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Preliminary communication

Aromatic lead(IV) compounds
I. The plumbylation of some aromatic ethers

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Continuing the investigations on metallation reactions[1,2] we have extended our interest to plumbylation reactions. Plumbylation of aromatic ethers with lead(IV) acetate has been reported for anisole[3] (in benzene and in acetic acid) and resorcinol dimethyl ether[4] (in benzene). After relatively long reaction times at 80° aryllead triacetates are obtained in rather low yields. We have succeeded in plumbylating some other aromatic ethers in acetic acid (Table 1). From the data it appears that plumbylation is a very selective electrophilic process.

TABLE 1

Compound	*Reaction time (days)*	*Temp. (°C)*	*Yield[a] (%)*	*M.p.[b] (°C)*	*Colour*
p-Methoxyphenyllead triacetate	4	80	25	139–141	white
p-Ethoxyphenyllead triacetate	4	80	23	133–136	white
p-n-Butoxyphenyllead triacetate	5	82	18	99–101	white
p-Phenoxyphenyllead triacetate	7	85	16	92–96	white
2,4-Dimethoxyphenyllead triacetate	2	70	50	148–151	yellow
2,4,6-Trimethoxyphenyllead triacetate	1[c]	70	12	174–176	yellow

[a] Yields are calculated on lead(IV) acetate.
[b] Melting points (under decomposition) are uncorrected.
[c] In benzene.

Plumbylation also occurs in excess of aryl ether as solvent, if some mercury(II) acetate (ca. 3 mole %) is present (Table 2). A possible explanation of the catalytic influence of mercury(II) acetate is the transfer of the aromatic group via a mercury intermediate to the lead(IV) compound[5].

TABLE 2

Compound	*Reaction time (h)*	*Temp. (°C)*	*Yield*[a] *(%)*	*M.p.*[b] *(°C)*	*Colour*
2,4-Dimethoxyphenyllead triacetate	5	80	45	148–151	yellow
2,4,6-Trimethoxyphenyllead triacetate	1½	70	80	174–176	yellow

[a] Yields are calculated on lead(IV) acetate.
[b] Melting points (under decomposition) are uncorrected.

The experimental procedure involved heating of lead(IV) acetate and the aromatic ether (in the solvent acetic acid or benzene, or in the presence of a catalytic amount of mercury(II) acetate) until most of the lead(IV) acetate had reacted. The acetic acid was removed by distillation under diminished pressure. After addition of water the mixture was extracted with benzene or chloroform. The benzene or chloroform layer was separated and filtered over "Hyflo". Light petroleum (b.p. 40–60°) was added to the filtrate and an almost pure precipitate of the aryllead triacetate was obtained. The product was recrystallized from benzene, or from benzene and light petroleum.

The compounds mentioned were characterized by PMR and IR spectroscopy, elemental analysis (C, H, O and Pb), and GLC analysis of the corresponding aryl iodides, obtained by cleaving the carbon–lead bond with KI. Full details will be published later.

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