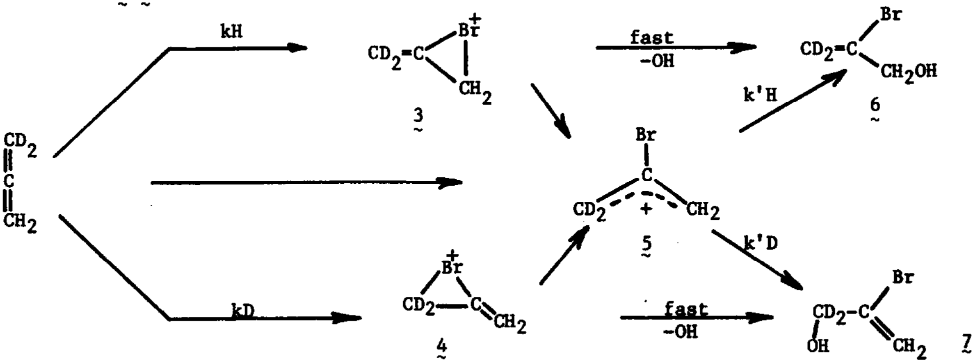
While most workers in the field accept the concept of initial "onium" ion formation, there is still some question regarding the possible intervention of the 2-substituted allyl cations (2) at a later stage of the mechanistic process.[4,5] Studies by Jacobs[5] and Caserio[6] on electrophilic additions to optically active allenes seem to indicate that



2-bromoallylcations can potentially intervene in such reactions. We wish to present direct kinetic evidence for the formation of a bromonium ion in the addition of HOBr to allene, evidence which will also be seen to exclude the subsequent intervention of the 2-bromoallyl cation.

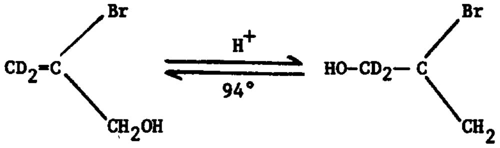
We have demonstrated the effectiveness of kinetic secondary deuterium isotope effects in probing the mechanism of allene cycloadditions.[7] Formation of bromonium ion 1 is formally a cycloaddition process and should thus give rise to predictable isotope effects.

In addition of Br^+ to 1,1-dideuterioallene k_D should be significantly greater than k_H if bromonium ions 4 or 3 are to be formed respectively. The excess of 4 would be reflected by the ratio of 7/6, as determined by nmr analysis. If on the other hand, the 2-bromoallyl cation, 5, is the initially formed intermediate, or if it intervenes after the bromonium ions 3 and 4, then the only observable isotopically discriminatory steps would be those of rapid carbonium ion destruction, k'_H and k'_D. Being a highly exothermic, low-activation-energy process,[8] with a transition state which would thus resemble most closely 5 rather than 6 or 7, a negligible isotope effect would be predicted for this mechanistic pathway. It should be said, however, that this reasonable prediction has never been experimentally tested.[9]



The reagent HOBr was chosen to generate the desired bromonium ion because of the stability to equilibration of the kinetically-controlled 2-bromoallyl alcohol products. We and others have shown that the allyl bromide products derived from Br_2 addition are very prone to isomerization with consequent equilibrations of the deuterium label.[11] HOBr[12] was added at room temperature to 1,1-dideuterioallene[14] in a closed system under vacuum.

Separation and purification of the deuterated 2-bromoallyl alcohols were achieved by glpc. The yield was 20% with the remainder of the allene having been competitively converted to acetone under the acidic aqueous conditions. There was no evidence of destruction of the 2-bromoallyl alcohol products by further reaction under the reaction conditions. The nmr spectrum of 2-bromoallyl alcohol (in CCl_4) exhibits peaks at δ 5.88 (doublet, 1H), 5.52 (doublet, 1H), 4.13 (singlet, 1H) and 3.85 (singlet, 2H). At least 10 integrations were utilized to produce a ratio of allylic to vinylic protons which gave a kinetic isotope effect of $k_H/k_D = 0.83 \pm .01$.



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In order to demonstrate that the isotope effect was indeed a kinetic effect, the deuterated 2-bromoallyl alcohol mixture was subjected to equilibration in $0.4NH_2SO_4$ solution[15] for 6 hours and then 10 hours at 94°. The observed equilibrium isotope effect was found to be $0.77 \pm .01$ after each equilibration. Such a determination of the thermodynamic isotope effect by a carbonium ion rearrangement process, has to our knowledge not been done before. This value corresponds to a $k_D/k_H = 1.17$ per deuterium at 25° and it compares well with the calculated value for such a process, 1.20.[16] One can moreover contrast this value with the observed equilibrium isotope effect, for the Cope rearrangement, 1.09,[17] which is considerably smaller. Our isotope effect corresponds to a $\Delta G° = 118$ cal/mole for the equilibration of 6 and 7.

The kinetic isotope effect is then of the same nature but, as expected, smaller than the equilibrium isotope effect. Such a result is most consistent with the intervention of the bromonium ions 3 or 4 in the reaction. Izawa and coworkers[18] similarly proposed an intermediate episulfonium ion when they observed an intermolecular $k_H/k_D = 0.84$ for the addition of 2,4-dinitrobenzene sulfenyl chloride to 1-phenylallene and its γ,γ-dideuterio analog. Our work, however, additionally demonstrates that the 2-bromoallyl cation 5 cannot intervene at any stage of the reaction.

Attempts to study the similar additions of HOCl to 1,1-deuterioallene also led to the observation of inverse isotope effects, thereby implicating the analogous chloronium ion.

However, these results were somewhat clouded by the fact that the 2-chloroallyl alcohol product was found not to be stable to HOCl under the reaction conditions.

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