ABSTRACT. Organocobalt complexes are used as radical precursors in biomimetic syntheses. Mechanistic studies demonstrate that carbon cobalt bonds can be either cleaved homolytically or heterolytically. In addition to these reactions, reductive eliminations occur as product forming steps.

Phosphoenolpyruvate reacts as C-3 unit with aldehyde functions of carbohydrates in enzymatic aldol reactions¹).
Because respective in vitro reactions fail in the absence of the enzymes, we have started biomimetic syntheses using radical methodology. For these reactions one has to find methods by which aldehyde functions of sugars are converted into radicals. Suitable radical precursors could be generated from aldehydes with trimethylsilyl phenyl selenide or from acetals with HBr.

As biomimetic synthons of phosphoenol pyruvate we have used methylenemalonic ester or an estersubstituted allylstannane.

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\begin{align*}
\text{RCHO} + \text{H}_2\text{C} \equiv \text{C} \text{CO}_2^- & \rightarrow \text{O} \text{H} \\
\text{RCH} + \text{CH}_2\text{CO}_2\text{H} &
\end{align*}
\]

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\text{RCH} + \text{CH}_2\text{CO}_2\text{H} &
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} \equiv \text{C} \text{CO}_2\text{Et} & \rightarrow \text{R} \text{CH} \text{CO}_2\text{Et} \\
\text{R} \text{CH} \text{CO}_2\text{Et} & \rightarrow \text{RCH} \text{CO}_2\text{Et} \\
\text{I-C}_2\text{H}_11\text{ONO} & \rightarrow \text{RCH} \text{CO}_2\text{Et} \\
\text{NOH} & \rightarrow \text{RCH} \text{CO}_2\text{Et} \\
\text{CH}_2\text{SnBu}_3 & \rightarrow \text{RCH} \text{CO}_2\text{Me} \\
\text{RCH} \text{CO}_2\text{Me} & \rightarrow \text{RCH} \text{CO}_2\text{Me} \\
\text{O}_3 & \rightarrow \text{RCH} \text{CO}_2\text{Me}
\end{align*}
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