Chemistry of phenoxo complexes. VI. Reactions of phenoxocopper(I) complexes with carbon tetrachloride

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The reactions of several substituted cuprous phenoxides with CCl_4 in acetonitrile were examined. Phenoxides without *ortho*-substituents usually gave high yields of tetraarylorthocarbonates. It is shown that the latter are also produced catalytically from sodium phenoxides and CCl_4 in the presence of small amounts of cuprous chloride. Cuprous phenoxides with *ortho*-chloro substituents, in the absence of facile hydrogen transfer agents, gave stable mixed oxidation state complexes of approximate composition: $Cu_2{}^{I}Cu^{II}Cl_2(OAr)_2$. In the presence of facile hydrogen atom transfer agents, such as free phenol or ascorbic acid, both the phenoxides without *ortho*-substituents and the *ortho*-chlorinated phenoxides gave moderate yields of triarylorthoformates. Some reactions of tritertbutylphenol and tritertbutylphenoxyl with copper complexes are described. The mechanisms of the various reactions are interpreted in terms of homo- and cross-coupling between phenoxyl and $\cdot CCl_3$ radicals.

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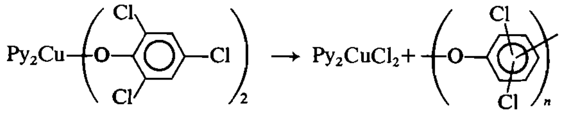
On a étudié les réactions de plusieurs phénolates cuivreux substitués avec le CCl_4 dans l'acétonitrile. Les phénolates qui ne portent pas de substituants en *ortho* conduisent généralement à de bons rendements d'orthocarbonates de tétraaryles. On a montré que l'on peut aussi obtenir ces derniers par une réaction catalytique des phénolates de sodium et du CCl_4 en présence de faibles quantités de chlorures cuivreux. Les phénolates cuivreux portant un chlore en *ortho*, en l'absence d'agents permettant des transferts faciles d'hydrogènes, conduisent à des complexes stables comportant des états d'oxydation mixtes et de composition approximative $Cu_2{}^{I}Cu^{II}Cl_2(OAr)_2$. En présence d'agents permettant des transferts faciles d'atomes d'hydrogène, tels du phénol libre ou de l'acide ascorbique, les phénolates sans substituants en *ortho* de même que les phénolates portant des chlores en *ortho* conduisent à des rendements moyens d'orthoformates de triaryles. On décrit quelques réactions du tri-*tert*-butylphenol et du radical tri-*tert*-butylphenoxyle avec des complexes de cuivre. On interprète les mécanismes des diverses réactions en termes de couplages homolytiques et croisés entre les radicaux phénoxyle et $\cdot CCl_3$.

[Traduit par le journal]

Introduction

An earlier paper (1) described a mechanistic study of reaction [1], first reported by Blanshard *et al.* (2).

[1] 

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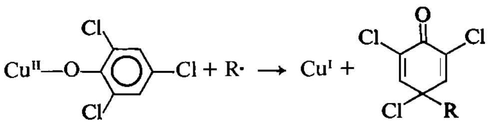
One conclusion of this study was that the initial step in reaction [1] is the homolytic ligand transfer from **1** to an initiator radical as depicted in [2] (1).

[2] 

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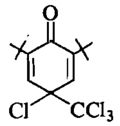
It was further suggested that one of the modes of participation of carbon tetrahalides in reaction [1] involved the formation and reaction of trihalomethyl radicals according to [2], to produce unstable trihalomethylcyclohexadienones, 3*a*, as intermediates (1).

Although a number of substituted trichloromethylcyclohexadienones have been synthesized, it is evident that their formation is favoured by alkyl substitution and strongly disfavoured by halogen substitution (3, 4). It is possible, however, that the latter empirical observation is the result of mechanistic rather than thermodynamic effects. To our knowledge there is a single reported example of a cyclohexadienone bearing both a chlorine and a trichloromethyl substituent on the same ring carbon.



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This compound, **4**, was prepared by Pirkle and Koser and although no specific reference to its ther-

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mal stability was made, it is certainly of relatively long-term stability under ambient conditions (5). Thus, the plausibility of 3*a* as an unstable intermediate in reaction [1], catalyzed by carbon tetrachloride, remained open to question.

In order to further test the plausibility of 3*a* as an intermediate it was decided to take advantage of the well known tendency of copper(I) complexes to undergo reaction with carbon tetrachloride according to reaction [3] (6, 7).

$$[3] \qquad Cu^{I} + CCl_4 \rightarrow Cu^{II}Cl + {}^{\bullet}CCl_3$$

By using a phenoxocopper(I) complex in reaction [3] the possibility existed that both phenoxocopper(II) species and trichloromethyl radicals could be generated simultaneously in high concentration, thereby fulfilling all of the requirements for testing reaction [2]. The results of such a study are reported in the present paper.

Results

The results of the reactions studied may be classified in terms of the principal products obtained. These products are (*i*) aryl orthocarbonates, (*ii*) aryl orthoformates, (*iii*) cyclohexadienone derivatives. Only in the case of cuprous tritertbutylphenoxide was the anticipated trichloromethylcyclohexadienone obtained as the major product.

All of the reactions described below were carried out in acetonitrile except where otherwise stated. Acetonitrile is particularly appropriate for the *in situ* preparation of cuprous phenoxides by reaction of cuprous chloride with the appropriate sodium phenoxide.

Orthocarbonate-forming Reactions

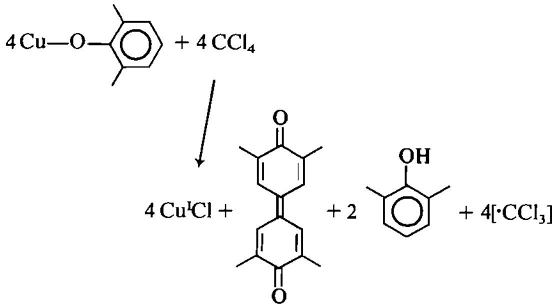
As previously reported (8), certain cuprous phenoxides undergo smooth reaction with CCl_4 under ambient conditions to produce the corresponding tetraarylorthocarbonate as the principal product. The most important criteria for success in this reaction are the requirements that there be no *ortho*-substituents on the phenoxo group and that the substituents not be exceptionally reactive towards radical attack.

The operation of the first criterion is illustrated by the high yields of orthocarbonate from reaction of 3-methyl and 4-methylphenoxocopper(I), but very low yields from 2-methylphenoxocopper(I).[1] A similar result was obtained with the monochlorophenoxo analogues.

The operation of the second criterion is illustrated by the failure of any methoxy-substituted phenoxide to yield orthocarbonate. This failure seemed to be due to the extreme ease of hydrogen atom abstraction from the methyl group. The mixtures of products obtained in such reactions were not characterised.

Reactions of *ortho*-methylated phenoxide gave products typical of phenoxyl radical coupling. The usual complex mixture, typical of oxidative coupling (9), was obtained from 2-methylphenoxocopper(I). The 2,6-dimethylphenoxo complex reacted rapidly and cleanly according to reaction [4]:

[4]



The precise fate of the $^{\bullet}CCl_3$ in reaction [4] was not determined. None of the reactions described herein was ever found to produce perchloroethane. A number of analyses by vpc all showed the presence of chloroform in solvent removed by distillation at the end of the reaction. It therefore seems reasonable to assume that $^{\bullet}CCl_3$ radicals are removed by hydrogen abstraction rather than coupling.

A reaction of dicopper(I) catecholate with CCl_4 produced the previously prepared bisphenylene orthocarbonate in good yield (10).

Since cuprous chloride is both a reactant and a product in the orthocarbonate forming reaction, it was anticipated that cuprous chloride would catalyse the reaction of a sodium phenoxide with CCl_4. A reaction in which an equimolar mixture of sodium 4-methylphenoxide and CCl_4 was reacted in the presence of 0.05 molar equivalents of cuprous chloride gave a high yield of orthocarbonate, thus confirming the expected catalysis.

Orthoformate-forming Reactions

The production of orthocarbonates described above only occurs in high yield under scrupulously anhydrous conditions. The use of undried acetonitrile as solvent led to the formation of triarylorthoformate as a major reaction product. Such reactions were also accompanied by precipitation of yellow cuprous oxide due to hydrolysis of the cuprous phenoxide.

An especially interesting case of orthoformate

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[1] Although small amounts of orthoesters were detected in the reaction product by ir they were not successfully separated.

TABLE 1. Some properties of aryl ortho esters

Compound	Mass spectrum m/e (abundance)			^{1}H nmr ($CDCl_3$)[c]	Melting point (°C)
Phenyl[a]	291(4)	228(1)	214(62)	7.75(m)	95 (lit. 96–98)
	170(28)	154(2)	77(100)		
3-Methyl phenyl[a]	333(100)	256(2)	242(3)	7.5(m); 2.55(s)(4:3)	84–85
	198(6)	182(16)	91(70)		
4-Methylphenyl[a]	333(100)	256(1)	242(2)	7.2(s); 2.35(s)(4:3)	101
	198(4)	182(5)	91(23)		
4-Chlorophenyl[a]	393(28)	282(2)	238(3)	7.98(d); 7.80(d)(1:1)	129–130
	222(3)	111(100)			
1,2-Phenylene[a]	228(100)	120(34)	92(68)	7.2(s)	109 (lit. 109)
	64(60)				
4-Methylphenyl[b]	333(1)	242(3)	227(76)	7.1(s); 6.5(s); 2.4(s)(12:1:9)	104
	198(4)	107(100)	91(73)		
2-Chlorophenyl[b]	393(100)	282(4)	266(4)	7.75(m)[d]	177
	247(3)	222(2)	111(44)		
2,4,6-Trichlorophenyl[b]	439(9)	404(100)	196(36)	7.6(3); 7.2(s)(6:1)	165–167
	179(27)				
Pentachlorophenyl[b]	555(1)	539(1)	291(1)	7.3(s)	224–226
	263(1)	247(1)	78(100)		

[a] Orthocarbonate.

[b] Orthoformate.

[c] Chemical shifts in δ units (s = singlet, d = doublet, m = multiplet). The figures in parentheses are the ratios of protons in the order of cited chemical shifts.

[d] The methine proton was coincident with the aromatic multiplet in this compound and was not assigned.

production was observed with cuprous 2,4,6-trichlorophenoxide. Under conditions normally used for the formation of orthocarbonate, the latter compound reacts to give a stable product of approximate composition $[Cu_2{}^{I}Cu^{II}Cl_2(OAr)_2]$. This reaction always leads to the production of a small amount of tris(trichlorophenyl)orthoformate and, by implication, cuprous chloride, thus rendering exact analysis of the Cu^{I}/Cu^{II} complex impossible. Equivalent results were obtained using cuprous pentachlorophenoxide.

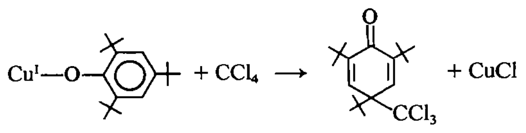
When the products of reactions of excess CCl_4 with either cuprous pentachloro- or trichlorophenoxide were treated with a facile hydrogen atom transfer agent such as ascorbic acid, or a reducing phenol such as 2,6-xylenol, the intense reddish-brown colour was rapidly bleached and workup of the reaction mixture gave the polyhalophenyl orthoformate in substantial yield (see Table 1). Reduction of the reddish-brown mixed oxidation state complex with stannous chloride also resulted in rapid bleaching, but no orthoformate could be detected in the product.

When the ascorbic acid reduction of the reddish-brown material was carried out in the presence of carbene scavengers such as cyclohexene or norbornene, no dichlorocarbene adducts were detected and the formation of orthoformate proceeded normally.

Reactions Involving Tritertbutylphenoxyl Species

The reaction of cuprous 2,4,6-tritertbutylphenoxide with CCl_4 was quite different from those of relatively unhindered phenoxides. The reaction shown in [5] occurred rapidly and cleanly:

[5]



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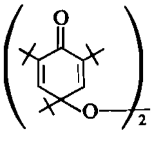
Since CuCl is generated in [5] and the cuprous phenoxide is easily formed from CuCl and sodium phenoxide, the cyclohexadienone can be synthesised in good yield from the reaction of CCl_4 and the sodium phenoxide in the presence of a catalytic amount of CuCl.

A reaction of equimolar amounts of 2,4,6-tritertbutylphenoxyl radical and cuprous trichlorophenoxide in the presence of CCl_4 also yielded **5** as the major product (ca. 50%). The remainder of the tertbutylphenoxyl radical was recovered as the peroxide, **6** (ca. 25%), and the quinol ether, **7** (ca. 25%). The product **6** resulted from oxygenation of unreacted radical during workup.



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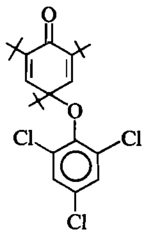

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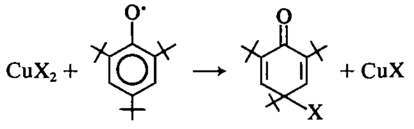
A similar reaction in which the tertbutylphenoxyl radical was replaced by 2,4,6-tritertbutylphenol resulted in a substantial increase in the yield of **7** at the expense of **5**.

No reaction occurred between tritertbutylphenoxyl and either bis(pyridine)bis(trichlorophenoxo)copper(II) or the mixed oxidation state product of the cuprous trichlorophenoxide/CCl_4 reaction.

Reaction [6] was found to proceed readily for X = Cl, but did not occur for X = CH_3COO, SCN, or OCH_3.

[6]



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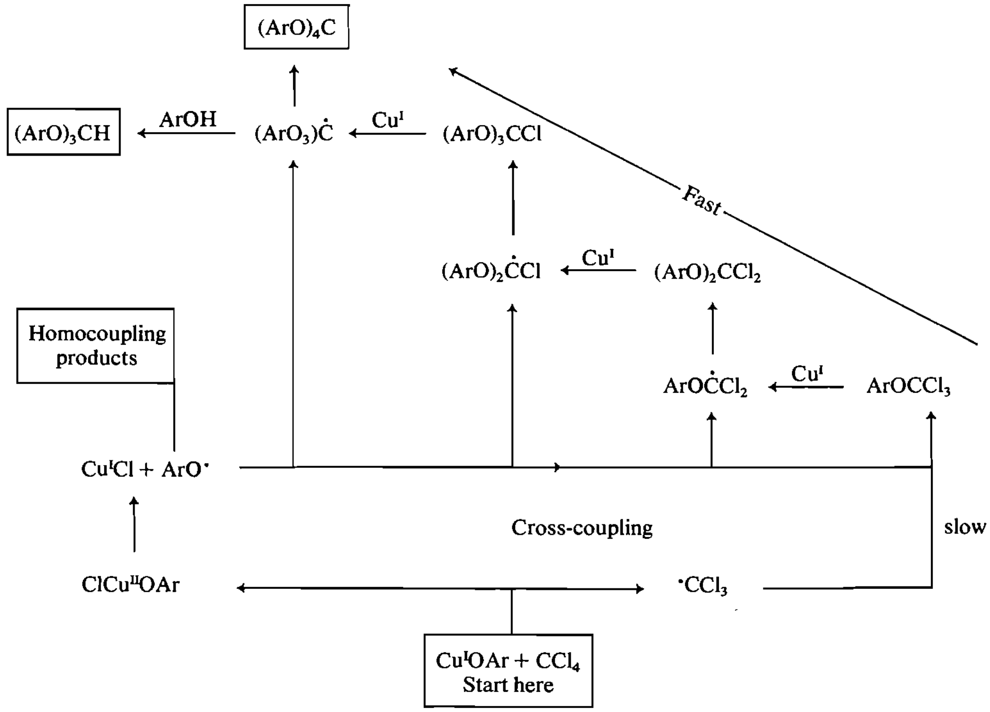
Discussion

Ortho Ester-forming Reactions

All of the experimental results described above can be accommodated by mechanisms involving free radicals. The production of ortho esters evidently occurs by an analogy of reaction [3] in which a copper(I)phenoxide generates a CCl_3 radical by chlorine atom abstraction from CCl_4 (see Scheme 1). If the phenoxide ligand is easily oxidised to the radical, such radical production should take place following oxidation of the Cu(I) by CCl_4. The simultaneously produced CCl_3 and phenoxyl radicals may undergo a number of different reactions, of which cross-coupling to produce an aryl trichloromethyl ether is presumably the precursor to ortho ester production. The fact that no mixed aryloxychloromethanes are observed in the ortho ester-producing reactions, even in the presence of a large excess of CCl_4, indicates that further substitutions into the trichloromethyl ethers are rapid compared to the initial substitution into CCl_4. The further substitutions could conceivably occur by simple nucleophilic attack by phenoxide (11) but the formation of orthoformates, as discussed below, is best explained on the assumption that they occur by a sequence of radical processes involving chlorine abstraction by copper(I).

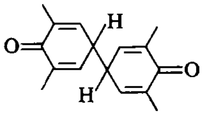
In the case of phenoxyl radicals that are unencumbered in the *ortho* positions the cross-coupling reaction to give ortho esters seems to occur with high efficiency. Alkyl substitution in the *ortho*-positions seems to favour homo-coupling of phenoxyl radicals relative to the cross-coupling reaction. This is probably a result of the reduced effectiveness of the bulky CCl_3 radical when it is competing with phenoxyl radical for a ring carbon position rather than for an unencumbered oxygen. Only in the case of the tritertbutylphenoxyl radical, where phenoxyl radical homocoupling is precluded, is carbon–carbon cross-coupling to CCl_3 observed.

The extreme rapidity of reaction [4] (complete



SCHEME 1. Production of ortho esters.

within a few minutes) suggests that phenoxyl radicals are generated in high concentration but that their rate of homo-coupling is much faster than either C—C, or C—O, coupling to trichloromethyl radicals. The stoichiometry of phenol production in the reaction also suggests that hydrogen abstraction from the primary coupling product, **9**, or its enol isomer, by phenoxyl radicals is fast compared to radical coupling, or to abstraction of hydrogen from solvent.



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The formation of diphenoquinone rather than C—O coupled phenolic oligomers conforms to the generally accepted view that the diphenoquinone is the normal product of the coupling of 2,6-dimethylphenoxyl *free* radicals.

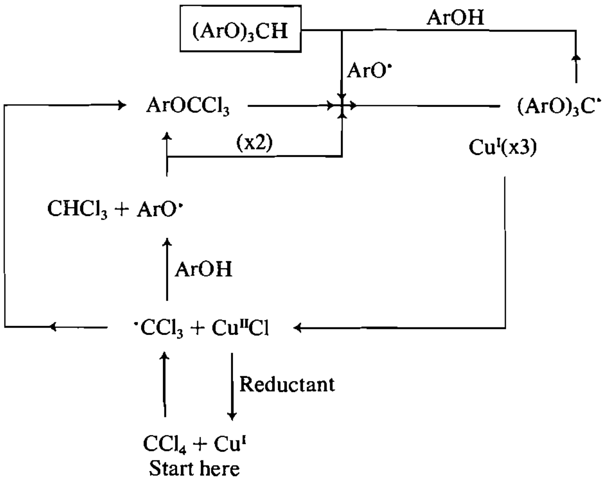
The observed formation of 2,4,6-trichlorophenyl orthoformate under certain reaction conditions proves that the steric impediment to cross-coupling at oxygen is not overly severe when both *ortho* positions are substituted with chlorine (in view of the similar steric size the same is surely true of methyl substituents). There is no doubt that the low stability of the homo-coupled phenoxyl dimers (either C—O or C—C) of the trichlorophenoxyl radical also directs the reaction towards orthoformate production. An examination of molecular models makes clear that orthocarbonate formation is sterically impossible in this case and it is expected that the triaryloxymethyl radicals will terminate by hydrogen atom abstraction. Even in the cases where there are no *ortho*-substituents the formation of orthoformate is observed when a facile hydrogen atom transfer agent, such as hydrolytically produced free phenol, is present. Since the mixed oxidation state products resulting from partial oxidation of cuprous penta- or trichlorophenoxides by CCl_4 are stable at room temperature, the generation of phenoxyl radicals in these systems most probably occurs via hydrogen atom abstraction from free phenol by other radicals in the system, and in particular by trichloromethyl radicals. Thus, in the absence of added hydrogen donor, a small amount of adventitious free phenol could yield phenoxyl radicals by hydrogen transfer to CCl_3 radicals generated by reaction [3].

The resulting phenoxyl radicals are then scavenged by cross-coupling with $CCl_3^{\cdot}$. The low yield of orthoformate results from the limited amount of $CCl_3^{\cdot}$ available and the inability of the phenoxide to recycle the Cu^{II} to Cu^{I} by reduction. These limiting factors are obviated by the addition of a protic reducing agent which can both recycle the Cu^{II} to Cu^{I} (thus ensuring a continuous supply of $CCl_3^{\cdot}$) and generate free phenol by protolysis of the phenoxide complexes (see Scheme 2).

The alternative possibility that orthoformate might be generated via insertion of dichlorocarbene into the O—H bond of free phenol is considered unlikely since no carbene derived products could be detected when the reactions were carried out in the presence of the carbene scavenger norbornene. It is not unlikely that dichlorocarbene might be extruded from an unstable trichloromethylcopper intermediate if it were formed. The present evidence provides little support for such a mechanism. The further possibility that orthoformate may arise from reaction of chloroform, resulting from hydrogen atom transfer to CCl_3 radicals, may be excluded on the grounds that chloroform was found to react only very slowly with cuprous phenoxides.

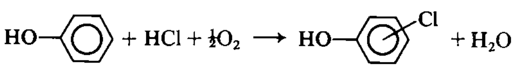
Reactions of Tritertbutylphenoxide and Tritertbutylphenol

All of the reactions of cuprous tritertbutylphenoxide and of tritertbutylphenol investigated in the present study gave products consistent with free radical mechanisms. The trichloromethylcyclohexadienone produced by reaction of cuprous tritertbutylphenoxide with CCl_4 is the expected product of cross-coupling between the phenoxyl radical and CCl_3 when steric hindrance precludes coupling at oxygen. The fact that only the 4-trichloromethyl derivative was isolated probably gives no clear indication of the stereoselectivity of the primary coupling process. The ^1H nmr spectrum of the crude reaction product indicated the presence of appreciable amounts of a 2-substituted cyclohexadienone. The failure to isolate such a compound may have been due to its spontaneous isomerisation to the more stable 4-isomer. The general failure to observe 2-substituted products from tritertbutylphenoxyl coupling reactions has previously been attributed to spontaneous isomerisation (12). The production of the quinol ether, **7**, in reactions of tritertbutylphenoxyl and tritertbutylphenol with cuprous trichlorophenoxide and CCl_4 is very likely due to protolysis of the cuprous trichlorophenoxide, followed by hydrogen abstraction from the free phenol to yield trichlorophenoxyl radicals. The reaction of tritertbutylphenoxyl with trichlorophenol is known to produce **7** in high yield (13). Since tritertbutylphenol introduces more protons into the system than the phenoxyl radical (where the protons come from hydroxylic impurities), it favours the formation of larger amounts of **7**.



SCHEME 2. Production of orthoformates from trichlorophenoxide.

The ligand abstraction reaction shown in [6], where X = Cl, is quite typical of ligand transfer reactions from cupric compounds to organic radicals (14); it is, we believe, the first such example involving an aryloxy radical. As such it raises some interesting speculation regarding the mechanisms of phenol substitution reactions mediated by metal complexes. For example, the well-known chlorination of phenols by cupric chloride is most simply explained by assuming the generation of a phenoxyl radical, followed by chlorine atom abstraction from $CuCl_2$ (15). Chlorine attachment at an unsubstituted *ortho-* or *para-*carbon would be followed by rapid enolisation to the phenol. In our study of reaction [6] it was also observed that use of $CuCl_2 \cdot 4H_2O$, rather than anhydrous $CuCl_2$, did not result in any decrease in the yield of **8**. Such behaviour parallels that of the reactions of alkyl radicals with copper(II) compounds, where the rates of transfer of chlorine or bromine atoms are very fast compared to reactions of ligands bonding through oxygen. The much higher reactivity of phenoxyl radicals towards chlorine ligand, rather than water or hydroxyl, also explains the relatively clean generation of monochlorophenol product in the copper catalyzed oxychlorination reaction [7] (16).

[7]


Given the fact that chlorination can occur by ligand transfer it is reasonable to ask whether there is any condition under which hydroxylation can occur by a similar process, particularly in view of the important role played by metalloenzymes in biological hydroxylation (17). In a number of preliminary experiments we were unable to effect reaction [6] where X = CH_3O, CH_3COO, or CNS. Although the compound **7** was isolated from reactions of tritertbutylphenoxyl and tritertbutylphenol with cuprous trichlorophenoxide, its formation was more likely due to the known reaction of tritertbutylphenoxyl with free trichlorophenol (13) than to ligand transfer. An unequivocal resolution of the latter uncertainty is very difficult since solutions of tritertbutylphenoxyl radical are difficult to free of hydroxylic impurities. Since the lowering of oxidation potential of the metal by ligation to oxygen, rather than chloride, impairs transfer of oxygen bonded ligands, the problem may be solved by design of a more suitable non-reacting ligand environment about the copper (e.g., more polarisable ligands such as those found in copper-containing oxidases (17)).

Experimental

Solvents were generally of reagent grade. Hydrocarbons were freshly distilled from sodium benzophenone dianion before use. Acetonitrile was distilled from calcium hydride and stored over molecular sieves. Ethanol was dried with sodium and distilled under dry nitrogen prior to use. Phenols were obtained as reagent grade materials and subject to either a single recrystallisation or distillation prior to use. Cuprous chloride was prepared according to a standard procedure (18) and stored under vacuum.

Preparation of Cuprous Phenoxides

A sample of the appropriate sodium phenoxide was prepared by dissolution of sodium (2.3 g) in dry ethanol (150 mL) under nitrogen. Following dissolution of the sodium the phenol was added in slight excess (1.05 equivalent) and solvent was removed by distillation until solid began to appear. The remaining solvent and excess phenol were removed by heating at 90°C and 0.001 Torr for 16 h. The resulting sodium phenoxide was ground to a fine powder under dry nitrogen and used immediately.

Sodium phenoxide (100 mmol) in deoxygenated, dry acetonitrile (200 mL) was stirred to achieve a fine suspension and then cuprous chloride (100 mmol) was added. After stirring for 1 h the white precipitate was sometimes filtered off under nitrogen and identified as sodium chloride (ca. 5.8 g), but normally the NaCl was not removed and further reactions were carried out directly on the solution of cuprous phenoxide.

Preparation of Orthocarbonates

A solution of cuprous phenoxide, prepared as above, was treated with CCl_4 (9 mL; 100 mmol). On contact with the solution the CCl_4 initially generated an intense blue colour which almost instantly turned dark brown. After stirring for 12 h the brown colour was usually either completely discharged or considerably faded. Sodium chloride was removed by filtration and the filtrate was evaporated to dryness on a rotary evaporator to yield a white, sticky solid. Extraction of the solid with CCl_4 yielded insoluble CuCl (~100 mmol). The remaining solution contained essentially pure orthocarbonate in the cases of phenyl, 4-methylphenyl, 3-methylphenyl, and 4-chlorophenyl (by ^1H nmr). Evaporation of CCl_4 and recrystallisation from absolute ethanol gave the pure orthocarbonates in ca. 50% yield. The product from the reaction of cuprous 2-chlorophenoxide contained a considerable amount of phenol and some ortho ester (by ir). Removal of the phenol by vacuum sublimation and recrystallisation of the residue from ethanol gave a small amount of tris(2-chlorophenyl) orthoformate (14% based on reactant phenol). Although the product of the cuprous 2-methylphenoxide reaction contained some ortho ester (by ir), neither orthocarbonate nor orthoformate was successfully isolated from the mixture of products.

A reaction of dicopper(I) catecholate (50 mmol) with CCl_4 (200 mmol) gave a dark green/black suspension with considerable evolution of heat. After stirring for 12 h the mixture was added to an excess of water, extracted with CH_2Cl_2, dried and evaporated to a dark brown viscous oil. The oil was deposited on a Florisil column and eluted with CH_2Cl_2 to yield pure bisphenylene orthocarbonate (50% yield).

Some properties of the orthocarbonates are summarised in Table 1.

Catalytic Synthesis of 4-Methylphenyl Orthocarbonate

To a stirred suspension of sodium 4-methylphenoxide (100 mmol) in acetonitrile (200 mL) was added cuprous chloride (5 mmol) and CCl_4 (100 mmol). After stirring for 12 h at room temperature the product was worked up as in the stoichiometric reaction and the yield of orthocarbonate was essentially the same.

Synthesis of 4-Methylphenyl Orthocarbonate in Wet Acetonitrile

The stoichiometric synthesis of 4-methylphenyl orthocarbonate was carried out using exactly the procedure described above, except for the use of reagent grade acetonitrile containing 0.2 to 0.3% water. Removal of a small amount of free phenol from the crude organic product by vacuum sublimation left a mixture of orthocarbonate and orthoformate in the ratio of 10:1 (by ^1H nmr).

Reaction of Cuprous 2,6-Dimethylphenoxide with CCl_4

Cuprous chloride (9.9 g) was added to a stirred suspension of sodium 2,6-dimethylphenoxide (14.4 g) in acetonitrile (100 mL). After 1 h CCl_4 (10 mL) was added. The mixture immediately turned dark brown, but after a few minutes the dark brown colour had completely faded to be replaced by the dark orange suspension of 2,2′,6,6′-tetramethyldiphenoquinone. The latter was filtered and washed with water to remove sodium chloride (yield: 5.8 g). The filtrate was evaporated to dryness and the resulting sludge was slurried with CCl_4 (100 mL). The precipitated CuCl was filtered off and the solution was evaporated to a brown oil. Sublimation of the oil under vacuum yielded xylenol (4.5 g) and left a dark brown tar (1.0 g) which contained a small amount of diphenoquinone together with other unidentified products.

Reactions of Cuprous 2,4,6-Trichlorophenoxide and Pentachlorophenoxide

Reactions of the title compounds with CCl_4 under the conditions described for orthocarbonate synthesis led to dark red-brown solutions of more or less indefinite stability at room temperature. The colour changes were much slower for the pentachlorophenoxide than for other phenoxides. Evaporation of the acetonitrile on a rotary evaporator gave an amorphous dark brown solid whose infrared spectrum was identical to that of the uncomplexed copper(II) trichloro- or pentachlorophenoxide (19).

Extraction of the solid derived from the trichlorophenoxide with ether yielded trichlorophenyl orthoformate in ca. 10% yield. Extraction of the solid derived from the pentachlorophenoxide with toluene yielded pentachlorophenyl orthoformate in ca. 10% yield.

Reactions in the Presence of Hydrogen Transfer Agents

A reaction of cuprous 4-methylphenoxide was carried out under the same conditions as the orthocarbonate synthesis but in the presence of one equivalent of 4-methylphenol. The crude organic product yielded cresol (77% based on total 4-methylphenoxyl) on vacuum sublimation and a residue containing only orthocarbonate and orthoformate in 2:1 molar ratio (by ^1H nmr) (50% based on sodium phenoxide).

A similar reaction with cuprous trichlorophenoxide and free trichlorophenol, using the same workup as that used in the stoichiometric orthocarbonate synthesis, yielded a crude organic product from which free phenol was sublimed (75% based on total trichlorophenoxyl) to leave essentially pure trichlorophenyl orthoformate (45% based on sodium phenoxide).

A solution of cuprous trichlorophenoxide, prepared from the sodium phenoxide (1.0 g) and cuprous chloride (0.46 g) in acetonitrile was reacted with CCl_4 (3 mL). 2,6-Dimethylphenol (0.58 g) was added and the solution was stirred until the dark brown colour was discharged. The precipitate was recovered and washed with water to yield 2,2′,6,6′-tetramethyldiphenoquinone (0.3 g). Evaporation of the filtrate to dryness and extraction with CCl_4 gave a crude organic fraction (1.1 g) containing mainly trichlorophenyl orthoformate, trichlorophenol, and xylenol. Removal of the phenols by vacuum sublimation left a residue consisting almost entirely of orthoformate (0.49 g; 44% yield).

Repetition of the latter reaction, but using ascorbic acid (0.88 g) in place of xylenol, resulted in a similar bleaching of the dark brown solution. The initial precipitate contained sodium chloride and unreacted ascorbic acid (only slightly soluble in CH_3CN). The CCl_4 extraction left a residue of CuCl mixed with dehydroascorbic acid. The CCl_4 soluble material was a mixture of trichlorophenol and trichlorophenyl orthoformate (0.91 g total weight). Removal of the phenol and recrystallisation of the residue from ethanol yield the pure orthoformate (0.36 g; 40%).

Synthesis of 2,4,6-Tritertbutyl-4-trichloromethylcyclohexa-2,5-dienone

Sodium tritertbutylphenoxide (1.29 g) was suspended in acetonitrile under nitrogen. Cuprous chloride (0.45 g) was added and the mixture was stirred for 1 h before addition of CCl_4 (5 mL). The mixture turned slowly from yellow, to green, to blue, and was left at room temperature several hours. The product was evaporated to dryness and the resulting green mass was extracted with CCl_4. Slow evaporation of the CCl_4 solution yields the product **5** as a pale yellow crystalline powder (1.38 g; 80%; mp 71–72°C, lit. 68–71°C (20)). *Anal.* calcd. for $C_{19}H_{29}OCl_3$: C 60.1, H 7.64, Cl 28.04; found: C 59.16, H 8.05, Cl 26.93. ^1H nmr (CCl_4): $\delta = 1.9$ (S, 27H); $\delta = 7.35$ (S, 2H); ir: $\nu_{C=O} = 1660$ and $1640\ cm^{-1}$ (KBr pellet).

A small amount of the peroxide **6** was isolated by concentration of the mother liquor. This product had properties identical to those previously reported (12).

A catalytic reaction was carried out using the sodium phenoxide (0.7 g; 2.5 mmol) and CuCl (0.025 g; 0.25 mmol) in acetonitrile (40 mL) and an excess of CCl_4. After stirring at room temperature for 5 h a conversion of phenoxide to **5** of 65% was estimated by ^1H nmr.

Reaction of the Cuprous Trichlorophenoxide/CCl_4 Reaction Product with 2,4,6-Tritertbutylphenoxyl

A solution of cuprous trichlorophenoxide was prepared by reaction of the sodium phenoxide (1.1 g) and cuprous chloride (0.5 g) in acetonitrile (15 mL). Following a standard procedure (21), the phenoxyl radical was prepared under N_2 by stirring tritertbutylphenyl (2.0 g) with MnO_2 (6 g) in benzene (100 mL). The radical solution was introduced into the cuprous phenoxide by filtration through a Schlenk filter under pressure of N_2. Carbon tetrachloride (3 mL) was injected and the mixture was stirred for 1 h. The product was evaporated to dry-

TABLE 2. Results of analyses of two complexes obtained from cuprous polyhalophenoxides*

	$Cu(I)TCP/CCl_4$	$Cu(I)PCP/CCl_4$
Approximate stoichiometry	[CuTCP][CuCl][CuClTCP]	[CuPCP][CuCl][CuClPCP]
Cu(I): calcd.	19.40	16.04
found	19.78	11.18
Cu(total): calcd.	29.11	24.05
found	26.68	23.83
Phenoxide: calcd.	60.04	66.99
found	59.6	68.5
Cl^-: calcd.	10.85	8.96
found	8.98	
C: calcd.	22.00	18.18
found	17.37	17.46
H: calcd.	0.61	0.00
found	1.01	0.55
Cl: calcd.	43.39	53.79
found	43.85	53.50

*TCP = trichlorophenoxide; PCP = pentachlorophenoxide.

ness and extracted with hexane. Slow evaporation of the hexane solution yielded the trichloromethylcyclohexadienone, **5** (1.5 g, 51% based on tritertbutylphenol). The residual mother liquor was shown by ^1H nmr to contain the peroxide **6** and the quinol ether **7** in roughly equal amounts. The compound **7** was crystallised by concentration of the mother liquor and its identity confirmed by comparison of its properties with those cited in the literature (22).

A similar reaction in which the tritertbutylphenol was used directly, without preoxidation to the radical, yielded a crude product which was shown by ^1H nmr to contain **5** and **7** in roughly equal proportions and only a small amount of **6**.

Reaction of 2,4,6-Tritertbutylphenoxyl with $CuCl_2$

The radical was prepared by oxidation of the phenol (2.62 g) with MnO_2 (12 g) in benzene (100 mL). The radical solution was filtered into a solution of anhydrous $CuCl_2$ (2.0 g) in acetonitrile (50 mL). The blue colour of the radical was discharged on contact with the $CuCl_2$ solution and on completion of the addition the solution was dark green/brown. Filtration, to remove precipitated CuCl, and evaporation yielded a sticky, black solid which was extracted with hexane. Evaporation of the hexane extract yielded an oil (2.2 g) which was shown by nmr to be a mixture of 4-chloro-2,4,6-tritertbutylcyclohexa-2,5-dienone, **8** (70%), and 4-hydroxy-2,4,6-tritertbutylcyclohexa-2,5-dienone, **10** (30%). The compound **8** was recovered by recrystallisation of the mixture from absolute ethanol (mp: 89–90°C, lit.: 94–96°C (23)), ir (thin film) 1665, 1645, 1370, 920 cm^{-1}; ^1H nmr (CCl_4): $\delta = 1.6$ (S, 9H); $\delta = 1.79$ (S, 18H); $\delta = 7.1$ (S, 2H).

Examination of a sample of the reagent radical solution showed it to be contaminated with **10** before reaction with the $CuCl_2$.

Treatment of a solution of **8** with CuCl in acetonitrile led to the rapid appearance of a dark blue colour, indicating the reversibility of reaction [6].

Similar reactions of the phenoxyl radical were carried out with bis(pyridine)bis(trichlorophenoxo)copper(II) and a number of other simple copper compounds. In each case the peroxide **6** was isolated in high (>75%) yield following aerobic workup of the reaction mixture. No ligand transfer products were identified.

Analysis of the Cuprous Polyhalophenoxides/CCl_4 Reaction Products

Samples of cuprous trichloro- or pentachlorophenoxide were prepared in acetonitrile as described above. Following removal of acetonitrile the orthoformate was removed from the product by washing with either ether (trichlorophenoxide) or toluene (pentachlorophenoxide). The resulting dark brown, amorphous powders were then dried under vacuum.

An accurately weighed sample was hydrolyzed in dilute nitric acid and carefully extracted with ether to remove phenol. The ether solution was evaporated and the phenol residue was weighed. The ionic chloride content of the aqueous hydrolysate was determined by both a gravimetric AgCl determination (23*a*) and by the Fajans method (23*b*).

The total copper and the relative amounts of Cu(I) and Cu(II) were determined using a procedure described by Kochi (24). Elemental analyses for C, H, and Cl were performed by Schwartzkopf Microanalytical Ltd. The results of these analyses are shown in Table 2.

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