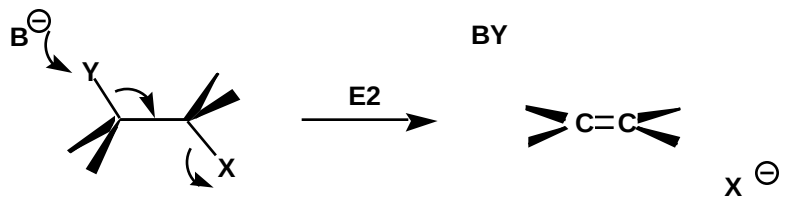
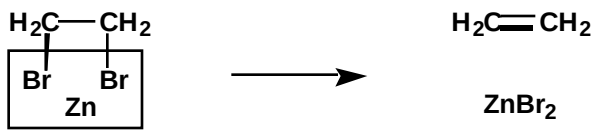
Text Related to Segment 13.06 ©2002 Claude E. Wintner

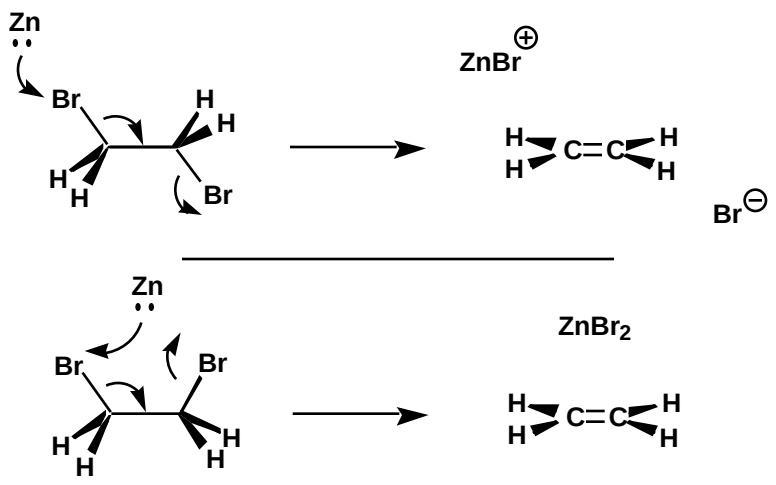
In the previous segment we specified a very particular, concerted, mechanism for the E2 reaction, involving only the conformation in which the atoms or groups to be eliminated are antiperiplanar to one another, that is, in the same plane and with a mutual dihedral angle of 180°:



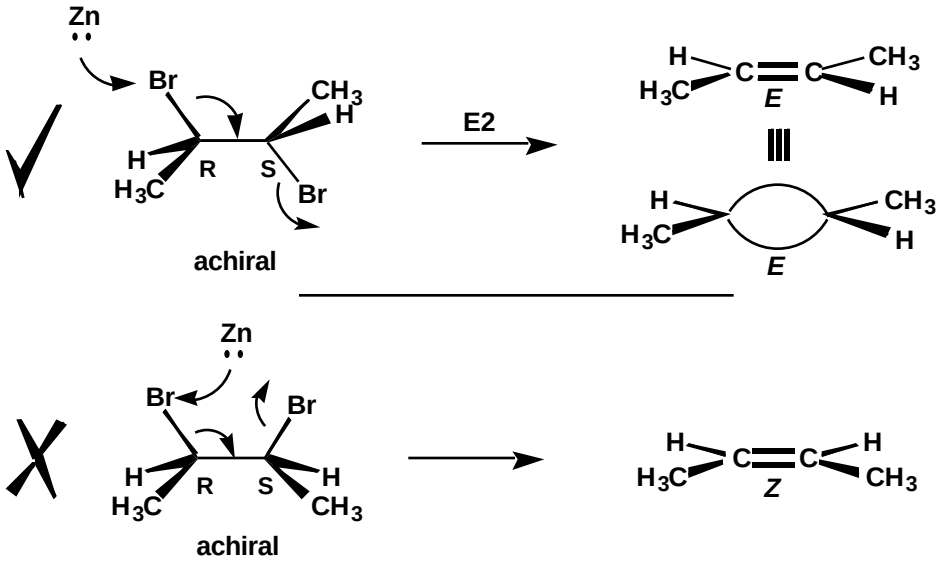
Elegant evidence for this mechanism is obtained through a stereochemical analysis of the debromination reaction that occurs when 1.2-dibromoalkanes (vicinal dibromoalkanes) react with zinc. To introduce this transformation, when 1,2-dibromoethane is treated with zinc, molecular bromine is eliminated from the molecule by the agency of the zinc, in a reaction exhibiting second-order kinetics, the resultant products being ethylene and zinc dibromide:



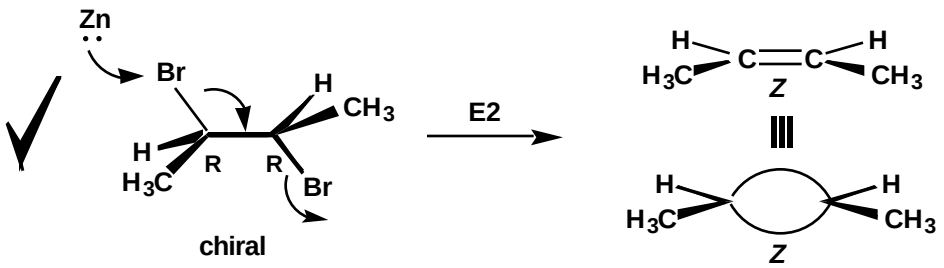
From the perspective of the previous segment, this reaction, occurring in a concerted manner, might take place in two extreme versions, one from the antiperiplanar conformation, the other from the synperiplanar conformation. However, as the following figure makes clear, the resultant product ethylene will contain no stereochemical information to provide insight into the transition state geometry:



Now, consider what may be expected if we start with *achiral* 2,3-dibromobutane as our substrate, instead of 1,2-dibromoethane. If the reaction is concerted, and if it takes place through an antiperiplanar transition state, we should observe only *E*-2-butene, as in the first line below. On the other hand, if the reaction is concerted, and if it were to take place through a synperiplanar transition state, we should observe only *Z*-2-butene, as in the second line:



In the event, only *E*-2-butene is observed. There is no leakage to *Z*-2-butene, confirming both the antiperiplanar nature of the transition state and the concertedness of the reaction, defining concerted to mean that the reaction must take place more rapidly than any rotation about the central C—C bond in an intermediate, a process which would lead to leakage to the *Z* isomer. Further confirmation for the stereospecificity of the reaction is obtained via the observation that from (either enantiomer of) *chiral* 2,3-dibromobutane only *Z*-2-butene is formed. Again, there is no stereochemical loss — in this case the leakage would be to *E*-2-butene — and so again the result does not permit a front-side ("syn") mechanism:



As just has been stated, the absence of stereochemical leakage indicates that the reaction must occur on a time scale more rapid than that of a single rotation about the central C—C bond in the transition state or in any intermediate we might postulate. In our figures the alternative τ bond notation has been offered as well as the σ/π, because it allows easy visualization of a "rear-side attack" — by the electron pair liberated as a result of the initial interaction with zinc — on the remaining C—Br bond, in turn releasing bromide ion. This view allows re-emphasis of the kinetic point just made, but from a slightly different perspective: the "attack" of an electron pair conceived in this way must occur more rapidly than does any central C—C bond rotation in the transition state.