Addition of a saturated hydrocarbon (\( \ce{R-H} \)) to an alkene to yield a saturated hydrocarbon of higher molecular weight is known as alklyation:

\[
\begin{align*}
\text{R-H} + \text{C=C} & \rightarrow \text{R-CCC-H} \\
\end{align*}
\]

Such reactions are used by the petroleum industry to produce medium-molecular-weight hydrocarbons from smaller molecules. A particularly important example is afforded by the addition of 2-methylpropane to 2-methylpropene in the presence of sulfuric acid or anhydrous hydrogen fluoride to yield 2,2,4-trimethylpentane:

\[
\begin{align*}
\text{CH}_3\text{C-H} + \text{CH}_3\text{C} & \rightarrow \text{CH}_3\text{C-H} \quad \text{CH}_3\text{C-CH}_3\text{-H} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

The overall reaction appears to be different from any so far discussed, because it involves addition of a nonpolar reagent (\( \ce{R-H} \)) to an alkene bond.

The key to the mechanism of hydrocarbon alkylation was provided by the discovery by P. D. Bartlett, in 1940, that a carbocation can react rapidly with a hydrocarbon having a tertiary hydrogen to yield a new carbocation and a new hydrocarbon. Some of these "hydrogen-transfer" reactions are extraordinarily fast and may be complete in seconds or less. The hydrogen is transferred with both bonding electrons. For example,

\[
\begin{align*}
\text{CH}_3\text{C-H} + \text{CH}_3\text{C} & \rightarrow \text{CH}_3\text{C-H} \quad \text{CH}_3\text{C-CH}_3\text{-H} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

With the knowledge that the hydrogen transfer is fast, the alkylation of 2-methylpropene with 2-methylpropane can be formulated as involving first polymerization of two 2-methylpropene molecules under the influence of the sulfuric acid catalyst to give the same octyl cation as was postulated for the dimerization of 2-methylpropene:

\[
\begin{align*}
2\text{CH}_2\text{C} & \rightarrow \text{CH}_3\text{C} \quad \text{CH}_3\text{C-CH}_3\text{C-CH}_3 \\
\end{align*}
\]

The octyl cation then can undergo a hydrogen-transfer reaction with 2-methylpropane to furnish 2,2,4-trimethylpentane and a tert-butyl cation:
Attack by the \textit{tert}-butyl cation on another molecule of 2-methylpropene produces an eight-carbon tertiary cation, which then proceeds to another molecule of "alkylate":

\[
\text{CH}_3\text{C}^\ominus\text{CH}_2\text{C}^\ominus\text{CH}_2 + \text{CH}_3\text{C}^\ominus\text{CH}_2\text{C}^\ominus\text{CH}_2 \rightarrow \text{CH}_3\text{C}^\ominus\text{CH}_2\text{C}^\ominus\text{CH}_2 + \text{CH}_3\text{C}^\ominus\text{CH}_2\text{C}^\ominus\text{CH}_2 \text{ etc.}
\]

This is an important example of a \textit{cationic chain} reaction.

\section*{References}

- John D. Robert and Marjorie C. Caserio (1977) \textit{Basic Principles of Organic Chemistry, second edition}. W. A. Benjamin, Inc., Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."