Pergamon

Tetrahedron Letters, Vol. 38, No. 47, pp. 8157-8158, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10222-2

The Effect of Lithium Bromide and Lithium Chloride on the Reactivity of SmI_2 in THF

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Abstract: Lithium bromide and lithium chloride salts have a profound influence on the reactivity of SmI_2. These salts increase the reducing power of SmI_2 and promote pinacol coupling. © 1997 Elsevier Science Ltd.

Samarium diiodide (SmI_2) is undoubtedly one of the most important reducing reagents presently utilized by organic chemists.[1] Numerous additives have been reported to promote or accelerate many types of reactions mediated by SmI_2. Lewis acids, including iron(III) compounds have been used to promote halide carbonyl coupling reactions.[2] Bases (KOH, $LiOCH_3$, and $LiNH_2$) have been employed in concert with SmI_2 to reduce esters, anhydrides, amides and carbonyls to the corresponding alcohols.[3] Cosolvents containing basic oxygen including HMPA, DMPU, and amines have been utilized to accelerate the reduction of organic functional groups and the coupling of halides with pi bonds.[1,4] First row transition metal catalysts have been employed with SmI_2 and proton donating cosolvents to reduce alkynes to alkenes.[5] Herein we report the effect of LiCl and LiBr on the reactivity of SmI_2.

During our initial electrochemical studies on the effect of cosolvents on the reducing power of SmI_2, we discovered that lithium halides containing a bromide or chloride counterion turned the blue SmI_2 solution to purple, reminiscent of the color change that occurs when HMPA is added as a cosolvent. The oxidation potential of SmI_2 in THF is -1.33V.[6] We initiated an electrochemical study designed to determine the effect of lithium halide salt concentration on the oxidation potential of SmI_2. The oxidation potential of SmI_2 containing 12 or more equivalents of LiBr was determined to be -1.98 ± 0.01 V while the oxidation potential of SmI_2 containing 12 or more equivalents of LiCl was -2.11 ± 0.01 V.[7] We initially suspected that the bromide and chloride ions were coordinating to the samarium and possibly displacing the iodide producing $SmBr_2$ or $SmCl_2$ *in situ*. We prepared $SmBr_2$[8] and $SmCl_2$[9] and found these reagents to be sparingly soluble in THF and numerous attempts to obtain their oxidation potentials were unsuccessful due to their low solubilities.

The negative oxidation potential of the species produced from the addition of LiBr and LiCl to SmI_2 led us to realize that this method may offer a convenient protocol for coupling carbonyls. The pinacol coupling of cyclohexanone was employed as a model in order to determine the possibility of using the lithium halide additives in SmI_2 mediated coupling reactions.[10] The influence of LiCl and LiBr on the reaction time and product yields are contained in Table 1. In all cases, the yields (both GC and isolated) are greater than 90% employing the lithium salts. Coupling reactions containing more than 12 equivalents of LiCl or LiBr displayed no further rate enhancement. It should be noted that the salts need to be dry in order for the reaction to produce the coupled product. Reactions performed with wet salts or with a few equivalents of added water produced only cyclohexanol.

Table 1. The Influence of Lithium Halide Salts on the Reaction Time and Yield of Pinacol Coupling of Cyclohexanone.

LiX Additive	Equivalents[a]	Reaction Time	GC Yield (%)	Isolated Yield
LiBr	4	10 min	98	92
LiBr	8	6 min	98	96
LiBr	12	4 min	97	93
LiCl	4	5 min	95	91
LiCl	8	3 min	97	95
LiCl	12	1 min	96	91

a) The equivalents of lithium halide based on the concentration of SmI_2.

We suspect that at higher concentrations of lithium salts, not only is the halide coordinating to the SmI_2, but the lithium may be coordinating to the carbonyl as well. This coordination effectively decreases the reduction potential of the carbonyl[11] and further enhances the rate of coupling. The ability to simultaneously increase the reducing power of SmI_2 while decreasing the reduction potential of carbonyls may provide a method for selective reductive coupling of carbonyls in the presence of a more easily reducible functional group. Work on the influence of lithium halides in SmI_2 mediated intra- and intermolecular carbonyl couplings is currently being investigated in our laboratory.

Acknowledgments: RAF is grateful to the donors of the Petroleum Research Fund, administered by the ACS, (29492-G1) for support of this research. JRF would like to thank the Proctor & Gamble Company and the University of Toledo Honors Program for undergraduate research funding.

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(*Received in USA* 15 *August* 1997; *revised* 17 *September* 1997; *accepted* 18 *September* 1997)