Tetrahedron Letters No. 49-50, pp 4409 - 4412, 1974. Pergamon Press. Printed in Great Britain.

# REACTION OF CUPROUS PHENOXIDES WITH CARBON TETRACHLORIDE. A SYNTHESIS OF ARYL ORTHOCARBONATES

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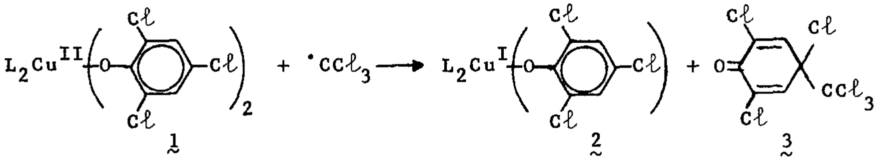
(Received in USA 15 October 1974; received in UK for publication 5 November 1974)

The aliphatic orthocarbonates have been known since 1864,[1] and their chemistry has been widely studied.[2] Although a number of cyclic orthocarbonates derived from catechols have been described,[3] there appears to be only a single report in the literature of the synthesis of a simple tetraarylorthocarbonate.[3] Orthocarbonate esters cannot be made, by simple substitution, from carbon tetrachloride.

We have previously suggested that, in the $CCl_4$ catalyzed decomposition of halophenoxocopper(II) complexes, trichloromethyl radicals participate in the following reaction:[4]



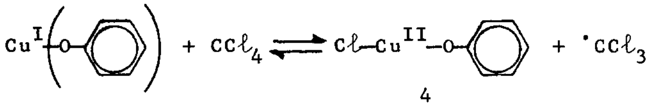
(1)

As part of a series of experiments designed to test the validity of (1), the reactions of cuprous phenoxides with carbon tetrachloride were investigated. In several cases the reaction products proved to be the corresponding aryl orthocarbonate.

Solutions of cuprous phenoxides in acetonitrile are readily prepared by metathesis between cuprous chloride and the appropriate sodium phenoxide; the air sensitive cuprous phenoxides so far prepared have all proved to be highly soluble in acetonitrile and the sodium chloride is quantitatively precipitated. (The preparation of cuprous phenoxide by reaction of methylcopper(I) with phenol in ether has recently been described. In this case the product was insoluble in the ether solvent used.[5])

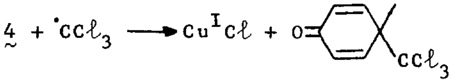
Asscher and Vofsi[6] showed that the equilibrium (2) is established in acetonitrile and that $CuC\ell/CC\ell_4$ is an excellent controlled source of trichloromethyl radicals. It therefore seemed reasonable that reactions (3) and (4) may occur and furnish both a useful route to cyclohexadienones and convincing support for the hypothetical reaction (1). However, in no case was there evidence for the occurrence of reaction (4).

$$CuC\ell + CC\ell_4 \rightleftharpoons CuC\ell_2 + {}^{\bullet}CC\ell_3 \qquad (2)$$



(3)

4



(4)

The simplest and most interesting reactions were observed with cuprous phenoxide, 4-methylphenoxide, 3-methylphenoxide and 4-chlorophenoxide. A typical procedure was as follows: To a solution of cuprous chloride (0.05 mole) in carefully dried acetonitrile (125 mℓ) under nitrogen was added solid sodium 4-methylphenoxide (0.05 mole). After stirring for one hour, degassed $CC\ell_4$ (0.1 mole) was added. The straw-coloured solution immediately turned dark blue and then dark brown. On stirring at room temperature for several hours the colour slowly faded. Filtration of the solution removed suspended $NaC\ell$ (0.05 mole) and evaporation under vacuum left a sludge of $CuC\ell$ mixed with a brown oil. The sludge was extracted with $CC\ell_4$, effecting an efficient separation of the organic product from the $CuC\ell$ (0.05 mole recovered). The p.m.r. spectrum of the $CC\ell_4$ solution showed the presence of only one product and slow evaporation of this solution gave white crystals of tetra(4-methylphenyl)orthocarbonate in near quantitative yield. The reaction of cuprous 3-methylphenoxide was virtually identical to that described above, but cuprous phenoxide differed in that there was little colour change on addition of $CC\ell_4$, there was an appreciable amount of air-sensitive acetonitrile-insoluble organic material removed at the $NaC\ell$ filtration step and the yield of orthocarbonate was only 50-60 per cent. The 4-chlorophenylcarbonate was also obtained in ca. 40 per cent yield using the above procedure.

The orthocarbonates were characterized by i.r., p.m.r. mass spectrometry and chemical analysis. In all cases the most prominent feature of the i.r. spectrum was a highly characteristic broad peak at ca. 1100 $cm^{-1}$. The mass spectra were characterized by the absence of a parent ion and by fragmentation patterns expected for the orthocarbonates. Some physical parameters for the compounds prepared are listed in the table.

Table: SOME PROPERTIES OF TETRAARYLORTHOCARBONATES

| Substituent | m/e (abundance) | pmr, ppm[a] | m.p(°C)[b] |
|---|---|---|---|
| None | 291(4) 228(1) 214(62) 170(28) 154(1) 77(100) | 7.75(m) | 95[c] |
| 3-methyl | 333(100) 256(2) 242(3) 198(6) 182(16) 91(70) | 7.5(m), 2.55(s) | 84-85 |
| 4-methyl | 333(100) 256(1) 242(2) 198(4) 182(5) 91(23) | 7.2(s), 2.35(s) | 101 |
| 4-chloro | 393(28) 282(2) 238(3) 222(3) 111(100) | 7.9(m) | 129-130 |

[a] Spectra measured on 10 per cent solutions in $CC\ell_4$ with internal TMS. m = multiplet, s = singlet.

[b] All samples recrystallized twice from ethanol. M.p's determined with calibrated apparatus.

[c] Lit. 96-98°.[3]

The reactions of cuprous 2-methyl and 2,6-dimethylphenoxides yielded no detectable orthocarbonates. The reaction of the 2,6-dimethylphenoxide occurred very rapidly, the initial dark brown colour fading in a few minutes. Workup of the products yielded tetramethyldiphenoquinone (40 per cent), dimethylphenol (40 per cent) and an unidentified oil (20 per cent). The reaction of the 2-methylphenoxide yielded 2-methylphenol (50 per cent) and an unidentified intractable oil.

Cuprous 2,4,6-trichlorophenoxide reacted rapidly with $CC\ell_4$ to give a dark brown solution. The dark brown solution showed no further evidence of reaction after 24 hours at room temperature but at ca. 60° rapidly precipitated poly(dichlorophenyleneoxide).[4] Workup of the reaction mixture either prior, or subsequent to precipitation of the polymer, failed to yield evidence for formation of either orthocarbonate or cyclohexadienone.

All reactions so far studied appear to proceed according to (3) as expected. In the case of those reactions which yield orthocarbonate, the product 4 presumably reacts with trichloromethyl radicals directly, or produces phenoxy radicals which couple selectively with them, to yield an aryltrichloromethyl ether and cuprous chloride. The high yields of orthocarbonate, even in the presence of excess $CC\ell_4$, suggest that any aryloxychloromethane intermediates undergo further aryloxy substitution much more rapidly than $CC\ell_4$ does. The presence of ortho-substituents completely suppresses coupling between phenoxy and trichloromethyl radicals and the observed products are those derived from reaction of phenoxy radicals with each other.[7]

Failure to observe any evidence for the occurrence of reaction (4) virtually excludes (1) as a plausible step in the $CC\ell_4$ catalyzed decomposition of halophenoxocopper(II) complexes.

Further studies are in progress to optimize yields in this orthocarbonate synthesis and to extend it to ortho-substituted products by modifying reaction conditions. Since $CuC\ell$ is both a reactant and product in the reaction, the catalyzed reactions of sodium phenolates with $CC\ell_4$ are also being explored.

Attempts to prepare alkyl orthocarbonates by this method have led only to complicated mixtures of products, with orthocarbonate present, if at all, in very poor yield.

Financial support for this work from the National Research Council of Canada is gratefully acknowledged.

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