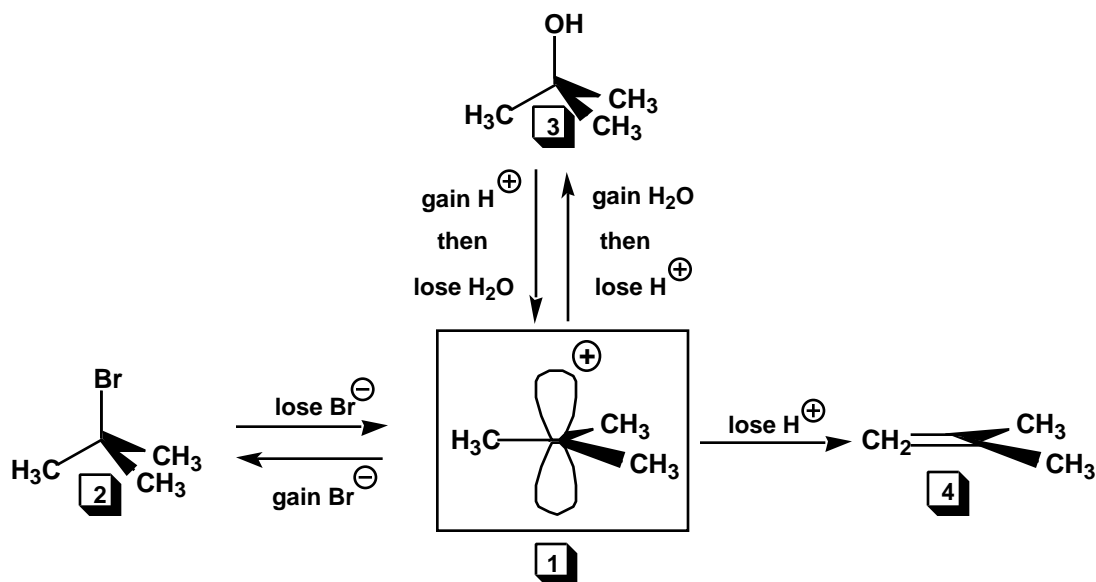


Text Related to Segment 14.04 ©2002 Claude E. Wintner

The figure below summarizes what has been said so far about reactions lying within the carbocation manifold, and also elaborates the theme. Transformations 3 → 1 → 2 and 2 → 1 → 3 are the S_N1 solvolysis reactions, governed by nucleophile concentration, that we have discussed:



the S_N1/E1 manifold, with its central carbocation

| | | | <u>Reaction Conditions</u> | | | |
|---|---|---|----------------------------|---|-------------------------------|--------------------------------------------------------------------------|
| 3 | → | 1 | → | 2 | S _N 1 "Solvolysis" | Concentrated HBr. |
| 2 | → | 1 | → | 3 | S _N 1 "Solvolysis" | Dilute acid - e.g., dilute H ₂ SO ₄ or dilute HBr. |
| 2 | → | 1 | → | 4 | E1 | Occurs as a side reaction with Sn1 **. |
| 3 | → | 1 | → | 4 | E1 | Concentrated H ₂ SO ₄ . |

****To drive this reaction efficiently, use base. But now this will be E2 - NO CARBOCATION!**

However, just as the E2 mechanism provides an alternative route, competing with the S_N2, so also reactions occurring by the S_N1 mechanism suffer a parallel competition from a unimolecular elimination pathway, E1, in which the carbocation

intermediate, instead of taking up with a new nucleophile, simply loses a proton to form an alkene. Thus, $2 \rightarrow 1 \rightarrow 4$ is a side reaction competing with $2 \rightarrow 1 \rightarrow 3$, resulting in a lowered yield of 3. The central carbon atom of the cation remains trigonal, the carbon atom giving up the proton changes from tetrahedral to trigonal, and the two electrons available from the bond formerly made with the leaving proton become the electrons of the new bond. The same leakage will occur for the reaction $3 \rightarrow 1 \rightarrow 2$, and indeed will accompany any transformation occurring by the S_N1 mechanism, always with consequent lowering of the yield of substitution product. Starting with an alcohol, elimination $3 \rightarrow 1 \rightarrow 4$ via the E1 mechanism becomes the preponderant result in concentrated sulfuric acid, where the thermodynamic driving force is to remove water from the alcohol, thus effectively diluting the sulfuric acid — a very exothermic process.

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