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THE CHEMISTRY OF ARYLLEAD(IV) TRICARBOXYLATES

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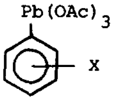
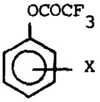
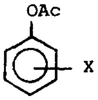
In a previous communication[1] we reported the trifluoroacetoxylation of a number of benzene derivatives with lead tetrakistrifluoracetate (LTTFA) in trifluoracetic acid (TFA), and suggested that aryllead tristrifluoroacetates were intermediates. In a later paper[2] we reported a number of these aryllead intermediates and showed that they may also be generated by metal-metal replacement when arylsilicon, arylthallium, and arylmercury compounds are treated with LTTFA in TFA.

During our study of the intermediate aryllead tristrifluoroacetates we investigated the preparation of the *p*-tolyl derivative from *p*-tolyllead triacetate by ligand exchange using TFA. There was a very rapid and almost quantitative formation of *p*-tolyl trifluoroacetate, which we assumed to proceed through *p*-tolyllead tristrifluoroacetate, although it could not be detected spectroscopically. In view of the availability of aryllead triacetates[3] we have investigated the reaction of a number of these compounds with TFA as a route to phenols, and to probe the mechanism of formation of aryl trifluoroacetates from aryllead tristrifluoroacetates in TFA.

It can be seen that for all aryllead triacetates listed in Table 1 there was a rapid reaction on addition of TFA leading to a high yield of the corresponding aryl trifluoroacetate, and in only one case (entry 6) did protodeplumbylation compete to any extent. However, the latter reaction was a major pathway with 2,4-dimethoxyphenyllead triacetate and 2-thiophenelead triacetate, 2,4-dimethoxybenzene and thiophene being formed in yields of 28 and 20% respectively.

TABLE 1: Reactions of aryllead(IV) triacetates with TFA [a]

Entry	Substrate [b]	Reaction Time	Products (%) [e]		
					
	X				
1	*p*-Me	*c*	96.7 (95.5)	<1 (<1)	<1 (<1)
2	H	*c*	82.5 (78.5)	<1 (<1)	<1 (<1)
3	*p*-Ph (m.p. 88-89°)	*c*	97.8 (96.7)	<1 (<1)	1-2 (1-2)
4	*p*-OMe	*d*	80.9 (75.2)	<1 (<1)	1-2 (1-2)
5	*m*-OMe (m.p. 98-98°)	*c*	79.2 (74.0)	<1 (<1)	<1 (<1)
6	*o*-Me (m.p. 139-140°	*c*	77.6 [f] (78.5) [f]	10.3 (8.9)	8.4 (7.4)

[a] Trifluoroacetic acid (10 ml) was added to the solid aryllead triacetate (200mg) at room temperature, the mixture shaken till homogeneous, and the reaction followed by n.m.r. spectroscopy.

[b] All new compounds gave analytical and spectral data consistent with the proposed structures.

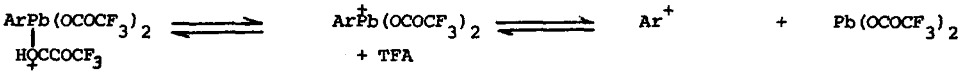
[c] Reaction complete in less than 15 seconds, i.e. the time necessary for the mixing of the reactants in the sample tube and inserting into the probe of the n.m.r. spectrometer.

[d] The half-time for the reaction is approx. 3 minutes.

[e] Reactions were carried out in duplicate, and the products analysed by g.l.c. using a 20% XE60 column on acid-washed and silanized Gas Chrom Q (100-200 mesh).

[f] Included in this figure is 2-4% of the corresponding phenol, formed by hydrolysis of the trifluoroacetate during removal of acid by washing with water.

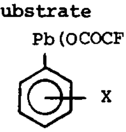
We propose that the conversion of the aryllead compounds into the aryl trifluoroacetates proceeds through the aryl cation, and involves the following equilibria:



$$\underset{H\overset{+}{O}CCOCF_3}{ArPb(OCOCF_3)_2} \rightleftharpoons \underset{+\ TFA}{Ar\overset{+}{P}b(OCOCF_3)_2} \rightleftharpoons Ar^+ + Pb(OCOCF_3)_2$$

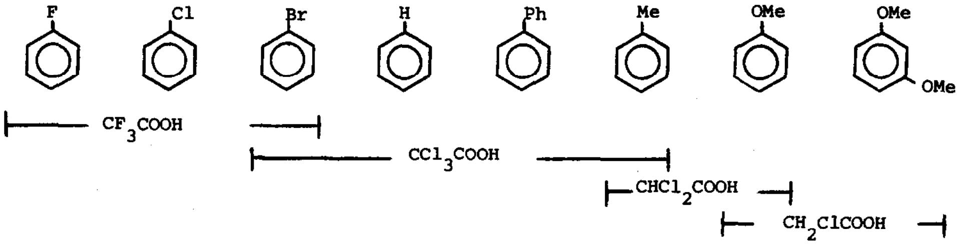
Our rate data (Tables 1 and 2) are consistent with this suggestion if the reasonable assumption is made that the formation of the aryl cation is the slow step. A triplet diradical cation structure, which at present accounts best for the chemical nature of aryl cations [4,5,6] is destablised by groups in the *meta* and *para* positions having a -I effect, and stablised by +R groups in the *meta* position[4]. Thus the relative rates of decomposition of the aryllead compounds to aryllead trifluoroacetates were found to be inversely proportional to the predicted relative stabilities of the corresponding aryl cations. We have also obtained evidence for a cationic intermediate from trapping experiments with reactive aromatic compounds[7].

TABLE 2: Half-times for conversion of aryllead tristrifluoroacetates to aryl trifluoroacetates [a]

Substrate  Substituent X	Compound used to generate the aryllead tristrifluoroacetate	$t^{\frac{1}{2}}$ (min) at 34°
p-NO_2	*p*-$NO_2C_6H_4HgOCOCF_3$	732
m-NO_2	*m*-$NO_2C_6H_4HgOCOCF_3$	1320
p-CF_3	*p*-$CF_3C_6H_4HgOCOCF_3$	24
m-CF_3	*m*-$CF_3C_6H_4HgOCOCF_3$	44.5
p-Br	*p*-$BrC_6H_4SiMe_3$	12
m-Br	*m*-$BrC_6H_4SiMe_3$	2.5
p-Cl	*p*-$ClC_6H_4SiMe_3$	22.5
m-Cl	*m*-$ClC_6H_4SiMe_3$	5.5
p-F	*p*-$FC_6H_4HgOCOCF_3$	90
m-F	*m*-$FC_6H_4HgOCOCF_3$	11

[a] The organometallic compound (0.38 mmol) from which the aryllead tristrifluoroacetate was generated was disolved in a 0.38 molar solution of LTTFA in TFA (1.0ml) and the reaction followed by n.m.r. spectroscopy.

The methods used for the synthesis of a number of the aryllead triacetates are worthy of comment. The *m*- and *o*- substituted compounds (entries 5 and 6, Table 1) were prepared by the method of Criegee *et al*[8]. The remaining compounds were synthesised by direct plumbylation [1,2]. This method has been used by de Vos *et al*[9,10] to obtain lead(IV) tricarboxylate derivatives of some aromatic ethers, including those of anisole and resorcinol dimethyl ether mentioned above. We extended the method to less reactive substrates[1] and now report the synthesis of *p*-tolyllead triacetate and 4-biphenyllead triacetate in high yield using lead tetraacetate and trichloroacetic acid, followed by metathesis with acetic acid. The wide applicability of this method is demonstrated in the formation of 2-thiophenelead triacetate (63%, m.p. 81-82°) in the same way, except that dichloroacetic acid was used in place of trichloroacetic acid. Thus by the use of lead tetraacetate with a halogenated acetic acid of the right strength, aromatics with a wide range of reactivities to electrophilic substitution may be plumbylated. A guide to the acid required is given below.



REFERENCES

1 J.R. Campbell, J.R. Kalman, J.T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, 1972, 1763.

2 J.R. Kalman, J.T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, 1972, 5369.

3 H. Shapiro and F.W. Frey, 'The Organic Compounds of Lead', Wiley, New York, 1968, p.295.

4 R.W. Taft, *J. Amer. Chem. Soc.*, 1961, 83, 3350.

5 R.A. Abramovitch and F.F. Gadallah, *J. Chem. Soc. (B)*, 1968, 497.

6 N. Kamigata, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Japan*, 1972, 45, 2047.

7 H.C. Bell, J.R. Kalman, J.T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, following paper.

8 R. Criegee, P. Dimroth, and R. Schempf, *Chem. Ber.* 1957, 90, 1337.

9 D. de Vos, J. Spierenburg, and J. Wolters, *Rec. Trav. Chim.*, 1972, 91, 1465

10 D. de Vos, J. Wolters, and A. von der Gen, *Rec. Trav. Chim.*, 1973, 92, 701.