

## THE EFFECT OF NITROGEN DONORS ON THE REACTIVITY OF COPPER(I) ARYLOXIDES : SYNTHESIS OF THIONCARBONATES

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**Abstract :** Significant changes in the reactivity of copper(I) aryloxides are observed in the presence of nitrogen bases leading to an easy method of synthesizing thioncarbonates.

Copper(I) phenoxide complexes have been studied in great detail in the recent past<sup>1,2</sup>. Several of them serve as models for biologically interesting copper(I) systems and hence their reactions with small molecules such as O<sub>2</sub> and CO have been investigated. We have recently shown that the reaction of simple copper(I) phenoxide with small molecules such as CS<sub>2</sub> can lead to a synthetically useful reaction<sup>3</sup>.

The reactivity of copper(I) phenoxide, however, depends on its nuclearity and the ancillary ligands in its coordination sphere. We describe here a few simple modifications of the structure of copper(I) phenoxide to control its reactivity towards CS<sub>2</sub> and related molecules and demonstrate its utility in preparing thioncarbonates. Thioncarbonates are normally synthesised from reacting thiophosgene with sodium aryloxide or alcoxide<sup>4</sup>. Aryl thioncarbonates are useful precursors in the synthesis of substituted thiophenols<sup>5</sup>. Although this method allows one to synthesize a variety of thioncarbonates and mixed thioncarbonates<sup>6</sup>, the difficulty of handling thiophosgene makes this synthetic route a difficult one. Further more the yields in these reactions are rather poor (10-28%)<sup>5</sup>.

Copper(I) phenoxides are conveniently generated through a metathesis reaction between CuCl and NaOAr in tetrahydrofuran or acetonitrile. This on treatment with two molar equivalent of a tertiary amine presumably leads to a binuclear bridged copper(I) complex 1<sup>7</sup>. Addition of carbondisulphide gives thioncarbonates in good to excellent yields after stirring for a few hours at room temperature, followed by an aqueous work up (see Table). The parent copper(I) phenoxide however does not give the thioncarbonate except when pyridine is used as a solvent. The yield in this case is rather poor.

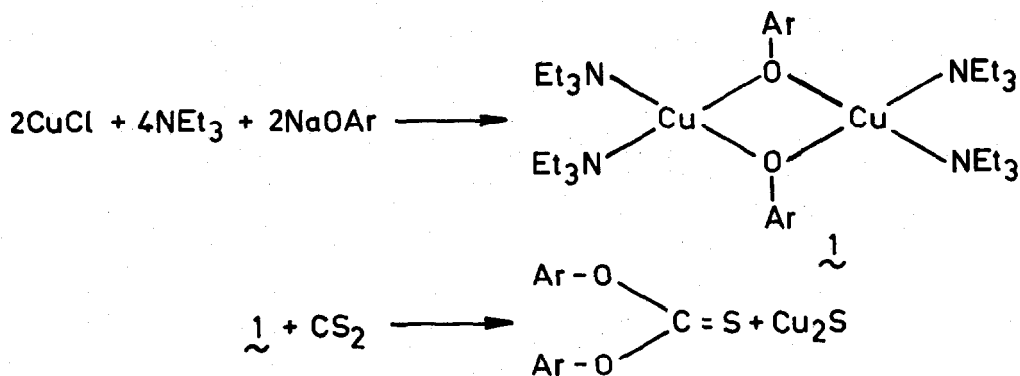


TABLE Thioncarbonates and Mixed Thioncarbonates

Substituent on starting Phenol	Some relevant data for thioncarbonates	
	m.p. <sup>a</sup>	yield %
4-Br	175-6	98 <sup>b</sup>
4-COOCH <sub>3</sub>	205-6	95 <sup>b</sup>
4-CHO	139-40	96 <sup>b</sup>
4-CN	210-12	70 <sup>b</sup>
4-Bu <sup>t</sup>	154-6	76 <sup>b</sup>
3,5-Dimethyl	158-60	71 <sup>b</sup>
4-OCH <sub>3</sub>	162-4	66 <sup>b</sup>
4-OCH <sub>3</sub>	162-4	88 <sup>c</sup>
H	105-6	40 <sup>d</sup>

Substituent on	Xanthate used	yield %
4-CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OCSS Na	91 <sup>c</sup>
4-CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub> OCSS Na	95 <sup>c</sup>
4-CH <sub>3</sub>	C <sub>2</sub> H <sub>3</sub> OCSS Na	85 <sup>e</sup>

- All melting points are uncorrected
- Triethylamine was used as a ligand
- Tetramethyl ethylenediamine was used as a ligand
- Pyridine as solvent and triethyl amine as a ligand
- 1,10-phenanthroline was used as a ligand

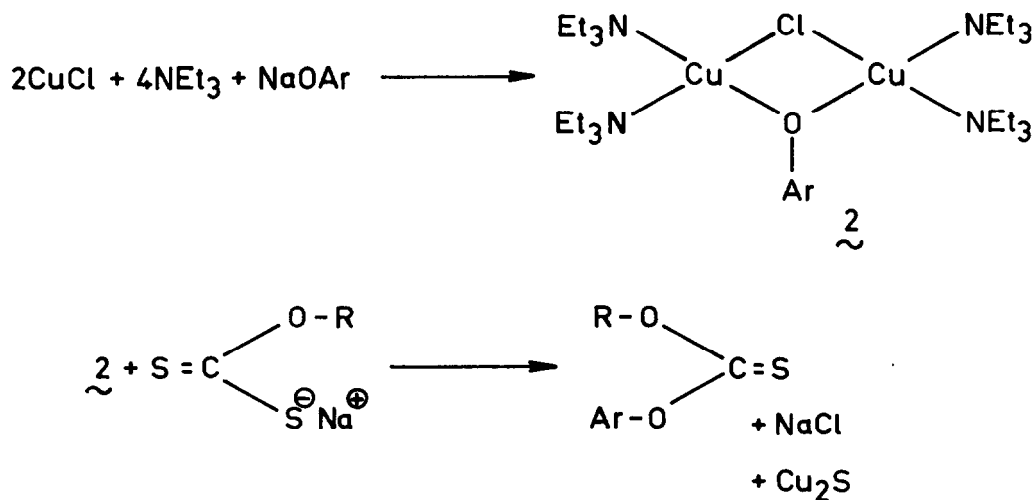
In a typical reaction anhydrous CuCl ( 5 mmol) was added to a suspension of sodium phenoxide in dry degassed acetonitrile (30 ml) under nitrogen. After one hour of stirring at room temperature, degassed triethylamine (10 mmol) was added as a solution in acetonitrile and the mixture stirred for

another hour, before adding carbondisulfide ( 5 mmol). After the reaction mixture had turned brown ( -4 hrs) the solvent and triethylamine were removed under reduced pressure and the residue was extracted with ether (3 x 20 ml) and dichloromethene (2 x 20 ml), and the combined organic layers washed with dil. NaOH and water to remove the unreacted phenol, dried and concentrated to give the crude thioncarbonate. Recrystallisation from absolute alcohol yielded analytically pure material.

Surprisingly when copper(I) aryloxides which failed to give reasonable yields of tetraaryloorthocarbonates were subjected to this procedure good yields of thioncarbonates were obtained. Our earlier conjecture that electron withdrawing groups reduce the nucleophilicity of the copper(I) aryloxides and hence lead to low yields of tetraaryloorthocarbonates seem to be borne out by these results. The presence of electron rich tertiary amines increase the nucleophilicity of the coordinated copper(I) phenoxide promoting the reaction with  $\text{CS}_2$ . The use of pyridines and less electron donating nitrogen bases considerably slows down the reaction. Furthermore the use of triarylphosphines which would also serve to attain the same coordination around the copper without providing increased electron density, do not lead to the formation of thioncarbonates in appreciable yield. A substantial increase in the rate of the reaction is also observed when the reaction is carried out in triethylamine as solvent and TMEDA as a ligand.

The increased nucleophilicity of the coordinated copper phenoxide however does not result in the substitution of the remaining sulfur on the thioncarbonate leading to the formation of tetraaryloorthocarbonates. Excess copper(I) phenoxide does not lead to further substitution. The severe steric restrictions that limit the synthesis of orthocarbonates are not operative in the synthesis of the thioncarbonates. This seems to be the result of the lower nucleolality of the complex 1 as opposed to simple copper(I) aryloxide.

The reaction may be further modified to synthesize mixed thioncarbonates. If cuprous chloride dissolved in THF containing one molar equivalent of TMEDA or 1,10-phenanthroline, is treated with



half an equivalent of sodium aryloxide complex 2 results<sup>7</sup>. Treatment of this with potassium alkyl xanthate gives mixed thioncarbonates in good yield, a few representative examples are given in the Table.

Synthesis of complex 2 was typically carried out in THF as solvent from CuCl and sodium aryloxide in the ratio 2:1. To this yellow solution was added the required amount of TMEDA dissolved in THF. An orange precipitate was formed at this stage. The sodium alkyl xanthate dissolved in THF was added to this precipitate in a dropwise fashion over a period of fifteen minutes. The mixture was stirred for 3-4 hrs till the precipitate turned brown. The solvent was removed under reduced pressure leaving a light brown precipitate which was extracted as before to yield the mixed thioncarbonates. The crude product was chromatographed on silica gel. Elution with petroleum ether (60-80<sup>o</sup>) yielded pure thioncarbonates.

Thus the reactivity of copper(I) phenoxides can be dictated by the ancillary ligands and synthetically useful reactions worked out by judicious choice of ligands and reactant. In the present case thioncarbonates have been synthesised in high yields, obviating the need for thiophosgene for preparing these compounds.

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#### References and Notes :

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