Addition of Bromine to Carbon–Carbon Double Bonds

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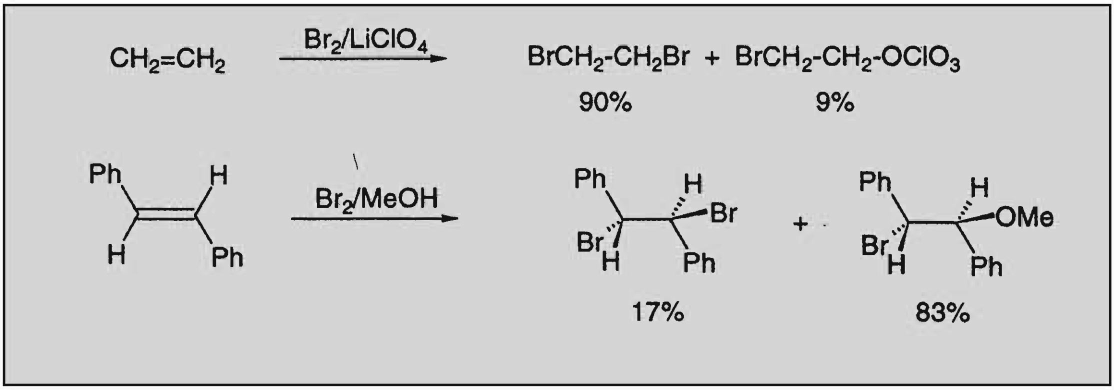
The carbon–carbon double bond is one of the key functionalities encountered in organic chemistry. There are many reactions available in the toolbox of organic chemists to prepare alkenes, compounds with carbon–carbon double bonds. Because of the presence of π-electrons in such double bonds they are nucleophilic, and as a result are attacked by electrophilic reagents. One such reagent is molecular bromine, Br_2. The bromination of a carbon–carbon double bond is one of the oldest known reactions in organic chemistry. Even though the outcome of the reaction appears to be an addition of bromine across the double bond, the details of the mechanistic and stereochemical aspects are quite fascinating. Many of these studies are covered in standard undergraduate text books but quite frequently students find some of the concepts difficult to understand. An effort is made in this classroom item to discuss a few of these concepts, and to provide the results of some more recent investigations.

It has long been suspected that the addition of bromine to the C=C bond involves an intermediate, since the reaction carried out in the presence of a competing nucleophile gives (in addition to the dibromide) an addition product of bromine and the nucleophile. Two such examples are shown in *Scheme 1*.

Scheme 1



Box 2

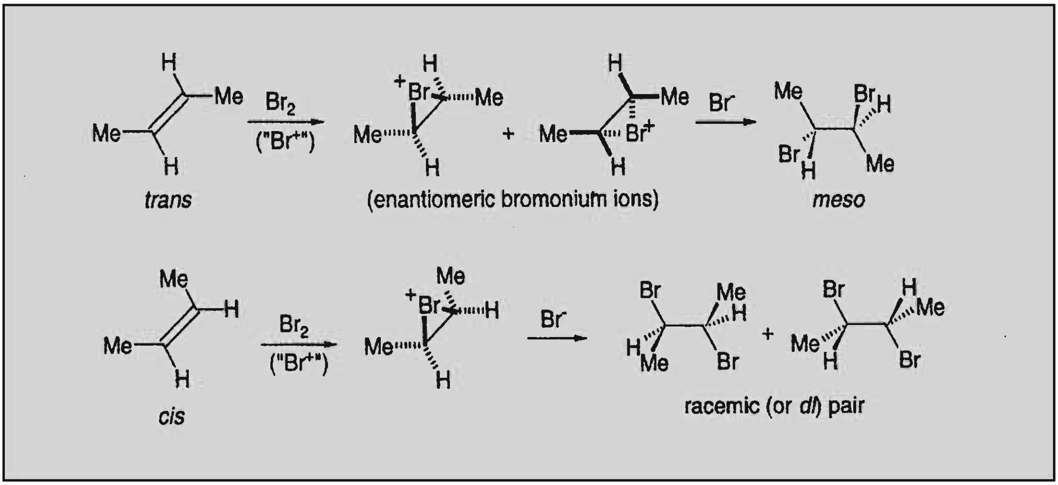
When two stereogenic (chiral) centers are present in a molecule, a total of four stereoisomers are possible in the form of two enantiomeric pairs. However, when the two centers are identical, there is only one enantiomeric pair (*dl* pair) and a *meso* compound. The *meso* compound may be thought of as a molecule having two identical chiral centers of opposite configuration, with the result that it is optically inactive. A meso compound in the Fischer projection will have a plane of symmetry. In its more stable *anti* conformation, however, a meso compound will show a center of symmetry.

Box 1

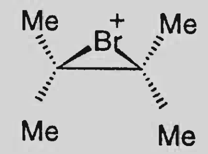
In general, if the alkene is symmetrical, *trans* addition of a reagent to a *trans* alkene, or *cis* addition to a *cis* alkene will produce *meso* products. The other two combinations would yield the racemic varieties. For unsymmetrical alkenes the nomenclature changes from *meso*/racemic to erythro/threo.

The stereochemical outcome of the bromination has also been studied in great detail. It was discovered that the overall addition of bromine is *anti*. In other words, the two bromine atoms appear to add from opposite faces of the double bond. This makes no difference if the alkene is ethylene, but if we take *cis* or *trans* 2-butenes as the substrates, *anti* addition to *trans* 2-butene would give the meso product (i.e., non-resolvable dibromide), whereas the *cis* isomer will produce the racemic mixture (i.e. resolvable dibromides).

These facts are consistent with the following mechanism, in which a bromonium ion is postulated as the intermediate.

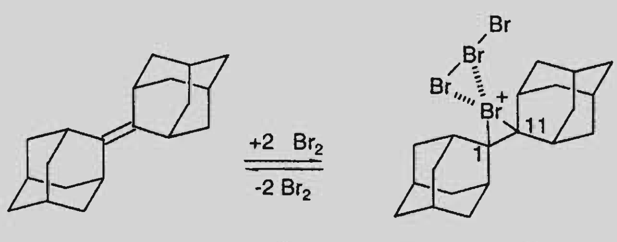


How does one prove the existence of the bromonium ion? There are, in general, two strategies for increasing the lifetime of a reactive species. One is to generate it at a low temperature in a medium which is highly non-nucleophilic. The other, which has also been described earlier in *Resonance*. Vol. 1. No. 7.p.62, July 1996 (tetra-*t*-butyltetrahedrane), is to surround the reactive functionality with bulky groups, so that the approach of the reagent is sterically difficult. Interestingly, both approaches have yielded positive results for the bromonium ion.



G A Olah has studied the proton nuclear magnetic resonance spectrum of a species generated upon the addition of bromine to tetramethylethylene. The spectrum at – 60°C showed a single line at 2.8 ppm, which is consistent with tetramethylethylene bromonium ion.

The other strategy involved the addition of bromine to a highly hindered alkene, adamantanylidene adamantane, shown here. Wynberg and coworkers brominated this alkene many years ago in CCl_4 to yield a yellow solid which was characterized to contain four bromine atoms, and was believed to be the bromonium ion tribromide. Upon attempted crystallization it gave off molecular bromine which was confirmed by its addition to cyclohexene. Brown and others finally succeeded in getting the X-ray crystal structure of this compound, which is shown below. There is no doubt from the crystal structure that it is indeed a cyclic bromonium ion!



C_1-Br 2.116 Å; C_{11}-Br 2.194 Å; C_1-C_{11} 1.497 Å

Bromination of normal unhindered double bonds is usually a very rapid reaction – and that is why it is frequently used as a test for unsaturation (decolourization of bromine colour). A nice experiment involving the reaction of bromine with double bonds has been described in the *Journal of Chemical Education* (Vol. 63. p. 1093, 1986). In this experiment, fresh tomato juice is poured in a graduated cylinder, and bromine water (*CAUTION*: bromine is extremely corrosive and must be handled with suitable eye and hand protection) is carefully layered on the top. A rainbow like colouration develops in the tomato juice layer. This results from the reaction of bromine with lycopene, a carotenoid present in tomato juice which contains 13 conjugated double bonds! A stable charge transfer complex with a blue colour is formed. Upon further reaction with bromine water lycopene essentially becomes pale yellow. The mixture of the blue colour with the reddish-orange of the tomato juice and the pale yellow cause the rainbow colours to form!

Why did the chicken cross the road?

Because it is a truth universally acknowledged that a single chicken, being possessed of a good fortune and presented with a good road, must be desirous of crossing. *Jane Austen*

It was the logical next step after coming down from the trees. *Charles Darwin*

Whether the chicken crossed the road or the road crossed the chicken depends on your frame of reference. *Albert Einstein*

It had sufficient reason to believe it was dreaming anyway. *Rene Descartes*

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