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ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS

VIII *. NEW COMPLEX REDUCING AGENTS

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Summary

Activated sodium hydride (NaH—RONa) was treated with Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Zr, Mo, Pd, W salts to give the new complex reducing agents NaH—RONa—MX_n (CRA). Their reactivities were examined for reduction of 1-bromonaphthalene. In most cases, the CRA exhibited very good reducing abilities, which can be varied by changing the solvent, the alkoxide, or the temperature. Moreover, some CRA act as coupling agents for aromatic halides. Easy to prepare and handle on a preparative scale, CRA must be regarded as very promising tools for organic synthesis.

Introduction

In recent years, considerable attention has been devoted to the reducing properties of transition metal hydrides as well as to those of mixtures of complex metal hydrides and transition metallic salts [1]. We have previously described [2] complex reducing agents (CRA), a new class of reagents which consist of mixtures of sodium hydride, sodium alkoxides and metallic salts "NaH—RONa—MX_n" (M = Ni, Co, Cu). They were first demonstrated to be effective for the reduction of aromatic halides [2] and *gem*-dihalogenocyclopropanes derivatives [3].

In some further preliminary communications we described their use for the reduction of alkenes, alkynes, enolisable ketones [4] and aliphatic halides [5]. Moreover, they have been shown to be of some interest in carbonylation [6],

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* For part VII see ref. 7.

oligomerisation [5] and coupling reactions [5]. Finally, we recently described a new, very active, heterogeneous hydrogenation nickel catalyst prepared from CRA [7].

A report by Ashby and Lin [8] of the reducing properties of $LiAlH_4$—transition metallic salts mixtures encouraged us to report our studies on the use of activated sodium hydride NaH—RONa [9] both for reductions of organic halides and for the preparation of CRA.

The present publication is the first of a series devoted to the extension of our preliminary results [2—7] and dealing with new CRA.

Design of complex reducing agents

One of the main features of the use of sodium hydride for preparation of reducing agents is that it does not involve ions other than Na^+. In addition, we have showed that in CRA, the basicity of NaH is strongly inhibited [4], thus largely removing one of the chief disadvantages of this hydride in reductions. Moreover, it is a cheap reagent, which can be easily handled, even on large scale.

In all our work on CRA, we deliberately performed all experiments on a preparative scale, using only commercial reagents and solvents of current grade for organic chemist. Control experiments were performed to reveal the differences, if any between CRA and one or two of its constituents. As we shall see, such experiments are very important in this kind of work, and can lead to somewhat unexpected results.

The goal of this work was to obtain not only very active NaH—RONa—MX_n systems but also milder ones, with a view to selective reductions.

In the light of previous results [2—7], reduction of 1-bromonaphthalene was chosen as test reaction.

Experimental

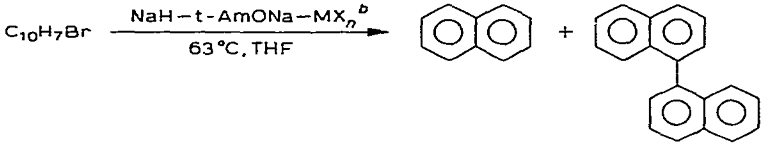
Fluka sodium hydride (50—60% in oil) was used, and was washed several times with the chosen solvent. All reactions were carried out under nitrogen or argon. Metallic salts were, if necessary, dried in vacuum for 8—12 h at 80—110°C. All solvents were distilled and stored over sodium wire. The absence of peroxides was confirmed in each case. The experiments were carried out by the following procedures:

Method A (exemplified for THF). t-AmOH (20 m*M*) in THF (10 ml) was added at 60—63°C to a vigorously stirred suspension of NaH (60 m*M*) in THF (10 ml), and the mixture refluxed for 2 h. The temperature was then decreased if necessary (to 0°C for $TiCl_4$, $TiCl_3$, $FeCl_3$, $MoCl_5$, WCl_6, 20°C for VCl_3, $Mn(OAc)_2$, $ZrCl_4$, $PdCl_2$, $Pd(OAc)_2$, $ZnCl_2$, $Zn(OAc)_2$, $CdCl_2$) and the metallic salt (10 m*M*) was added, followed by 10 ml of THF. After refluxing for 4 h, the reagent was ready for use (typical colourations are given in Table 1). 1-Bromonaphthalene (10 m*M*) in THF (10 ml) was then added. Each run was repeated twice: first with an internal standard (tetradecane) for GLPC analysis and secondly without the standard to determine isolated yields after ordinary work-up.

Method B (exemplified for DME). The metallic salt (10 m*M*) was added, at room temperature or below (see method A) to a stirred suspension of NaH

TABLE 1

REDUCTION OF 1-BROMONAPHTHALENE IN THF[a] (Method A)



Metallic salt	Reaction medium colouration	Reaction time	Naphthalene (%)[c]	1,1'-Binaphthyl (%)[c]
$TiCl_4$	grey	40—45 h	8—10	—[d]
Cp_2TiCl_2	black	2—3 h	70—75	traces[e]
$TiCl_3$	black	60—65 h	50—55	traces[e]
VCl_3	black	13—15 h	80—85	traces[e]
$CrCl_2$	blue, then black	15—17 h	70—75	—[e]
$Cr(OAc)_3$	black	16—18 h	70—75	traces[e]
$Mn(OAc)_2$	marroon	40—45 h	35—40	—[e]
$FeCl_3$	black	3—4 h	70—75	15—20[e]
$Co(OAc)_2$	black	1.5—2 h	85—90	—
$NiCl_2$	black	25—30 h	80—85	—[e]
$(Ph_3P)_2NiCl_2$	black	1.5—2 h	60—65	20—25[e]
$NiBr_2$	black	15 min	90—95	—
$Ni(OAc)_2$	black	5 min	90	—
$Cu(OAc)_2$[f]	black	17 h	60—65	20[e]
$ZnCl_2$	grey	3 h	90—95	—
$Zn(OAc)_2$	grey	1.5—2 h	95	—
$CdCl_2$	grey	2.5—3 h	50	35—40[e]
$ZrCl_4$	yellow	4—5 h[g]	55	25[e]
$MoCl_5$	black	145 h	30—35	traces[e, h]
$PdCl_2$	black	5 min	85—90	—
$Pd(OAc)_2$[i]	black	5 min	90—95	—
WCl_6	blue	100 h	5—10	—[d]

[a] 40 ml. [b] ratio NaH/t-AmONa/MX_n/$C_{10}H_7Br$ = 40/20/10/10 (in m*M*). [c] Isolated yields after column chromatography. [d] 80% starting material recovered. [e] Unidentified heavy by-products were formed. [f] Result of ref. 2. [g] Hardly reproducible. [h] 45% recovered starting material. [i] NaH/t-AmONa/$Pd(OAc)_2$/$C_{10}H_7Br$ = 20/10/5/5 m*M*.

(60 m*M*) in DME (20 ml). The temperature was raised to 60—65°C and t-AmOH (20 m*M*) in DME (10 ml) was added. After refluxing for 45—60 min the reagent was ready for use and the experiments were conducted as for method A.

Control experiments

NaH reductions. 1-Bromonaphthalene (10 m*M*) in 10 ml of the desired solvent was added at 60—63°C to a stirred suspension of NaH (60 m*M*) in 30 ml of solvent. The reaction was monitored by GLPC analysis of small aliquots.

NaH—t-AmONa reductions. 1-Bromonaphthalene (10 m*M*) in 10 ml of solvent was added at 60—63°C to the NaH—t-AmONa (40—20 m*M*), prepared as in method A in 30 ml solvent. The reaction was monitored as before.

NaH—MX_n reductions. The metallic salt (10 m*M*) was added at the appropriate temperature (see method A) to a stirred suspension of NaH (60 m*M*) in 30 ml of solvent. The temperature was raised to 63°C. After 4 h with good stirring, 1-bromonaphthalene (10 m*M*) was added. The reaction was monitored as before.

t-AmONa—MX$_n$ reductions. t-AmONa (60 mM) was prepared by adding t-AmOH (60 mM) in the solvent (10 ml) to a stirred suspension of NaH (60 mM) in 20 ml of the solvent at 60—63°C. After 2 h with good stirring, the temperature was decreased and the metallic salt (10 mM) was added (for relevant temperatures see method A). After 4 h of stirring at 63°C 1-bromonaphthalene (10 mM) in THF (10 ml) was added. The reaction was monitored as before.

Results

Reduction of 1-bromonaphthalene was first tried with several NaH—t-AmONa—MX$_n$ systems in THF, using method A (see experimental). Results are recorded in Table 1.

The control experiments can be summarized as follows:

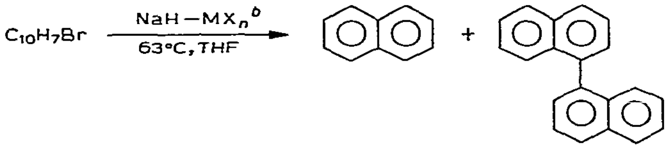
NaH reduced 1-bromonaphthalene in 35—40% yield after 170 h in refluxing THF. Much tar was formed.

No reaction was observed with t-AmONa after 65 h in refluxing THF.

Reductions by NaH—t-AmONa (40—20 mM) were rather erratic. Thus yields

TABLE 2

CONTROL EXPERIMENTS - REDUCTION OF 1-BROMONAPHTHALENE IN THF [a]



Metallic salt	Reaction medium colouration	Reaction time (h)	Naphthalene (%) [c]	1,1'-Binaphthyl (%) [d]	Unreacted [c] 1-bromonaphthalene (%)
$TiCl_4$	white	40—45	20—25	—	65—70
Cp_2TiCl_2	dark marroon	50—55	85—90	10	none
$TiCl_3$	purple	75—80	traces	—	90
VCl_3	purple	110	0—5	—	90
$CrCl_2$	marroon	65—70	50	—	45
$Cr(OAc)_3$	black	15—20	5—10	—	80
$Mn(OAc)_2$	marroon	55—60	20	—	75
$FeCl_3$	black	35—40	60	traces	35
$Co(OAc)_2$	purple	25—30	5—10	—	90
$NiCl_2$	black	25—30	0—5	—	95
$(Ph_3P)_2NiCl_2$	marroon	40—45	25—30	55—60	none [e]
$NiBr_2$	black	40—45	40—45	traces	40
$Ni(OAc)_2$	black	40—45	60	0—5	none [e]
$Cu(OAc)_2$	black	35—40	60	—	40
$ZnCl_2$	grey	10—15	85—90	—	none [e]
$Zn(OAc)_2$	grey	50—55	60—65	—	25 [e]
$CdCl_2$	grey	40—45	65—70	—	30
$ZrCl_4$	grey	35—40	10—15	—	80
$MoCl_5$	marroon	120	15—20	—	80
$Pd(OAc)_2$	black	3—4	45—50	—	50
WCl_6	dark purple	110	traces	—	100

[a] 40 ml; [b] NaH/MX$_n$/$C_{10}H_7Br$ = 60/10/10. [c] Determined by GLPC analysis with internal standards. [d] Isolated yields. [e] Unidentified heavy by-products.

varied from 30 to 85% and reaction times from 14 to 210 h. These results confirm the reducing properties of NaH—RONa systems. However the reductions are often of poor reproducibility in THF.

All the t-AmONa—MX_n systems were examined. Except for two cases ($CrCl_2$ and $Pd(OAc)_2$) reduction yields were very low (<10%; the observed reductions may be due to the presence of a small excess of the NaH used to prepare the alkoxide). With $CrCl_2$ the reduction yields reached 45—50% after 110—120 h of reaction. The result observed with $Pd(OAc)_2$ is noteworthy; 25—30% of naphthalene were obtained accompanied by 40—45% of 1,1'-binaphthyl. For both salts, it has been demonstrated that no reaction occurred without t-AmONa.

Finally, experiments performed with NaH—MX_n are recorded in Table 2. In some cases good yields were obtained but reaction times were always longer than for the reductions with CRA. Results obtained with $(Ph_3P)_2NiCl_2$, and further investigations [10] indicate that the presence of ligands on the metal atom facilitates the reduction of nickel salts by NaH and leads to reagents which are more effective for coupling (however, they are far less reactive than NaH—t-AmONa—$Ni(OAc)_2$—Ph_3P [10]).

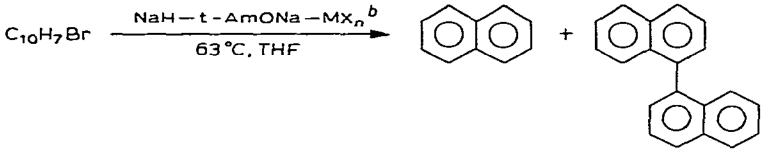
Comparison of Tables 1 and 2 shows that t-AmONa generally increases the reducing ability of NaH—MX_n mixtures, leading, in most cases, to powerful reducing agents. Six metallic salts ($TiCl_4$, $TiCl_3$, $Mn(OAc)_2$, $NiCl_2$, $MoCl_5$, WCl_6) lead to CRA systems less active than NaH—t-AmONa. It is noteworthy that in five cases (Table 1) formation of 1,1'-binaphthyl occurred. These observations indicated that CRA might also be useful as coupling reagents, and this was confirmed by some preliminary results [5].

In order to get more informations about CRA, some of the main parameters to their preparation were studied.

It appeared from the results reported in Table 1 that the most reactive CRA were obtained from metal(II) salts, other metal salts leading to milder reducing reagents. This mildness might have been due to a wrong ratio of the reagents, and so we performed further experiments with NaH/t-AmONa/MX_n/$C_{10}H_7Br$ equal to 40/20/20 : n/20 : n (where n is the oxidation degree of the metal) instead of 40/20/10/10. From these latter experiments it appeared that for $TiCl_3$, VCl_3,

TABLE 3

REDUCTION OF 1-BROMONAPHTHALENE IN THF [a] (Method B)



Metallic salt	Reaction time	Naphthalene (%) [c]	1,1'-Binaphthyl [c]
Cp_2TiCl_2	1.5 h	65—70	traces [d]
$Co(OAc)_2$	1.5 h	90—95	—
$Ni(OAc)_2$	5 min	85—90	—
$Zn(OAc)_2$	1.5—2 h	90—95	—

[a] 40 ml. [b] NaH/t-AmONa/MX_n/$C_{10}H_7Br$ = 40/20/10/10 m*M*. [c] Isolated yields. [d] Unidentified heavy by-products.

TABLE 4

REDUCTION OF 1-BROMONAPHTHALENE BY NaH—t-AmONa-$Ni(OAc)_2$ [a] IN VARIOUS SOLVENTS (Method B)

Solvent [b]	T (°C)	Preparation time	Reaction time	Naphthalene (%) [c]
THF	63	45 min	5 min	90
DME	63	45 min	5 min	95—100
Benzene	63	4 h	2.5 h	80—85 [d]
Cyclohexane	63	4 h	40 h	10 [e]
Anisole	63	45 min	2.5—3 h	65—70 [d]
Diethyl ether	33	4 h	10 h	70 [d]

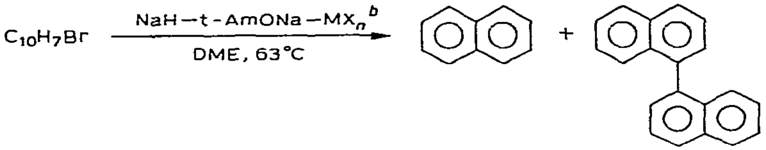
[a] NaH/t-AmONa/$Ni(OAc)_2$/$C_{10}H_7Br$ = 40/20/10/10 m*M*. [b] 40 ml. [c] Isolated yields. [d] Unidentified heavy by-products. [e] 85% unreacted starting material.

$Cr(OAc)_3$, $FeCl_3$, $ZrCl_4$ there was no increase in reactivity; with $TiCl_4$, $MoCl_5$ and WCl_6, the reducing properties were close to those of NaH—t-AmONa.

In the light of the above results, we examined the influence of the preparation procedure on the reactivity of CRA. Thus we prepared them by addition of the

TABLE 5

REDUCTION OF 1-BROMONAPHTHALENE IN DME [a] (Method B)



Metallic salt	Reaction medium colouration	Reaction time	Naphthalene (%) [c]	1,1'-Binaphthyl (%) [c]
$TiCl_4$	white	160 h	20	— [f]
Cp_2TiCl_2	black	1 h	70—75	traces [d]
$TiCl_3$	white	17 h	traces	— [d, f]
VCl_3 [e]	grey	140 h	10	— [d, f]
$CrCl_2$	black	2—3 h	80—85	5 [d]
$Cr(OAc)_3$ [e]	grey	7 h	95—100	—
$Mn(OAc)_2$	marroon	55 h	85—90	8—10
$FeCl_3$	black	1—2 h	65—70	20—25 [d]
$Co(OAc)_2$	black	2 h	85—90	—
$NiCl_2$	black	17 h	80	8—10 [d]
$(Ph_3P)_2NiCl_2$	black	1—2 h	45—50	30—35 [d]
$NiBr_2$	black	15 min	65—70	traces [d]
$Ni(OAc)_2$	black	5 min	95—100	—
$Cu(OAc)_2$	black	20 h	80—85	5—10
$ZnCl_2$	grey	2—3 h	95—100	—
$Zn(OAc)_2$	grey	2—3 h	85—90	traces
$CdCl_2$	dark green	2—3 h	95	—
$ZrCl_4$	white	50—55 h	35—40	25—30 [d]
$MoCl_5$	marroon	70 h	25—30	— [d, g]
$PdCl_2$	black	30 min	90—95	—
$Pd(OAc)_2$	black	30 min	85—90	—
WCl_6 [e]	purple	30 h	80—85	— [d]

[a] 40 ml. [b] Unless otherwise noted, NaH/t-AmONa/MX_n/$C_{10}H_7Br$ = 40/20/10/10 m*M*. [c] Isolated yields. [d] Unidentified heavy by-products. [e] NaH/t-AmONa/MX_n/$C_{10}H_7Br$ = 40/20/20 : *n*/20 : *n*. [f] 80% recovered starting material. [g] 50% recovered starting material.

alcohol to NaH—MX$_n$ mixtures in the relevant solvent (method B). A few experiments of this kind are reported in Table 3. Qualitatively, the results were the same as for method A and reaction times were generally similar. However, preparation times were obviously shorter. Thus, method B appeared more suitable, and this alternative procedure was generally used in later experiments.

The influence of the solvent on CRA properties was also briefly studied. The main results are summarized in Table 4. In each case the characteristic black colour of the CRA appeared, more or less quickly depending upon the nature of solvent. DME and THF led to the best results. However non polar solvents should be of interest for selective reductions.

These results encouraged us to perform a series of experiments using DME (method B) as solvent with the goal of improving the reduction obtained in THF. The experiments reported in Table 5 show that solvent effects are in fact not easy to predict. In most cases, DME was a better solvent than THF, but for some salts ($TiCl_3$, VCl_3, $ZrCl_4$) the opposite was true. Furthermore, the coupling ability of some reagents seemed to depend upon the solvent ($Mn(OAc)_2$, $NiCl_2$, $Cu(OAc)_2$, $CdCl_2$).

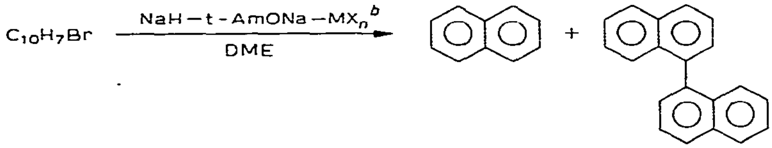
In DME, reduction of 1-bromonaphthalene by NaH was very slow and incomplete, while reduction by NaH—t-AmONa was reproducibly achieved in 17 h. Thus in DME, five salts ($TiCl_4$, $TiCl_3$, VCl_3, $MoCl_5$, WCl_6) lead to CRA systems less active than NaH—t-AmONa.

Temperature variation was briefly examined (Table 6). As expected reaction rates were increased by raising the reaction temperature, but for the two coupling systems used the lower the temperature the higher the yield of 1,1′-binaphthyl.

Finally with reference to complex bases [11], it might be thought that the feasibility of preparing CRA and also their reducing powers might be dependent upon the activating alkoxide. These expectations were verified, as shown in Table 7, which clearly indicates that several kinds of alcohols may be used. The most important feature is that the variation of the nature of the activating alkoxide allows controlled variation of the CRA properties.

TABLE 6

REDUCTION OF 1-BROMONAPHTHALENE IN DME [a] (Method B). TEMPERATURE EFFECT

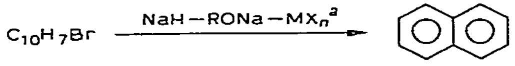


Metallic salt	T (°C)	Reaction time	Naphthalene (%) [c]	1,1′-Binapthyl (%) [c]
$Ni(OAc)_2$	RT	1.5 h	80—85	— [d]
$Ni(OAc)_2$	63	5 min	95—100	—
$(Ph_3P)_2NiCl_2$	RT	20 h	30—35	50 [d]
$(Ph_3P)_2NiCl_2$	63	1—2 h	45—50	30—35 [d]
$FeCl_3$	RT	15 h	50—55	35—40 [d]
$FeCl_3$	63	1—2 h	65—70	20—25 [d]

[a] 40 ml. [b] NaH/t-AmONa/MX$_n$/$C_{10}H_7Br$ = 40/20/10/10 mM. [c] Isolated yields. [d] Unidentified heavy by-products.

TABLE 7

REDUCTION OF 1-BROMONAPHTHALENE. VARIATION OF THE ACTIVATING ALKOXIDE

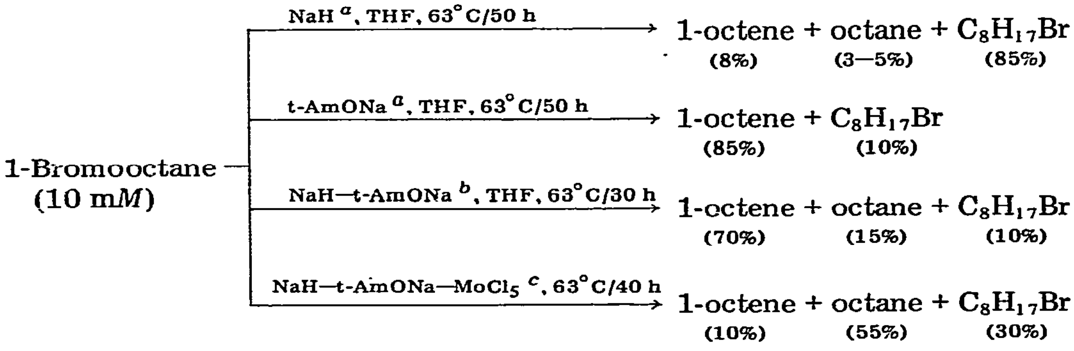


Alcohol (ROH)	Metallic salt	Solvent[b] (Method)	T (°C)	Reaction time	Naphthalene (%)
MeOH	$Ni(OAc)_2$	DME (B)	63	—	—[c]
EtOH	$Ni(OAc)_2$	DME (B)	63	5 h	75—80[d]
EtOH	$ZnCl_2$	THF (A)	63	3.5 h	90—95
$Et(OCH_2CH_2)_2OH$	$Ni(OAc)_2$	DME (B)	20	2.5 h	90—95
iPrOH	$Ni(OAc)_2$	DME (B)	20	2 h	85—90[e]
iPrOH	$ZnCl_2$	THF (A)	63	1 h	75—80[e]
2-octanol	$Ni(OAc)_2$	DME (B)	20	3.5 h	70—75[e]
2-octanol	$ZnCl_2$	THF (A)	63	16 h	40—45[f]
cyclohexanol	$Ni(OAc)_2$	DME (B)	20	3—4 h	70—75[e]
cyclohexanol	$ZnCl_2$	THF (A)	63	3 h	90—95
t-BuOH	$Ni(OAc)_2$	DME (B)	20	2 h	85—90
t-BuOH	$ZnCl_2$	THF (A)	63	2 h	90—95
t-AmOH	$Ni(OAc)_2$	DME (B)	20	1.5 h	80—85[e]
t-AmOH	$ZnCl_2$	THF (A)	63	3 h	90—95
phenol	$Ni(OAc)_2$	DME (B)	20	9—10 h	90—95[e]
phenol	$ZnCl_2$	THF (A)	63	1.5 h	70—75[e]

[a] NaH/RONa/MX$_n$/$C_{10}H_7Br$ = 40/20/10/10 m*M*. [b] 40 ml. [c] The black colouration was not observed and no reaction occurred. [d] Often erratic. [e] Unidentified heavy by-products. [f] 45% recovered starting material.

It was noted above that $TiCl_4$, $MoCl_5$ and WCl_6 gave NaH—t-AmONa—MX$_n$ mixtures of low reactivity towards 1-bromonaphthalene, in both DME and THF. These reagents may, however, be of potential value as exemplified for $MoCl_5$ in Scheme 1.

SCHEME 1



[a] 60 mM. [b] 40/20 m*M*. [c] 40/20/10 m*M*.

These experiments clearly confirm that CRA properties are fundamentally different from those of the components. Moreover they suggest that mild reducing CRA may find further applications in selective reductions.

Conclusion

It is evident that reactions of NaH—RONa with metallic salts leading to CRA are general. CRA constitute new versatile reducing reagents, the properties may be easily varied. Some applications of this potential selectivity have already been described [5,12]. From the practical viewpoint, it must be emphasized that CRA are cheap, and easily prepared and handled. Moreover, work now in progress confirms that in many cases reductions may be achieved with metallic salts as catalysts, and we shall show in further publications how CRA may be used to perform selective as well as rapid quantitative reductions.

Acknowledgments

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