We already have seen (for example, in Segment 11.04) that a hydrogen atom attached to a carbon atom $\alpha$ to a carbonyl group can have enhanced acidity as a result of the relative (three-orbital-four-electron) stability of enolate anions, and hence can be removed by bases, but we have not explored the consequences of this reactivity. In both aqueous acid and aqueous base, if the water is deuterated, then deuterium is incorporated at these reactive positions:

\[\text{H}_3\text{C} = \text{CH}_3 \quad \xrightarrow{\text{D}_2\text{O}/\text{OD}} \quad \text{D}_3\text{C} = \text{CD}_3\]

\[\text{H}_3\text{C} = \text{CH}_3 \quad \xrightarrow{\text{D}_2\text{O}/\text{OD}} \quad \text{D}_3\text{C} = \text{D}_3\text{D}_3\]

\[\text{H}_3\text{C} = \text{H} \quad \xrightarrow{\text{D}_2\text{O}/\text{OD}} \quad \text{D}_3\text{C} = \text{H}\]

\[\text{H}_3\text{C} = \text{H} \quad \xrightarrow{\text{D}_2\text{O}/\text{OD}} \quad \text{D}_3\text{C} = \text{H}\]

\[\text{H}_3\text{C} = \text{H} \quad \xrightarrow{\text{D}_2\text{O}/\text{OD}} \quad \text{D}_3\text{C} = \text{H}\]
Thus, as in the figure (and assuming a molar excess of deuterium), as a result of deuterium exchange in either acidic or basic deuterium oxide, acetone yields hexadeuteroacetone, 3-pentanone yields 2,2,4,4-tetradeutero-3-pentanone, acetaldehyde gives 2,2,2-trideuteroacetaldehyde, and propanal gives 2,2-dideuteropropanal. In each case protons are removed at the acidic $\alpha$ position, the evidence being that, upon their replacement in the deuterated environment, they reappear as deuterons.

In line [2] of the following figure the enolization reaction responsible for deuterium exchange is interpreted as the E2 counterpart to nucleophilic attack at carbonyl carbon as in line [1], for which we already (in Segment 16.01) have made the case that it is fundamentally an $S_N2$ reaction. Lines [3] and [4] interpret the same two transformations using the alternative $\tau$ bond notation. Line [5] states the acidic variant.
enolate and enol formation interpreted as members of the E2 family of reactions

The final figure outlines the completing step of these deuterium exchange reactions, in base and in acid:
completion of deuterium exchange reaction in base (by enolate anion) and in acid (by enol)