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ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING "COMPLEX REDUCING AGENTS" V[1]
SOME PROPERTIES OF $FeCl_3$ COMPLEX REDUCING AGENTS (FeCRA)

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Since a few years, considerable attention has been devoted to the study of reducing agents which consist of mixtures of transition metal salts and metal hydrides[2]. When we started our works on this subject, sodium hydride had scarcely been used for the preparation of this kind of reagents. In previous publications, we showed that NaH-RONa-MX_n systems, designated Complex Reducing Agents (abbreviated CRA), are new useful tools for the reduction of halides[3,4], ketones, alkenes and alkynes[5].

Current investigations in our laboratory pointed out[6] that $FeCl_3$ was one of the transition metal salts which give active CRA for the reduction of organic halides. On the other hand, FUJISAWA, SUGIMOTO and OHTA reported that $FeCl_3$, and principally $FeCl_2$, in the presence of NaH, provide effective systems for the reduction of carbonyl[7] as well as ethylenic or acetylenic compounds[8]. However, these reactions needed large excess of NaH and $FeCl_3$ (NaH/$FeCl_3$/substrate = 21/7/1). Moreover, yields were low for the reduction of monosubstituted alkynes because of simultaneous formation of oligomeric products[8]. Our previous work on alkene and alkyne reductions by NiCRA[5] led us to think that most part of these disadvantages would be removed by using NaH-t.BuONa-$FeCl_3$ (FeCRA) instead of NaH-$FeCl_3$. Ferric chloride appeared more interesting to us than $FeCl_2$ because of its easy availability from commercial sources and over all its more easy storage and handling without alteration.

We wish to report here that FeCRA is, indeed, a more efficient system for the reduction of alkenes and alkynes to the corresponding saturated hydrocarbons. Furthermore, FeCRA, which does not reduce ketones, is exemplified as an attractive reagent for selective reductions.

Preparation of FeCRA

To a stirred suspension of NaH (60 mM)[9] (washed with dry THF) in THF (25 ml), was added $FeCl_3$[10] (10 mM) at room temperature under nitrogen atmosphere. The reaction mixture was warmed to 45°C and a solution of t.BuOH (20 mM) in THF (5 ml) was added dropwise. A green colour rapidly developed (with gas evolution) and then turned to deep black. After stirring for 1 hour at 45°C the reagent was ready for use.

Alkene reductions

Exploratory experiments conducted with 1-octene indicated that quantitative reduction to octane may be obtained after 25 hours at 25°C. However, reaction time was decreased to 6 hours by performing the reaction at 45°C, while incomplete reductions were observed at 65°C (probably due to partial destruction of the reducing species). Typical reductions of alkenes are provided in Table I.

Table I : Reduction of alkenes (7,5 mM) by NaH-t.BuONa-$FeCl_3$ (40/20/10 mM)$^{(a)}$ in 10 ml THF

Alkene	Reaction temp. °C	Reaction time (hr)	Products	yield %$^{(b)}$
1-octene	25	25	octane	90-95$^{(c)}$
1-octene	45	6	octane	90-95$^{(c)}$
1-hexene	45	15	hexane trans 2-hexene	80-85$^{(c)}$ traces
cis 2-hexene	45	20	hexane trans 2-hexene	75-80$^{(c)}$ 5-10
trans 2-hexene	45	20	hexane trans 2-hexene	80-85 5-10
cyclohexene	45	24	cyclohexane cyclohexene	75-80 25-20
cyclooctene	45	15	cyclooctane cyclooctene	45-50 50-45$^{(d)}$
styrene	25	3	ethylbenzene	55-60

(a) i.e. NaH/t.BuONa/$FeCl_3$/alkene = 5,32/2,66/1,33/1

(b) Determined by GLPC analysis (50 m Squalene capillary column) with internal standards (C_6-C_{10} saturated hydrocarbons)

(c) Isomerisations to 2-alkenes were observed during the reduction

(d) No further evolution is observed in 160 hrs

The overall results favorably compare with those described with NaH-$FeCl_3$[8]. For example, reduction of 1-octene by NaH-$FeCl_3$ was performed[8] in 90 % yield after 40 hours at room temperature. However this reaction needed a NaH/$FeCl_3$/substrate ratio as high as 21/7/1. The same ratio was used for the reduction of styrene ; ethylbenzene was obtained in 50 % yield after 42 hours at 0-5°C[8]. The observed activity of FeCRA points out the dramatic effect of the alcoholate (t.BuONa) on the reducing ability of NaH-$FeCl_3$, a result in accordance with our previous observations on the activation of $NaNH_2$[11], NaH[12] and NaH-MX_n (M = Ni, Co, Cu)[3].

The superiority of FeCRA for this kind of reaction was confirmed by reduction of alkynes (Table II). (In this case, a two fold excess of FeCRA was used).

Table II : Reduction of alkyne (7,5 mM) by NaH-t.BuONa-$FeCl_3$ (80/40/20 mM) in 40 ml THF

Alkyne	Reaction temp. °C	Reaction time (hr)	Product	Yield %[(a)]
1-octyne	35	9	octane	95
2-hexyne	45	8	hexane	95
phenylacetylene	35	6	ethylbenzene	98

(a) Determined by GLPC analysis (50 m Squalene capillary column) with internal standards (C_6-C_{10} saturated hydrocarbons)

It is noteworthy that even with phenylacetylene quantitative yields were obtained without formation of polymeric products (a side reaction observed with NaH-$FeCl_3$). These results clearly indicated that FeCRA are far more convenient systems than NaH-$FeCl_3$ for the reduction of alkynes.

Competitive reductions

FeCRA stand out in sharp contrast to NaH-$FeCl_3$ systems in that they do not reduce ketones (experiments not reported here). Thus we thought that FeCRA would be effective for selective reductions and we performed the reactions reported in Table III.

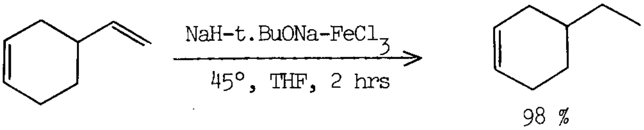
Table III : Reduction of 1-octene (7,5 mM) by NaH-t.BuONa-$FeCl_3$ (40/20/10 mM) in the presence of ketone (10 mM) in 40 ml THF

Ketone	Reaction temp. °C	Reaction time (hr)	Products	Yield %[(a)]
cyclohexanone	45	20	octane cyclohexanone	98 95
5-nonanone	45	16	octane 5-nonanone 5-nonanol	98 90 5
methylphenylketone	45	20	octane trans 2-octene $C_6H_5COCH_3$ $C_6H_5CHOHCH_3$	95 4 90 5

(a) Determined by GLPC analysis (50 m Squalene or Carbowax capillary column) with internal standards (C_6-C_{10} unsaturated hydrocarbons).

Ketone were only slightly reduced (if not at all) and could be recovered without alteration while 1-octene was quantitatively transformed to octane. Thus FeCRA appears as an attractive reagent for selective reductions.

Potential selective reductions of non conjugated dienes were emphasized in the case of 4-vinylcyclohexene (see Scheme).



In conclusion, the results reported in this communication clearly exemplify the activation of reducing agents by sodium alcoholates and confirm that Complex Reducing Agents are new versatile tools in the field of reductions. Moreover, in the near future[13], we shall report that CRA also provide a source of new very active catalysts for heterogeneous hydrogenations.

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References and notes

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