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ARYLATION WITH ARYLLEAD TRIACETATES PRODUCED *IN SITU* BY MERCURY-LEAD EXCHANGE

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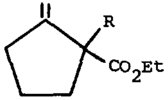
Reaction of a diarylmercury with lead tetraacetate to give an aryllead triacetate has been found to be a rapid reaction. The *in situ* generation of aryllead triacetates is thus an attractive alternative to the use of the purified reagents in the various electrophilic arylation reactions of these compounds.

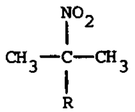
Recently we have shown that aryllead triacetates are highly effective electrophilic C-arylating agents, giving excellent yields of α-arylated derivatives with a variety of β-dicarbonyl compounds,[1-3] nitroalkanes,[4] and some enamines.[5] The aryllead reagents may be prepared by a number of methods,[6] the most convenient being direct plumbation of an aromatic compound using lead tetraacetate in acetic acid or a haloacetic acid. Aromatic plumbation is, however, limited to a relatively small number of compounds and a more general route to these reagents is that involving treatment of a diarylmercury with lead tetraacetate.[7]

$$Ar_2Hg + Pb(OAc)_4 \rightarrow ArPb(OAc)_3 + ArHgOAc$$

Various routes to the mercury compounds have been developed, with the most commonly used method being the reaction of a Grignard reagent and mercury(II) chloride. As can be seen from the above scheme, the corresponding arylmercury acetate always accompanies the aryllead triacetate and although the reaction is high yielding, isolation of the pure lead reagent in good yield is not always readily achieved. Although Criegee[7] employed a reaction time of 3 days for the synthesis of phenyllead triacetate from diphenylmercury the reaction is in fact very fast, being complete within 5 minutes at room temperature. Since arylmercury acetates are relatively unreactive compounds, the reaction lends itself to the preparation of a solution of an aryllead triacetate which may then be reacted directly with a nucleophile. We have investigated this simple arylation procedure with ethyl 2-oxocyclopentanecarboxylate (1a) and 2-nitropropane (2a) and a number of arylmercury compounds, and the results are shown in Table 1.



(1a) R = H
(1b) R = Ph
(1c) R = $\underline{p}$-FC_6H_4
(1d) R = $\underline{o}$-MeC_6H_4
(1e) R = $\underline{o}$-$MeOC_6H_4$
(1f) R = 3,4-$(MeO)_2C_6H_3$



$$CH_3-\overset{\overset{\large NO_2}{|}}{\underset{\underset{\large R}{|}}{C}}-CH_3$$

(2a) R = H
(2b) R = Ph

Table 1. Arylation reactions of aryllead triacetates formed *in situ* from arylmercuries and lead tetraacetate.[a]

Entry	Substrate	R^1HgR^2	Product[b]	Isolated Yield(%)
1	(1a)	$R^1 = R^2 = \mathrm{Ph}$	(1b)	69
2	(1a)	$R^1 = \mathrm{PhCH_2}$, $R^2 = \mathrm{Ph}$	(1b)	65
3	(1a)	$R^1 = R^2 =$ *p*-$\mathrm{FC_6H_4}$	(1c)	60
4	(1a)	$R^1 = R^2 =$ *o*-$\mathrm{MeC_6H_4}$	(1d)	64
5	(1a)	$R^1 = R^2 =$ *o*-$\mathrm{MeOC_6H_4}$	(1e)	78
6	(1a)	$R^1 = R^2 =$ 3,4-$\mathrm{(MeO)_2C_6H_3}$	(1f)	62
7	(2a)	$R^1 = R^2 = \mathrm{Ph}$	(2b)	63

[a] For entries 1-6 the arylmercury compound (2.5 mmol) was stirred with acetic acid-free lead tetraacetate (2.5 mmol) in chloroform (3-4 ml) for 20 min. at 40°. The substrate (2.0 mmol) and pyridine (2.5 mmol) were added, the volume adjusted to 6 ml with chloroform, and the reaction mixture was stirred at 40° for 3 h. For entry 7 the aryllead triacetate was formed as above and the chloroform removed. A solution of the substrate (2.0 mmol) in dry dimethyl sulfoxide (6 ml) was added and the reaction mixture stirred under nitrogen at 40° for 30 h.

[b] Products were isolated by p.l.c. All new compounds gave the expected analytical and spectroscopic data.

Although only two substrates have been investigated there would appear to be little doubt that the method is applicable to those reactions we have reported for the purified aryllead triacetates. Actual yields are similar to those obtained using the isolated lead reagents, being somewhat higher than those shown in Table 1, which are for pure isolated products. Of particular interest is the reaction of keto ester (1a) with a benzylphenylmercury/lead tetraacetate mixture (entry 2) which gave the phenyl derivative (1b) in similar yield to that obtained using diphenylmercury (entry 1). Benzylphenylmercury is readily produced by the reaction of phenylmagnesium bromide with benzylmercury chloride, and therefore this approach may well be preferred in the case of less accessible aryl halides when conversion of 50% of the aromatic compound to unreactive arylmercury acetate would not be acceptable.

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