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REACTIONS OF LEAD TETRAKISTRIFLUOROACETATE WITH AROMATIC AND METALLOAROMATIC COMPOUNDS. A NEW ROUTE TO PHENOLS

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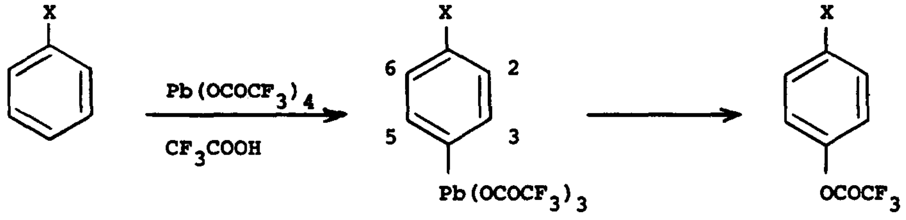
Recently we reported the trifluoroacetoxylation of a number of benzene derivatives with lead tetrakistrifluoroacetate (LTTFA) in trifluoroacetic acid (TFA) and showed that the reaction proceeds by an electrophilic substitution mechanism[1]. We also obtained NMR spectroscopic evidence that the p-halophenyllead tristrifluoroacetates (1a), (1b), and (1c) are intermediates in the formation of the corresponding p-halophenyl trifluoroacetates (2a), (2b), and (2c) from fluorobenzene, chlorobenzene, and bromobenzene respectively with LTTFA in TFA. Of these intermediates the p-fluoro compound (1a) is the most stable and can be isolated readily. The NMR data for (1a), (1b), and (1c) are given in Table 1.



(1)

(2)

a, X = F
b, X = Cl
c, X = Br
d, X = CH_3

TABLE 1: NMR data for compounds (1a), (1b), and (1c)

Chemical shifts are in p.p.m. ex TMS[a] for *ca.* 5% w/v solutions in TFA

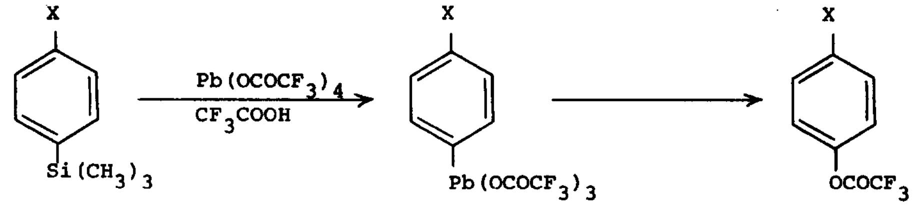
Compound	Chemical Shift	
	H-2 and H-6	H-3 and H-6
(1a)	7.47	7.99
(1b)	7.72	7.86
(1c)	7.79	7.89

[a] Because of the instability of TMS in the reaction mixture, chemical shifts were measured from CH_2Br_2 added as an internal standard, and converted by adding the chemical shift of CH_2Br_2 ex TMS in TFA.

In the case of the reaction of toluene with LTTFA in TFA to yield p-tolyl trifluoroacetate[1], we have been unable as yet to obtain NMR evidence for the intermediacy of (1d). However, we believe that (1d) is an intermediate since treatment of p-tolyllead triacetate[2] with TFA led to very rapid formation of p-tolyl trifluoroacetate and it is known[3] that aryllead tricarboxylates undergo ligand exchange with carboxylic acids.

The above examples of electrophilic attack by LTTFA on aromatic substrates, resulting in displacement of a proton by lead(IV), prompted us to examine the possibility of displacing other species by LTTFA. Initially we were interested in the possibility of metal-metal exchange with arylthallium(III)[4], arylmercury(II)[5], and arylsilicon[6] compounds and LTTFA. In fact we have observed at least one example of each of these reactions (Table 2). Addition of p-fluorophenylthallium(III) bistrifluoroacetate[7], p-chlorophenylthallium(III) bistrifluoroacetate[7], and p-bromophenylthallium(III) bistrifluoroacetate[7] to LTTFA in TFA at 39-40° led to the immediate appearance in the NMR spectrum of the characteristic signals (Table 1) due to (1a), (1b), and (1c) respectively, which under these conditions gave as before[1] (2a), (2b), and (2c) respectively at readily observable rates (Table 2). It should be noted that Taylor, McKillop and co-workers[8] have suggested that aryllead intermediates might be involved in their reactions of arylthallium(III) bistrifluoroacetates with lead tetracetate in TFA. In fact we have been able to show that (1a) is formed from p-fluorophenylthallium(III) bistrifluoroacetate under their conditions[8].

An exactly analogous reaction was observed on treatment of p-fluorophenylmercury(II) trifluoroacetate and the four p-substituted phenyltrimethylsilanes (3a)[9], (3b)[9], (3c)[9] and (3d)[10] under the same conditions with LTTFA in TFA. As can be seen from the data in Table 2, the reactions proceed by metal-metal exchange, and not by replacement of the metal by a proton followed by plumbylation of the aromatic ring[1].



(3) (1) (2)

a, X = F c, X = Br
b, X = Cl d, X = CH_3

TABLE 2: Relative rates of reactions

Substrate 		Half-time for displacement of X by $Pb(OCOCF_3)_3$ with LTTFA in TFA	Half-time for displacement of X by H with TFA (sec)	Half-time for formation of p-Y-C_6H_4-Pb-$(OCOCF_3)_3$ from Y-C_6H_5 (sec)	Half-time for conversion of p-Y-C_6H_4-Pb-$(OCOCF_3)_3$ to p-Y-C_6H_4-$OCOCF_3$ (sec)
X	Y				
$Tl(OCOCF_3)_2$	F	*a*	*a*	*ca.* 50	1950 ± 200
$Tl(OCOCF_3)_2$	Cl			*ca.*190	590 ± 20
$Tl(OCOCF_3)_2$	Br			*ca.*120	250 ± 10
$HgOCOCF_3$	F	*b*	255 min	*ca.* 50	1950 ± 200
$SiMe_3$	F		55 ± 5	*ca.* 50	1950 ± 200
$SiMe_3$	Cl		300 ± 20	*ca.*190	590 ± 20
$SiMe_3$	Br		410 ± 20	*ca.*120	250 ± 10
$SiMe_3$	Me		*b*	*c*	*c*

[Footnotes over-page]

Footnotes to Table 2

a Not estimated since the arylthallium compounds are insoluble in TFA. However, in the presence of LTTFA they do dissolve quite readily in TFA and while dissolving the NMR spectra show only the signals due to the aryllead compounds.

b The reaction was virtually complete in the time necessary for the mixing of the reactants in the sample tube and inserting into the probe of the NMR spectrometer, i.e. the half-time for the reaction is less than *ca*. 30 seconds.

c The reaction of toluene to give p-tolyl trifluoroacetate is complete in under 2 minutes.

The reactions of the arylsilicon compounds (3a), (3b), (3c) and (3d) were particularly clean and the yields of the corresponding aryl trifluoroacetates (1) were practically quantitative. Thus the method offers a useful route from an aryl halide to a phenol. The reaction proceeds equally well if LTTFA is generated *in situ* from lead tetraacetate and TFA, and this is therefore the more convenient synthetic procedure. It is noteworthy that we have not observed a similar reaction between (3a) and lead tetraacetate in acetic acid, even at reflux.

ACKNOWLEDGMENTS

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