

REDUCTION OF UNSATURATED CARBON-CARBON BONDS BY MEANS OF IRON CHLORIDE - SODIUM HYDRIDE SYSTEM

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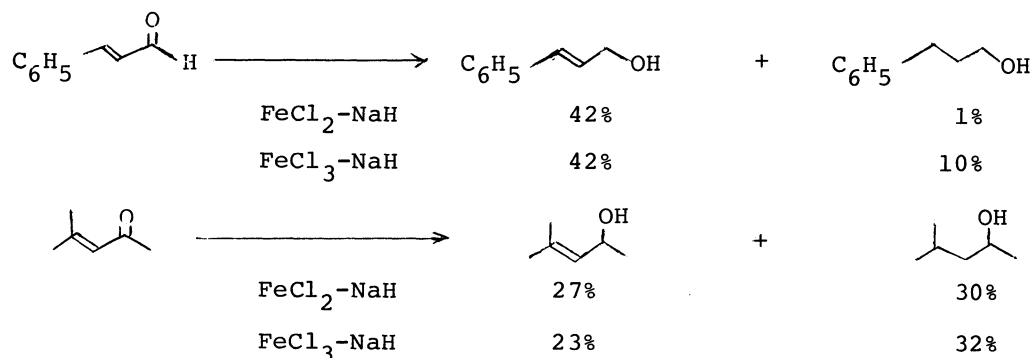
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The reagent consisting of iron(II or III) chloride and sodium hydride in tetrahydrofuran was found to reduce both carbonyl and olefin bonds in an enone. Olefins and acetylenes were also hydrogenated by the reagent giving the corresponding saturated hydrocarbons under mild conditions.

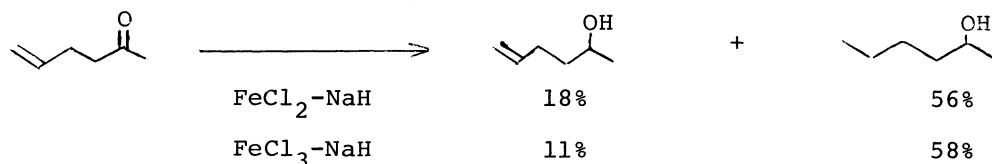
For the reduction of organic functional groups, a wide variety of mixed hydrides consisting of metal salts and complex metal hydrides such as lithium aluminum hydride and sodium borohydride have been utilized.¹⁾ For example, a combination of lithium aluminum hydride and iron(III) chloride or cobalt(II) chloride has been utilized for the hydrogenation of olefins,²⁾ although the system cannot be applied to the reduction of enones.³⁾ In addition, sodium borohydride and platinum, rhodium, ruthenium, osmium, iridium or nickel salts have been described as an effective hydrogenation system for unsaturated carbon-carbon bonds.⁴⁾ On the other hand, sodium hydride is the most widely used strong bases in organic syntheses, but is rarely used as a reducing agent.⁵⁾ The reagent consisting of iron(II or III) chloride and sodium hydride in tetrahydrofuran, however, was recently reported from our laboratory to provide an effective system for the reduction of ketones and aldehydes to the corresponding alcohols under mild conditions.⁶⁾ We now report here that the above system is also effective for the reduction of unsaturated carbon-carbon bonds to the corresponding saturated hydrocarbons.

When the reduction system prepared by an addition of iron(II or III) chloride to sodium hydride in THF was applied to the reduction of enones, different results from those of the usual hydride reductions⁷⁾ were obtained. Cinnamaldehyde gave cinnamyl alcohol as a major product along with a small amount of

saturated alcohol, 3-phenylpropanol, while the amount of saturated product, 4-methylpentan-2-ol exceeded the amount of unsaturated product, 4-methyl-3-penten-2-ol, on the reduction of mesityl oxide under the optimum conditions for



carbonyl compounds.⁶⁾ An example of such simultaneous reduction of ketonic and olefinic double bonds in an enone has been described for the unusual reduction of cinnamaldehyde by means of lithium aluminum hydride, which is believed to involve an addition of the metal hydride to the allyloxyaluminum compound intermediately formed.⁸⁾ Although the isolated double bond is generally stable to lithium aluminum hydride, the major product of the reduction of 5-hexen-2-one in THF with the iron chlorides-sodium hydride systems was also the saturated alcohol, hexan-2-ol, and the yield of the unsaturated alcohol, 5-hexen-2-ol, was



low. These findings show the possible applicability of the systems not only to carbonyl compounds but also to unsaturated carbon-carbon bonds.

Table I reveals that the reagents are effective for the hydrogenation of various olefins and acetylenes. The results show that the aromatic olefins are more reactive than the aliphatic ones, the terminal than the inner, and the cis than the trans. Although inner acetylenic bonds were reduced effectively, phenylacetylene gave ethylbenzene in only a 27% yield along with unidentified oligomeric products, due to complex side reactions caused by the acidic proton.

Since the reduction proceeds after some period of stirring of the mixture of iron chloride and sodium hydride, the active species for the reduction is considered to result from the reaction of the two reagents. Although evolution of hydrogen was observed throughout the reduction, a substitution of the reaction atmosphere with hydrogen instead of argon had no effect to the

reduction rates and the yields of products. Thus the reaction does not seem to proceed via catalytic hydrogenation over a low valent iron compound. Then, the reaction is supposed to involve an addition step of some kind of iron hydride⁹⁾ similar to that of diborane.¹⁰⁾ Because of the different thermal stabilities of the reagents derived from trivalent and bivalent iron chlorides, it is necessary to select appropriate reaction conditions depending on the reagents used, similarly to the case of the reduction of carbonyl compounds.⁶⁾ In addition, proper amounts of the reagents are also depend on the substrates. For example, styrene gave a better result by using two fold excess of the reducing reagent derived from iron(II) chloride than using ten fold excess, while other olefins required a large excess of the reagent.

Typical experimental procedures are as follows.

Reduction of Styrene with FeCl_2 -NaH System: To a suspension of sodium hydride (50%, 390 mg, 8 mmol), which was washed with dry THF, in THF (15 ml), was added iron(II) chloride (510 mg, 4 mmol) at 0°C under an atmosphere of argon. After stirring for 15 min, a solution of styrene (212 mg, 2 mmol) in THF (2 ml) was added dropwise and the reaction mixture was continued to stir at 0 - 5°C for 24 hr. Then water was added to the resulting mixture and the organic layer was extracted with ether and the product, ethylbenzene, was analyzed by glpc.

Reduction of 5-hexen-2-one with FeCl_3 -NaH System: To a suspension of sodium hydride

Table I Reduction of unsaturated compounds with iron chloride-sodium hydride system

Substrate	Reagent (molar ratio)	Molar Ratio FeCl_x /Substrate	Reaction Temp. (°C)	Time (hr)	Product (Yield*, %)
Styrene	FeCl_2 -NaH(1:2)	2	0 - 5	24	Ethylbenzene (85)
	FeCl_2 -NaH(1:2)	10	0 - 5	24	Ethylbenzene (69)
	FeCl_3 -NaH(1:3)	7	r.t.	42	Ethylbenzene (50)
1-Octene	FeCl_2 -NaH(1:2)	10	0 - 5	24	Octane (96)
	FeCl_3 -NaH(1:3)	7	r.t.	40	Octane (90)
trans-1-propenylbenzene	FeCl_2 -NaH(1:2)	10	0 - 5	24	Propylbenzene (93)
trans-3-Octene	FeCl_2 -NaH(1:2)	10	0 - 5	146	Octane (57)
cis-3-Octene	FeCl_2 -NaH(1:2)	10	0 - 5	100	Octane (84)
4-Methylcyclohexene	FeCl_2 -NaH(1:2)	10	0 - 5	162	Methylcyclohexane (63)
Phenylacetylene	FeCl_3 -NaH(1:3)	7	r.t.	12	Ethylbenzene (27)
Methylphenylacetylene	FeCl_2 -NaH(1:2)	10	0 - 5	15	Propylbenzene (90)
Butylethylacetylene	FeCl_2 -NaH(1:2)	10	0 - 5	48	Octane (65)

*Yields were determined by glpc.

(50%, 2.02 g, 42 mmol), which was washed with dry THF, in THF (3 ml), was added dropwise a solution of iron(III) chloride (2.27 g, 14 mmol) in THF (17 ml) with cooling in an ice bath and stirred for 4 hr at room temperature. Then a solution of 5-hexen-2-one (193 mg, 2 mmol) in THF (2 ml) was added to the yellow suspension. The reaction mixture was stirred continuously at room temperature for 40 hr to become a black suspension, followed by a treatment with aqueous ammonium chloride. The resulting 2-hexanol and 5-hexen-2-ol were extracted with ether, and analyzed by glpc.

References and Notes

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- 4) H. C. Brown and C. A. Brown, J. Amer. Chem. Soc., 84, 1494, 1495 and 2827 (1962) and *ibid.*, 85, 1003 and 1005 (1963).
- 5) Non-enolizable ketones are reduced by sodium hydride to the corresponding alcohols at elevated temperatures. See F. W. Swamer and C. R. Hauser, J. Amer. Chem. Soc., 68, 2647 (1946) and P. Caubère and J. Moreau, Bull. Soc. Chim. France, 3270 and 3276 (1971).
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