130–180 °C at 6 °C/min) for **6**–**8** and the internal standard. The GC areas were obtained with the aid of a planimeter (scanned four times and averaged) and normalized against the internal standard. The slope of semilogarithmic plots of $[(\text{area})_t - (\text{area})_\infty]/(\text{area})_0$ vs. time provided the observed first-order rate constant, k_{obsd}. All rate constants were evaluated by the method of least squares.

Registry No. 1, 1196-55-0; **2**, 700-77-6; **2** semicarbazone, 74924-96-2; **3**, 40599-78-8; **4**, 16484-17-6; **5**, 18335-58-5; **6** (axial isomer), 74924-97-3; **6** (equatorial isomer), 74924-98-4; **7**, 74924-99-5; **8**, 74925-00-1; **9**, 24112-80-9; **10**, 74925-01-2.

Selectivity of the Aromatic Plumbylation Reaction

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Received March 20, 1980

The plumbylation of toluene in dichloroacetic acid yields initially 5.4% 2-, 1.8% 3-, and 92.7% 4-methylphenyllead(IV) dichloroacetates. The toluene to benzene rate ratio under these conditions is 59.5. The partial rate factors are $o_f^{\text{Me}} = 9.64$, $m_f^{\text{Me}} = 3.21$, and $p_f^{\text{Me}} = 331$. The plumbylation of toluene in trifluoroacetic acid yields aryl trifluoroacetates and biaryls. Analysis of these products suggests that the plumbylation reaction yields 17.9% 2-, 3.2% 3-, and 78.9% 4-methylphenyllead(IV) trifluoroacetates in the initial step of the reaction. The toluene to benzene rate ratio is 114 under these conditions. The partial rate factors are $o_f^{\text{Me}} = 61.2$, $m_f^{\text{Me}} = 10.8$, and $p_f^{\text{Me}} = 540$. These observations suggest that the plumbylation reaction is a typical electrophilic substitution and that the reaction is significantly more selective than thallation or mercuration.

The use of lead(IV) acetates for the nuclear oxidation of benzene derivatives has been known for some time.[1] Subsequently attention has been drawn to the involvement of aryllead(IV) compounds as intermediates in these reactions. DeVos, Norman, and Sternhell and their associates have investigated the factors governing the formation of these compounds.[2–4] Their work has led to the development of good procedures for the preparation of a variety of aryllead(IV) compounds which are valuable synthetic intermediates. For example, the aryllead(IV) compounds react with other aromatic compounds to form biaryls[4e] and with 1,3-dicarbonyl compounds to form 2,2-diaryl-1,3-dicarbonyl derivatives.[5] The aryllead compounds also react quantitatively with halogens to form aryl chlorides, bromides, and iodides as well as substances with aryl sulfur, nitrogen, and carbon linkages.[6]

$$\text{ArH} + \text{Pb(OAc)}_4 \rightarrow \text{ArPb(OAc)}_3 + \text{HOAc}$$

It is intriguing that the isomer distributions in the plumbylation of toluene depend significantly upon the solvent. It may be inferred from the results of Sternhell and his co-workers that the reaction of lead(IV) trifluoroacetate with toluene in trifluoroacetic acid yields about 25% 2-, 5% 3-, and 70% 4-methylphenyllead(IV) trifluoroacetates.[4a] DeVos and his associates report that the reaction of lead(IV) acetate with excess toluene in the presence of dichloro- and trichloroacetic acids yields the 4-methylphenyllead(IV) derivatives exclusively.[3a] They suggest that further reactions may selectively consume the 2 and 3 isomers. In addition, there may be a substantial difference in the selectivity of lead(IV) dichloroacetate and lead(IV) trifluoroacetate as electrophilic reagents. These interpretations are certainly reasonable; however, the isomer distributions for the reaction in trifluoroacetic acid may differ because substitution occurs by an electron-transfer process in that solvent. The considerations coupled with our interest in the use of metallic reagents as catalysts in electrophilic aromatic substitution reactions prompted us to study the selectivity of the reaction of lead(IV) compounds with benzene and toluene in dichloroacetic acid and trifluoroacetic acid.[7]

Table I. Isomer Distribution for Plumbylation of Toluene in Dichloroacetic Acid at 25 °C

% reaction[a]	% $CH_3C_6H_4OH$[b]	isomer distribution, % 2-	3-	4-
26	8.2	4.6	1.0	94.3
32	13.9	6.3	2.1	91.5
40	13.4	5.2	2.3	92.4
	average value	5.4 ± 1.2	1.8 ± 0.7	92.7 ± 1.4

[a] Based on the consumption of lead(IV) acetate. [b] The average isomer distribution for the cresols was 40% 2-, 17% 3-, and 43% 4-isomers.

Results

Plumbylation in Dichloroacetic Acid. The plumbylation of benzene and toluene proceeded smoothly in dichloroacetic acid at 25 °C to yield a mixture of aryllead(IV) dichloroacetates and aryl dichloroacetates. Biaryls were not formed. The aryl dichloroacetates formed slowly from the aryllead(IV) dichloroacetates under the conditions of these experiments. In order to obtain ac-

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(1) Preuss, F. R.; Menzel, R. *Arch. Pharm.* **1958** *291*, 350 and subsequent papers in the series.

(2) (a) Harvey, D. R.; Norman, R. O. C. *J. Chem. Soc.* **1964**, 4860. (b) Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc. B* **1970**, 421. (c) Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *Ibid.* **1971**, 518. (d) Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 325.

(3) (a) Willemsens, L. C.; DeVos, D.; Spierenburg, J.; Wolters, J. *J. Organomet. Chem.* **1972**, *39*, C61. (b) DeVos, D.; Spierenburg, J.; Wolters, J. *Recl. Trav. Chem. Pays-Bas* **1972**, *91*, 1465. (c) DeVos, D.; Boschman, F. E. H.; Wolters, J.; van der Gen, A. *Ibid.* **1973**, *92*, 467. (d) DeVos, D.; Wolters, J.; vander Gen, A. *Ibid.* **1973**, *92*, 701. (e) DeVos, D.; van Barneveld, W. A. A.; van Beelen, D. C.; van der Kooi, H. O.; Wolters, J.; van der Gen, A. *Ibid.* **1975**, *94*, 97. (f) DeVos, D. Thesis, University of Leiden, The Netherlands, 1975.

(4) (a) Campbell, J. R.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Tetrahedron Lett.* **1972**, 1763. (b) Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Ibid.* **1972**, 5369. (c) Bell, H. C.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Ibid.* **1974**, 853, 857. (d) Bell, H. C.; Kalman, J. R.; Pinhey, J. T.; Sternhell, S. *Aust. J. Chem.* **1979**, *32*, 1521. (e) Bell, H. C.; Kalman, J. R.; May, G. L.; Pinhey, J. T.; Sternhell, S. *Ibid.* **1979**, *32*, 1531. (f) Bell, H. C.; Pinhey, J. T.; Sternhell, *S. Ibid.* **1979**, *32*, 1551.

(5) Pinhey, J. T.; Rowe, B. A. *Aust. J. Chem.* **1979**, *32*, 1561.

(6) Lodochnikova, V. I.; Panov, E. M.; Kocheshkov, K. A. *Zh. Obshch. Khim.* **1967**, *37*, 547. (b) Aylward, J. B. *J. Chem. Soc. B* **1967**, 1268. (c) Stock, L. M.; Wright, T. L., unpublished results.

(7) (a) Stock, L. M.; Wright, T. L. *J. Org. Chem.* **1977**, *42*, 2875. (b) Stock, L. M.; Wright, T. L. *Ibid.* **1979**, *44*, 3467.

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Table II. Relative Rates for Plumbylation of Toluene and Benzene in Dichloroacetic Acid at 25 °C

concentration, M				
$[C_6H_6]$	$[C_6H_5CH_3]$	$[Pb(O_2CCH_3)_4]$	% reaction[a]	k_T/k_B
1.76	0.238	0.19	40	58.2
1.78	0.222	0.18	28	61.3
2.51	0.286	0.19	32	60.1
4.39	0.313	0.20	26	58.5
			average value	59.5 ± 1.4

[a] Based on the consumption of lead(IV) acetate.

Table III. Product Distribution for Oxidation of Toluene with Lead(IV) Trifluoroacetate in Trifluoroacetic Acid at 25 °C

% reaction[a]	% methylbiphenyls[b]	isomer distribution, %		
		2-cresol	3-cresol	4-cresol
33	0.3	20.3	3.1	76.6
65	3.6	17.1	3.5	79.4
85	3.8	20.5	3.2	76.3
93	3.7	16.8	3.6	79.6

[a] Based on the consumption of lead(IV) acetate. [b] The percent of biaryl in the biaryl and cresol product fraction.

Table IV. Product Distribution for Biaryls Formed in the Competitive Plumbylation of Benzene and Toluene in Trifluoroacetic Acid at 25 °C

% reaction[a]	% biphenyl	% methylbiphenyl		dimethylbiphenyl		
		2-	4-	2,2-	2,4'-	4,4'-[b]
65	8.6	1.2	59.0	3.1	12.4	7.4
85	14.1	0.6	66.8	1.0	8.8	8.5
93	14.3	1.2	70.8	2.7	5.5	5.4
100	12.3	2.3	60.3	2.6	16.4	6.1

[a] Based on the consumption of lead(IV) trifluoroacetate. [b] Includes the 3,4'-isomer.

Table V. Relative Rate of Plumbylation of Toluene and Benzene with Lead(IV) Trifluoroacetate in Trifluoroacetic Acid at 25 °C

concentration, M				
$[C_6H_6]$	$[C_6H_5CH_3]$	$[Pb(O_2CCF_3)_4]$	% reaction[a]	k_T/k_B
1.56	0.108	0.0325	65	109
1.75	0.0831	0.0324	100	115
1.89	0.130	0.0434	85	115
2.14	0.0992	0.0338	93	118

[a] Based on the consumption of lead(IV) trifluoroacetate.

curate data for the product distribution in the initial plumbylation reaction, we interrupted the reactions after only 25 to 40% of the lead(IV) acetates had been consumed to minimize the decomposition of the aryllead(IV) compounds. The reactions were quenched by the addition of aqueous potassium iodide which reacts instantly with the aryllead(IV) compounds to produce the aryl iodides. The aryl iodide mixture was analyzed by gas chromatography and high-resolution NMR spectroscopy. 4-Iodotoluene was produced exclusively. The aryl dichloroacetates which were also produced in these reaction mixtures were hydrolyzed in dilute aqueous base to the corresponding cresols prior to analysis by gas chromatography. The results were normalized to establish the initial isomer distribution for the plumbylation reactions of toluene (Table I).

Competition methods were employed to determine the toluene to benzene rate ratio. The same methods used for the determination of the isomer distribution were used for the analysis of the relative rate which was calculated by the familiar Ingold-Shaw expression.[8] The results are summarized in Table II.

Plumbylation in Trifluoroacetic Acid. The reaction of toluene with freshly prepared lead(IV) trifluoroacetate was carried out in trifluoroacetic acid at 25 °C. The aryllead(IV) trifluoroacetates produced under these conditions rapidly solvolyze to yield aryl trifluoroacetates and biaryls.[4e] We were unable to obtain consistent results by the analysis of the esters. Accordingly, the reaction products were hydrolyzed to provide the cresols and biaryls. The composition of this mixture could be reliably determined by gas chromatography and high-resolution NMR spectroscopy. The composition of the product mixture is summarized in Table III.

The toluene to benzene rate ratio was determined by competition experiments with benzene in large excess. The reaction mixture was analyzed as already described. The isomer distribution for the cresols is shown in Table III. The composition of the biaryl fraction depended, of course, on the concentration of benzene and toluene. 4-Methylbiphenyl was the dominant product in the presence of excess benzene. Neither 3-methylbiphenyl nor 2,3′-dimethylbiphenyl could be detected among the reaction products. The 3,4′- and 4,4′-dimethylbiphenyls were not separated by the analytical procedures. The product distributions for four independent experiments are summarized in Table IV.

The information presented in Tables III and IV was normalized to estimate the isomer distribution for the initial plumbylation reaction of toluene in trifluoroacetic acid to be 17.9 ± 1.7% 2-, 3.2 ± 0.2% 3-, and 78.9 ± 1.5% 4-methylphenyllead(IV) trifluoroacetates.

The extent of the conversion of benzene to phenol and biphenyl and the extent of the conversion of toluene to the cresols, methylbiphenyls, and dimethylbiphenyls were also measured in four experiments. The manner in which the data were treated is noted in the Experimental Section. The relative rate of the plumbylation of toluene and benzene is presented in Table V.

As an aid to the interpretation of the product distributions in the reactions of the intermediate aryllead(IV) compounds with toluene, we also measured the product distribution in the phenylation of toluene with benzenediazonium tetrafluoroborate in trifluoroacetic acid at 25 °C. The decomposition of the diazonium ion gave a mixture of about 65% phenyl trifluoroacetate and 35% methylbiphenyls with an isomer distribution of 51.6% 2-, 23.1% 3-, and 25.3% 4-methylbiphenyls.[9]

Discussion

The plumbylation reaction in dichloroacetic acid proceeds smoothly to give the aryllead(IV) compounds in good yield. Only a small quantity of the aryllead(IV) dichloroacetates is solvolyzed to aryl dichloroacetates under the mild experimental conditions. Biaryls are not formed in a detectable amount. The observation that the aryl dichloroacetate mixture is rich in the 2 and 3 isomers

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[8] Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.

[9] We are indebted to P. Y. Kwok for this determination.

[10] Olah, G. A.; Hasimoto, I.; Lin, H. C. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 4121.

[11] Kwok, P. Y.; Stock, L. M.; Wright, T. L. *J. Org. Chem.* **1979**, *44*, 2309.

[12] Brown, H. C.; Wirkkala, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 1447.

Table VI. Partial Rate Factors for the Electrophilic Metalation of Toluene

reaction conditions	partial rate factors o_f^{Me}	m_f^{Me}	p_f^{Me}
plumbylation, $Pb(O_2CCF_3)_4$, CF_3CO_2H, 25 °C[a]	61.2	10.8	540
plumbylation, $Pb(O_2CCHCl_2)_4$, Cl_2CHCO_2H, 25 °C[a]	9.64	3.21	331
thallation, $Tl(O_2CCF_3)_3$, $CF_3CO_2H_2$, 25 °C[b]	9.6	5.7	168
thallation, $Tl(O_2CCF_3)_3$, $CF_3CO_2H_2$, 25 °C[c]	12.7	4.5	226
mercuration, $Hg(O_2CCF_3)_2$, CF_3CO_2H, 25 °C[d]	3.62	2.55	46.9
mercuration, $Hg(O_2CCF_3)_2$, CF_3CO_2H, 0 °C[d]	18.8	3.18	82.8
mercuration, $Hg(O_2CCH_3)_2$, $HClO_4$, CH_3CO_2H, 25 °C[e]	4.98	2.25	32.9
mercuration, $Hg(O_2CCH_3)_2$, CH_3CO_2H, 25 °C[e]	5.71	2.23	23.0

[a] This study. [b] Reference 10. [c] Reference 11. [d] Reference 12. [e] These are representative results for the mercuration reaction in acetic acid, ref 13.

suggests that the 2- and 3-methylphenyllead(IV) compounds are solvolyzed more rapidly than the 4 isomer, with the result that 4-methylphenyllead(IV) dichloroacetate is obtained as the dominant product as proposed by DeVos and his associates.[3e,f]

The quantities of the aryllead compounds and aryl esters were both considered in the definition of the isomer distribution for the plumbylation reaction, Table I, and in the definition of the relative rate, Table II. The partial rate factors based on these observations are $o_f^{Me} = 9.64$, $m_f^{Me} = 3.21$, and $p_f^{Me} = 331$.

The plumbylation reaction in trifluoroacetic acid differs considerably from the reaction in dichloroacetic acid. The initial product consists of aryl trifluoroacetates and biaryls. As already noted, the aryl dichloroacetates were hydrolyzed prior to analysis. Although the isomer distribution for the cresol fraction could be measured reproducibly, the product distribution for the biaryl fraction depends somewhat upon the experimental conditions. Consequently, the product distribution inferred from these results for the plumbylation of toluene and the relative rate are less well-defined than in the other case. The best values for the isomer distribution for the plumbylation reaction are 17.9 ± 1.7% 2-, 3.2 ± 0.2% 3-, and 78.9 ± 1.57% 4-methylphenyllead(IV) trifluoroacetates. These results and the relative rate data, Table V, yield the partial rate factors $o_f^{Me} = 61.2$, $m_f^{Me} = 10.8$, and $p_f^{Me} = 540$.

There is a significant difference in the partial rate factors for plumbylation in dichloroacetic acid and in trifluoroacetic acid. As in many other cases, this reaction proceeds more rapidly and more selectively in trifluoroacetic acid. This feature of the results is illustrated by the data for the other electrophilic metalation reactions of toluene presented in Table VI.

The partial rate factors indicate that the plumbylation reaction is substantially more selective than either thallation or mercuration.[3f] The reaction constants, ρ^+, estimated from the para partial rate factors are about −9 for plumbylation, −7.5 for thallation, and −5.5 for mercuration in trifluoroacetic acid. These observations suggest that the transition states for the reactions differ considerably with more benzenonium ion character in the transition state for the plumbylation reaction than in the transition state for the mercuration reaction. While little is known about the factors governing the selectivity of electrophilic reagents, it is notable that iodine is the most selective molecular halogen and that the phenylsulfonium ion is more selective than the phenylacylonium ion under comparable conditions.[13] These fragmentary observations suggest that the transition states for aromatic substitution reactions are more similar to the benzenonium ions for the electrophiles of the higher periods and higher groups of the periodic table. Presumably, these reagents are less electrophilic than the other less polarizable electrophiles of the lower periods and require the fuller development of the character of the benzenonium ion at the energy maximum.

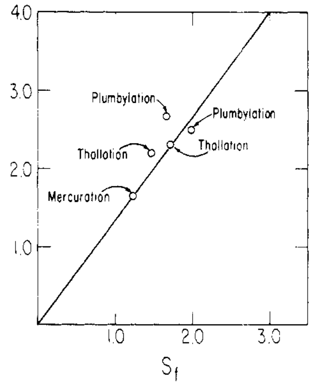


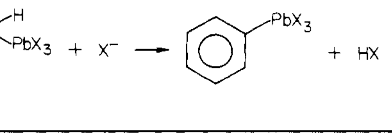
Figure 1. Relationship between log p_f^{Me} and S_f, log (p_f^{Me}/m_f^{Me}), for electrophilic metalation reactions of toluene. Data for the plumbylation, thallation and mercuration reactions are presented in Table VI.

The relationship between intermolecular selectivity and intramolecular selectivity was examined by comparison of the data for the electrophilic metalation reactions with the data for other electrophilic substitution reactions of toluene, Figure 1.

Only the observations for the plumbylation reaction in trifluoroacetic acid exhibit a significant deviation from the selectivity relationship established for about 100 other reactions. As already noted, the partial rate factors for this reaction are somewhat less certainly established than the results for the other reactions. Consequently, we conclude that the factors governing the electrophilic metalation reactions are the same as the factors governing the other substitution reactions and that there is no reason to postulate the involvement of electron-transfer processes in these reactions. Thus, although the evidence is quite incomplete, the available information[2-4] suggests that the plumbylation reaction is a typical electrophilic substitution reaction in which the electrophilicity of the lead(IV) compound is enhanced by protonation or protonation followed by dissociation. A weak complex between the lead(IV) cation and the aromatic compound may be formed prior to the more significant electrophilic substitution reaction in which the benzenonium ion is formed. In the rate-determining reaction, a proton is removed from this ion to provide the first stable intermediate, the aryllead(IV) compound.[14]

$$PbX_4 + H^+ \rightleftharpoons PbX_4H^+ \rightleftharpoons PbX_3^+ + HX$$

$$PbX_3^+ + ArH \rightleftharpoons ArH{\cdot}PbX_3^+$$



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[13] Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

The aryllead(IV) trifluoroacetates, unlike the related arylmercury and arylthallium derivatives, are quite unstable in trifluoroacetic acid. The acid-catalyzed decomposition reactions of these products to form aryl cations have been discussed by Sternhell and his associates.[4c] It seems only necessary to note that the behavior of the aryl cation depends upon the polarity of the solvent. The phenylation of toluene with phenyllead(IV) triacetate in dichloroacetic acid yields 11% 3-methylbiphenyl, whereas the reaction of the lead(IV) compound produces 17% of this isomer in trifluoroacetic acid.[4c] Under the same conditions, we found that the benzenediazonium ion yields 23% of the 3 isomer. The reaction in acetonitrile or sulfolane is reported to give 26% of this compound.[15] These results suggest that the phenyl cation has not equilibrated with its surroundings and is best described as an encumbered ion, e.g., $\overline{\mathrm{Ar^{+}Pb(O_2CCF_3)_2}}$, rather than an unassociated phenyl cation. Additional work will be required to characterize these intermediates with confidence.

Experimental Section

Materials. Lead(IV) acetate was recrystallized from acetic acid prior to use. All other reagents and solvents were purified by conventional methods as necessary. The compounds which were used as reference materials in the chromatographic or spectroscopic work were purified by fractionation or crystallization and demonstrated to be free of isomeric impurities by appropriate analytical methods.

Lead(IV) Trifluoroacetate. A suspension of red lead oxide (7.5 g) in trifluoroacetic acid (26 g) and trifluoroacetic anhydride (25 g) was stirred for 4 to 5 days under nitrogen until the mixture became virtually homogeneous. The light yellow mixture was filtered and the filtrate was evaporated in vacuo to yield a pale yellow or white solid which consisted of 1 part lead(IV) and 2 parts lead(II) trifluoroacetates. All the experiments with this compound were carried out in a drybox.

Competitive Plumbylation of Toluene and Benzene in Dichloroacetic Acid. In a typical experiment, a solution of lead(IV) acetate (1.97 g, 4.44 mmol) in dichloroacetic acid (17 g) was added to a stirred solution of benzene (3.24 g, 41.6 mmol) and toluene (0.516 g, 5.6 mmol) in dichloroacetic acid (20 g). The reaction mixture was light yellow. After 10 min, the reaction was quenched in a solution of potassium iodide (3 g) in water (50 mL). A heavy yellow precipitate formed immediately. After the mixture was stirred for 30 min, sodium bisulfite was added to destroy the iodine that was formed. The mixture was extracted with ether containing 4-nitrotoluene which served as the internal standard. The ether layer was filtered to remove residual lead(II) iodide and dried over sodium sulfate. The solution was analyzed by gas chromatography for iodobenzene and iodotoluene on a Carbowax 20M column. The iodotoluenes were isolated and analyzed by NMR at 270 MHz to determine the isomer distribution. Only the 4 isomer was present. Control experiments established that 0.5% of the other isomers could have been detected. The solution was also analyzed by gas chromatography for phenyl and tolyl dichloroacetates and biaryls on an OV-101 column. Biaryls were not detected in any of the experiments. The esters were hydrolyzed to the corresponding phenol and cresols for analysis by the following procedure. The ether was removed in vacuo and 4 M sodium hydroxide was added to the residue. The solution was stirred vigorously for 2 h. The solution was acidified with 10% hydrochloric acid, neutralized with sodium hydrogen carbonate, and extracted with ether. The ether layer was analyzed for phenol and 2- and 4-cresol on the OV-101 column. The aryl dichloroacetate peaks were no longer present, indicating that hydrolysis was complete. The 3- to 4-cresol ratio was determined on a trixylenol phosphate column. The combined yields of the iodides, phenols, and cresols were used to define the isomer distribution and the relative rate.

The absence of 2- and 3-iodotoluenes in the iodotoluene fraction was confirmed in several independent experiments. For example, the reaction mixture was poured into a solution of sodium iodide and iodine in sufficient chloroform to maintain a homogeneous solution. The solution was stirred for 48–67 h or refluxed for 24 h and then worked up as usual. Analysis showed only 4-iodotoluene.

Competitive Plumbylation of Toluene and Benzene in Trifluoroacetic Acid. A solution of lead(IV) trifluoroacetate (2.76 g, 1.40 mmol) in trifluoroacetic acid (25 mL) was added rapidly to a stirred solution of benzene (5.23 g, 67.1 mmol) and toluene (0.426 g, 4.63 mmol) in trifluoroacetic acid (25 mL). After 5 min the reaction mixture was poured into water and extracted with ether containing 4-nitrotoluene. Ether and trifluoroacetic acid were removed in vacuo. The residue was dissolved in a small quantity of ether and shaken with 1.0 N sodium hydroxide to hydrolyze the aryl trifluoroacetates. Dilute hydrochloric acid was then added until the mixture was acidic. The aqueous layer was then removed and the ether layer was washed with sodium hydrogen carbonate and dried over sodium sulfate. The composition of this solution was determined as outlined previously.

Other competitive experiments were carried out differently. The order of the addition of the reagent was reversed in several experiments and the lead solution was added slowly in others. The same results were obtained, indicating the absence of mixing effects. In other experiments the reaction was quenched in water and stirred for 24 h to hydrolyze the aryl trifluoroacetate products. The same results were realized. It was also established that the reaction could be quenched by the addition of chloroform and that the aryl trifluoroacetate fraction could be reliably analyzed by gas chromatography if precautions were taken to exclude moisture. However, erratic results were obtained when portions of the esters were inadvertently hydrolyzed.

Certain of the biaryls can form from either phenyl or tolyl cations. Accordingly, some simplifying assumptions were necessary for the analysis of the data. As a first approximation we assumed that the resultant cations exhibited the same inter- and intramolecular selectivity as the phenyl cation. The merit of this assumption was tested by the calculation of the composition of the product mixture based upon the derived partial rate factors. Reasonable agreement between the calculated and observed product distributions was realized.

Phenylation with Benzenediazonium Ion. In a typical experiment, toluene (0.921 g, 10.0 mmol) and benzenediazonium tetrafluoroborate (0.575 g, 3.0 mmol) were dissolved in trifluoroacetic acid (10 mL) in a constant-temperature bath at 25.3 °C. The reaction was allowed to proceed for 48 h (about 9 half-lives). The ester to biaryl product ratio was about 2:1. The isomer distribution was determined to be 52.5% 2-, 22.4% 3-, and 25.1% 4-methylbiphenyls by the procedures already described. Replicate experiments gave similar results.

Acknowledgment is made to D. DeVos for information concerning the most effective procedures for the preparation of the aryllead(IV) compounds and to the U.S. Army Research Office, Grant ARO DAAG-29-76-6-025, for support of this work.

Registry No. Lead(IV) acetate, 546-67-8; lead(IV) trifluoroacetate, 16656-82-9; toluene, 108-88-3; benzene, 71-43-2; benzenediazonium tetrafluoroborate, 369-57-3; 2-methylbiphenyl, 643-58-3; 3-methylbiphenyl, 643-93-6; 4-methylbiphenyl, 644-08-6.

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[14] The kinetic isotope effect for the plumbylation of anisole-*4-d* is 4.5.[3e]

[15] Abramovitch, R. A.; Gadallah, F. F. *J. Chem. Soc. B* **1968**, 497.