Organosodium chemistry

Organosodium chemistry is the chemistry of organometallic compounds containing a carbon to sodium chemical bond.\[1\]\[2\] The application of organosodium compounds in chemistry is limited in part due to competition from organolithium compounds in the same group 1 elements row of the periodic table. Yet several important compounds exist.

Organometal bonds in group 1 are characterised by high polarity and high nucleophilicity on carbon (compare electronegativity of carbon (2.55) to that of lithium 0.98, sodium 0.93 potassium 0.82 rubidium 0.82). The principal organosodium compound of importance is sodium cyclopentadienide that is prepared from sodium metal and cyclopentadiene:

\[
2 \text{Na} + 2 \text{C}_5\text{H}_6 \rightarrow 2 \text{NaC}_5\text{H}_5 + \text{H}_2
\]

The higher alkali metals are known to metalate even unactivated hydrocarbons and are known to self-metalate

\[
2 \text{NaC}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 \text{Na}_2 + \text{C}_2\text{H}_6
\]

Another side-reaction is beta-elimination:

\[
\text{NaC}_2\text{H}_5 \rightarrow \text{NaH} + \text{C}_2\text{H}_4
\]

The carbanionic nature of these compounds can be reduced by resonance stabilization for instance in Ph\(_3\)CM compounds.

Sodium can also react with hydrocarbons in one-electron reduction. With naphthalene it forms sodium naphthalenide solutions.

\[
\text{C}_{10}\text{H}_8 + \text{Na} \rightarrow \text{Na}^+\text{[C}_{10}\text{H}_8]^{-}\nonumber
\]

In the Wanklyn reaction (1858)\[3\][4] sodium replaces magnesium in a Grignard type reaction with carbon dioxide:

\[
\text{C}_2\text{H}_5\text{Na} + \text{CO}_2 \rightarrow \text{C}_2\text{H}_4\text{CO}_2\text{Na}
\]

In the original work the alkylsodium compound was accessed from the dialkylmercury compound for example diethylmercury in the Schorigin reaction or Shorygin Reaction\[5\][6]:

\[
(\text{C}_2\text{H}_5)_2\text{Hg} + 2\text{Na} \rightarrow 2\text{C}_2\text{H}_5\text{Na}
\]

Higher alkali metals

The higher alkali metals, organopotassium, organorubidium and organocaesium, are even more reactive than organosodium and of limited utility. A notable reagent is Schlosser's base, a mixture of \(n\)-butyllithium and potassium \(\text{tert}\)-butoxide. This reagent reacts with propene to the compound allyl potassium (KCH\(_2\text{CHCH}_2\)). \(\text{cis}\)-2-Butene and \(\text{trans}\)-2-butene equilibrate when in contact with alkali metals. Whereas isomerization is fast with lithium and sodium, it is slow with the higher alkali metals. The higher alkali metals also favor the sterically congested conformation.\[7\]
References

[6] P. Schorigin, Ber. 41, 2711, 2717, 2723 (1908)
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