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REACTIONS OF ARYLLEAD(IV) TRIACETATES WITH PHENOLS.

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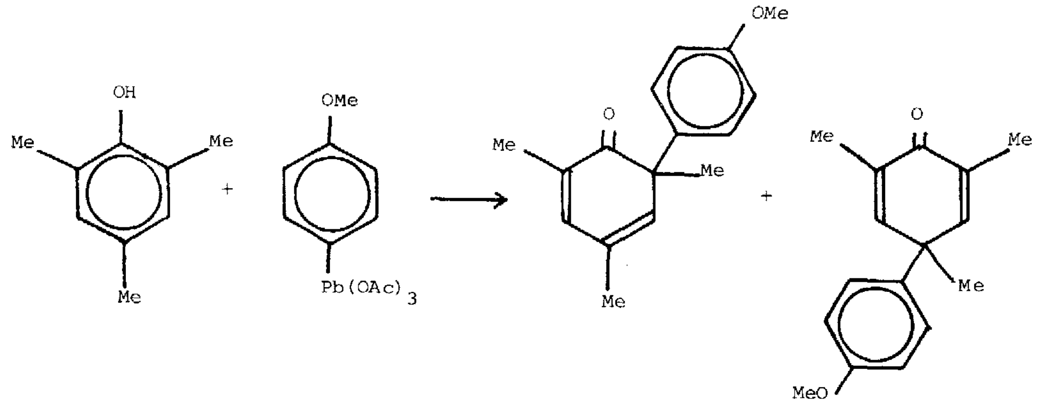
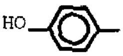
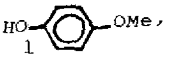
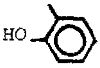
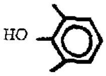
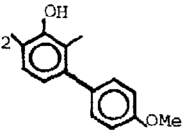
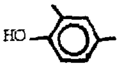
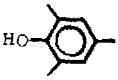
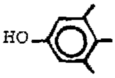
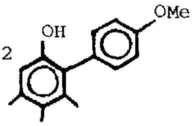
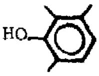
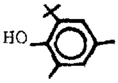
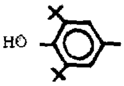
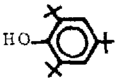
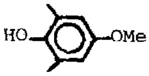
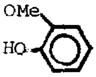
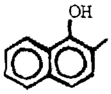
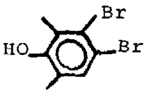
In the course of an investigation of the chemistry of aryllead(IV) derivatives[1-4] we have reported[4] that aryllead(IV) tricarboxylates react smoothly with a variety of electron-rich arenes in the presence of trifluoroacetic acid to give significant to excellent yields of biaryls. We have since extended these results to demonstrate[5] that by substitution of appropriate Lewis acids for trifluoroacetic acid high yields of biaryls can also be obtained with moderately electron-rich arenes (such as benzene and toluene), and we reasoned that analogous reactions with highly electron-rich aromatics (such as phenols) may proceed in the absence of strong acid catalysts. Indeed the reaction of mesitol (1) with *p*-methoxyphenyllead (IV) triacetate (2) in glacial acetic acid gave the expected 2,4- and 2,5-cyclohexadienones (3) and (4) in a total yield of approximately 20%. The yields of the dienones increased dramatically on using a 1:1 mole ratio of (1) and (2) in chloroform at room temperature in the presence of 1 mole of pyridine (Table 1).



(1) (2) (3) (4)

Table 1: Reaction of *p*-methoxyphenyllead (IV) triacetate with phenols[a]

Entry	Substrate	Products (%)				
		o-Dienone[b]	*p*-Dienone[c]	Recovered Substrate	Anisole	Other
1		-	-	46	12	 1, d
2		5-10	-	61	5	d
3		75-90 (40)[e]	-	5-7 (38)[e]	3	1-2 
4		18	*ca.*5	51	3	d
5		75	20	5	1-3	
6		-	12	45	4	22 
7		75[f]	-	*ca.* 5	*ca.* 1	
8		65[g]	5-7	19	9	
9		-	30	52	31	
10		-	-	18	23	
11		26	58	2	7	
12		48	-	45	6	d
13		-	-	25-30	29	
14		56	-	20	13	
15		67[h]	-	28	4	

Footnotes to Table 1

[a] Reactions were carried out in chloroform at room temperature by mixing equimolar amounts of the substrate (*ca.* 5-10% w/v in $CHCl_3$), pyridine and *p*-methoxyphenyllead (IV) triacetate. The yields of products were determined by a combination of GLC and NMR methods, while isolation was effected by thin layer chromatography. All isolated products had the expected elementary analyses and spectroscopic properties.

[b] Products analogous to (3).

[c] Products analogous to (4).

[d] Polyarylated substrate.

[e] Reaction performed in the absence of pyridine.

[f] Of which 30% corresponded to arylation at C2 and 45% to arylation at C6.

[g] Arylation at C6.

[h] Of which 35% corresponded to arylation at C2 and 32% to arylation at C6.

Clearly this reaction represents a convenient synthesis of a variety of arylated cyclohexadienones which are not readily accessible by other methods, and which have not been previously reported. Although the full scope of the reaction remains to be investigated, the following comments may already be made:

(i) The reaction fails with phenols bearing only electron-withdrawing substituents (e.g. nitrophenols, polychlorophenols) and the reaction rate is markedly lower for 3,4-dibromo-2,6-dimethylphenol (entry 15) than for 2,6-dimethylphenol (entry 3). Similarly an increase in the number of methyl groups increases the rate of reaction as measured by the rate of consumption of lead (IV). Thus the reaction is complete with mesitol (entry 5) in 15 minutes, compared with *o*-cresol (entry 2) which requires 24 hrs.

(ii) In the case of mono- and di-alkylated phenols (e.g. entries 1, 2 and 4) the overall yields of dienones are lower than for more heavily alkylated phenols, with more of the unreacted substrate and polyarylated materials being present. A possible explanation is that arylation at the unsubstituted *ortho* or *para* positions produces phenols which are more reactive than the original substrate, thus leading to polyarylation.

(iii) One mole of pyridine appears to lead to optimum yields of the dienones. There is NMR evidence of a reaction, presumably ligand exchange, between aryllead (IV) triacetates and pyridine, but solutions containing only these reagents appear to be indefinitely stable and do not react with electron-rich arenes, such as mesitylene. We therefore conclude that the role of pyridine is formation of the phenolate anion.

(iv) The reaction proceeds with a variety of aryllead (IV) triacetates, e.g. with phenyl-, p-fluorophenyl-, and p-tolyllead (IV) triacetates in similar yields to those listed in Table 1.

(v) There is a distinct preference for *ortho* attack (entries 4, 5, and 8) and a preference for attack *ipso* to methoxyl groups compared with methyl groups (entries 5 and 11, 2 and 12) which are reminiscent of the Wessely acetoxylation.[6]

Although the above observations could be explained by a formal nucleophilic displacement of lead by phenol or phenolate anion with the driving force provided by the change of oxidation state of lead, a mechanism involving electron transfer is equally probable.

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References

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6. W.A. Bubb and S. Sternhell, *Tetrahedron letters*, 1970, 4499 and refs. therein.