The High Reactivity of Radical-anion-prepared Sodium Hydride: Reaction with Benzyl Chloride

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Summary Sodium hydride prepared by the reaction of sodium dihydronaphthylide with hydrogen reacts readily with benzyl chloride to give hydrogen, toluene, bibenzyl, and stilbene.

RECENTLY, we[1] and others[2,3] have reported a preparation of sodium hydride (I) by the reaction of sodium dihydronaphthylide and hydrogen in tetrahydrofuran solution. A feature of the reaction is the unusually high reactivity of this hydride as compared with the commercially available sodium hydride prepared at high temperature.[1] We now report that sodium hydride prepared by the radical-anion method reacts readily at room temperature with benzyl chloride, which does not react with commercial sodium hydride in tetrahydrofuran,[4] reacts only very slowly at high temperature with commercial sodium hydride activated by hexamethylphosphortriamide.[5]

Equimolar addition of benzyl chloride to a suspension in tetrahydrofuran of (I) (prepared by the reaction of sodium dihydronaphthylide and hydrogen catalysed by titanium isoproproxide[2]) at room temperature produced an immediate evolution of hydrogen. After centrifugation of the reaction mixture, g.l.c. analysis revealed that all of the benzyl chloride had reacted. The products of the reaction were isolated by g.l.c. and identified by spectroscopic methods.

$$\begin{aligned}&\mathrm{NaH} + \mathrm{PhCH_2Cl} \rightarrow\\ &\qquad \mathrm{H_2} + \mathrm{PhMe} + \mathrm{PhCH_2{\cdot}CH_2Ph} + \mathrm{PhCH{:}CHPh}\end{aligned}$$

The yields based on benzyl chloride are 15% for hydrogen and 30, 21, and 17% for toluene, bibenzyl, and stilbene, respectively.

A mechanism involving a carbene precursor could account for the products according to the following scheme:

$$\begin{tikzcd}
\mathrm{H^-} + \mathrm{PhCH_2Cl} \arrow[rr] & & \mathrm{Ph\bar{C}HCl} + \mathrm{H_2} \arrow[d] \\
\mathrm{Ph\bar{C}H_2} \arrow[d] \arrow[dr] & & \mathrm{Ph\ddot{C}H} + \mathrm{Cl^-} \arrow[ll, "\mathrm{H^-}"'] \arrow[d] \\
\mathrm{PhCH_3} & \mathrm{(PhCH_2)_2} & \mathrm{PhCH{:}CHPh}
\end{tikzcd}$$

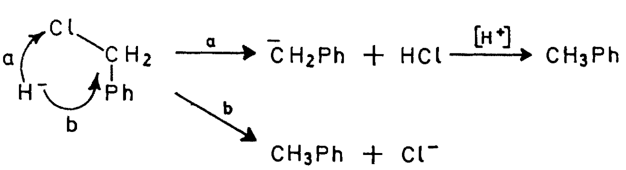
A carbene mechanism was ruled out, however, by the following experiments. When the reaction was conducted in a 5 molar excess of cyclohexene, no phenylnorcarane could be detected and cyclohexene was recovered unchanged. Equally important, reaction of α,α-dideuteriobenzyl chloride with sodium hydride gave rise to toluene which was 100% dideuterio-substituted. The complete absence of monodeuteriotoluene rules out any component of a carbene or carbenoid mechanism.

Since stilbene in control experiments is stable to the reaction conditions the formation of bibenzyl must be independent of stilbene. We suggest a nucleophilic displacement on chlorine followed by an S_N2 reaction of the resultant benzyl anion on unreacted benzyl chloride.

$$\mathrm{H^-} + \mathrm{ClCH_2Ph} \rightarrow \mathrm{PhCH_2^-} + \mathrm{HCl}$$
$$\mathrm{PhCH_2^-} + \mathrm{PhCH_2Cl} \rightarrow \mathrm{PhCH_2{\cdot}CH_2Ph} + \mathrm{Cl^-}$$

It is likely that hydride, a "soft" base, would displace the "softer" acid, chlorine, rather than carbon.[6] Moreover, this is a less hindered approach and gives rise to a strong H–Cl bond.

There are indications that stilbene is produced by an alternative mechanism which is currently being studied. Toluene formation, on the other hand, could occur either by displacement on chlorine followed by protonation, or by nucleophilic displacement on carbon. The low yield of H_2 (15%) cannot rule out path (a), since the HCl produced would be expected to protonate the benzyl anion rapidly rather than to react with hydride to form hydrogen. To support this contention, trityl chloride which cannot react by displacement on carbon reacts vigorously with sodium hydride, producing low yields of both hydrogen and the trityl anion (identified by carbonation and deuteriation). As predicted from path (a), the major product is triphenylmethane. Although there is not sufficient evidence as yet to rule out displacement on carbon, these results and the implication of the benzyl anion in the formation of bibenzyl favour displacement on chlorine.



In sum, the reactivity of radical-anion-prepared sodium hydride is remarkable, and suggests many synthetic applications.

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