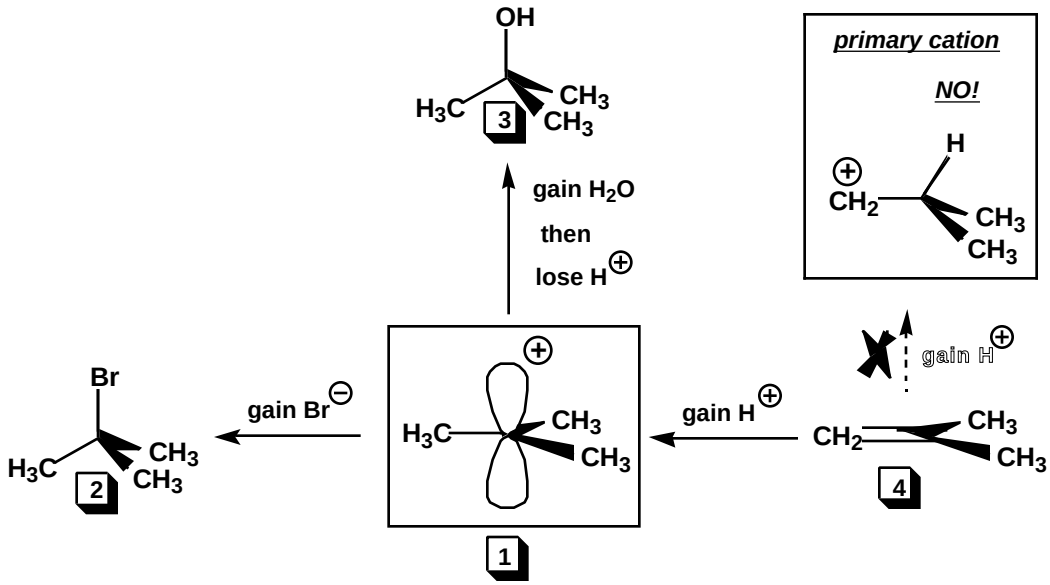
Text Related to Segment 15.01 ©2002 Claude E. Wintner

Entrance to the same carbocation energy surface already discussed (for example, in Segment 14.04) is gained by a pathway which is just the reverse of the E1 route. Here we repeat the figure of that segment, altered to suit the present purpose:



addition reactions on the carbocation manifold:
THE MORE STABLE CARBOCATION ALWAYS IS FORMED

		Reaction Conditions
4 → 1 → 2	**Addition**	**Concentrated HBr.**
4 → 1 → 3	**Addition**	**Dilute acid - e.g., dilute H_2SO_4 or dilute HBr.**

If isobutylene 4 is treated with concentrated HBr, the *addition* reaction 4 → 1 → 2 to form t-butyl bromide takes place. The initial interaction is between a proton from HBr and a molecule of isobutylene acting as a Lewis base. The π electrons are used to form a new bond to the proton, and in the process a carbocation is generated. Clearly, there would be two possibilities: the resultant cation either might be the tertiary carbocation 1, or it might be the primary carbocation shown in the upper-right-

hand corner of the figure, depending upon which carbon atom of the double bond in isobutylene received the proton. However, *in fact there is no choice;* the primary carbocation will not form! *The more stable carbocation always is formed.* Although it is simply a corollary of the carbocation stability data that we have analyzed previously, estimating that a solvated primary carbocation has a free energy some 30 kcal/mole higher than does a solvated tertiary carbocation, this important rule, along with its predictive usefulness, cannot be overemphasized. Given the carbocation 1 and the circumstances of an excess of bromide ion — as provided by the concentrated HBr — t-butyl bromide 2 must be the outcome. The net result has been to add HBr across the double bond of isobutylene in a *regiospecific* manner, directed by the stability of the carbocation intermediate. Extension of the same argument to aqueous mineral acid conditions leads to the conclusion that, in dilute H_2SO_4 or HBr solutions, addition to isobutylene can take place to yield t-butyl alcohol via 4 → 1 → 3; again it will be the tertiary carbocation 1 that forms, but now the nucleophile in excess in the medium is water, and an alcohol is the result. Here the net effect has been to add water across the double bond, again in the regiospecific sense directed by the stability of the carbocation intermediate.

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