

A CONVENIENT SYNTHESIS OF COPPER(I) CARBOXYLATES

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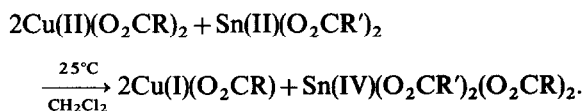
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Abstract—A simple procedure is described for the synthesis of aliphatic and aromatic copper(I) carboxylates by the reduction of copper(II) carboxylates with commercially available tin(II) 2-ethylhexanoate. In this way copper(I) acetate, benzoate and stearate have been prepared in good yield and purity from the corresponding copper(II) carboxylates.

Copper(I) carboxylates have found wide application as catalysts and stoichiometric reagents in organic chemistry,¹ and have served as starting materials in the synthesis of novel copper(I) complexes.² These air- and moisture-sensitive compounds are usually prepared by one of the methods described by Edwards and Richards.³ One procedure involves the reaction of copper(I) oxide with a carboxylic acid, with azeotropic removal of the water by-product. Reaction times are long (*ca* 12 h) and the several manipulations must be carried out under inert atmosphere. A second route involves treating a carboxylic acid solution of the copper(II) carboxylate with a reductant such as copper(0) or hydrazine hydrate. To employ this procedure, however, the acid must be a liquid at ambient conditions. Further, non-volatile carboxylic acids can be difficult to remove from the copper(I) product.

Recently several examples of the *in situ* generation of catalytically active copper(I) by the tin(II) reduction of copper(II) compounds have been reported.^{4,5} In our study of the copper-catalyzed decomposition of diaryliodonium salts,⁵ we employed tin(II) 2-ethylhexanoate to generate copper(I) carboxylate catalysts from the corresponding copper(II) carboxylates. The subject of this report is our development of the tin(II) reduction of simple copper(II) carboxylates as a convenient method for preparing copper(I) carboxylates of good purity in good isolated yield:



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RESULTS AND DISCUSSION

We have prepared three copper(I) carboxylates [copper(I) acetate, stearate and benzoate] in good yield (65–85%) from the corresponding commercially available copper(II) salts by reduction with tin(II) 2-ethylhexanoate in CH_2Cl_2 solution under an inert atmosphere. The occurrence of carboxylate exchange between copper and tin was ruled out by the IR spectrum of copper(I) benzoate which showed only strong absorbances due to aromatic C—H stretching; no absorbance due to aliphatic C—H stretching was observed. In addition, elemental and mass spectroscopic analyses indicated that the desired products were obtained in high purity.

Relative to the procedures of Edwards and Richards,³ advantages of the method described here include the short reaction time and the simple apparatus and work up. Critical for some applications⁵ is the fact that the reaction product produced by this method is obtained free of excess carboxylic acid or coordinating solvent. The tin(II) reductant, further, is inexpensive and readily available.

Isolation of a product of high purity requires the use of copper(II) carboxylates free of insoluble impurities such as copper oxides or halides.⁶ Some commercially available copper(II) carboxylates are of modest purity; thus, the reduction of a commercial copper(II) caprylate gave the copper(I) salt (identified by FDMS and high-resolution EI mass spectroscopic experiments) in good yield, but elemental analysis revealed the presence of about 10% of a copper-containing impurity, presumably a copper(I) halide. The presence of small amounts of impurities may be of less concern in some application of the copper(I) carboxylates as a reaction catalyst.⁴

The method described here applies only to copper(II) carboxylates which have at least slight

solubility in the organic solvent. Our attempts to reduce copper(II) gluconate and glycolate, which are extremely insoluble in CH_2Cl_2 and CHCl_3 , were unsuccessful. Conversely, it appears that high solubility of the copper(I) carboxylate may result in over-reduction of the product [to copper(0)]. Therefore, in reactions involving substituted carboxylates it may be necessary in some instances to substitute other reaction solvents.

EXPERIMENTAL

Commercially available copper(II) carboxylates were dried in a vacuum oven at 80°C overnight and used without further purification. Tin(II) 2-ethylhexanoate (stannous "octoate") was used without purification (except for degassing) in the synthesis of copper(I) benzoate and stearate, but was distilled under vacuum (*ca* 0.005 torr, b.p. $155\text{--}165^\circ\text{C}$) through a short fractionating column for the synthesis of copper(I) acetate. A good commercial grade of CH_2Cl_2 was used after degassing on a vacuum line. We preferred to carry out the syntheses in an inert atmosphere glove box, but the reaction has also been carried out in a three-neck flask with a nitrogen blanket over the solution. Removal of the reaction and wash solvents from the copper(I) product can be accomplished with a cannula or a filtering side arm. Loss of the very fine copper(I) product through the fritted filter appears to be the major factor lowering the isolated yield. The representative synthesis of copper(I) benzoate is described below.

Copper(I) benzoate

In an inert atmosphere glove box, a mixture of copper(II) benzoate (0.016 mol) and tin(II) 2-ethylhexanoate (0.009 mol) in 25 cm^3 CH_2Cl_2 was prepared. While stirring at room temperature, the color of the solution changed from blue [due to copper(II)] to a faint grey-green color over about 4 h. The very fine whitish precipitate [copper(I) benzoate] was isolated by suction filtration [the tin(II) reagent and the tin(IV) product are very soluble in the organic solvent]. The product was

washed 4 times with CH_2Cl_2 , leaving a whitish-grey solid which was dried *in vacuo* for several hours. The moderately air-sensitive copper(I) benzoate was isolated in 84% yield and stored under nitrogen.

Found: Cu, 34.20; C, 45.30; H, 2.73. Calc. for $\text{CuC}_7\text{H}_5\text{O}_2$: Cu, 34.4; C, 45.5; H, 2.73%. IR (KBr) major bands at 3050(m), 1590(s), 1530(br, s), 1490(m), 1410(br, sh, 845(m), 710(s), 690(s) and $555(\text{m})\text{ cm}^{-1}$.

Copper(I) acetate

Isolated as a very pale yellow solid in 75% yield. Found: Cu, 51.60; C, 19.59; H, 2.41. Calc. for $\text{CuC}_2\text{H}_3\text{O}_2$: Cu, 51.83; C, 19.60; H, 2.47%.

Copper(I) stearate

Isolated as a pale yellow solid in 65% yield: Found: Cu, 18.15; C, 62.08; H, 9.95. Calc. for $\text{CuC}_{18}\text{H}_{35}\text{O}_2$: Cu, 18.33; C, 62.33; H, 10.10%.

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