Preparation and Reactions of Highly Active Cadmium and Zinc Slurries by Metal Atom–Solvent Cocondensations

Summary: Active cadmium and zinc slurries were prepared by the cocondensation of the metal vapor with excess solvent at 77 K, followed by warming to room temperature, and then allowed to react with alkyl bromides and iodides in several solvents, polar and nonpolar.

Sir: There are a few limited reports in the literature dealing with the direct reaction of cadmium metal with alkyl halides. Only alkyl iodides and unsaturated bromides were found to react in the highly polar solvating media hexamethylphosphoric triamide (HMPT), DMSO, and DMF.[1] As would be expected, the RCdX and R_2Cd were formed as solvent adducts, e.g., RCdI·HMPA. Similarly, there are reports of zinc dust reactions with alkyl iodides and bromides in solvents such as dimethoxyethane, diglyme, DMSO, and DMF with formation of solvated RZnI and RZnBr.[2] High temperature and/or zinc–copper couples have been employed for zinc activation for direct RX reactions.[3] In addition, Rieke and co-workers[4] have reported that the reduction of $ZnBr_2$ with potassium in diglyme or dimethoxyethane also yields a very active form of zinc.

We report here a procedure for production of very active slurries of cadmium and zinc in pure, clean, finely divided forms that are reactive with alkyl halides in all types of solvents, polar and nonpolar.

Cadmium slurries in diglyme, dioxane, THF, hexane, and toluene were produced by condensing ~9 g of Cd with ~60 ml of solvent at 77 K. Colored matrices were formed that turned black on melt down (cf. Table I for exact amounts of reagents). Alkyl iodides were added usually before melt down, followed by warming and then reflux. For example

$$\text{Cd vapor} + \text{hexane} \xrightarrow{77\text{ K}} \xrightarrow{\text{warm}}$$

$$\text{Cd*–hexane slurry} \xrightarrow[\text{reflux}]{\text{RI}} R_2Cd + CdI_2$$

The amount of RCd species present was determined by hydrolysis with 10% HCl, followed by quantitative determination of RH formed by vacuum line manipulations, pressure–volume measurements, and GLC techniques. The highest yields of RCd compounds were obtained in diglyme and dioxane solvents although in hexane, toluene, and THF the yields were still acceptable (cf. Table I). We have not yet carried out a detailed investigation concerning whether RCdI or R_2Cd are produced in different solvents or as solvent adducts. Only a small amount of Et_2Cd was isolable by vacuum pumpoff from a Cd–toluene slurry–EtI reaction (1% Et_2Cd by hydrolysis).

Dialkylzinc compounds were isolable from Zn*RX reactions by vacuum pumpoff. Usually, however, the yields of RZn species were simply determined by hydrolysis of the reaction mixture. In diglyme quantitative yields of R_2Zn (presumably) were obtained. Lower yields were observed in hexane and toluene. The Zn slurries retained their activity if manipulated under an atmosphere of dry nitrogen.

Table I. Zn and Cd Reactions with Alkyl Halides

Mol of Zn	RX	Mol of RX	Reflux time, h[a]	% yield of R_2M[b]	Solvent
0.127	EtBr	0.04	18	100.0	Diglyme
0.107	*n*-PrBr	0.04	23	100.0	Diglyme
0.077	*n*-BuBr	0.04	17	100.0	Diglyme
0.149	*n*-PrBr	0.04	23	93.5	Dioxane
0.357	*n*-PrBr	0.04	22	89.0	THF
0.203	*n*-PrBr	0.04	17	57.7	Hexane
0.126	*n*-PrBr	0.04	16	28.5	Toluene
Mol of Cd	**RX**	**Mol of RX**	**Reflux time, h**	**% yield**	**Solvent**
0.083	EtI	0.04	19.5	82.7	Diglyme
0.026	EtI	0.04	12.5	74.0	Dioxane
0.088	EtI	0.04	20.5	61.8	Hexane
0.069	EtI	0.04	17.5	61.7	THF
0.115	EtI	0.04	18.0	54.5	Toluene

[a] At reflux temperature of solvent–substrate mixture at reduced pressure. [b] Yield based on RX as limiting reagent.

These slurries were produced by the codeposition of metal vapors (atoms) and excess solvent on the walls of a metal atom reactor[5] at 77 K, followed by warming. The method is quite versatile since many metals and a wide range of solvents can be employed. In some cases the slurries are so fine that they can be handled by syringe, similar to Mg–THF slurries which we reported earlier.[6] There is need for a great deal of research in this area since different clustered forms with different properties are produced when different solvents are employed (with the same metal).[7]

$$\text{Zn*–solvent} + RX \rightarrow R_2Zn + ZnX_2$$

$$X = Br, I$$

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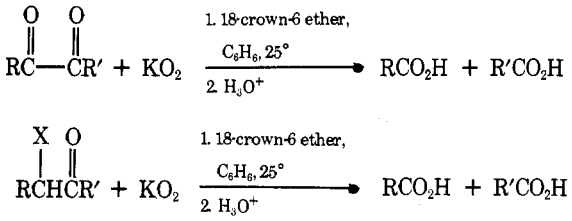
Oxidative Cleavage of α-Keto, α-Hydroxy, and α-Halo Ketones, Esters, and Carboxylic Acids by Superoxide[1]

Summary: The reaction of α-keto, α-hydroxy, and α-halo ketones, esters, and carboxylic acids with potassium superoxide in benzene in the presence of 18-crown-6 ether results in the oxidative cleavage of these compounds to carboxylic acids in a reaction which, in several respects, is reminiscent of the behavior of certain dioxygenases.

Sir: In previous reports we have demonstrated that superoxide is a potent and synthetically useful oxygen nucleophile.[2,3] This communication describes the results of our continuing investigation of the reactivity of this reagent and in particular its reactions with α-keto, α-hydroxy, and α-halo ketones, esters, and carboxylic acids. These studies reveal that such substrates undergo facile oxidative cleavage to produce the respective carboxylic acids in fair to excellent yields. A summary of the results obtained on treatment of various representative substrates is given in Table I.



R′ = OH, OR, alkyl, aryl; X = OH, Cl, Br

The following description is typical of the experimental procedures employed in the reaction of potassium superoxide[4] with α-keto, α-hydroxy, and α-halo ketones, esters, and carboxylic acids. *dl*-Camphoroquinone (0.831 g, 5.00 mmol) was added to a mixture of 18-crown-6 ether[5] (0.528 g, 2.00 mmol) and powdered potassium superoxide (1.42 g, 20.0 mmol) in dry benzene.[6] The resulting mixture was vigorously stirred for 12 h, then cautiously poured into 20 ml of water. The aqueous layer was separated and acidified with 3 M HCl and subsequently extracted with three 40-ml portions of ethyl ether. The combined ether extracts were dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The residual white solid was recrystallized from aqueous ethanol to give 0.87 g (87%) of *dl*-camphoric acid, mp 205–206° (lit.[7] mp 208°).

Certain aspects of this reaction deserve brief comment. First, the results shown in Table I indicate that the oxidative cleavage of α-substituted ketones, esters, and carboxyl-

Table I. Reactions of Potassium Superoxide with Various α-Keto, α-Hydroxy, and α-Halo Ketones, Esters, and Carboxylic Acids

Substrate	mM of KO_2/mM of substrate[a]	Product[b]	Yield,[c] %
Benzil	3/1	Benzoic acid	87
Camphoroquinone	4/1	Camphoric acid	87
1,2-Cyclohexadione	4/1	Adipic acid	53
2-Ketoglutaric acid	4/1	Succinic acid	42[d]
2-Ketophenylacetic acid	4/1	Benzoic acid	93
Ethyl 2-ketophenylacetate[e]	4/1	Benzoic acid	93
Benzoin	3/1	Benzoic acid	98
2-Hydroxycyclohexanone	4/1	Adipic acid	69
Mandelic acid	4/1	Benzoic acid	94 (81)[f]
2-Hydroxystearic acid	12/1	Heptadecanoic acid	77
1-Hydroxycycloheptanecarboxylic acid	4/1	1-Hydroxycycloheptanecarboxylic acid	*g*
1-Cyclohexylmandelic acid	4/1	1-Cyclohexylmandelic acid	*g*
Ethyl Mandelate	4/1	Benzoic acid	93
2-Chlorocyclohexanone	4/1	Adipic acid	60
2-Chlorocyclooctanone	4/1	Octanedioic acid	62
3-Bromocamphor	4/1	Camphoric acid	54
Phenacyl chloride	4/1	Benzoic acid	72
2-Bromo-2-phenyl-acetic acid	4/1	Benzoic acid	90
2-Bromooctanoic acid	4/1	Heptanoic acid	58[h]
Methyl 2-bromo-2-cyclohexane acetate	4/1	Cyclohexanecarboxylic acid	54[h]

[a] Unless otherwise indicated, all reactions were carried out for 24 h using a 1:10 ratio of 18-crown-6 to KO_2. Understandably, reaction times were noticeably shorter at higher ratios. [b] Products were characterized by comparison of spectral data. Solids were further characterized by their melting points and liquids by their GLC retention times. [c] Unless otherwise indicated, reported values refer to isolated, recrystallized product yields, based on substrate. [d] Because of its solubility characteristics, considerable difficulty was experienced in isolating this material from the crude reaction mixture. Control experiments suggest that the values given represent minimal isolated yields. Conversion yields generally ranged from 20 to 30% higher. [e] For a discussion of the cleavage of esters by superoxide, see ref 2b. [f] Carried out in dry DMSO. [g] A nearly quantitative recovery of starting material was obtained in this instance. [h] Determined by GLC analysis.