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SYNTHESIS OF ARYLLEAD(IV) TRIACETATES BY TIN-LEAD EXCHANGE

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Aryltributylstannanes undergo a high yielding mercury (II) catalysed reaction with lead tetraacetate in chloroform to give the aryllead triacetate, which is readily separated from the other product of the reaction, tributyltin acetate. The synthetic utility of the reaction is demonstrated in the preparation of 6-methoxy-2-naphthyllead triacetate which is readily converted into the anti-inflammatory drug, naproxen.

In view of the utility of aryllead triacetates as electrophilic C-arylating agents,[1-4] there is a need for the development of general methods of synthesis of these compounds. Direct plumbation of aromatics[5] is the most convenient method of synthesis; however, it is dependent on the nature of the existing substituents and is limited to a relatively small number of compounds. All other useful methods involve metal-metal exchange and the most general route developed so far involves treatment of a diarylmercury with lead tetraacetate.[6] Although the reaction proceeds in high yield, difficulty can be experienced in separating the other product, the arylmercury acetate, from the lead compound.[5]

Some years ago we showed that aryltrimethylsilanes undergo silicon-lead exchange with lead tetraacetate in trifluoroacetic acid;[5,7] however, the method is not a generally useful one, since under the conditions many aryllead tristrifluoroacetates are converted very rapidly into aryl trifluoroacetates. We have now found that an analogous tin-lead exchange occurs with aryltributylstannanes, even in the absence of acid. The reaction, which takes place simply on mixing the stannane with lead tetraacetate in chloroform, is accelerated by the addition of a catalytic amount of mercury(II) acetate or mercury(II) trifluoroacetate (Scheme 1). The other product of the reaction, tributyltin acetate, is readily removed from the lead compound by washing with light petroleum.

$$\underset{(1)}{ArSnBu_3} + Pb(OAc)_4 \xrightarrow[Hg(O_2CR)_2]{CHCl_3} \underset{(2)}{ArPb(OAc)_3} + Bu_3SnOAc$$

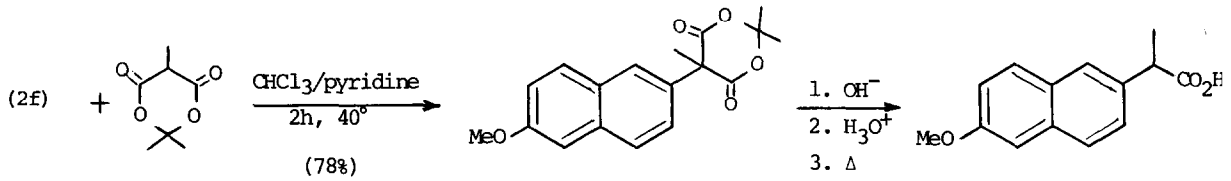
Scheme 1.

(a) Ar = o-$MeOC_6H_4$
(b) Ar = C_6H_5
(c) Ar = p-FC_6H_4
(d) Ar = 3,4-$(MeO)_2C_6H_3$
(e) Ar = p-$F_3CC_6H_4$
(f) Ar = 6-methoxy-2-naphthyl

A number of stannanes have been studied and from the results (Table 1) it can be seen that yields are generally high, being similar for compounds in which the aromatic ring is substituted with either

electron withdrawing or electron releasing substituents. The catalysis of the reaction by mercury(II) compounds is clearly indicated in the reactions of compound (1a) (entries 1, 2, and 3, Table 1), which also show that mercury(II) trifluoroacetate is more effective than the acetate.

To demonstrate the use of this reaction we have prepared 6-methoxy-2-naphthyllead triacetate (2f) from the stannane (1f) (entries 8 and 9, Table 1), which was obtained (Grignard route, 76%) from 6-bromo-2-methoxynaphthalene. The lead compound (2f) was readily converted into the antiflammatory drug, naproxen (3) under conditions previously described by us [4] (Scheme 2).



Scheme 2

Table 1. Reactions of aryltributylstannanes with lead tetraacetate.[a]

Entry	$ArSnBu_3$	Catalyst(mol%)	Time(h)	Product	Yield(%)[b]
1	(1a)	-	24	(2a)	60[c]
2	(1a)	$Hg(O_2CCH_3)_2$ (5)	5	(2a)	90[c]
3	(1a)	$Hg(O_2CCF_3)_2$ (5)	2	(2a)	92
4	(1b)	$Hg(O_2CCF_3)_2$ (5)	24	(2b)	69
5	(1c)	$Hg(O_2CCF_3)_2$ (5)	20	(2c)	76
6	(1d)	-	1	(2d)	84
7	(1e)	$Hg(O_2CCF_3)_2$ (12)	24	(2e)	75
8	(1f)	-	16	(2f)	86
9	(1f)	$Hg(O_2CCH_3)_2$	2	(2f)	87

[a] The stannane was stirred in chloroform at 40° with acetic acid-free lead tetraacetate (1.01 equivalents) and catalyst. Substrate concentrations were in the range 0.3-0.7M. The reaction mixture was filtered through Celite and the product was washed with light petroleum and crystallised from chloroform/hexane. New compounds gave the expected analytical and spectroscopic data.

[b] Isolated yields unless otherwise specified. [c] Yield determined by n.m.r. spectroscopy.

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