

Ni, D.; Wei, Y.; Ma, D. Angew. Chem. Int. Ed. 2018, 57, Early view (DOI: 10.1002/anie.201805905).

More than 10 years ago, a graduate student in the M. E. Jung's Lab @ UCLA synthesized allyl alcohol 2 by DIBAL-H reduction of 1. The spectroscopic data for 2 were identical to those they reported earlier. However, when compound 2 was allowed to stand without solvent at $21^{\circ} \mathrm{C}$ for 5 days, it completely rearranged to a new compound 3 , which could be isolated in a highly pure state in $52 \%$ yield. Propose a mechanism for the rearrangement. They assumed that there must had been traces of either Al (III) salts or acid present in the sample of $\mathbf{2}$ resulting from the DIBAL-H reduction.


To prove the structure of 3 , the graduate student decided to prepare an authentic sample of a simple derivative. Since compound 4 was known in the literature, he decided to prepare its methylated derivative 5 and compare it to the product of simple debromination of $\mathbf{3}$. Methylation of 4 proved to be successful to give the 5 -methyl enone $\mathbf{5}$; However, when the bromide $\mathbf{3}$ was treated with AIBN and $\mathrm{Bu}_{3} \mathrm{SnH}$ in refluxing benzene, he isolated a compound 6 that was clearly different from the expected product 3. Propose a structure of the compound $\mathbf{6}$ and the mechanism for its formation.

${ }^{1} \mathrm{H}-\mathrm{NMR}$ data for $\mathbf{6}: \delta 2.73$ (dd, $1 \mathrm{H}, J=18.1,6.7 \mathrm{~Hz}$ ), $2.35(\mathrm{~m}, 1 \mathrm{H}), 2.14(\mathrm{t}, 2 \mathrm{H}, J=7.5 \mathrm{~Hz}), 2.08$ (dd, $1 \mathrm{H}, J=18.1,2.2$ $\mathrm{Hz}), 2.03(\mathrm{~s}, 3 \mathrm{H}), 1.40(\mathrm{tq}, 2 \mathrm{H}, J=7.5,7.4 \mathrm{~Hz}), 1.15(\mathrm{~d}, 3 \mathrm{H}, J=7.5 \mathrm{~Hz}), 0.87(\mathrm{t}, 3 \mathrm{H}, J=7.4 \mathrm{~Hz})$.
${ }^{13} \mathrm{C}-\mathrm{NMR}$ data for 6 : $\delta 212.3,168.5,139.4,40.9,39.7,25.2,21.8,17.3,16.9,14.2$.
M. E. Jung and D. Yoo, JOC, 2007, 72, 8565.

