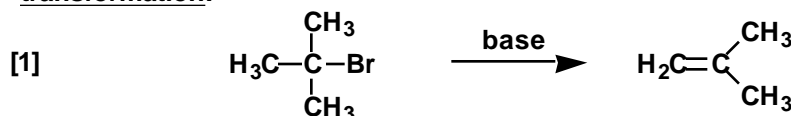


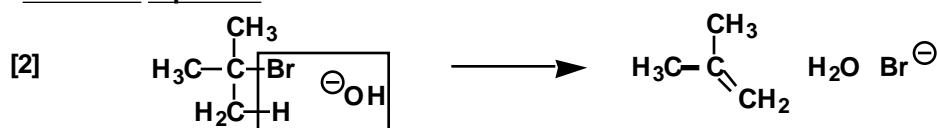
Text Related to Segment 13.05 ©2002 Claude E. Wintner

We concluded the last segment by stressing that, in fact, a reaction *does* take place [1] when t-butyl bromide (2-bromo-2-methylpropane) is treated with bases, but that it is *not* a *substitution* reaction. The product is isobutylene (isobutene, 2-methyl-1-propene), the result of elimination of HBr by the base.

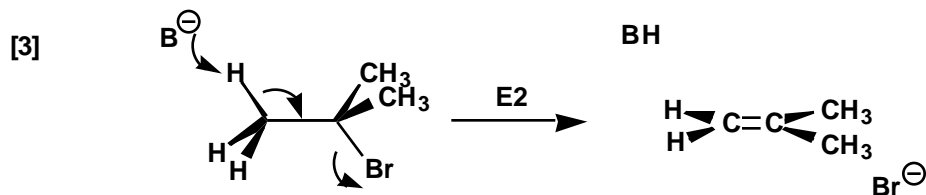
transformation:



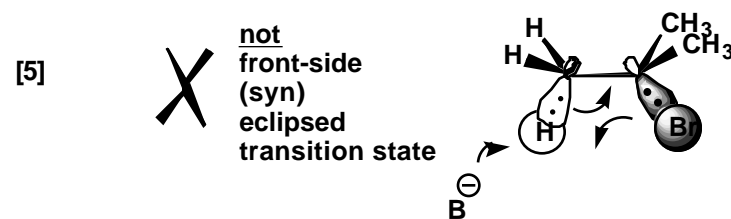
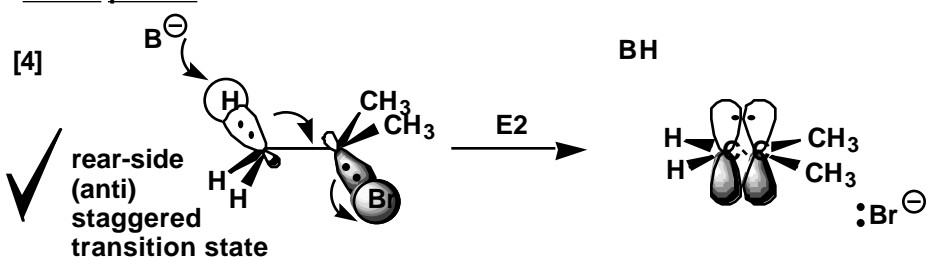
balanced equation:



mechanism:



orbital picture:

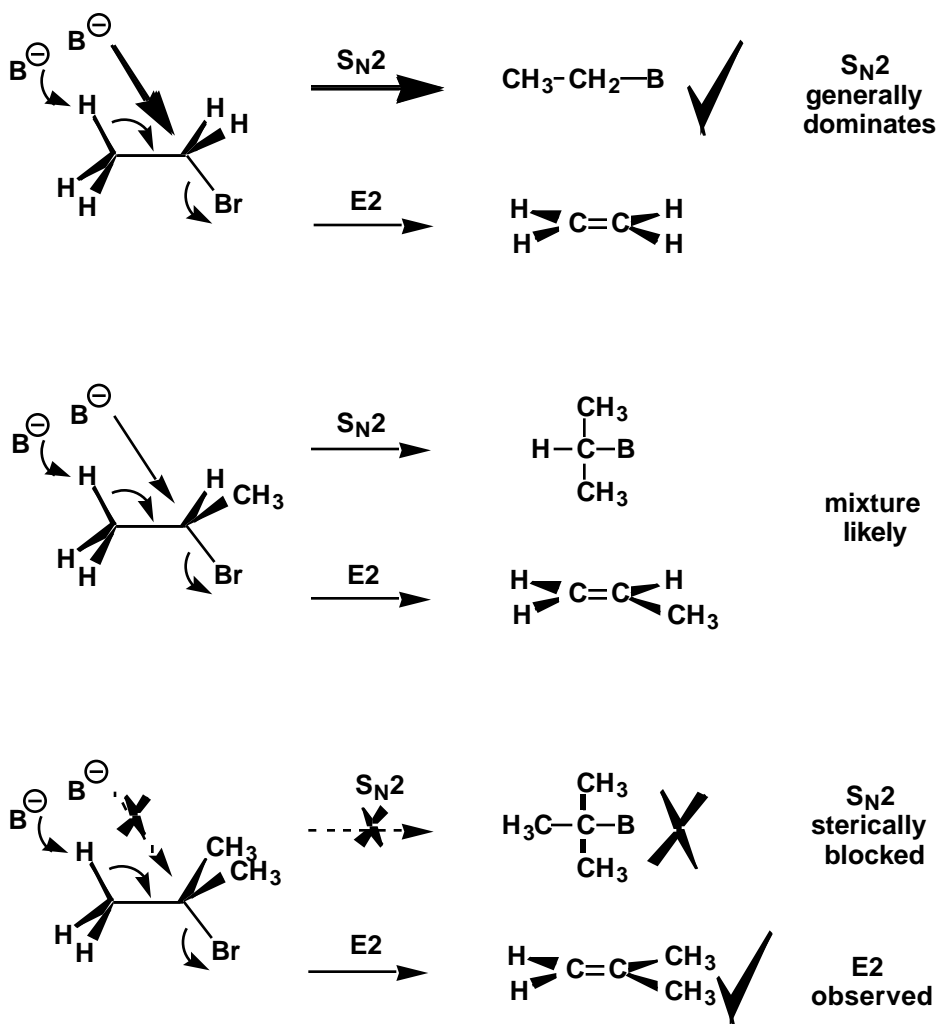


several perspectives on the reaction of t-butyl bromide with base, governed by the E2 mechanism

The rate is second order, depending on both base and substrate, and the mechanism is classified as E2 (elimination, bimolecular). Attention to the overall balanced equation [2] reveals a clear thermodynamic driving force: in effect, hydrogen bromide is torn from the molecule, and it and the base are neutralized. From a variety of stereochemical experiments — one of which, the stereospecific zinc debromination of chiral versus achiral 2,3-dibromobutane, will be analyzed in the next segment — E2 reactions are understood to occur in the manner illustrated in [3], as regards both the conformation of the reactant and the potential configuration of the product. The orbital picture [4] may be visualized as one in which two sp^3 orbitals arranged in an anti conformation in the reactant develop into two p orbitals that mix to become a π bond in the product, the hybridization at the relevant carbon atoms changing from sp^3 to sp^2 and the substituent groups thus moving up or down into a planar arrangement. In particular, we shall see evidence that E2 reactions do *not* occur via a front-side, or "syn" mechanism [5], which would entail an eclipsed transition state that in fact possesses characteristics suspiciously reminiscent of an anti-aromatic four-electron system!

The E2 mechanism may be thought of as providing a more or less constant alternative to the S_N2 pathway, for the thermodynamic driving force toward elimination to which we have just alluded always is present, regardless of whether the halide is primary, secondary, or tertiary. However, from the point of view of relative rate, as we move from primary to tertiary halides the S_N2 mechanism is rendered less competitive, and finally totally noncompetitive, with the result that the E2 reaction becomes dominant. As a general rule, the more nucleophilic the attacking reagent, the better are the chances for observing an S_N2 reaction; we already have emphasized that sulfur nucleophiles tend to perform well in this regard, in particular since their base strength is relatively low. On the other hand, as base

strength increases, elimination of HX will be favored increasingly. If the base is very strong, the S_N2 mechanism already may be entirely noncompetitive with E2 in secondary cases, and even for primary cases a great deal of elimination may be the observed result. The competitive situation between the S_N2 and E2 mechanisms for ethyl, isopropyl, and t-butyl bromides is summarized in the pictorial analysis given in the following figure:



competition between S_N2 and E2 mechanisms involving ethyl, isopropyl, and t-butyl bromides