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ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING "COMPLEX REDUCING AGENTS" VI[1]
SOME NEW COMPLEX REDUCING AGENTS AND SOME NEW APPLICATIONS

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Our previous publications showed that Complex Reducing Agents (CRA) NaH-RONa-MX_n (where RONa was a sodium alcoholate and MX_n Ni, Co or Cu salts) are new cheap, easily prepared and handled reagents. They are useful in reductions[2,3,4] as well as carbonylations[5]. Continuing our investigations in this area, we wish to report in the present paper results concerning some new CRA and some of their applications.

New Complex Reducing Agents

Our main results are summarized in the Table I where reduction of 1-bromonaphthalene was selected as an appropriate test reaction.

Table I : 1-Br-$C_{10}H_7$ + NaH (40 mM) - t.AmONa (20 mM) - MX_n $\longrightarrow$ $C_{10}H_8$

Run	1-Br-$C_{10}H_7$ (mM)	MX_n (mM)	Solvent (50ml)	T°C	Reaction time	Reduction (a) Rdt %	By-product % (a)
1	10	$Ni(OAc)_2$ (10)	THF	60	1 h	90 (b)	
2	10	$Ni(OAc)_2$ (10)	DME	60	5 mn	100	
3	10	$Ni(OAc)_2$ (10)	DME	20	1 h 30	85	
4	10	$(Ph_3P)_2NiCl_2$ (10)	THF	60	17 h	40	1,1-binaphthyl (60)
5	10	$FeCl_3$ (10)	DME	60	1 h 30	64	– (c)
6	10	$CrCl_2$ (10)	DME	60	16 h	75	(c)
7	5	$ZrCl_4$ (5)	DME	60	94 h	35	1,1-binaphthyl (27) (c)
8	10	$ZnCl_2$ (10)	THF	60	3 h	90	
9	4	$MoCl_5$ (4)	THF	60	20 h	70	
10	3,3	WCl_6 (3,3)	DME	60	31 h	80	
11	10	$Mn(OAc)_2$ (10)	THF	60	40 h	35	(c)
12	10	Cp_2TiCl_2 (10)	THF	60	42 h	73	(c)
13	10	Cp_2TiCl_2 (10)	DME	60	60 h	72	(c)

(a) Isolated yields (b) From reference [2] (c) Heavy by-products were obtained.

As anticipated[2] the solvent had a dramatic influence on the rate of the reductions (runs 1-3). Moreover, it appears that besides the metallic salts used precedently[2], a wide variety of other ones provide active systems. Of course, the nature of the metal plays a very important part on the reducing ability of CRA.

It is noteworthy that reagents prepared from $ZrCl_4$ (run 7) and $(Ph_3P)_2NiCl_2$ (run 4) lead to appreciable amounts of 1,1'-binaphthyl.We shall see (vide infra) applications of this last observation.

Reduction of organic halides

Until now, results were obtained from aromatic halides[2] or gem-dihalogenocyclopropane compounds[3]. However, it was of interest to know if our reagents were able to reduce other kinds of halides. As seen from Table II, CRA appear effective in the reduction of various kinds of halides.

Table II : Reduction of some organic halides (10 mM) by NaH (40 mM) - t.AmONa (20 mM) - MX_n (10 mM)

Run	MX_n	Substrate	Solvent (50 ml)	T°C	reaction time	Yield %
14	$Ni(OAc)_2$	$1\text{-}ClC_8H_{17}$	DME	60	15 mn	95[(a)]
15	$Ni(OAc)_2$	$1\text{-}BrC_8H_{17}$	DME	20	15 mn	98[(a)]
16	$Ni(OAc)_2$	$2\text{-}BrC_8H_{17}$	DME	20	20 mn	100[(a)]
17	$Ni(OAc)_2$	$4\text{-}BrC_8H_{17}$	DME	20	30-60 mn	95[(a)]
18	$Ni(OAc)_2$	$1\text{-}BrC_{12}H_{25}$	DME	20	1 h 15	93[(b)]
19	$Ni(OAc)_2$	$Br\text{-}Cyclo\text{-}C_6H_{11}$	DME	20	30 mn	95[(a)]
20	$Ni(OAc)_2$	1-Br Adamantyl	DME	60	15 mn	90[(a)]
21	$Ni(OAc)_2$	$C_6H_5CH_2Cl$	DME	20	30 mn	80[(c)]
22	$Ni(OAc)_2$	$2\text{-}MeOC_6H_4Br$	DME	60	5 mn	90
23	$ZnCl_2$	$1\text{-}BrC_8H_{17}$	THF	20	18 h	95
24	$ZnCl_2$	$1\text{-}BrC_8H_{17}$	THF	60	65 mn	95
25	$ZnCl_2$	$1\text{-}IC_8H_{17}$	THF	20	45 mn	95
26	$ZnCl_2$	$4\text{-}BrC_8H_{17}$	THF	20	16 h	0
27	$ZnCl_2$	$1\text{-}BrC_{12}H_{25}$	THF	60	2 h	100
28	$ZnCl_2$	$Ph\text{-}CH{=}CH\text{-}CH_2Br$	DME	15	1 h - 1h30	80[(a)]

(a) Determined by GLPC analysis with internal standards

(b) Isolated yield

(c) 20 % of bitolyl were formed

Not reported experiments pointed out that some other metallic salts (for example $FeCl_3$, $ZrCl_4$, WCl_6) allowed reductions of 1-bromooctane. However ethylenic derivatives were formed in about 20 % yield.

Table II reveals that selective reductions would be possible (compare runs 14 and 15, 23 and 26). This selectivity is exemplified by competitive experiments reported in Table III.

Table III : Competitive reductions of halides by CRA[(a)]

Run	Substrate (mM)	MX_n (10mM)	Solvent (50 ml)	T°C	t	Reduction product % (b)	Recovered starting material % (b)
29	$1\text{-}BrC_8H_{17}$ (10) + $4\text{-}BrC_8H_{17}$ (10)	$ZnCl_2$	THF	40	6 h	C_8H_{18} (100)	$4\text{-}BrC_8H_{17}$ (100)
30	$1\text{-}BrC_8H_{17}$ (10) + $1\text{-}ClC_8H_{17}$ (10)	$Ni(OAc)_2$	DME	60	3 mn	C_8H_{18} (100)	$1\text{-}ClC_8H_{17}$ (100)
31	$C_6H_5CH_2Cl$ (10) + $1\text{-}Br\text{-}C_8H_{17}$ (10)	$Ni(OAc)_2$	DME	20	30 mn	$C_6H_5CH_3$ (c) (85)	$1\text{-}BrC_8H_{17}$ (90)

(a) NaH (40 mM) - t.AmONa (20 mM)

(b) Determined by GLPC with internal standards

(c) Isolation of 15 % $(C_6H_5CH_2)_2$

Note that the result of run 31 is rather surprising considering runs 15 and 21 (Table II).

Anyway, it is clear that CRA allowed a wide range of reductions and constitute very promising reagents.

Coupling and oligomerisation reactions

We saw before (run 4 Table I) that $(Ph_3P)_2NiCl_2$ induced some coupling of 1-bromonaphthalene. We thought that the preparation of CRA in the presence of Ph_3P would lead to new reagents able to couple organic halides instead of reduce them.

Indeed this was the case. However some side reactions, just now studied, intervened and after some preliminary experiments we chose bipyridyl as a convenient ligand. Our first results are reported in the Table IV.

Table IV : Coupling of aromatic halides by NaH-t.AmONa-Ni(OAc)$_2$-Bipyr$^{(a)}$ in THF (50ml) at 60°C

Run	Substrate (10 mM)	t (h)	Coupled product % (b)	Reduction Product % (c)
32	1-BrC_8H_7	1,5	1,1'-binaphtyl (70)	C_8H_8 (25)
33	2-Cl-C_6H_4-CH_3	24	2,2'-bitolyl (80)	$C_6H_5CH_3$ (20)
34	4-Cl-C_6H_4-CH_3	20	4,4'-bitolyl (85)	$C_6H_5CH_3$ (15)

(a) Reagents ratio mM : 40/20/10/20

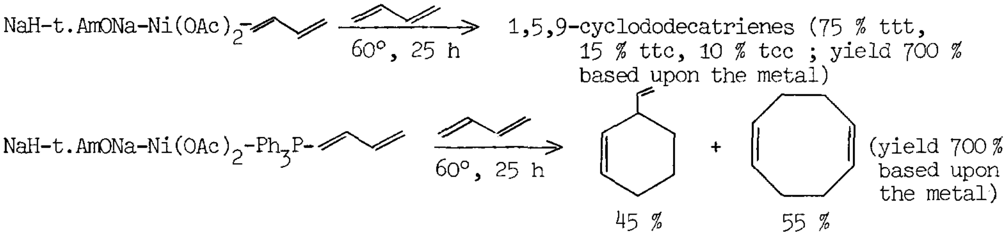
(b) Isolated yield (c) Determined by GLPC with internal standards

Wanting just now to emphasize this new property, we did not optimise reaction conditions.

From our whole results, we postulated that without additional ligand, the reaction of NaH-t.AmONa with metallic salts led to hydride reducing species (as briefly shown earlier[4]). On the other hand, in the presence of an additional ligand, the reaction takes another course and leads to stabilised low valent metallic species able to give, for example, coupling reactions.

Taking account of the literature results[6] this hypothesis is strongly supported by the reactions performed with butadiene (see Scheme).

Scheme :



Both reactions were conducted in THF under normal pressure with the help of a very efficient cold condenser. Besides trimerisation we observed small quantities formation of 3-vinyl cyclohexene and 1,5-cyclooctadienes. Besides dimerisation low amount of unknown by-products was formed. We are now extending the results briefly outlined in the present note and developing some new applications.

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