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SYNTHESIS OF ARYL ORTHOCARBONATES

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Abstract: A simple and efficient method of preparing tetraaryl orthocarbonates from copper phenoxide and carbon disulfide is described.

Simple substitution reactions on carbon tetrachloride with sodium alkoxide or phenoxide do not yield orthocarbonates[1]. However, the use of tin[2] and thallium[3] alkoxides has simplified the procedure for making alkyl orthocarbonates. Similarly some improvement has been made in the synthesis of aryl orthocarbonates by the use of copper phenoxide and carbon tetrachloride[4]. Unfortunately, this reaction has severe limitations; it cannot be used for preparing aryl orthocarbonates with substituents susceptible to radical attack, such as methoxy or carbomethoxy.

We wish to report a novel reaction of carbon disulfide with copper(I) phenoxides to yield aryl orthocarbonates in high yield (see Table). This method works consistently well except when the starting phenol has an ortho substituent or when an $-NH_2$, $-CN$ or $-NO_2$ group is present. Several hitherto inaccessible tetraaryl orthocarbonates have thus been prepared.

$$CS_2 + [CuOPh]_4 \longrightarrow C(OPh)_4 + 2Cu_2S$$

In a typical reaction sodium phenoxide (10 mmol), prepared in situ by the reaction of sodium hydride and phenol in acetonitrile (50 ml), was reacted with cuprous chloride (10 mmol) to yield yellow copper phenoxide. To this stirred acetonitrile suspension was added carbon disulphide (10 mmol) and an excess of 10% sodium hydroxide solution in succession. The dark brown sludge formed was extracted with ether and the ether was dried and concentrated to yield the crude orthocarbonate. Recrystallisation was effected with 95% ethanol.

Unlike the reaction of cuprous phenoxide with carbon tetrachloride, the reaction with carbon disulfide can be run in the presence of water, without generating orthoformates. When the reaction was run with sodium phenoxide generated from sodium hydroxide and phenol the yield of the orthocarbonate was only 10% less than that reported in the table.

Table Tetraaryl Orthocarbonates

Substituent on starting Phenol	Some relevant data for tetraaryl orthocarbonates			
	pmr,ppm[a]	m.p.(°C)[b]	Yield(%)	Ref.
H	6.94-7.46(m)	95.0	92	1
4-CH_3	7.0(s), 2.28(s)	101	85	4
4-OCH_3	6.66-7.33(m), 3.73(s)	94-96	83	d
4-OCH_2CH_3	6.6-7.2(m), 3.97(q), 1.36(t)	92-93	79	d
4-$COOCH_3$	6.76-8.22(m), 3.9(s)	124-125	64	d
4-Cl	6.97-7.3(m)	130	88	4
3-CH_3	6.66-7.26(m), 2.27(s)	84-85	33	4
3-CHO	7.33-7.79(m), 9.9(s)	136-138	37	d
2-OH[c]	7.0(s)	109-110	84	1
2,4,6-trichloro	7.32(s)	175-6	15	d

[a] All measurements were made on a Varian 60 MHz instrument in deuterochloroform with TMS as internal standard.

[b] All melting points are uncorrected.

[c] In the case of catechol the spiroorthocarbonate was obtained.

[d] All new compounds gave satisfactory elemental analysis and/or mass spectra and other spectral data.

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