

## Copper(I) Alkoxides. Synthesis, Reactions, and Thermal Decomposition<sup>1</sup>

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**Abstract:** Alkoxides and phenoxides of copper(I) can be prepared by the heterogeneous reaction between alcohols and phenols and methylcopper(I). These organocopper(I) compounds are useful reagents for the formation of ethers by displacement of halide from organic halides. The reaction of copper(I) alkoxides with aryl halides yields alkyl aryl ethers under particularly mild conditions. Thermal decomposition of primary alkoxy copper(I) reagents generates intermediate alkoxy radicals. Thermal decomposition of secondary alkoxy copper(I) reagents apparently can take place either by a free-radical mechanism or by a mechanism tentatively suggested to involve copper(I) hydride as an intermediate. The structural factors determining which mechanism will predominate for a given compound have not been established.

The utility of alkyl- and arylcopper(I) reagents in organic synthesis is based on their high nucleophilicity toward carbon, and on their ability to take part in electron-transfer reactions.<sup>2-4</sup> They also show low basicity toward protons, an affinity for carbon-carbon double bonds, and an ability to coordinate with soft Lewis bases. Since the mechanisms by which copper(I) influences the reactivity of carbanions are not clearly understood, it is difficult to predict the behavior of new types of organocopper(I) compounds. Nevertheless, there is obvious reason to hope that organic derivatives of copper(I) other than those belonging to the well-explored class of compounds containing carbon-copper bonds might also show useful

reactivity. This paper describes studies of one such class: alkoxides of copper(I). These studies had three objectives: synthesis and characterization of alkoxides and phenoxides of copper(I); determination of the behavior of these substances in reactions whose usefulness with alkylcopper reagents has already been established; and examination of the mechanisms of their thermal decomposition.

Copper(I) alkoxides and phenoxides have been implicated previously as intermediates in a variety of copper-catalyzed reactions,<sup>4,5</sup> and poorly characterized examples of these substances have been prepared.<sup>6</sup> A useful synthesis of copper(I) *tert*-butoxide<sup>7</sup> is not applicable to the preparation of the thermally unstable copper(I) primary and secondary alkoxides that were of central interest in our work. The preparation of copper(I) phenoxide by a procedure analogous to that described here has been reported.<sup>8</sup> Copper(I) alkoxides

(1) Supported by the National Science Foundation, Grants GP-28586X and GP-14247, and by the International Copper Research Association.

(2) J. F. Normant, *Synthesis*, 2, 63 (1972); G. H. Posner, *Org. React.*, 19, 1 (1972).

(3) G. Bähr and P. Burba in "Methoden der Organischen Chemie" (Houben-Weyl), Vol. XIII/1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, p 731 ff.

(4) O. A. Chaltkyan, "Copper-Catalytic Reactions," A. E. Stubbs, trans., Consultants Bureau, New York, N. Y., 1966; P. E. Fanta, *Chem. Rev.*, 64, 613 (1964); R. G. R. Bacon and H. A. O. Hill, *Quart. Rev., Chem. Soc.*, 19, 95 (1965); J. Peisach, P. Aisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper," Academic Press, New York, N. Y., 1966.

(5) J. K. Kochi, *Proc. Int. Congr. Pure Appl. Chem.*, 23rd, 4, 377 (1971), and references cited therein.

(6) C. E. H. Bawn and F. J. Whitby, *J. Chem. Soc.*, 3926 (1960); G. Costa, A. Camus, and N. Marsich, *J. Inorg. Nucl. Chem.*, 27, 281 (1965).

(7) T. Saegusa, T. Tsuda, and T. Hashimoto, *J. Amer. Chem. Soc.*, 94, 658 (1972).

(8) T. Kawaki and H. Hashimoto, *Bull. Chem. Soc. Jap.*, 45, 1499 (1972).

have been suggested as "holding groups" in mixed copper ate complexes,  $\text{Het(R)CuLi}$ .<sup>9</sup>

## Results

**Synthesis and Characterization of Copper(I) Alkoxides and Phenoxides.** Copper(I) alkoxides were obtained by heterogeneous reaction between dry, oxygen-free alcohols and halide-free methylcopper(I) at 0° under a nitrogen atmosphere (eq 1). With the exception of



copper(I) methoxide, the copper(I) alkoxides were soluble in ether at 0°; most were also soluble in hydrocarbon solvents, although copper(I) cyclohexoxide and cyclopentoxide provide notable exceptions (*vide infra*). Copper(I) alkoxides were precipitated from ether solutions as light yellow solids on cooling to -78°, and were purified by washing with cold ether. Copper(I) methoxide and copper(I) phenoxides were obtained using a similar reaction; however, since these substances are insoluble in ether, their formation was heterogeneous throughout. This procedure for the preparation of copper(I) alkoxides is a reasonably general one, although high molecular weight alcohols sometimes react slowly or incompletely with methylcopper(I). Further, the isolated yields of copper(I) alkoxides are more variable than one would like (*vide infra*). Vigorous agitation of the suspension of methylcopper(I) in the solution of excess alcohol in ether is required to achieve high yields of copper(I) alkoxides. Similar procedures have been applied to the synthesis of copper(I) carboxylates, and seem to work smoothly.

Copper(I) alkoxides are hydrolyzed on contact with water and rapidly oxidized by air. Their thermal stability depends on their structure: copper(I) derivatives of tertiary alcohols are stable for hours at temperatures less than 170°, while those of primary alcohols decompose rapidly at room temperature. The sensitivity of many of these compounds precluded combustion analysis as a method of establishing empirical composition. Instead, samples were hydrolyzed, and the ratio of alkoxy to copper moieties ( $R = \text{RO}/\text{Cu}$ ) in these samples was determined. These analyses indicated values of  $R$  in satisfactory agreement with the expected value  $R = 1.0$ : for copper(I) methoxide,  $R = 1.06$ ; for copper(I) *n*-butoxide,  $R = 0.98$ ; for copper(I) *tert*-butoxide,  $R = 1.04$ ; for copper(I) cyclohexoxide,  $R = 1.04$ ; for copper(I) isopropoxide,  $R = 1.01$ . These results leave no doubt that the materials obtained using the procedure outlined in eq 1 are copper(I) alkoxides.

For certain synthetic applications, it proved convenient to use an alternative procedure for the preparation of copper(I) alkoxides. Reaction of lithium alkoxide with a suspension of copper(I) chloride in dimethoxyethane at 0° resulted in formation of a homogeneous solution containing organometallic species whose reactivity was essentially indistinguishable from that of pure copper(I) alkoxides. The observation that cooling these solutions did not result in precipitation of copper(I) alkoxides suggested that

lithium chloride was complexed with organocopper species present in solution, and no serious efforts were made to isolate pure copper(I) alkoxides from these solutions. Nevertheless, since alkali metal alkoxides are frequently more readily obtained in large quantity than is methylcopper(I), this procedure will be the more convenient for the preparation of what are presumed, on the basis of reactivity, to be copper(I) salts of these alkoxides, at least for practical applications involving large quantities of these materials.

**Oxidation of Copper(I) Alkoxides.** The dimerization of organic groups by oxidative coupling of the organic moieties of copper(I) alkyls, aryls, and acetylenes seems to have no analogy in the chemistry of copper(I) alkoxides: reaction with molecular oxygen occurs smoothly, but yields only copper(II) alkoxides; reaction of copper(I) *n*-butoxide with nitrobenzene yields *n*-butanal in 22% yield.

**Reactions of Copper(I) Alkoxides and Phenoxides with Organic Halides.** Coupling of organic groups by nucleophilic displacement of halide ion from an organic halide by the alkyl moiety of a lithium dialkylcuprate is one of the most useful reactions of organocopper(I) compounds.<sup>2</sup> Analogous nucleophilic reactions between alkyl halides and copper(I) alkoxides, prepared according to eq 1, give moderate yields of dialkyl ethers (Table I).<sup>10</sup> These yields respond to changes in

Table I. Reactions of Copper(I) Alkoxides with Alkyl Halides

ROM	R'X	Solvent	Temp, C	ROR, %
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCu	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	Et <sub>2</sub> O	25	2
		Et <sub>2</sub> O-HMPA		28
		Diglyme		1
			100	11
		Pyridine	25	65
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Cl		115	55
				25
			25	60
				95
				25
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> OCu	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>tert</i> -C <sub>4</sub> H <sub>9</sub> Br		3
		Bromocyclohexane		< 1
		(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> Br		< 1
				55
				55
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> I			53
				100
				62 <sup>b</sup>
				75 <sup>c</sup>
				54 <sup>c</sup>

<sup>a</sup> The starting concentration of ROCu was approximately 0.2 *N*; R'X was present in 50% excess. All reactions were allowed to proceed for 24 hr at the temperature indicated. Yields were determined by glpc, and are based on the assumption that the yield of copper(I) alkoxide isolated from reaction of methylcopper(I) with alcohol was *ca.* 50%. The text contains a discussion of this point.

<sup>b</sup> Isolated yield based on methylcopper(I). <sup>c</sup> Yields were determined by glpc, and, to make comparison with the corresponding yields from the copper(I) alkoxides possible, are reported on the assumption that the yield of lithium alkoxide from reaction of methylcopper(I) with alcohol was *ca.* 50%. In reality, this yield is probably quantitative, so that the true yield of ROR' based on ROLi is half of that given.

(10) Conventional methods for the preparation of alkyl and aryl ethers are surveyed by C. A. Beuhler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970, Chapter 6, and by H. Meerwein in "Methoden der Organischen Chemie" (Houben-Weyl), VI 3, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1965, p 1 ff.

(9) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Amer. Chem. Soc.*, **95**, 7788 (1973); see also W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39**, 400 (1974).

reaction conditions and reactant structure in a fashion that is qualitatively similar to that characterizing the Williamson ether synthesis: production of ethers is favored by the use of pyridine<sup>11</sup> or polar aprotic solvents;<sup>11</sup> elimination is a serious side reaction in displacements at secondary centers. The yields of ethers formed by reaction of copper(I) alkoxides and alkyl-X decreased in the order  $X = \text{OTs} > \text{Br} \simeq \text{I} > \text{Cl}$ ; the corresponding order for aryl-X was  $X = \text{I} > \text{Br} \gg \text{OTs} > \text{Cl}$ . The reaction of copper(I) alkoxides with alkyl halides offers certain advantages over the Williamson synthesis of ethers in that reaction conditions in the former are milder than those usually employed in the latter, and elimination appears to be a smaller problem; however, it suffers from the disadvantage that copper(I) alkoxides are ordinarily less readily available and more sensitive to temperature and oxygen than are alkali metal alkoxides.

The reaction of copper(I) alkoxides with aryl halides produces aryl aryl ethers in good yields (Table II).

**Table II.** Reaction of Copper(I) Alkoxides with Aryl and Vinylic Halides<sup>a</sup>

ROM <sup>b</sup>	ArX <sup>c</sup>	Solvent	Temp. °C	ArOR, % <sup>d</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCu	Phenyl <i>p</i> -toluenesulfonate	Pyridine	25	12
		Diglyme		1
		Pyridine	100	29
	Iodobenzene	Pyridine	25	64
			115	90
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCu <sup>e</sup>	Chlorobenzene			<1
	Bromobenzene			65
	Iodobenzene			98
		Dimethoxyethane-HMPA <sup>f</sup>	85	96
			25	75
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OLi (10% CuCl)	Iodobenzene	Pyridine	115	70
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCu <sup>e</sup>	3-Iodotoluene			55 <sup>g</sup>
	4-Iodotoluene			65 <sup>g</sup>
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> OCu	Bromobenzene			45 <sup>g</sup>
	Iodobenzene			85
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> OCu				86
				96 <sup>h</sup>
C <sub>6</sub> H <sub>5</sub> OCu				94
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OCu	1-Bromocyclohexene			85
				33 <sup>g</sup>

<sup>a</sup> The starting concentration of copper alkoxide was approximately 0.1 N. Reactions were carried out for 12 hr. <sup>b</sup> Copper(I) alkoxides were prepared by the reaction of methylcopper(I) with the alcohol, unless otherwise noted. <sup>c</sup> A 50% excess of the aryl halide was employed. <sup>d</sup> Yields are determined by glpc based on the copper(I) alkoxide, unless otherwise noted. <sup>e</sup> The copper(I) alkoxide was prepared by the reaction of the lithium alkoxide with cuprous chloride. <sup>f</sup> The DMF contained 4 equiv of HMPA/equiv of lithium. <sup>g</sup> Isolated yield based on methylcopper(I). The ethers produced in these reactions were isomerically pure within the limits of detection of the analysis ( $\pm 5\%$ ). <sup>h</sup> Copper(I) *tert*-butoxide was prepared by the reaction of potassium *tert*-butoxide with cuprous chloride.

Within the limited range of reactions examined, comparable yields of alkyl aryl ethers are obtained from copper(I) alkoxides prepared according to eq 1, from

(11) Reaction of copper(I) carboxylates with alkyl halides occurs best in pyridine: A. H. Lewin and N. L. Goldberg, *Tetrahedron Lett.*, 491 (1972). Magnesium alkoxides react with alkyl halides in hexamethylphosphoramide to give ethers in good yield: Y. Leroux, M. Larcheveque, and J.-C. Combret, *Bull. Soc. Chim. Fr.*, 3258 (1971).

the species (or mixture of species) obtained by reaction of lithium alkoxides with cuprous chloride, and from lithium alkoxide in the presence of approximately 10 mol % cuprous<sup>12</sup> chloride. Again, pyridine or ethereal solvents containing HMPA provide the best reaction media. Higher temperatures or longer reaction times are required for these reactions than for the reactions of copper alkoxides with alkyl halides, although these displacements do take place at a serviceable rate even at room temperature. One important function of pyridine in these reactions seems to be that of stabilizing the copper alkoxides against thermal decomposition;<sup>13</sup> it may also change the reactivity or extent of aggregation of the copper alkoxides by coordination.

These reactions provide the best available procedure for the conversion of aryl halides into aryl alkyl ethers. Alternative preparations based on reactions between potassium alkoxides and aryl halides require more vigorous conditions and produce lower yields of products, and in addition suffer from the possibility that intervention of an aryne mechanism in any new example may lead either to a mixture of products or to a single product in which the position of the ether linkage is ambiguous.<sup>14</sup>

#### Thermal Decomposition of Copper(I) Alkoxides.

The thermal stability of copper(I) alkoxides is appreciably higher than that of copper(I) alkyls: for example, on warming to room temperature from  $-78^\circ$ , copper(I) *n*-butoxide is stable for 12 hr, while *n*-butylcopper(I) decomposes in 20 min. Nonetheless, thermal decomposition of copper alkoxides is an important competing process when reactions of certain of these substances are carried out at temperatures above ambient, and information concerning these thermal decompositions is pertinent to their synthetic application.

Many pathways exist for the thermal decomposition of transition metal organometallic compounds in general,<sup>15-22</sup> and of organocopper(I) compounds in particular.<sup>15-22</sup> Although it has been possible to define certain details of these decompositions, it is still very difficult to *predict* the process that will dominate for a particular organometallic reagent. Comparison

(12) R. G. R. Bacon and S. C. Rennison, *J. Chem. Soc. C*, 312 (1969) have noted that the nucleophilicity of sodium alkoxides toward aryl halides is increased by the presence of copper salts.

(13) A similar function is served by triarylphosphines; however, the presence of stoichiometric quantities of phosphines in organic reaction mixtures complicates their work-up.

(14) M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, **45**, 89 (1965); J. S. Bradshaw, E. Y. Chen, R. H. Hales, and J. A. South, *J. Org. Chem.*, **37**, 2051 (1972); D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).

(15) P. S. Braterman and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 657 (1972).

(16) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972); G. M. Whitesides, D. Bergbreiter, and P. E. Kendall, *ibid.*, **96**, 2806 (1974).

(17) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968).

(18) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

(19) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968); **93**, 247 (1971); A. Cairncross, H. Omura, and W. A. Sheppard, *ibid.*, **93**, 248 (1971).

(20) M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, **42**, 205 (1972).

(21) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 232 (1972).

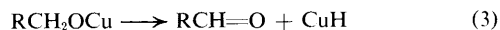
(22) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970).

of the mechanism(s) of thermal decomposition of corresponding copper(I) alkyls and alkoxides should help to define the factors that determine the dominant decomposition pathways.

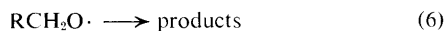
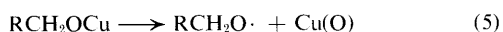
The major products of the thermal decomposition of primary and secondary copper(I) alkoxides are copper metal, alcohol, and the ketone or aldehyde formally derived from oxidation of the alcohol (eq 2).



Two fundamentally different types of mechanisms were considered in trying to account for these products. One, represented by eq 3 and 4, involves an initial elim-



ination of copper(I) hydride from one copper(I) alkoxide moiety, followed by reduction of a second copper(I) alkoxide by this copper(I) hydride. This mechanism has been established for the decomposition of *n*-butyl(tri-*n*-butylphosphine)copper(I),<sup>20-22</sup> but clearly cannot be important in the thermal decomposition of, e.g., copper(I) *tert*-butoxide, for which vicinal copper(I) hydride elimination is impossible. The second mechanism (eq 5 and 6) requires homolytic



scission of a copper-oxygen bond, followed by generation of products from the initially formed alkoxy radicals; this mechanism would also be applicable to the decomposition of *tert*-alkoxycopper(I) compounds. By way of precedent, thermal decomposition *via* free alkyl radicals is of established importance for copper(I) alkyls containing no hydrogen atoms  $\beta$  to the carbon-copper bond.<sup>21</sup> Thus, a problem of central concern in determining the mechanism of thermal decomposition of a copper(I) alkoxide is that of determining whether copper(I) hydride or free alkoxy radicals are intermediates in the decomposition.<sup>23</sup>

Our first approach to this problem centered on a study of the influence of solvent on the distribution of products from the thermal decomposition of representative copper(I) alkoxides (Table III). If free alkoxy radicals are intermediates in these thermal decompositions, then the yield of alcohol produced relative to that of the carbonyl-containing product should be higher in solvents that are more active hydrogen donors toward alkoxy radicals than in those that are less active.<sup>24</sup> The copper(I) alkoxides examined fell into two categories: those (e.g., copper(I) *n*-heptoxide, cyclohexoxide, and cyclopentoxide) for which the ratio

**Table III.** Solvent Effects on the Distribution of Products from the Thermal Decomposition of Copper(I) Alkoxides<sup>a</sup>

ROCu	Solvent (H donor ability) <sup>b</sup>	Alcohol/carbonyl <sup>c</sup>	Product balance, %
<i>n</i> -C <sub>7</sub> H <sub>15</sub> OCu	Toluene (1.0)	3.1	92
	Pentane (2.6)	2.9	79
	THF (23)	10	88
Copper(I) cyclohexoxide	Benzene (0.0004)	1.04	100
	Cumene (2.5)	2.71	
	Pentane (2.6)	2.32	91
Copper(I) cyclopentoxide	THF (23)	8.73	86
	Pentane (2.6)	1.18	84
	THF (23)	7.68	72
CH <sub>3</sub> CH(OCu)C <sub>3</sub> H <sub>7</sub>	Pentane (2.6)	0.74	89
	THF (23)	0.89	83
C <sub>2</sub> H <sub>5</sub> CH(OCu)C <sub>2</sub> H <sub>5</sub>	Benzene (0.0004) <sup>d</sup>	0.96	
	Tetralin (4.3) <sup>e</sup>	0.79	90
	Ether (23) <sup>f</sup>	1.83	100
C <sub>6</sub> H <sub>5</sub> CH(OCu)C <sub>6</sub> H <sub>5</sub>	Toluene (1.0)	1.19	86
	Pentane (2.6)	0.72	
	THF (23)	1.39	80
Copper(I) cyclobutoxide	Pentane (2.6)	0.80	72
	THF (23)	0.80	72

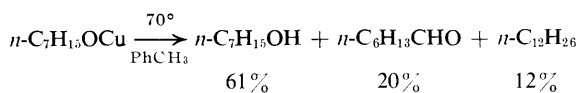
<sup>a</sup> The decompositions were carried out by heating solutions originally 0.3 + 0.1 *M* in copper(I) alkoxide for 20 hr at 115°, unless noted otherwise. <sup>b</sup> The method used to estimate these numbers is described in ref 24. <sup>c</sup> "Alcohol/carbonyl" is the ratio of the alcohol- and carbonyl-containing products derived from the alkoxy moiety of the copper(I) alkoxide. <sup>d</sup> Decomposition temperature 85°. <sup>e</sup> Decomposition temperature 100°. <sup>f</sup> Decomposition temperature 160°.

of alcoholic to carbonyl-containing products increased significantly as the solvent was changed from relatively ineffective hydrogen atom donors such as pentane or toluene to an efficient donor, tetrahydrofuran, and those (e.g., copper(I) 2-pentoxide, 3-pentoxide, cyclobutoxide, and 1,1-diphenylmethoxide) for which a change in solvent had no significant influence on this ratio. These yields are reasonably reproducible; small variations may be due to adventitious hydrolysis in some of the samples. The physical appearance of all of the samples during decomposition was similar, with two exceptions: copper(I) cyclohexoxide and cyclopentoxide were much less soluble than the other copper(I) alkoxides examined, and their decompositions were at least in part heterogeneous.

The high yields of alcohols observed in decompositions of the first group of alkoxides in solvents of high hydrogen atom donor capability, and the variation in this yield on changing the solvent, are qualitatively compatible with the intermediacy of free alkoxy radicals in the decompositions. It is difficult to estimate quantitatively the change in the ratio of alcohol- to carbonyl-containing products expected on changing solvent in these reactions, assuming an alkoxy radical to be an intermediate, since a number of reactions (radical combination and disproportionation, attack on solvent, reaction with undecomposed copper(I) alkoxide) are conceivably open to such a radical. Further qualitative support for the intermediacy of free alkoxy radicals in these reactions was provided by the observation of fragmentations and ring closures characteristic of alkoxy radicals in certain thermal decompositions. Thus, thermal decomposition of copper(I) *n*-heptoxide at 70° in toluene yielded 1-heptanol, *n*-heptaldehyde, and dodecane. The formation of dodecane can best be explained as the result of

(23) A number of variants are conceivable for a free-radical decomposition. At one extreme, initial decomposition of the copper(I) alkoxide could yield a dialkyl peroxide, which would decompose in a subsequent step to free alkoxy radicals. As precedent, decomposition of vinylic and aromatic organocopper(I) compounds produce organic dimers in a reaction that does not involve free-radical intermediates.<sup>18,19</sup> Alternatively, alkoxy radicals generated by homolytic scission of a carbon-copper bond might attack copper(I) alkoxide to induce radical formation. Regardless, the most immediate mechanistic distinction to be made is that between those reaction schemes that involve intermediate free alkoxy radicals, and those that do not.

(24) The hydrogen atom donor abilities listed for the solvents used in Table III are those estimated on a per molecule basis from data for reactions of *tert*-butoxy radicals with these substances: cf. W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966; C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967); A. L. Williams, E. A. Oberriecht, and J. W. Brooks, *J. Amer. Chem. Soc.*, **78**, 1190 (1956); J. A. Howard, *Advan. Free Radical Chem.*, **4**, 49 (1972).



the fragmentation of an intermediate heptoxyl radical to an *n*-hexyl radical, and subsequent combination of two of these radicals.<sup>25</sup> Similarly, thermal decomposition of the copper(I) salt of 4-penten-1-ol at 90° in toluene yielded 3–4% of 2-methyltetrahydrofuran.<sup>26</sup>

The behavior of primary alkoxycopper(I) compounds on thermal decomposition, and of cyclohexoxy- and cyclopentoxycopper(I), indicates that the dominant mechanism for decomposition of these substances generates free alkoxy radicals. Establishing a mechanism for the remaining secondary alkoxycopper(I) compounds examined is less straightforward, although several lines of evidence are compatible with a mechanism involving elimination and subsequent reaction of copper(I) hydride. First, the relative insensitivity of product distributions from decomposition of these substances to the hydrogen donor ability of the solvent is expected for a mechanism involving generation and consumption of an intermediate copper(I) hydride. Second, an effort to detect fragmentation of the cyclobutyl ring during the thermal decomposition of copper(I) cyclobutoxide was unsuccessful: the only products observed were cyclobutanol and cyclobutanone. The oxidation of cyclobutanol has been the object of careful study;<sup>27</sup> its two-electron oxidation leads to cyclobutanone, while its one-electron oxidation leads almost exclusively to ring-opened products. Although the reaction conditions used to effect the thermal decomposition of copper(I) cyclobutoxide are significantly different than those of Roček, the observations that no ring-opened products were obtained,<sup>28</sup> and the yields of ring-closed products were good (Table III), both provide strong support for the contention that the cyclobutoxy radical is not an intermediate in this decomposition. Both observations are also compatible with a decomposition mechanism involving elimination of copper(I) hydride. Third, if copper(I) hydride is generated in these decompositions, it must convert copper(I) alkoxides to alcohols (eq 4) at a rate that is at least comparable to its rate of formation: the ratio of the yields of alcohols and ketones produced in the thermal decomposition never falls much below unity, as it must if the elimination of copper(I) hydride (eq 3) were to be rapid compared with its subsequent reaction. Experimentally, reaction of copper(I) hydride<sup>29</sup> with equimolar quantities of either copper(I) cyclohexoxide in toluene or copper(I) 3-pentoxide in ether at 100° results in conversion of alkoxy moieties en-

tirely to alcohol; no ketones were detected in either reduction. Thus the transformation of copper(I) alkoxides to alcohols by copper(I) hydride is rapid. Fourth, if copper(I) hydride were produced during thermal decomposition of copper(I) alkoxides, some quantity of molecular hydrogen might be found among the products of the decomposition, since thermal decomposition of copper(I) hydride to hydrogen is a rapid reaction under the conditions encountered in these reactions. Examination of the thermal decomposition products of pentane solutions of copper(I) cyclobutoxide and 2-pentoxide indicated the presence of approximately 1% molecular hydrogen based on copper alkoxide; those from copper(I) *n*-butoxide and cyclohexoxide also showed small (~0.1–0.2%) yields. The quantities of hydrogen detected from decomposition of copper(I) cyclobutoxide and 2-pentoxide are only 4–6% of that required to account fully for the difference in the yields of ketone and alcohol generated in these reactions; nevertheless, they are again compatible with the presence of copper(I) hydride in the decomposition. Finally, brief examination of the kinetics of these thermal decompositions revealed behavior very similar to that observed both by Kochi<sup>20,30</sup> and by Stedronsky<sup>31</sup> for the thermal decomposition of alkylcopper(I) compounds in which the elimination of copper(I) hydride is of established importance: decomposition of copper(I) 2-pentoxide in pentane shows an induction period of variable duration, followed by a decomposition whose time course varies from sample to sample. The induction period can be eliminated by the addition of 5 mol % copper(I) hydride. Curiously, the kinetics of the thermal decomposition of copper(I) *n*-heptoxide shows similar, erratic, behavior.

## Discussion

The reaction of methylcopper(I) (and presumably other thermally stable, basic, organocopper(I) reagents)<sup>32–34</sup> with alcohols and phenols provides one convenient route to copper(I) alkoxides and phenoxides; materials of similar reactivity may also be obtained by reaction between lithium alkoxides and cuprous chloride. The two types of reactions in which these reagents seem to have immediate synthetic potential are those involving the formation of ether linkages, particularly by displacement of halide ion from an aromatic nucleus, and those requiring the thermal generation of primary alkoxy radicals.<sup>35</sup> In the former reaction, copper(I) alkoxides seem clearly superior to

(25) For comparison, *n*-butoxy radicals, generated at 195° in the vapor phase, decompose to propyl radicals to the extent of 29%: E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discuss. Faraday Soc.*, **10**, 242 (1951).

(26) Irradiation of the nitrite ester of 4-penten-1-ol results in yields of cyclized products up to 68%: R. D. Rieke and N. A. Moore, *Tetrahedron Lett.*, **25**, 2035 (1969).

(27) K. Meyer and J. Roček, *J. Amer. Chem. Soc.*, **94**, 1209 (1972); J. Roček and A. E. Radkowsky, *J. Org. Chem.*, **38**, 89 (1973); *J. Amer. Chem. Soc.*, **95**, 7123 (1973).

(28) The observation that no butyraldehyde or suberaldehyde were detected in this reaction is not necessarily very significant, since copper(I) alkoxides are sufficiently strongly basic to destroy sensitive carbonyl compounds under the conditions of these reactions.

(29) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969); J. A. Dilts and D. F. Shriver, *ibid.*, **90**, 5769 (1968); **91**, 4088 (1969); G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970).

(30) K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

(31) E. R. Stedronsky, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.

(32) T. Cohen and A. H. Lewin, *J. Amer. Chem. Soc.*, **88**, 4521 (1966).

(33) A. Cairncross, J. R. Roland, R. M. Henderson, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **92**, 3187 (1970).

(34) T. L. Cohen and R. A. Schambach, *J. Amer. Chem. Soc.*, **92**, 3189 (1970).

(35) A brief examination of the thermal decomposition of copper(I) phenoxides was carried out in the hope that this reaction might generate phenoxy radicals, and might accordingly provide a method of oxidatively coupling phenols. The results of this study were disappointing: although diglyme solutions of copper(I) 2,6-dimethylphenoxide yielded 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl in yields up to 60% on rapid decomposition at >200°, much lower yields (~20%) were also obtained under apparently similar conditions. Thermal decomposition of copper(I) phenoxide yielded mixtures of dihydroxybiphenyls in no more than 5% yield. Details of these experiments may be found in the Ph.D. Thesis of J. S. Sadowski, Massachusetts Institute of Technology, Cambridge, Mass., 1972.

other presently available reagents. The ability of copper(I) to facilitate reactions that involve formal nucleophilic displacements at  $sp^2$  carbon centers is well known,<sup>4</sup> and evidence has been presented that these reactions may in some instances involve free-radical intermediates.<sup>32</sup> We have no concrete evidence concerning the mechanism of the displacement of halide ion from aromatic nuclei by copper alkoxides. Small quantities ( $\sim 1\%$ ) of biphenyl are observed in reactions with phenyl iodide; this observation is consistent with, but does not demand, either a free radical or an aryl-copper intermediate in the reaction. The pronounced effect of solvents, particularly HMPA, on the reaction, the suggestion of radical character, and the facility with which alkoxides of copper(I) (as opposed to other metals) participate are compatible with mechanisms of the  $S_{RN}1$  type,<sup>32,36</sup> but oxidative addition to Cu(I) might also be involved,<sup>37</sup> and additional work is required to define a mechanism convincingly.

As a method of generating primary alkoxy radicals, the thermolysis of copper(I) alkoxides offers at the same time the advantages that these substances are much easier to obtain, and safer to manipulate, than are primary alkyl peroxides, and the disadvantage that they are more sensitive to air and water than these peroxides.

The examination of the mechanisms of thermal decompositions of copper(I) alkoxides provides two convincing, if qualitative, pieces of evidence indicating that free alkoxy radicals are important intermediates between primary copper(I) alkoxides and products: the response of product yields to changes in the hydrogen atom donor ability of the solvent, and the production of fragmentation and cyclization products characteristic of alkoxy radicals. These data do not require either that a free-radical mechanism be followed exclusively (although it appears to be a dominant pathway for primary copper(I) alkoxides), or that the alkoxy radicals necessarily be generated by homolysis of an oxygen-copper bond (although this pathway seems *a priori* the most likely). Regardless, it is evident that at least one additional mechanism—most probably involving the generation and reaction of copper(I) hydride—is operative in the thermal decomposition of secondary alkoxy copper(I) compounds. The evidence supporting the involvement of copper(I) hydride in this second mechanism is more compatible than obligatory: the nature and relative yields of decomposition products are relatively insensitive to solvent; more ketone than alcohol is produced in certain of the decompositions; traces of hydrogen are detected among the products; copper(I) hydride rapidly reduces copper(I) alkoxides to alcohols. These observations are all very similar to those made in establishing copper(I) hydride as an intermediate in the thermal decomposition of *n*-butyl-(tri-*n*-butylphosphine)copper(I), and make an analogous mechanism for the decomposition of copper(I) alkoxides attractive.

The identification of these two mechanisms does not clarify the structural factors that control the path

followed by a particular organocopper(I) compound in its thermal decomposition. Indeed, the elimination of copper(I) hydride from a copper(I) alkoxide would seem energetically more attractive than its elimination from a copper(I) alkyl, both because the energy change associated with the conversion of a carbon-oxygen single bond to a carbonyl group is more favorable than that of a carbon-carbon single bond to a double bond, and because a copper(I)-oxygen bond is expected to be more polar, and less susceptible to homolytic scission, than a copper(I) carbon bond. The failure of this reasoning suggests that other factors entirely—the structure of the organometallic aggregates, the presence of trace metal catalysts, the availability of vacant coordination sites on the metal—may ultimately determine the decomposition mechanisms and thermal stabilities of these and other organometallic reagents.

## Experimental Section<sup>38</sup>

**Iodo[bis(di-*n*-butyl sulfido)]copper(I).** Commercial copper(I) iodide (195 g, 1.05 mol) was stirred with di-*n*-butyl sulfide (290 g, 2.00 mol) in a 500-ml erlenmeyer flask. The reaction mixture was warmed to 80° for 30 min and the resulting amber liquid filtered through a Buchner funnel and stored at room temperature.

**Methylcopper(I).** Iodo[bis(di-*n*-butyl sulfido)]copper(I) (1.4 g, 2.8 mmol) and 30 ml of ether were added to a flame-dried, serum-stoppered, 40-ml centrifuge tube containing a Teflon-coated stirring bar and six to eight 3-mm glass beads to aid in subsequent heterogeneous reactions with the alcohols. The solution was cooled to  $-78^\circ$  in a Dry Ice-isopropyl alcohol bath and methylolithium (1.5 ml of a 1.6 *N* solution in diethyl ether, 2.4 mmol) was added, producing an immediate precipitate of bright yellow methylcopper(I). The solid was compacted by centrifugation at room temperature and the supernatant liquid removed by cannula. Fresh ether (30 ml) was added while keeping the methylcopper(I) cold in a Dry Ice-isopropyl alcohol bath, and the tube was shaken and centrifuged. The ether was again removed and the washing procedure repeated an additional two times.

**Copper(I) alkoxides** were prepared by a common procedure, illustrated here by the preparation of copper(I) *n*-butoxide. To a suspension of 2.4 mmol of methylcopper(I), prepared as described above, was added *n*-butyl alcohol (0.22 ml, 2.4 mmol). The reaction mixture was stirred at 0° for 3 hr under nitrogen. The resulting homogeneous solution was cooled to  $-78^\circ$ ; copper(I) *n*-butoxide precipitated as a light yellow powder. The solid was com-

(38) All melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer, Model 237, grating spectrophotometer. Nmr spectra were determined with a Varian T-60 nmr spectrometer. Mass spectra were determined on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Combustion analyses were performed by Midwest Microlabs, Ltd., of Indianapolis, Ind. Analytical glpc analyses were performed on F&M Model 810 and Perkin-Elmer Model 990 flame ionization instruments. Hydrogen analyses were carried out by glpc using nitrogen carrier gas, a thermal conductivity detector, and methane as internal standard. Absolute yields of products were calculated from peak areas using internal standard techniques, with response factors obtained from authentic samples. Diethyl ether and tetrahydrofuran were distilled from lithium aluminum hydride or calcium hydride before use. Dimethoxyethane and pentane were distilled from disodium benzophenone dianion under nitrogen; pyridine and benzene were distilled from calcium hydride under nitrogen; hexamethylphosphoramide was distilled from sodium at reduced pressure. Alcohols were distilled, dried over 3A molecular sieves, and deoxygenated using a stream of nitrogen. Organic halides were passed through a column of alumina, and deoxygenated using a stream of nitrogen. Halide-free methylolithium (1.6 *M* in ether) was purchased from Foote Mineral Corp. Cyclopentyl-, *n*-butyl-, and *tert*-butyllithium reagents were supplied by Foote Mineral Corp. *sec*-Butyllithium was supplied by Alfa Inorganics, Inc. Lithium reagents were analyzed by the Gilman double titration method.<sup>39</sup> All reactions involving organometallic reagents were carried out under prepurified nitrogen, using standard inert atmosphere techniques.<sup>40</sup>

(36) J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972); J. A. Zoltewicz and T. M. Oestreich, *J. Amer. Chem. Soc.*, **95**, 6863 (1973), and references cited in each.

(37) Nucleophilic coupling of gold(I) ate complexes with alkyl halides involves oxidative addition of the alkyl moiety to the gold atom: A. Tamaki and J. Kochi, *J. Organometal. Chem.*, **51**, C39 (1973).

(39) H. Gilman, F. K. Cartledge, and S.-Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963); G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).

(40) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapter 7.

pacted by centrifugation at  $-78^{\circ}$  and the supernatant liquid removed by cannula. Fresh ether was added while keeping the copper(I) *n*-butoxide cold in a Dry Ice-isopropyl alcohol bath, and the tube was shaken and centrifuged. The ether was again removed and the washing procedure repeated. The yields (*vide infra*) of copper(I) alkoxides obtained using this procedure were not particularly reproducible, for two reasons: the heterogeneity of the reaction in ether and the restrictions imposed by the method of analysis.

When the alkoxide was generated as an intermediate, the reaction was homogeneous (pyridine dissolves methylcopper(I)), and a two-fold excess of alcohol was used. When the alkoxide was to be isolated, the reaction was heterogeneous (diethyl ether does not dissolve methylcopper(I)), and 1 equiv of alcohol was used. The washing and centrifuging had to be done at  $-78^{\circ}$ , as the alkoxides are very ether soluble at higher temperatures. These manipulations were technically difficult. Because the acid quench regenerated the starting alcohol, care had to be taken to remove excess alcohol before quenching the alkoxide, and only 1 equiv of alcohol was used. The isolated yield of alkoxide probably varied over a wider range than did the nonisolated yield of alkoxide intermediate. Average yields (per cents and ranges) observed for various copper alkoxides were: methoxide  $\sim 70$ ; *n*-butoxide  $\sim 55$  (48–66); *tert*-butoxide  $\sim 65$  (52–83); cyclohexoxide  $\sim 80$ ; phenoxide  $\sim 45$  (35–57); and isopropoxide  $\sim 50$ .

**Analysis of Copper(I) Alkoxides.** To a solution of copper(I) alkoxide (1–4 mmol) in ether at  $0^{\circ}$  was added 0.5 ml of concentrated hydrochloric acid. Addition of internal standard permitted glpc analysis of the resulting homogeneous solution for alcohol on a 15% Carbowax 20M on Chromosorb W column. The copper content of the solution was then determined by adding to it 10 ml of concentrated nitric acid, diluting to 200 ml with distilled water, and analyzing following the procedure of Flaschka and Abdine.<sup>41</sup>

**Small Scale Reactions of Copper(I) Alkoxides with Organic Halides.** The procedures used for most of these reactions were similar, and are illustrated here by the method used for the reaction of copper(I) *n*-butoxide with *n*-butyl bromide. A 2.4-mmol sample of methylcopper(I) was prepared. The bulk of the ether used in the final washing was removed, pyridine (20 ml) and *n*-butyl alcohol (0.22 ml, 2.4 mmol) were added, and the centrifuge tube was capped with two serum stoppers. (The second served to slow the rate of leakage of oxygen into the flask.) The solution was stirred for 3 hr at  $0^{\circ}$ ; then *n*-butyl bromide (0.32 ml, 3.6 mmol) was added and the reaction mixture was stirred for an additional 24 hr at room temperature. Analysis by glpc on an 8-ft, 10% TCEP on Chromosorb W column indicated a yield of di-*n*-butyl ether of 64%.

**Purification of Cuprous Chloride.**<sup>42</sup> Cuprous chloride (50 g) was ground in a mortar with *ca.* 10 ml of 1 *N* sulfuric acid. The resulting paste was added to 700 ml of 6% sulfurous acid. The suspension was stirred for 10 min; the suspended solid and the pale blue supernatant liquid were separated by filtration. The filtered solid was washed with 300 ml of glacial acetic acid, 250 ml of ethanol, and 250 ml of ether. The off-white solid was dried under vacuum and stored at  $5^{\circ}$ .

**Reaction of Iodobenzene with Copper(I) *n*-Butoxide by the Reaction of Lithium *n*-Butoxide with Cuprous Chloride.** Cuprous chloride (0.20 g, 2.0 mmol) was added to a serum-stoppered, flame-dried, 40-ml centrifuge tube containing a Teflon-coated stirring bar, and the tube was flushed with nitrogen. A solution of lithium *n*-butoxide, prepared by reaction of 0.148 g (2.0 mmol) of *n*-butyl alcohol with 2.0 mmol of methyl lithium in 5 ml of DME, was added and the mixture stirred for 30 min. Pyridine (20 ml) was added to the resulting yellow solution, and this mixture allowed to react with iodobenzene (0.61 g, 3.0 mmol) for 12 hr at reflux. Glpc analysis indicated that *n*-butyl phenyl ether was present in 98% yield, based on copper(I) alkoxide yield.

**Reaction of lithium *n*-butoxide with iodobenzene in the presence of 10% cuprous chloride** was carried out in an analogous manner, with the exception that only 0.02 g (0.2 mmol) of cuprous chloride was used. Analysis on a 6-ft, 3% OV-17 on Chromosorb Q column showed a 70% yield of *n*-butyl phenyl ether.

**Preparative Scale Reaction of Copper(I) *sec*-Butoxide with Bromobenzene.** Dimethoxyethane (30 ml) and 2-butanol (5.6 g, 75

mmol) were added to a serum-stoppered, flame-dried, 100-ml erlenmeyer flask containing a Teflon-coated stirring bar. The resulting solution was cooled in an ice bath and methyl lithium (47 ml of a 1.6 *N* solution in ether, 75 mmol) was added slowly. Cuprous chloride (7.5 g, 75 mmol) was placed in a serum-stoppered, flame-dried, 500-ml, round-bottomed flask equipped with a Teflon-coated stirring bar and a serum-stoppered reflux condenser. The apparatus and its contents were flushed with nitrogen, the lithium *sec*-butoxide solution was added, and the mixture was stirred for 30 min at  $25^{\circ}$ . Pyridine (200 ml) and bromobenzene (11.8 g, 75 mmol) were added to the resulting solution and the reaction mixture was refluxed for 12 hr. Solvent was removed by distillation through a 30-cm Holzmann column, and the residue was distilled through the same column at reduced pressure, yielding 5.1 g (45%) of *sec*-butyl phenyl ether having bp  $91^{\circ}$  (15 mm): nmr ( $\text{CCl}_4$ )  $\delta$  6.8 (s, 5, aromatic CH), 4.0 (m, 1, OCH), 2.0–0.8 (m, 8,  $\text{CH}_2$  and  $\text{CH}_3$ ).

**Preparation Scale Reaction of 1-Bromobutane with Copper(I) Phenoxide.** A magnetic stirring bar and 15.3-mm glass beads (to increase the rate of solid solution reactions by grinding) were placed in each of two 200-ml centrifuge bottles. The bottles were stoppered, and flamed under nitrogen. Methylcopper(I) (50 mmol) was prepared in each tube. To the washed suspensions of methylcopper(I) in ether (50 mmol) was added 8.8 ml of phenol (0.1 mol) and 100 ml of pyridine. The mixture was stirred for 3 hr at  $0^{\circ}$ . Butyl bromide (8.05 ml, 0.075 mol) was added to each bottle and the mixtures were stirred at room temperature under nitrogen for 48 hr. The reaction mixtures were poured onto ice and the combined organic products extracted into ether. Ammonium hydroxide (30 ml) was added to complex copper as water-soluble Cu(II) species. The extracts were washed with aqueous KOH and with ice-water; the ether was removed on a rotary evaporator. On distillation under reduced pressure, 9.3 g (62%) based on methyl lithium of *n*-butyl phenyl ether was obtained: nmr ( $\text{CCl}_4$ )  $\delta$  6.7–7.2 (m, 5, aromatic CH), 3.8–4.0 (t, 2,  $\text{OCH}_2$ ), 0.8–2.0 (m, 7,  $\text{CH}_2$  and CH); ir ( $\text{CCl}_4$ ) 2960, 2940, 2880, 1600, 1500, 1290  $\text{cm}^{-1}$ ; *m/e* 150.

**Preparative Scale Reaction of 1-Bromocyclohexene with Copper(I) *n*-Butoxide.** The reaction was carried out on a 70-mmol scale in a manner analogous to that described above; the reaction time was 24 hr. A reduced pressure distillation yielded 3.6 g (33%) of 1-butoxycyclohexene:  $n_D^{20}$  1.4635; nmr ( $\text{CCl}_4$ )  $\delta$  4.45 (m, 1,  $=\text{CH}$ ), 3.55 (t, 2,  $\text{OCH}_2$ ), 0.95–2.0 (m, 15,  $\text{CH}_2$  and  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3075, 2900, 1665, 1450, 1435, 1375, 1190  $\text{cm}^{-1}$ ; *m/e* 154.

**Reaction of Copper(I) Phenoxide with Iodobenzene.** A solution of halide-free methylcopper(I) (2.0 mmol) in 20 ml of pyridine was transferred to a flame-dried, 40-ml centrifuge tube containing phenol (0.87 g, 2.0 mmol), and stirred at  $25^{\circ}$  for 30 min. The resulting amber solution was transferred to a flame-dried, 50-ml, round-bottomed flask equipped with a Teflon-coated stirring bar and a serum-stoppered reflux condenser. Iodobenzene (0.61 g, 3.0 mmol) was added and the reaction mixture refluxed for 12 hr. Analysis of the reaction mixture by glpc using an 8-ft, 15% Carbowax 20M column indicated a 94% yield of diphenyl ether.

Cyclobutanol was prepared using the procedure of Caserio, Graham, and Roberts.<sup>43</sup>

**Thermolysis of Copper(I) Alkoxides.** Approximately 2-ml aliquots of copper(I) alkoxide solution were transferred under nitrogen into dry 8-mm Pyrex tubes, the contents of the tubes were frozen in liquid nitrogen, and the tubes were sealed under vacuum. The tubes were heated in a bomb oven for the requisite time, cooled, and opened. Internal glpc standards were added, and the mixtures were analyzed by glpc. The copper content of these solutions was determined by the procedure of Flaschka and Abdine.<sup>41</sup>

**Thermal Decomposition of Copper(I) Alkoxides in the Presence of Copper(I) Hydride.** Solutions of, *e.g.*, copper(I) cyclohexoxide (5.0 mmol) in 10 ml of toluene and copper(I) 3-pentoxide (3.2 mmol) in 10 ml of ether were transferred to 40-ml centrifuge tubes containing 3.0-mmol samples of copper(I) hydride.<sup>29</sup> The resulting mixtures were decomposed in sealed tubes at  $115^{\circ}$  and analyzed as described above.

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(41) H. Flaschka and H. Abdine, *Mikrochim. Acta*, 770 (1956).

(42) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, 2, 1 (1946).

(43) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 11, 171 (1960).