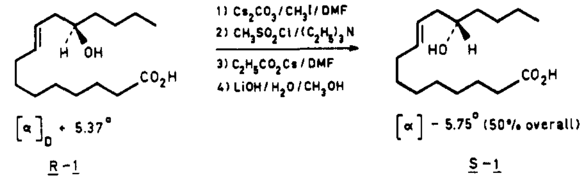

(2)

ether nor $C_2H_5O_2CNNCO_2C_2H_5/(C_6H_5)_3P/C_6H_5CO_2H$ gave acceptable results.[9,10]

Acknowledgment. We thank Professor D. Seebach, ETH Zürich, for providing us with an unpublished method for the transesterification of propionate esters.[11]

Registry No. (*R*)-1, 540-12-5; (*S*)-2-octanol, 6169-06-8; (1*R*)-menthol, 2216-51-5; 5α-cholestan-3β-ol, 80-97-7; ethyl (*S*)-2-hydroxypropionate, 687-47-8; methyl (*S*)-2-hydroxy-2-phenylacetate, 21210-43-5; (*S*)-2-hydroxy-2-phenyl-*N*,*N*-dimethylacetamide, 79043-43-9; benzyl methanesulfonate, 55791-06-5; (*RS*)-2-bromooctane, 60251-57-2; *trans*-3-hexen-1-ol, 928-97-2; 1-iodoheptane, 4282-40-0; ethyl-(*RS*)-2-bromopropionate, 41978-69-2; cesium propionate, 38869-24-8; cesium benzoate, 17265-04-2.

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[9] In the reaction of the methyl ester of (*R*)-1 with $C_2H_5O_2CN=NCO_2C_2H_5/(C_6H_5)_3P/C_6H_5CO_2H$ the benzoate obtained was almost completely racemic. The cause of the racemization has not been determined. The mesylate of the methyl ester of (*R*)-1 with excess KO_2/dibenzo-18-crown-6 gave impure methyl ester of (*S*)-1 in poor yield; separation from the large excess of crown ether was difficult.

[10] For a recent report on the use of cesium fluoride in DMF as a catalyst see: (a) Mukaiyama, T.; Murakami, M.; Yamaguchi, M. *Chem. Lett.* **1980**, 529. (b) Mukaiyama, T.; Pai, F.-C.; Onaka, M.; Narasaka, K. *Ibid.* **1980**, 563.

[11] Seebach, D.; Hungerbühler, E.; Schnurrenberger, P.; Weidmann, B.; Züger, M., submitted for publication in *Synthesis.*

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Preparation of Highly Reactive Metal Powders. A New Procedure for the Preparation of Highly Reactive Zinc and Magnesium Metal Powders

Summary: Highly reactive zinc and magnesium metal powders can be prepared by the lithium reduction of the corresponding metal salt with a catalytic amount of naphthalene as an electron carrier. Applications to the Reformatsky reaction, the Grignard reaction, and cyclopropanation (with dibromomethane) are described.

Sir: Earlier we had reported the preparation of highly reactive zinc and magnesium metal powders from the potassium or sodium reduction of the corresponding metal salt.[1-4] We now report a new general approach for the preparation of these highly reactive metal powders, using lithium as a reducing agent.[5] In the case of zinc, this results in far more reactive metal powders which can be used in several reactions with special advantage.

The highly reactive zinc is readily prepared by the reduction of anhydrous zinc chloride with 2.1 equiv of lithium and a small amount of naphthalene (10% based on the number of moles of lithium) in freshly distilled glyme under an argon atmosphere.[8] The solution is stirred at room temperature for 15 h to complete the reduction. When the stirring is stopped, the very finely divided black zinc particles settle out, leaving a clear colorless solution above the black powder. In some cases, the solution may appear more or less green due to the presence of some lithium naphthalide. This causes no problems in further reactions and can be ignored or, if desired, the clear solution can be removed by syringe and replaced with fresh dry glyme (this process being repeated 2 or 3 times). In this manner, the naphthalene which acts as an electron carrier in the reduction can be removed and a variety of other solvents added if desired.[15] With regard to the solvent in which the reduction is carried out, glyme is definitely the best solvent. Use of tetrahydrofuran leads to a zinc powder of much reduced reactivity and reduction does not proceed at all in diethyl ether. Also, the anion is of critical importance, with chloride being clearly superior.

The exceptional reactivity of the zinc powders is clearly demonstrated by several reactions. The reduction of anhydrous zinc chloride with potassium in glyme yields a zinc powder which will react with bromobenzene.[10] When the solution is refluxed in glyme for 18 h, 41% of the bromobenzene reacted. In contrast, zinc prepared by lithium reduction of zinc chloride in glyme reacts with bromobenzene under reflux to give 73% reaction in only 10 h.

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[1] Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178.

[2] Rieke, R. D.; Hudnall, P. M.; Uhm, S. *J. Chem. Soc., Chem. Commun.* **1973**, 269.

[3] Rieke, R. D.; Bales, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 789.

[4] Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

[5] We had earlier reported using this approach to prepare highly reactive transition metals.[6,7]

[6] Rieke, R. D.; Kavaliunas, A. V.; Rhyne, L. D.; Fraser, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 246.

[7] Kavaliunas, A. V.; Rieke, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5944.

[8] An example of a typical reduction for zinc is as follows. Into a 50-mL, two-necked, round-bottomed flask is placed 0.35 g (0.0504 mol) of lithium,[9] 3.27 g (0.0240 mol) of zinc chloride, 0.65 g (0.00507 mol) of naphthalene, and 16.0 mL (0.154 mol) of 1,2-dimethoxyethane. This is stirred at room temperature until the reduction is complete (about 15 h). The activated zinc appears as a fine black powder which settles out of the solution after the stirring is stopped for some time (about 1 h). The zinc chloride was purchased from Cerac, Inc., Milwaukee, WI, and was 99.5% pure and anhydrous. The combination Li (1.84 g, 0.265 mol), $ZnCl_2$ (17.21 g, 0.126 mol), naphthalene (2.23 g, 0.0174 mol), 1,2-dimethoxyethane (95 mL, 0.912 mol) in a 250-mL flask has also been successfully used.

[9] Lithium (99.9%, rod, 1.27-cm diameter) from Alfa has been used extensively in our studies. The lithium is cut under oil, rinsed in hexane, and trasferred to a tared 24/40 adapter with a stopcock and rubber septum which has been filled with argon. The adapter is evacuated to pump off the hexane, filled with argon, and weighed. The lithium is then transferred to the reaction vessel under an argon stream.

[10] For exact details for the preparation of zinc with potassium or sodium, see ref 11.

[11] Rieke, R. D.; Uhm, S. J. *Synthesis* **1975**, 452.

[12] A 1:1 ratio of α-halo ester to aldehyde or ketone was normally employed. The ratio of zinc to α-halo ester was normally 1:0.9.

[13] A typical reaction follows. A 50-mL, two-necked, round-bottomed flask is equipped with a Teflon-coated magnetic stirring bar, rubber septum, and condenser connected to an argon inlet. The flask is charged with 0.224 g (0.033 mol) of freshly cut lithium,[9] 1.57 g (0.0165 mol) of anhydrous magnesium chloride (Cerac, Inc.), 0.436 g (0.0034 mol) of naphthalene and 10-20 mL of tetrahydrofuran. The mixture is stirred vigorously at room temperature for 24 h.[14] After complete reduction, the highly reactive magnesium appears as a dark gray to black powder, which slowly settles when stirring is stopped. In some cases, the tetrahydrofuran has a slight olive green color due to a small amount of lithium naphthalide. This can be ignored when the highly reactive magnesium is reacted. If desired this can be removed by syringing off the THF and adding fresh dry tetrahydrofuran or other solvent.

[14] It is important that the reaction be stirred vigorously and that the lithium make frequent contact with the stirring bar, as the lithium has a tendency to be coated with magnesium, stopping the reduction from continuing. If reduction does stop, it can be initiated again by gently rubbing the piece of lithium against the wall of the flask with a metal spatula. The rubber septum can be temporarily removed under a stream of argon to carry out this procedure.

[15] One can also remove the solvent and electron carrier by filtering through a medium frit under an argon atmosphere.

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More dramatic and of much more importance is the reaction of zinc with dihalomethanes. Zinc metal prepared by potassium reduction reacts rapidly with diiodomethane, and when this is reacted in the presence of cyclohexene, a Simmons–Smith reaction occurs to yield bicyclo[4.1.0]-heptane. A wide variety of conditions were tried but a maximum yield of 25–30% was realized. This zinc also reacted rapidly with dibromomethane but only a 5% yield of bicyclo[4.1.0]heptane was obtained. The zinc prepared by lithium reduction, in contrast, gave excellent results. The zinc powder was prepared in the usual manner by lithium reduction in glyme. The solution was allowed to settle and then the glyme was removed via a syringe. The black powders can be washed with fresh dry glyme to remove the bulk of the naphthalene. Finally, the remaining glyme is removed with the aid of a vacuum pump. Anhydrous diethyl ether is then injected into the flask. Cyclohexene (0.5 equiv, based on zinc) is then injected into the reaction followed by the slow (10–15 min) addition of dibromomethane (1.0 equiv, based on zinc). The reaction is somewhat exothermic during the addition. The solution is then refluxed for 6 h, yielding 94% bicyclo[4.1.0]heptane and 6% cyclohexene. Dichloromethane appears to be unreactive under these conditions, and diiodomethane due to its very high reactivity gives somewhat erractic results. Thus dibromomethane is the reagent of choice. The Simmons–Smith reaction can be extended to even more unreactive dihalides. Reaction of 1,1-dibromoethane with cyclohexene under the above conditions produces both *exo*-7-methylbicyclo[4.1.0]heptane (12%) and *endo*-7-methylbicyclo[4.1.0]heptane (12%).

The zinc powders prepared by potassium reduction have been previously shown to be very useful in the Reformatsky reaction.[11] Similarly, the zinc powders prepared by lithium reduction lead to near quantitative yields in this reaction. As in the Simmons–Smith reaction, once the zinc powders are prepared the glyme is removed and replaced with diethyl ether. Ethyl α-bromoacetate (0.1 equiv) is added to the zinc powder at ice bath temperatures. A mixture of cyclohexanone and the remaining ethyl α-bromoacetate are added dropwise over 15 min.[12] The reaction mixture is then stirred at room temperature for 1 h and the quenched with aqueous acid. Analysis by GLC and isolation indicated near quantitative yields (yields ranged from 95% to 98%) of the β-hydroxy esters. The reaction proceeds equally well with aldehydes.

The reaction can also be carried out with ethyl α-chloroacetate. The only change in reaction conditions is that the reaction is refluxed for 2 h instead of being stirred at room temperature for 1 h. Yields are in the range of 85–90%.

Earlier we had also reported the preparation of highly reactive magnesium metal powders prepared by the reduction of magnesium halides, using potassium or sodium.[1,3,4] We now report that magnesium powders of equal reactivity can be readily and conveniently prepared by using lithium along with an electron carrier as the reducing agent. The highly reactive magnesium is prepared by the reduction of anhydrous magnesium chloride with 2 equiv of lithium and a small amount of naphthalene or biphenyl (10% based on the number of moles of lithium) in freshly distilled glyme or tetrahydrofuran under an argon atmosphere.[13] The solution is stirred vigorously at room temperature for 24 h. After complete reduction, the highly reactive magnesium appears as a dark gray to black powder, which slowly settles when stirring is stopped. Grignard reagents or other reactions can be prepared right in the reaction vessel by injecting the appropriate halide. If desired, the magnesium powder can be washed with fresh solvent to remove the electron carrier as described for zinc. Also, one can add a variety of other solvents if it is desired to carry out a reaction in a solvent other than glyme or THF. Grignard reagents prepared from this magnesium appear to react as normal Grignard reagents prepared from magnesium turnings. For example, they react with CO$_2$ to give the corresponding acid and add to ketones to give the corresponding alcohol.

In summary, high reactive zinc and magnesium powders are easily and safely prepared by lithium reduction of the corresponding salts. These metals are of equal or in the case of zinc superior reactivity to those metals prepared by potassium or sodium reduction. We will report the full details of these metals in the near future.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Army Office (supported work on zinc) and the Division of Chemical Sciences, Department of Energy (Contract No. DE-AC02-80ER10603, supported work on magnesium).

Registry No. Zinc, 7440-66-6; zinc chloride, 7646-85-7; magnesium, 7439-95-4; magnesium chloride, 7786-30-3; lithium, 7439-93-2.

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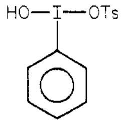
Functionalization of Alkenes and Alkynes with [Hydroxy(tosyloxy)iodo]benzene. Bis(tosyloxy)alkanes, Vinylaryliodonium Tosylates, and Alkynylaryliodonium Tosylates

Summary: [Hydroxy(tosyloxy)iodo]benzene (1) reacts with various alkenes to give bis(tosyloxy)alkanes and with various alkynes to give either vinylaryliodonium tosylates or alkynylaryliodonium tosylates. In the presence of 1, 1,1-diphenylethylene undergoes oxidative rearrangement and phenyliodination.

Sir: We report that [hydroxy(tosyloxy)iodo]benzene (1)[1-6] reacts with various alkenes to give bis(tosyloxy)alkanes and, in one case, a vinylaryliodonium salt and a product of oxidative rearrangement. With various alkynes, either vinylaryliodonium tosylates or alkynylaryliodonium tosylates are obtained.



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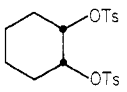

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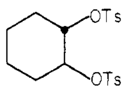

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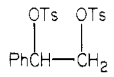
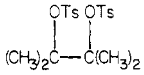


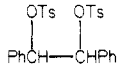
$\mathrm{PhCH(OTs){-}CH_2(OTs)}$

4



$\mathrm{(CH_3)_2C(OTs){-}C(OTs)(CH_3)_2}$

5



$\mathrm{PhCH(OTs){-}CHPh(OTs)}$

6

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(6) G. F. Koser and R. H. Wettach, *J. Org. Chem.*, **45**, 4988 (1980).

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