zine, 40127-91-1; 4-chlorothiophenol, 106-54-7; 3,4-dichloroaniline, 95-76-1; 3,4-dichlorobenzylamine, 102-49-8; 2,4-dichlorobenzylamine, 95-00-1; sulfanilamide, 63-74-1; diethylamine, 109-89-7; ethyl 4-aminobenzoate, 94-09-7; potassium acetate, 127-08-2; 1-pyrrolidino-1-cyclohexene, 1125-99-1; ethylene glycol, 107-21-1; benzyl mercaptan, 100-53-8; *N*-methyl-*p*-nitroaniline, 100-15-2; *p*-nitroaniline, 100-01-6; guanidine, 113-00-8.

References and Notes

(1) For the previous paper in this series, see E. C. Taylor and P. A. Jacobi, *J. Am. Chem. Soc.*, submitted for publication.

(2) This work was supported by a grant (CA-12876) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

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(14) Prepared by cyclization of **5k** with guanidine in methanol in the presence of sodium methoxide; the methyl ester is formed by transesterification.

(15) Prepared by cyclization of **5k** with guanidine in ethanol in the presence of sodium ethoxide.

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Thallium in Organic Synthesis. XL. Preparation and Synthetic Utility of Diarylthallium Trifluoroacetates[1,2]

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Two methods are described for the preparation of diarylthallium trifluoroacetates: (1) the "disproportionation" of arylthallium ditrifluoroacetates by heating in acetone, and (2) the reaction of arylmagnesium bromides with thallium(III) trifluoroacetate (TTFA) to give diarylthallium bromides, conversion of the latter to diarylthallium hydroxides, and, finally, treatment with trifluoroacetic acid (TFA). Although it has been widely believed that diarylthallium(III) compounds are chemically inert, it is shown that these diarylthallium trifluoroacetates are useful, versatile intermediates for the synthesis of unsymmetrical biphenyls (by irradiation in benzene), aryl iodides (by heating with iodine in chloroform), and phenols (by reaction with lead tetraacetate–triphenylphosphine in TFA solution, followed by alkaline hydrolysis of the resulting aryl trifluoroacetates).

Diarylthallium(III) derivatives have been known for over 50 years, but the reported chemistry of these compounds is prosaic, perhaps as a result of a widespread belief that they are "amongst the most stable and least reactive organometallic compounds known".[3] We report that this reputed lack of reactivity is a myth, and that diarylthallium trifluoroacetates are useful and versatile intermediates for the preparation of unsymmetrical biphenyls, aryl iodides, and phenols.

Preparation of Diarylthallium Trifluoroacetates. Literature methods for the preparation of diarylthallium compounds involve the reaction of thallium(III) halides with arylboronic acids, with diarylmercury compounds, or with Grignard reagents.[4a–c] Two new methods for their preparation are described below.

Thallation of aromatic substrates with thallium(III) trifluoroacetate (TTFA) is now a well-known process[5a,b] in which the position taken by thallium with respect to substituents already present can often be controlled by a combination of kinetic, thermodynamic, and chelation factors.[6] We have reported previously on the "disproportionation" of the resulting arylthallium ditrifluoroacetates to give diarylthallium trifluoroacetates upon treatment with triethyl phosphite.[7] It was found in the course of this work that attempted recrystallization of the arylthallium ditrifluoroacetates from water or from acetone resulted in partial "disproportionation". We have now found that heating arylthallium ditrifluoroacetates in acetone for 1 hr, followed by addition of water, results in smooth conversion to diarylthallium trifluoroacetates in good to excellent yield (method A). This simple procedure thus supplements the triethyl phosphite "disproportionation" method utilized previously.[7] Representative compounds prepared by method A are listed, along with yield and melting point, in Table I.

Table I
Representative Diarylthallium Trifluoroacetates by Method A[a]

$$ArTl(OCOCF_3)_2 \xrightarrow[water]{acetone} Ar_2TlOCOF_3$$

$Ar_2TlOCOF_3$ registry no.	Ar	Yield, %	Mp, °C[b]
27675-18-9	4-$CH_3C_6H_4$	99	289–291
27675-21-4	3,4-$(CH_3)_2C_6H_3$	93	274–276
27675-19-0	2,4-$(CH_3)_2C_6H_3$	93	278–280
27675-20-3	2,5-$(CH_3)_2C_6H_3$	64	243–245
27675-22-5	2,4,6-$(CH_3)_3C_6H_2$	99	214–216
55073-42-2	2-Dibenzylfuranyl	47	286–287

[a] Melting points and elemental analyses were determined after one recrystallization of the diarylthallium trifluoroacetate from ethyl acetate. Satisfactory C, H analyses were reported for each compound listed in the table. [b] All of the compounds melted with decomposition.

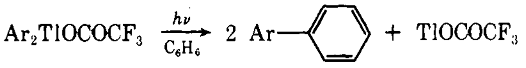
Table II
Representative Diarylthallium Trifluoroacetates by Method B[a]

$$\mathrm{ArBr} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Mg^\circ}} \mathrm{ArMgBr} \xrightarrow[\mathrm{Et_2O}]{\mathrm{TTFA}} \mathrm{Ar_2TlBr} \xrightarrow[\mathrm{EtOH\text{-}H_2O}]{\mathrm{KOH}} \mathrm{Ar_2TlOH} \xrightarrow[\mathrm{H_2O}]{\mathrm{TFA}} \mathrm{Ar_2TlOCOCF_3}$$

$Ar_2TlOCOCF_3$ registry no.	Ar	Yield, %[b]	Mp, °C[c]	Molecular formula	Analysis, %, Found (calcd) C	H
55073-43-3	$2\text{-}CH_3C_6H_4$	71	244–246	$C_{16}H_{14}F_3O_2Tl$	38.57 (38.46)	2.76 (2.82)
55073-44-4	$3\text{-}CH_3C_6H_4$	50	247–249	$C_{16}H_{14}F_3O_2Tl$	38.77 (38.46)	2.83 (2.82)
55073-45-5	$3\text{-}ClC_6H_4$	70	267–270	$C_{14}H_8Cl_2F_3O_2Tl$	31.62 (31.11)	1.65 (1.49)
55073-46-6	$3\text{-}BrC_6H_4$	68	256–259	$C_{14}H_8Br_2F_3O_2Tl$	28.02 (26.72)	1.68 (1.28)
55073-47-7	$3\text{-}CH_3OC_6H_4$	43	250–251	$C_{16}H_{14}F_3O_4Tl$	34.53 (36.15)	2.69 (2.65)
55073-48-8	1-Naphthyl[d]	44[e]	247–248	$C_{22}H_{17}O_2Tl$	50.84 (51.03)	3.27 (3.31)
55073-49-9	2-Naphthyl[d]	55[f]	272–273	$C_{22}H_{17}O_2Tl$	50.58 (51.03)	3.47 (3.31)

[a] Melting points and elemental analyses were determined after one recrystallization or trituration of the diarylthallium trifluoroacetate or acetate with ethyl acetate. [b] Based on thallium(III) trifluoroacetate (TTFA). [c] All of the compounds melted with decomposition. [d] Since treatment of the diarylthallium hydroxide with aqueous TFA resulted in extensive decomposition, the corresponding acetate was prepared with HOAc. [e] Based on TTFA. The yield is 68% based on di(1-naphthyl)thallium hydroxide. [f] Based on TTFA.

Table III
Conversion of Diarylthallium Trifluoroacetates to Biphenyls



Ar	Yield, %[a]
C_6H_5[6,7]	95
$4\text{-}CH_3C_6H_4$	61[b]
$2\text{-}CH_3C_6H_4$	46[c]
$3\text{-}BrC_6H_4$	41[d]
$3\text{-}ClC_6H_4$	53[e]
$3\text{-}CH_3OC_6H_4$	67[f]
$3,4\text{-}(CH_3)_2C_6H_3$	65[g]

[a] Yields were determined by GLC analysis of the crude photolysis product. [b] Product contained 3% 4,4′-dimethylbiphenyl, 2% biphenyl, and <2% toluene. [c] Product contained 8% 2,2′-dimethylbiphenyl. [d] Product contained 9% biphenyl and 39% bromobenzene. [e] Product contained 4% biphenyl, 7% chlorobenzene, and 18% of an unidentified biaryl. [f] Product contained 2% biphenyl and 3% anisole. [g] Product contained 3% 3,3′,4,4′-tetramethylbiphenyl, 2% biphenyl, 3% o-xylene, and 14% of an unidentified biaryl.

A characteristic feature of the "disproportionation" procedure described above is its regiospecificity; no detectable scrambling of the aryl–thallium bond occurs, and the orientation of thallium with respect to ring substituents remains the same in the diarylthallium trifluoroacetates as it was in the starting arylthallium ditrifluoroacetates. A complementary route to diarylthallium trifluoroacetates which would provide access to derivatives with different orientations of substituents would be most useful. We have found such a procedure in the reaction of arylmagnesium bromides with TTFA. The initial product of the reaction, a diarylthallium bromide, was converted to the diarylthallium hydroxide by treatment with aqueous ethanolic potassium hydroxide, and the corresponding trifluoroacetate derivatives were then prepared by reaction with aqueous trifluoroacetic acid (TFA).[8] Representative compounds prepared by method B are listed in Table II, which also summarizes yield, melting point, and microanalytical data.

That methods A and B indeed yield the same compounds was confirmed by the synthesis of di-4-tolylthallium trifluoroacetate by both routes; the products were identical in all respects.

Synthesis of Unsymmetrical Biphenyls. We have reported previously that photolysis of arylthallium ditrifluoroacetates in benzene suspension results in replacement of the thallium substituent by a phenyl group (i.e., phenylation) to give unsymmetrical biphenyls in excellent yield.[9] We have now found that the same conversion can be effected in comparable yields utilizing diarylthallium trifluoroacetates as the organometallic precursors. Unsymmetrical biphenyls prepared by this photolysis route are listed in Table III.

We suggest that the initial photolytic reaction is homolysis of a C–Tl bond to give an aryl radical and the unstable thallium(II) species ArTl(II)OCOCF$_3$. The former serves as a precursor for 1 equiv of biaryl, while the latter disproportionates to give a second aryl radical and thallium(I) trifluoroacetate. This reaction sequence is thus analogous to that postulated previously for the photolysis of arylthallium ditrifluoroacetates in benzene to give unsymmetrical biphenyls.[9] The observed formation of small amounts (<5%) of biphenyl as well as symmetrical biaryls is in accord with the proposed mechanism.

This synthesis of unsymmetrical biphenyls complements and extends the related procedure which utilizes arylthallium ditrifluoroacetates,[9] since the substituent pattern possible with diarylthallium trifluoroacetates prepared by method B may be different from that accessible by method A (which must be identical with the pattern present in the arylthallium ditrifluoroacetate precursors).

Synthesis of Aryl Iodides. We have described previously a remarkably simple synthesis of aryl iodides which involves treatment of arylthallium ditrifluoroacetates with aqueous potassium iodide at room temperature. Reaction is complete in a matter of seconds, and the aryl iodide is formed in quantitative yield.[5b,10] We now report that diarylthallium trifluoroacetates, although stable to aqueous potassium iodide, may be converted to aryl iodides by reflux-

Table IV
Conversion of Diarylthallium Trifluoroacetates to Aryl Iodides

$$\mathrm{Ar_2TlOCOCF_3} \xrightarrow[\mathrm{HCCl_3}]{\mathrm{I_2}} 2\ \mathrm{ArI} + \mathrm{TlOCOCF_3}$$

Ar	Reaction time, hr[a]	Product	Yield, %[b]
C_6H_5[6,7]	16	Iodobenzene	80
$2\text{-}CH_3C_6H_4$	16	2-Iodotoluene	89
$3\text{-}CH_3C_6H_4$	16	3-Iodotoluene	74
$4\text{-}CH_3C_6H_4$	15	4-Iodotoluene	86
$3,4\text{-}(CH_3)_2C_6H_3$	19	4-Iodo-*o*-xylene	88
$3\text{-}ClC_6H_4$	18	3-Iodochlorobenzene	94
$1\text{-}C_{10}H_7$[c]	12	1-Iodonaphthalene	90
$2\text{-}C_{10}H_7$[c]	16	2-Iodonaphthalene	90
$2\text{-}C_{12}H_7O$	16	2-Iododibenzofuran	93

[a] All iodinations were done at the reflux temperature of chloroform (61°). [b] Yields were determined by GLC analysis of the crude organic products. [c] The corresponding acetate was used.

ing a solution in chloroform with an excess of molecular iodine. Representative aryl iodides prepared in this manner are listed in Table IV, along with appropriate experimental data.

The overall stoichiometry for the above conversion is given in eq 1. We suggest that the initial reaction is formation of an arylthallium trifluoroacetate iodide (eq 2) which spontaneously decomposes to give a second mole of aryl iodide and thallium(I) trifluoroacetate (eq 3). Support for

$$\mathrm{Ar_2TlOCOCF_3} + \mathrm{I_2} \longrightarrow 2\mathrm{ArI} + \mathrm{TlOCOCF_3} \tag{1}$$

$$\mathrm{Ar_2TlOCOCF_3} + \mathrm{I_2} \longrightarrow \mathrm{ArI} + \mathrm{ArTl(OCOCF_3)I} \tag{2}$$

$$\mathrm{ArTl(OCOCF_3)I} \longrightarrow \mathrm{ArI} + \mathrm{TlOCOCF_3} \tag{3}$$

this interpretation comes from the observation that treatment of di-4-tolylthallium trifluoroacetate with 1 equiv of iodine resulted in the formation of 2 equiv of 4-tolyl iodide (91%) and thallium(I) trifluoroacetate (88% recovery); no thallium(I) iodide could be detected. Independent support for the spontaneous disproportionation of arylthallium trifluoroacetate iodides (eq 3) comes from the previously reported observation[5b] that treatment of phenylthallium ditrifluoroacetate with 1 equiv of potassium iodide resulted in instantaneous formation of iodobenzene in quantitative yield, with no concomitant formation of thallium(I) iodide.

The conversion of diarylthallium trifluoroacetates to aryl iodides by treatment with molecular iodine is thus analogous to the well-known conversion of diarylmercury derivatives with iodine to a mixture of the aryl iodide and an arylmercury iodide,[11] but it is much more effective as a synthetic tool because of the spontaneous decomposition to product of the arylthallium trifluoroacetate iodide intermediate (corresponding to the stable arylmercury iodide). The present route constitutes a practical synthetic procedure for the ultimate conversion of aryl Grignard reagents to aryl iodides.

Synthesis of Phenols. We also report that phenols may be prepared from diarylthallium trifluoroacetates in the same manner as previously reported for the conversion of arylthallium ditrifluoroacetates to phenols,[12] i.e., by treatment with lead tetraacetate in TFA followed by addition of triphenylphosphine. The resulting aryl trifluoroacetates are hydrolyzed to the phenols with aqueous base. Representative conversions and experimental details are given in Table V.

Table V
Conversion of Diarylthallium Trifluoroacetates to Phenols

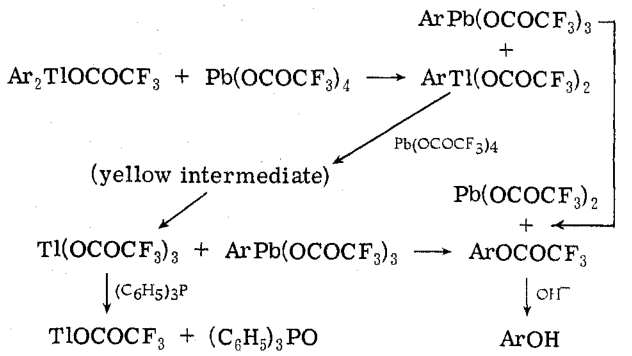
$$\mathrm{Ar_2TlOCOCF_3} \xrightarrow[\text{2. Ph}_3\text{P}]{\text{1. 2Pb(IV)}} 2\mathrm{ArOCOCF_3} \xrightarrow{\mathrm{OH^-}} 2\mathrm{ArOH}$$

Ar	Reaction conditions[a]		Phenol	Yield, %[b]
	Temp, °C	Time, hr		
C_6H_5[6,7]	41	1.0	Phenol	39
$4\text{-}CH_3C_6H_4$	22	0.1	*p*-Cresol	58
$3\text{-}CH_3C_6H_4$	22	1.0	*m*-Cresol	50
$2\text{-}CH_3C_6H_5$	22	1.0	*o*-Cresol	55
$3,4\text{-}(CH_3)_2C_6H_3$	22	0.5	*o*-4-Xylenol[c]	69
$2,5\text{-}(CH_3)_2C_6H_3$	22	0.5	*p*-2-Xylenol	67
$2,4,6\text{-}(CH_3)_3C_6H_2$	22	0.5	2,4,6-Mesitol	21
$3\text{-}ClC_6H_4$	73	0.5	3-Chlorophenol	55
$3\text{-}BrC_6H_4$	73	1.2	3-Bromophenol	44
$3\text{-}CH_3OC_6H_4$[d]	22	0.4	3-Methoxyphenol	29

[a] These conditions refer to the period after the Pb(IV) addition and before the Ph_3P addition. [b] Yields were determined by GLC analysis of the crude product. [c] Product contained 1% *o*-3-xylenol. [d] Ph_3P was omitted.

As was observed for the analogous phenol synthesis from arylthallium ditrifluoroacetates,[13] a bright yellow solid separated from the TFA reaction mixture after addition of lead tetraacetate, but before addition of triphenylphosphine. Examination of this yellow solid showed it to be identical with the intermediate complex prepared from arylthallium ditrifluoroacetates and lead tetraacetate in TFA solution.[13] It thus appears that the reaction of lead tetra(trifluoroacetate) (formed in situ from lead tetraacetate and TFA[14a]) with diarylthallium trifluoroacetates proceeds as shown in Scheme I. The yellow intermediate (presumed to be a thallium–lead complex[13]) is formed by reaction of the arylthallium ditrifluoroacetate with the second equivalent of lead tetra(trifluoroacetate). Aryllead tri(trifluoroacetates) are known to decompose spontaneously to lead ditrifluoroacetates and aryl trifluoroacetates.[14a,b] In further support of this proposed reaction course, we have observed that treatment of di-4-tolylthallium acetate with lead tetraacetate in glacial acetic acid gave 4-tolylthallium diacetate and 4-tolyllead triacetate.

Scheme I



The reason for the effectiveness of triphenylphosphine addition remains uncertain, although oxidation to triphenylphosphine oxide, presumably by TTFA released in the metal–metal exchange reaction between the arylthallium ditrifluoroacetate and lead tetra(trifluoroacetate), has been confirmed.[13]

It should be mentioned that while it was not directly determined whether complete metathesis of lead tetraacetate to lead tetra(trifluoroacetate) in TFA solution occurred in our experiments,[14a] the following evidence suggests that this metathesis process was probably complete. When a solution of lead tetraacetate in TFA was added to a TFA solution of phenylthallium ditrifluoroacetate,[7] phenyl trifluoroacetate was the only ester detected; no phenyl acetate was formed.[15] Furthermore, dissolution of 4-tolyllead triacetate in TFA results only in the formation of 4-tolyl trifluoroacetate.[14a,b,15]

This phenol synthesis from diarylthallium trifluoroacetates complements the corresponding synthesis from arylthallium ditrifluoroacetates. Yields are only moderate, but the procedure represents a viable conversion of aryl Grignard reagents to phenols. There is clearly no advantage, however, in employing the present method for phenol synthesis from arylthallium ditrifluoroacetate precursors utilizing method A (initial "disproportionation"), since the latter organothallium compounds can be converted directly to phenols.[12]

It thus appears that diarylthallium trifluoroacetates (and presumably other diarylthallium derivatives as well) are not exceptionally stable substances, and may be utilized under appropriate reaction conditions as intermediates in a variety of useful aromatic substitution reactions.

Experimental Section[16]

Synthesis of Diarylthallium Trifluoroacetates. Method A. By Disproportionation of Arylthallium Ditrifluoroacetates. The general procedure is illustrated by the disproportionation of 3,4-dimethylphenylthallium ditrifluoroacetate to di(3,4-dimethylphenyl)thallium trifluoroacetate. A solution of 8.00 g (0.015 mol) of 3,4-dimethylphenylthallium ditrifluoroacetate in 15 ml of acetone was heated under reflux for 30 min and cooled, and 40 ml of water was added. The white crystalline solid which separated was collected by filtration, washed with water, and dried to give 3.66 g (93%) of white silky crystals, mp 269–275° dec. The analytical sample, mp 274–276° dec, was recrystallized from ethyl acetate.

Data for other diarylthallium trifluoroacetates obtained in the same manner from arylthallium ditrifluoroacetates are summarized in Table I.

Method B. By Reaction of Aryl Grignard Reagents with Thallium(III) Trifluoroacetate (TTFA). The general procedure is illustrated by the conversion of 2-bromotoluene to di-2-tolylthallium trifluoroacetate. Thus, 17.10 g (0.10 mol) of 2-bromotoluene was converted to the corresponding Grignard reagent in the normal fashion. To a solution of this Grignard reagent in diethyl ether, under nitrogen, was added by means of a dropping funnel a solution of 10.86 g (0.02 mol) of dry TTFA in 30 ml of anhydrous ether. The rate of addition was adjusted so that the exothermic reaction was maintained under control. The resulting stirred heterogeneous reaction mixture was heated gently under reflux for 15 min and then cooled to 0°. Excess Grignard reagent was destroyed by addition of 50 ml of water, and the resulting precipitate was collected by filtration, suspended in 50 ml of pyridine, and heated under reflux for 2 hr. The suspended solids were removed by filtration and the filtrate was evaporated under reduced pressure to give a residual solid (di-2-tolylthallium bromide) to which was added 20 ml of 3 *M* potassium hydroxide and 20 ml of ethanol. The resulting suspension was heated under reflux for 18 hr, and the white solid was collected by filtration, washed with distilled water, and dried in vacuo for 2 hr at 50° to give 6.64 g (82%) of di-2-tolylthallium hydroxide.

A suspension of 4.00 g of the above material in 40 ml of TFA and 40 ml of water was stirred for 15 min, an additional 80 ml of water was added, and the resulting solid was collected by filtration to give 4.33 g (87%) of di-2-tolylthallium trifluoroacetate as a white, microcrystalline solid, mp 244–246° dec. The microanalytical sample was prepared by recrystallization *from ethyl acetate* (see Table II). Representative data for other diarylthallium trifluoroacetates prepared by method B are summarized in Table II.

Di(1-naphthyl)thallium Acetate. *Di(1-naphthyl)thallium* hydroxide was prepared from 1-bromonaphthalene by the general procedure described above. A solution of 4.90 g (0.01 mol) of di(1-naphthyl)thallium *hydroxide was dissolved* in 25 ml of pyridine and 25 ml of acetic anhydride, and the resulting solution was heated on a steam bath for 20 min and then cooled to approximately 2°. Addition *of 50 ml* of water resulted in precipitation of a solid which was collected by filtration, washed well with water, and dried to give 3.62 g (68%) of di(1-naphthyl)thallium acetate. The analytical sample was prepared by trituration with boiling ethyl acetate, and melted at 247–248° dec (see Table II).

Preparation of Unsymmetrical Biphenyls. The general procedure for the photochemical synthesis of unsymmetrical biphenyls is illustrated by the conversion of di-4-tolylthallium trifluoroacetate to 4-methylbiphenyl. Thus, a suspension of 1.25 g (0.0025 mol) of di-4-tolylthallium trifluoroacetate in 300 ml of benzene was placed in a 500-ml quartz tube fitted with a reflux condenser. The stirred reaction suspension was purged with nitrogen for 15 min and then irradiated, with continuous stirring, for a period of 18 hr with 300-nm light in a Rayonet photochemical reactor. The benzene solvent was then removed by distillation under reduced pressure, and the residue was taken up in 100 ml of *n*-hexane–ether (1:1). The latter solution was extracted with 30 ml of water, the aqueous layer was extracted again with 25 ml of *n*-hexane–ether (1:1), and the organic extracts were combined and passed through 10 g (200 mesh, <0.08 mm) of silica gel. The combined eluates were dried ($MgSO_4$) and evaporated under reduced pressure to give 0.55 g of crude product. GLC analysis of this crude product showed that it contained 0.50 g of 4-methylbiphenyl (61%), as well as 4,4′-dimethylbiphenyl (3%), biphenyl (2%), toluene (<2%), and 2-methylbiphenyl (2%).

Other unsymmetrical biphenyls prepared in analogous fashion are listed in Table III. All compounds were identified by ir spectral comparison or by a comparison of GLC retention times with those of authentic samples.

Synthesis of Aryl Iodides. The general procedure for the synthesis of aryl iodides is illustrated by the conversion of di-2-tolylthallium trifluoroacetate to 2-iodotoluene. Thus, a stirred mixture of 0.50 g (0.001 mol) of di-2-tolylthallium trifluoroacetate and 0.51 g (0.002 mol) of iodine in 20 ml of chloroform was heated under reflux, protected from light, for 16 hr. To the cooled reaction mixture was added a solution of 2.00 g (0.01 mol) of $Na_2S_2O_5$ in 25 ml of water, and the two-phase solution was vigorously stirred until the purple color of iodine had been completely discharged. The heavy yellow precipitate of thallium(I) iodide was removed by filtration through Celite, the chloroform layer in the filtrate was separated, and the aqueous layer was extracted with an additional 25-ml portion of chloroform. The combined chloroform extracts were washed with water, dried ($MgSO_4$), and evaporated to give 0.39 g (89%) of GLC-pure 2-iodotoluene.

Representative data for the conversion of other diarylthallium trifluoroacetates to aryl iodides are given in Table IV.

Reaction of Di-4-tolylthallium Trifluoroacetate with 1 Equiv of Iodine. A mixture of 0.50 g (0.001 mol) of di-4-tolylthallium trifluoroacetate and 0.25 g (0.001 mol) of iodine in 20 ml of chloroform was heated under reflux for 18 hr, by which time the purple iodine color had been completely discharged. The cooled reaction mixture was concentrated to half volume under reduced pressure, cooled, and then filtered to give 0.27 g of thallium(I) trifluoroacetate. Addition of petroleum ether to the chloroform filtrate and cooling yielded an additional 0.01 g of thallium(I) trifluoroacetate, combined yield 0.028 g (88%(= MP [[5–[[7°/ Evaporation of the filtrates then gave 0.40 g (91%) of 4-iodotoluene, *identical* with an authentic sample.

Synthesis of Phenols. The general procedure is illustrated by the conversion of di-2-tolylthallium *trifluoroacetate to o-cresol.* Thus, to a cooled (2°), stirred suspension of 2.50 g (0.005 mol) of di-2-tolylthallium trifluoroacetate in 10 ml of TFA was added by means of a dropping funnel *a solution of 4.61 g (0.01 mol) of* lead tetraacetate in 10 ml of TFA. After addition was complete, the reaction mixture was allowed to warm to room temperature, *stirred for an additional 60 min, and cooled again to 2°*, and a solution of 2.62 g (0.01 mol) of triphenylphosphine in 10 ml of TFA was added rapidly. Excess TFA was then removed under reduced pressure, 25 ml of 6 *N* hydrochloric acid was added, and lead(II) and thallium(I) chlorides were removed by filtration. The filtrate was extracted with two 25-ml portions of methylene chloride, the extracts were combined, and 50 ml of 2 *N* sodium hydroxide was added. The two-phase solution was stirred for 30 min at room temperature, the methylene chloride layer was separated and extracted with an additional 25-ml portion of 2 *N* sodium hydroxide, and the combined aqueous alkaline layers were acidified with hydrochloric acid. The acidic aqueous solution was then extracted with three 25-ml portions of methylene chloride, the combined extracts were washed with 25 ml of saturated sodium bicarbonate solution to remove residual TFA, the basic washings were extracted in turn with 25 ml of methylene chloride, and the combined organic extracts were washed with water, dried ($MgSO_4$), and evaporated to give 0.59 (55%) of GLC-pure *o*-cresol, identical with an authentic sample.

Representative experimental data for the synthesis of other phenols from diarylthallium trifluoroacetates are given in Table V.

Reaction of Di-4-tolylthallium Acetate with Lead Tetraacetate. To a stirred suspension of 2.00 g (0.004 mol) of di-4-tolylthallium trifluoroacetate in 15 ml of aqueous ethanol (1:1) was added 0.4 g (0.01 mol) of sodium hydroxide. The heterogeneous mixture was stirred for 30 min at room temperature, and the precipitated white solid was collected by filtration, washed well with water, and dried to give 1.61 g (>99%) of di-4-tolylthallium hydroxide. This material was dissolved in 10 ml of glacial acetic acid and the solution was stirred for 30 min at room temperature. Removal of the acetic acid under reduced pressure then gave 1.35 g (76%) of di-4-tolylthallium acetate as a colorless, crystalline solid, mp 264–265° dec.

Anal. Calcd for $C_{16}H_{17}O_2Tl\cdot 0.5\ H_2O$: C, 42.26; H, 3.99. Found: C, 42.54; H, 3.95.

A suspension of 1.25 g (0.0028 mol) of di-4-tolylthallium acetate hemihydrate (prepared as described above) and 1.15 g (0.0025 mol) of lead tetraacetate in 20 ml of glacial acetic acid was stirred for 18 hr at room temperature. The initially opaque mixture became clear after ~45 min. Excess acetic acid was removed by evaporation under reduced pressure, the residue was stirred with 30 ml of benzene, and the suspended colorless solid was collected by filtration and dried, yield 1.14 g (98%), mp 223–225° dec. The ir spectrum of this compound was identical with that of authentic 4-tolylthallium diacetate (vide infra).

Addition of petroleum ether (bp 30–60°) to the filtrate and cooling resulted in the separation of 0.46 g (38%) of 4-tolyllead triacetate monohydrate, mp 98–101° dec (lit.[17] mp 86–88°).

Anal. Calcd for $C_{13}H_{16}O_6Pb\cdot H_2O$: C, 31.64; H, 3.68. Found: C, 32.04; H, 3.96.

4-Tolylthallium Diacetate. To a solution of 5.21 g of 4-tolylthallium ditrifluoroacetate in 20 ml of acetonitrile was added 10 ml of 5 *M* sodium hydroxide, and the yellow suspension which formed immediately was stirred at room temperature for 5 min. The yellow solid (4-tolylthallium oxide) was then collected by filtration, washed thoroughly with water, and dried (3.11 g, >99%). A suspension of 0.80 g of 4-tolylthallium oxide in 10 ml of chloroform containing 0.45 g of glacial acetic acid was stirred for 1 hr at room temperature, the resulting solution was evaporated to dryness under reduced pressure, and the residual white solid (1.01 g, 95%) was recrystallized from 1,2-dichloroethane, mp 222–223° dec.

Anal. Calcd for $C_{11}H_{13}O_4Tl$: C, 31.94; H, 3.17. Found: C, 32.18; H, 3.21.

Behavior of 4-Tolyl Acetate in Trifluoroacetic Acid. A solution of 0.15 g of 4-tolyl acetate in 20 ml of TFA was stirred at room temperature for 20 min and then evaporated under reduced pressure. The residual oil was partitioned between 10 ml of methylene chloride and 10 ml of 6 *N* HCl by stirring for 10 min. After the methylene chloride layer was separated, the aqueous acid layer was extracted with 3 × 40 ml of methylene chloride, and the extracts were combined with the methylene chloride layer above and washed with saturated sodium bicarbonate solution, then with water, dried ($MgSO_4$), and evaporated under reduced pressure. Mass spectral analysis of the residual oil showed *only* the presence of 4-tolyl acetate; no evidence for 4-tolyl trifluoroacetate could be found. In addition, the NMR spectrum of the residual oil showed two methyl group resonances (δ 2.23 and 2.32) of equal intensity.

Conversion of 4-Tolyllead Triacetate to 4-Tolyl Trifluoroacetate in TFA. A solution of 0.24 g of 4-tolyllead triacetate monohydrate in 10 ml of TFA was stirred for 20 min at room temperature and then evaporated under reduced pressure. The residual oil (which possessed a strong phenolic odor) was stirred vigorously with 5 ml of dichloromethane and 5 ml of 6 *N* HCl, the precipitated lead dichloride was separated by filtration, the aqueous layer was extracted with three 20-ml portions of dichloromethane, and the combined dichloromethane extracts were washed with saturated aqueous sodium bicarbonate and then with water and dried ($MgSO_4$). Evaporation then gave 0.07 g (70%) of 4-tolyl trifluoroacetate, identified by comparison (GLC, NMR, ir) with authentic material.

Registry No.—4-Tolylthallium ditrifluoroacetate, 23586-55-2; 3,4-dimethylphenylthallium ditrifluoroacetate, 23586-56-3; 2,4-dimethylphenylthallium ditrifluoroacetate, 34202-98-7; 2,5-dimethylphenylthallium ditrifluoroacetate, 34202-99-8; 2,4,6-trimethylphenylthallium ditrifluoroacetate, 23586-57-4; 2-dibenzofuranylthallium ditrifluoroacetate, 55073-50-2; 2-bromotoluene, 95-46-5; 3-bromotoluene, 591-17-3; 3-bromochlorobenzene, 108-37-2; 1,3-dibromobenzene, 108-36-1; 3-bromoanisole, 2398-37-0; 1-bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; di-2-tolylthallium bromide, 55073-51-3; di-3-tolylthallium bromide, 55073-52-4; di(3-chlorophenyl)thallium bromide, 55073-53-5; di(3-bromophenyl)thallium bromide, 55073-54-6; di(3-methoxyphenyl)thallium bromide, 55073-55-7; di(1-naphthyl)thallium bromide, 55073-56-8; di(2-naphthyl)thallium bromide, 55073-57-9; di-2-tolylthallium hydroxide, 55073-58-0; di-3-tolylthallium hydroxide, 55073-59-1; di(3-chlorophenyl)thallium hydroxide, 55073-60-4; di(3-bromophenyl)thallium hydroxide, 55073-61-5; di(3-methoxyphenyl)thallium hydroxide, 55073-62-6; di(1-naphthyl)thallium hydroxide, 55073-63-7; di(2-naphthyl)thallium hydroxide, 55073-64-8; di-4-tolylthallium hydroxide, 55073-65-9; di-4-tolylthallium acetate, 50795-46-5; 4-tolylthallium diacetate, 55073-66-0; 4-tolyllead triacetate, 3076-56-0.

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