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Reactions of Cuprous Acetate with Organic Halides

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Cuprous acetate was prepared from phenylcopper and acetic acid, and its reactivity for organic halides was investigated. The mixed anhydrides containing an acetyl group are formed easily from cuprous acetate and acyl halides. The reaction of cuprous acetate with CH_3I, C_2H_5I, $CH_2{=}CHCH_2Br$, and $PhCH_2Cl$ in acetonitrile gives the corresponding ester. The addition of ethylenediamine converts the above reaction to a reductive coupling reaction, resulting in bibenzyl (50% yield) from benzyl chloride and 1,5-hexadiene (95—98% yield) from allyl chloride or bromide. The reaction of cuprous acetate-ethylenediamine with aryl bromide or iodide in DMF gives a reductively dehalogenated product, *i.e.*, the corresponding hydrocarbon, in a small yield.

Although numerous copper salts have been utilized in organic syntheses, little has been investigated about cuprous acetate. Cuprous acetate was first prepared from cuprous oxide and acetic anhydride by Calvin.[1] Recently, Sheppard[2] reported to obtain this compound quantitatively from *m*-(trifluoromethyl)phenylcopper octamer and acetic acid. It has also been reported that cuprous acetate activates the molecular hydrogen in quinoline,[1,3] and that cuprous acetate executes

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[1] M. Calvin, *J. Amer. Chem. Soc.*, **61**, 2230 (1939).

[2] A. Cairncross, J. R. Foland, R. M. Henderson, and W. A. Sheppard, *ibid.*, **92**, 3187 (1970).

[3] S. Weller and G. A. Mills, *ibid.*, **75**, 770 (1953).

a reductive dehalogenation on aryl halides in nitrogen heterocyclic solvents.[4] However, the reaction of cuprous acetate with organic halides has not yet been fully investigated. Therefore, we prepared cuprous acetate from phenylcopper and acetic acid, and examined its reactions with acyl halides and some aliphatic and aromatic halides.

Results and Discussion

Although Sheppard used *m*-(trifluoromethyl)phenylcopper as an organocopper, we found that cuprous acetate can be synthesized quantitatively from phenylcopper and acetic acid;

$$\mathrm{PhCu} + \mathrm{CH_3COOH} \rightarrow \mathrm{Cu(OCOCH_3)} + \mathrm{PhH}$$

As cuprous acetate was easily decomposed by both oxygen and moisture, it was isolated and characterized as a complex with triphenylphosphine according to the usual procedures for Cu(I) complexes.[5,6] It is a white crystalline oxygen-stable compound, is soluble in an organic solvent and has the composition of CuOAc-$(PPh_3)_2$.

Reactions of Cuprous Acetate with Acyl Halides. Cuprous acetate similar to cuprous alkoxides reacted with acyl halides to produce the corresponding anhydrides in fairly good yields, as is shown in Table 1. The yield of anhydride diminishes with the increase in the carbon chain in the acyl group. This fact may be attributable to the increase in the electron-releasing ability in the order of $-CH_3 < -C_2H_5 < -C_3H_7$. Mixed anhydrides have been synthesized from carboxylic acid or its metal salts[7] and acyl halide. Recently, Taylor[8] reported that mixed anhydrides could be prepared in high yields by utilizing Tl-(OCOR). Considering that thallium salts are very toxic, the above reaction seems to be a useful method of synthesizing mixed anhydrides containing acetyl group.

Table 1. Reactions of CuOAc with acyl halides in ether[a]

Acyl halide	Product	Yield (%)
CH_3COCl	$CH_3COOCOCH_3$	76.5
C_2H_5COCl	$CH_3COOCOC_2H_5$	39.4
n-C_3H_7COCl	$CH_3COOCOC_3H_7$	26.5

a) CuOAc, 0.01 mol; acyl halide, 0.01 mol; in refluxing ether for 5 hr.

Reactions of Cuprous Acetate with Aliphatic Halides. The halogen-exchange reactions of copper salts with organic halides have been studied by many investigators. Therefore, the reactions of cuprous acetate with organic halides were examined, as is shown in Table 2.

It is clear from Table 2 that all alkyl halides except bromobenzene and iodobenzene are converted to the corresponding esters in acetonitrile. Cohen[9] reported that cuprous benzoate reacts with aryl halides in diglyme to produce aryl benzoate in good yields and that organocopper ArCuOCOPh is an intermediate in the reaction. Cuprous phenoxide[10] also reacted with aryl halides in diglyme to produce aryl phenyl

Table 2. Reaction of CuOAc with halides in acetonitrile[a]

Halide	Solvent	Temp. (°C)	Product	Yield (%)
CH_3I	CH_3CN	60	CH_3OAc	46.2
C_2H_5I	CH_3CN	80	C_2H_5OAc	50.8
$CH_2{=}CHCH_2Br$	CH_3CN	60	$CH_2{=}CHCH_2OAc$	68.3
$PhCH_2Cl$	Diglyme	87	$PhCH_2OAc$	63.5
	CH_3CN	150	$PhCH_2OAc$	42.7
PhBr, PhI	Diglyme	87	—	
		150	—	

a) CuOAc, 0.01 mol; halides, 0.01 mol; reaction time, 5 hr.

Table 3. Effects of the addition of ligands in acetonitrile[a]

Halide	Ligand	Temp (°C)	Product and Yields (%)	
$PhCH_2Cl$	en[b]	87	$PhCH_2CH_2Ph$ (40.2)	$PhCH_2OAc$(18.2)
$PhCH_2Cl$	2en	87	$PhCH_2CH_2Ph$ (50.1)	$PhCH_2OAc$(19.8)
$PhCH_2Cl$	dipy[c]	87	$PhCH_2CH_2Ph$ (1.8)	$PhCH_2OAc$(18.8)
$CH_2{=}CHCH_2Br$	en	80	1,5-hexadiene(97.8)	
$CH_2{=}CHCH_2Cl$	en	65	1,5-hexadiene(95.3)	
PhBr, PhI	en	87	—	

a) CuOAc, 0.01 mol; halides, 0.01 mol; reaction time, 5 hr. b) en=ethylenediamine. c) dipy=dipyridyl.

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[4] R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, **19**, 95 (1965).

[5] G. Costa, E. Reisenhofer, and L. Stefani, *J. Inorg. Nucl. Chem.*, **27**, 2581 (1965).

[6] F. H. Jardine, L. Ruleand, and A. G. Voha, *J. Chem. Soc., A*, **1970**, 238.

[7] R. Schijf and W. Stevens, *Rec. Trav. Chim., Pays-Bas* **85**, 627 (1966).

[8] E. C. Taylor, G. W. Mclay, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2422 (1968).

[9] T. Cohen and A. H. Lewin, *ibid.*, **88**, 4521 (1966).

[10] T. Kawaki and H. Hashimoto, This Bulletin, **45**, 1499 (1972).

ether. However, cuprous acetate did not react with aryl halides under similar experimental conditions. As toluene has not been detected in the reaction of cuprous acetate with benzyl chloride, the reaction of cuprous acetate with organic halide seems not to proceed through an organocopper intermediate of the RCuOAc type, but seems to proceed through the four-centered mechanism proposed by Bacon.

The Effect of Ligands on the Reactions with Aliphatic Halides. Although cuprous acetate was expected to have more reducing power than the other cuprous salts, it could not dehalogenate organic halides. It has been reported that the reducing power of cuprous chloride is remarkably enhanced by the addition of ethylenediamine in acetonitrile[11] and that the resulting complex dehalogenates benzyl chloride. Table 3 shows the effects of the addition of ligands on the reactions of the cuprous acetate with halides in acetonitrile. In the reaction with benzyl chloride, the addition of 1 mol of ethylene diamine enhanced the reducing power of cuprous acetate, resulting in a higher yield of bibenzyl. Dipyridyl would stabilize cuprous acetate too strongly resulting in a much smaller yield of bibenzyl. Allyl chloride and bromide were converted to 1,5-hexadiene quantitatively without any formation of the ester. Cuprous acetate–ethylenediamine is expected to have more reducing power in DMF because ethylenediamine stabilizes the higher valent state of copper. However, even under these conditions, the reductive coupling product of iodo- and bromobenzene could not be prepared, although the reductively dehalogenated products were obtained in low yields, as is shown in Table 4.

Because the coupling products were not detected when oxygen was bubbled into the reaction mixture prior to hydrolysis, it seems that organocopper is not an intermediate in this reaction. Bacon and his coworkers[4] proposed the following mechanism in the reaction of cuprous acetate with aryl halides in pyridine or quinoline;

Table 4. Reactions of CuOAc-ethylenediamine with aryl halides in DMF[a]

Aryl halide	Product	Yield (%)
PhI	benzene	6.8
PhBr	benzene	5.4
p-$CH_3C_6H_4Br$	toluene	23.0
p-BrC_6H_4Br	bromobenzene	10.9
p-$NO_2C_6H_4Br$	nitrobenzene	8.2

a) CuOAc, 0.01 mol; aryl halide, 0.01 mol; reaction time, 2 hr; reaction temperature, 150°C.

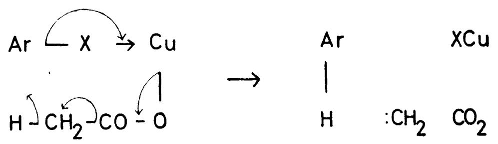

Fig. 1

The reaction of cuprous acetate–ethylenediamine with aryl halides in DMF may also proceed through a similar process.

Experimental

Preparation of Cupous Acetate and its Characterization as the Triphenylphosphine Complex. Phenylcopper was prepared according to the direction of Costa.[12] To the phenylcopper (0.1 mol) suspended in fresh ether under nitrogen was added a slight excess of acetic acid at 0—20°C, after which the mixture was stirred for 4 hr. The resulting white solid of CuOAc was washed several times with ether and dried under nitrogen. CuOAc is so air-sensitive that we failed in elemental analysis under the usual conditions.

Triphenylphosphine (0.02 mol) was added to CuOAc (0.01 mol) suspended in benzene under nitrogen, and the mixture was refluxed for 5 hr. The reaction mixture was then decanted, and the supernatant solution was concentrated to deposit $CuOAc(PPh_3)_2$.

Found: C, 70.81; H, 5.20; Cu, 10.06%. Calcd for $CuOAc(PPh_3)_2$: C, 70.53; H, 5.13; Cu, 9.80%.

Reactions of Cuprous Acatate with Oraganic Halides. Organic halide or acyl halide (0.01 mol) was added to CuOAc (0.01 mol) suspended in acetonitrile or ether under nitrogen, and the mixture was heated under the conditions shown in Tables 1 and 2. The yields of the products were determined by gas chromatography.

The Effect of Addition of Ethylenediamine. Ethylenediamine (0.01 mol) was added to CuOAc (0.01 mol) suspended in acetonitrile under nitrogen, and the mixture was refluxed for 0.5 hr, after which organic halide (0.01 mol) was dropped in. Then, the mixture was stirred under the conditions shown in Table 3. The reactions in DMF were also conducted in a manner similar to the experiment described above.

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[11] K. Wada and H. Hashimoto, This Bulletin, **41**, 3601 (1968).

[12] G. Costa, A. Camus and L. Gatti, *J. Organometal. Chem.*, **5**, 568 (1966).