Reactions of Aryloxycopper(I) with Organic Halides

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Some aryloxycoppers were synthesized by the interaction of phenylcopper with phenols and then characterized. The reaction of aryloxycopper and organic halide in diglyme generally gave the corresponding ether. From these and other results, it is suggested that aryloxycopper(I) is an intermediate in the Ullmann condensation, *etc.*

A number of reactions utilizing cuprous salts have been reported by numerous investigators. However, the preparations and reactions of alkoxy- or aryloxycopper(I), as well as of $CuOCOCH_3$, Cu(acac) and $CuNO_3$, have not been studied thoroughly, though Costa[1] reported the preparation of unstable methoxycopper(I) and its decomposition reaction. Aryloxycopper(I) has been assumed to be an intermediate of some copper-promoted reaction.[2,3] Weingarten[4,5] reported that aryloxycopper(I) is an intermediate of the Ullmann condensation reaction. In the oxidative coupling reaction of substituted phenols, this compound was also reported by Hay and his co-workers[6] to play an important role. The aim of this work is to examine the preparation of aryloxycopper(I) and its reactivity.

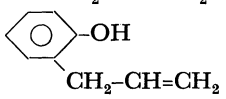
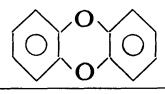
Results and Discussion

Preparation and Properties of Phenoxycopper(I). Phenoxycopper(I) was prepared by adding a small excess of phenol to phenylcopper suspended in anhydrous diethyl ether; the details will be specified in the Experimental section. Phenoxycopper(I) is a violet micro-crystalline, oxygen-sensitive compound; it is soluble in dyglime and DMF and insoluble in benzene and ether.

Group Ib metal halides in the low oxidation state are well known to form stable complexes with triphenylphosphine (PPh_3). Recently, several investigators have reported halogenocopper(I) complexes with PPh_3.[7,8] Phenoxycopper(I) also formed a complex with the composition of $Cu(OPh)(PPh_3)_3$ by refluxing with PPh_3 in benzene. This complex is a white crystalline compound, stable to oxygen and soluble in an organic solvent.

Reactions of Aryloxycopper(I) with Organic Halides. Cuprous salts promoted the reaction of aryl halide with alkali metal phenoxide to give aryl ether.[5,9] This reaction was suggested, from the study of the ESR, to be a nucleophilic replacement reaction of the ate complex of phenoxycopper(I) on aryl halide. It appeared to be interesting to investigate the reactions of aryloxycopper(I) with organic halides in connection with the Ullmann condensation reaction. Table 1 shows the results of the reactions between aryloxycopper(I) and some organic halides. It is obvious that, under mild conditions, these reactions do not proceed successfully, but under rigorous conditions they proceed to obtain the corresponding ethers. In the reaction of No. 2, diphenyl ether was obtained from bromobenzene in a 38% yield. This result gives some support to the

Table 1. Reaction of CuOAr with organic halides in diglyme

No.	Ar in CuAr	Halide	Temp. (°C)	Time (hr)	Product	Yield (%)
1	Ph	PhBr	100	4	PhOPh	6.8
2	Ph	PhBr	124	17	PhOPh	38
3	Ph	CH_3I	40	17	$PhOCH_3$	20
4	Ph	$PhCH_2Cl$	100	4	$PhOCH_2Ph$	16
5	Ph	CH_2=CH–CH_2Cl	r.t.	0.5	$PhOCH_2$–CH=CH_2	3.8
						17[a]
6	*p*-CH_3-C_6H_4	PhBr	125	17		28
7	*p*-NO_2-C_6H_4[b]	PhBr	125	17	—	
8	*p*-CH_3O-C_6H_4[b]	PhBr	125	17	—	
9	*o*-Br-C_6H_4	PhBr	125	17		trace

a) Plus several unidentified high-boiling products. b) Heterogeneous reaction.

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hypothesis that aryloxycopper(I) is an intermediate of the Ullmann condensation reaction.

To investigate the substituent effects, *p*-methyl-, *p*-nitro-, and *p*-methoxyphenoxycopper(I) were prepared and reacted with bromobenzene, but only *p*-methylphenoxycopper(I) gave the corresponding ether. The result may be due to the fact that *p*-nitro- and *p*-methoxyphenoxycopper(I) were insoluble in diglyme. The reaction of phenoxycopper(I) with allyl chloride is abnormal with respect to producing *o*-allylphenol and several high-boiling by-products at room temperature. The formation of *o*-allylphenol can not be attributed to a Claisen rearrangement of the resulting allyl phenyl ether under very mild reaction conditions used.

TABLE 2. THE EFFECT OF LIGANDS IN THE REACTION OF CuOPh WITH PhBr AT 125°C FOR 17 hr IN DIGLYME

Ligand	Ligand/CuOPh (mol/mol)	Yield of PhOPh(%)
—	0	38
Pyridine	3	46
PPh_3	3	8.2

The effect of the addition of pyridine or PPh_3 in the reaction of phenoxycopper(I) and bromobenzene is shown in Table 2. The addition of pyridine increased the yield of diphenyl ether, and that of PPh_3 decreased significantly the yield of diphenyl ether. Bacon and his co-worker[2] proposed the following four-centered mechanism for the halogen exchange of ary halide with cuprous salts:

$$ArX + CuY \rightleftharpoons \left[\begin{matrix} & X & \\ Ar & & Cu \\ & Y & \end{matrix}\right] \longrightarrow ArY + CuX$$

X; Y=Cl, Br, I

The above reaction of phenoxycopper(I) with bromobenzene may be thought to proceed through a similar process.

Reactions of Phenoxycopper(I) with Acyl Halides. Phenoxycopper(I) as well as other metal alkoxides reacted with acyl halides very rapidly at room temperature to form the corresponding ester. For example, phenoxycopper(I) was reacted with benzoyl chloride and acetyl chloride in ether at room temperature for 2 hr to produce phenyl benzoate (74% yield) and phenyl acetate (64% yield) respectively.

Oxidation of 2,6-Di-t-butylphenoxycopper(I). 2,6-Di-*t*-butylphenoxycopper(I) was prepared by the same method as phenoxycopper(I) and was oxidized by passing air through its suspension in ether to give only 2, 2′,6,6′-tetra-*t*-butyldiphenoquinone as the reaction product. It has been reported[6] that the oxidative coupling of 2,6-di-*t*-butylphenol catalyzed with cuprous chloride and pyridine also gave 2,2′,6,6′-tetra-*t*-butyldiphenoquinone. It seems from the results of this experiment that aryloxycopper(I) is an intermediate of the oxidative coupling of phenols catalyzed with copper salts.

Experimental

Preparation of Phenoxycopper(I). Phenlycopper was prepared according to the directions of Costa.[10] Phenyllithium (0.02 mol) was added to cuprous bromide (0.02 mol) suspended in absolute ether at −10°C under a nitrogen atmosphere. The resulting white precipitate of phenylcopper was washed several times with ether under the applied pressure of nitrogen.

To the above phenylcopper (0.02 mol) suspended in fresh ether at room temperature, we added a slight excess of phenol under nitrogen; the mixture was then stirred for 2 hr. The resulting violet solid of CuOPh was washed several times with ether and dried under nitrogen. The IR spectra showed the absorption bands of a trace of unreacted phenylcopper, which had little influence on the following reactions. The other aryloxycoppers were prepared in a similar way.

Preparation of Cu(OPh)(PPh_3)$_3$. PPh_3 (0.04 mol) was added to CuOPh (0.01 mol) suspended in benzene, after which the mixture was refluxed for 5 hr. The reaction mixture was then concentrated to deposit Cu(OPh)(PPh_3)$_3$.

Found: C, 76.16; H, 5.25; Cu, 6.38%. Calcd for $C_{60}H_{50}OP_3Cu$: C, 76.62; H, 5.25; Cu, 6.70%.

Reactions of Aryloxycopper with Organic Halides. All the reactions were carried out *in situ* without any drying of the aryloxycoppers prepared as described above. Organic halide (0.02 mol) was added to CuOAr (0.02 mol) suspended in ether under nitrogen, after which the mixture was heated under the conditions shown in Table 1. The yields of the products were determined by gas chromatography.

Reactions of Phenoxycopper(I) with Acyl Halides. Acetyl chloride or benzoyl chloride (0.02 mol) was added to phenoxycopper(I) (0.02 mol) suspended in ether as described above, and the mixture was stirred at room temperature for 2 hr.

Oxidation of 2,6-Di-t-butylphenoxycopper(I). Oxygen was bubbled into a suspension of 2,6-di-*t*-butylphenoxycopper in ether at room temperature for 10 hr. The mixture was hydrolyzed with dilute hydrochloric acid, and then the ether layer was separated. The ether was subsequently removed to give solid 2,2′,6,6′-tetra-*t*-butyldiphenoquinone in a yield of 16%; this substance was identified by elemental analysis, IR, and NMR and by its failure to depress the melting point of an authentic sample.

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