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ORGANOTHALLIUM COMPOUNDS
XIII*. DITHALLATION OF SOME MONOCYCLIC AROMATIC COMPOUNDS**

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Summary

Thallation of anisole and phenetole with an equimolar amount of thallic trifluoroacetate in trifluoroacetic acid yields predominantly the para-thallated derivatives using short reaction times, but ortho-thallated species using long reaction times. With an excess of thallic trifluoroacetate, dithallation occurs and 2,4-bis[bis(trifluoroacetato)thallio]-anisole and -phenetole have been isolated. Each gives the corresponding 1-alkoxy-2,4-diiodobenzene as the sole organic product on treatment with aqueous sodium iodide. Complete dithallation of thiophen has been achieved on reaction with an excess of thallic trifluoroacetate in acetonitrile, as indicated by quantitative formation of 2,5-diiodothiophen on treatment of the thallation product with aqueous iodide ions. Use of an excess of thallic trifluoroacetate in refluxing trifluoroacetic acid causes partial dithallation of toluene, m-xylene, and benzene.

Introduction

No examples of dithallation or polythallation of monocyclic aromatics have been reported [3-9], except in the preliminary account of the present study [2]. Dithallation of 2,2'-bithiophen [3] and biphenyl [9] is known, but only one thallium substitutes per aromatic ring. By contrast, dimercuration is common [10], even to the point of complicating some preparations of monomercurated arenes [11], and it is now possible to permercurate a wide range of aromatic compounds [12]. This difference in behaviour has

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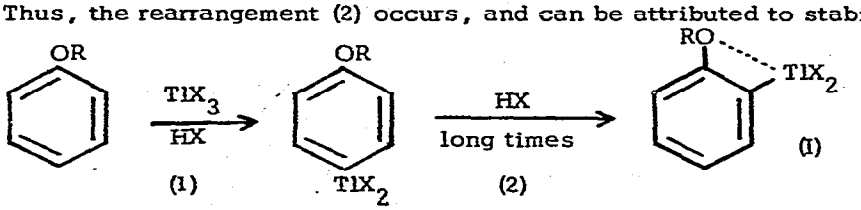
* Part XII, Ref. [1]. ** Preliminary communication, Ref. [2].

been attributed [9, 13] to the powerful electron withdrawing effect of the $-Tl(O_2CCF_3)_2$ substituent [9, 13, 14], whereas mercury substituents have a small electronic effect [15] (for a somewhat dissenting view, see [16]). However, despite the deactivating effect of thallium substituents, we have now achieved partial or substantial dithallation of several aromatics. In addition, we have observed a rearrangement reaction of para-thallated anisole and phenetole in trifluoroacetic acid at room temperature.

Results and Discussion

1. Thallation of Anisole and Phenetole

Details of the thallation of anisole and phenetole are given in Tables 1 and 2. To facilitate identification, all products were converted into the corresponding iodoarenes by treatment with aqueous iodide ions. (The reaction is known to place iodine in the position previously occupied by thallium [3].) Using a substrate:thallium ratio of 1:1, the predominant products are the para-substituted alkoxybenzenes [reaction (1)] when the reaction time is short (in agreement with earlier results for anisole [3]), and the ortho-substituted alkoxybenzenes when the reaction time is long. Thus, the rearrangement (2) occurs, and can be attributed to stabilization



(R = Me or Et) (X = CF_3CO_2)

of the ortho isomers (I) by intramolecular oxygen-thallium coordination giving a four membered chelate ring. In the absence of such an interaction, the ortho isomers (I) would probably be destabilized by steric repulsion. The complete absence of the meta isomers indicates that the rearrangement does not simply involve a statistical equilibration of isomers, as in the mercuration of toluene [10]. The conclusion that the ortho-thallated alkoxybenzenes are thermodynamically the most stable isomers is consistent with the predominant formation of ortho-thallated anisole in the transthallation reaction between phenylthallium bistrifluoroacetate and anisole [17]. An earlier observation [3], confirmed in this work (Table 1), that thallation of anisole using short reaction times gives more ortho isomer at room temperature than at low temperatures, is readily explicable by the occurrence of (2). However, a claim [4] that thallation of an excess of anisole with thallic trifluoroacetate gives exclusively the ortho isomer using a short reaction

TABLE 1

THALLATION OF ANISOLE IN TRIFLUOROACETIC ACID

Reactants			Products (% Yield) [b]			
Mol. ratio [a]	Time (hr.)	Temp. (°C)	A	B	C	Total
1:1	0.25	-25	4	70	-	74
	0.02	25	9	61	-	70
	0.25	25	15	72	-	87
	1.0	25	20	58	-	78
	168	25	46	13	13	72
1:2.4	0.05	25	6 [c]	49 [c]	-	55 [c]
2:1	65	25	30	9	33	72
3:1	24	73	19	13	12	44
	69	25	11	4	55	70

[a] Thallic trifluoroacetate:anisole. Concentration of $Tl(O_2CCF_3)_3$ ca. 1 M in trifluoroacetic acid. [b] Yields of iodoanisoles based on anisole, after treatment of the products with iodide ions. A = 2-iodoanisole, B = 4-iodoanisole, C = 2,4-diiodoanisole. [c] Yields based on thallic trifluoroacetate.

TABLE 2

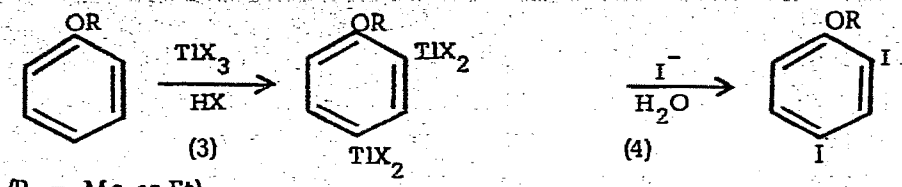
THALLATION OF PHENETOLE IN TRIFLUOROACETIC ACID

Reactants			Products (% Yield) [b]			
Mol. ratio [a]	Time (hr.)	Temp. (°C)	A	B	C	Total
1:1	0.25	25	19	69	6	94
	1.0	25	32	43	9	84
	168	25	40	18	4	62
3:1	72	25	20	5	54	79
6:1	216	25	-	-	94	94

[a] Thallic trifluoroacetate:phenetole. [b] Yields of iodophenetoles based on phenetole, after treatment of the products with iodide ions. A = 2-iodophenetole, B = 4-iodophenetole, C = 2,4-diiodophenetole.

time could not be verified (Table 1). Para-thallation predominated, as expected. Reaction (2) contrasts with known [5] rearrangements of para-thallated arenes, which give meta-thallated isomers, and with previous ortho-thallations [5], which proceed via five- and six-membered chelate rings under conditions of kinetic control.

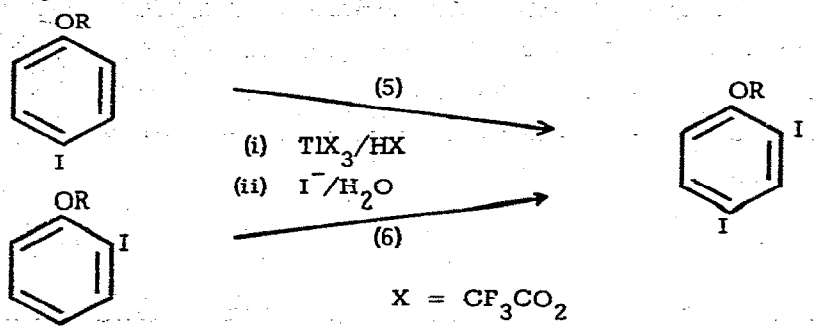
Thallation of anisole and phenetole with an excess of thallic trifluoroacetate followed by treatment of the product with iodide ions gives 2,4-diiodo-anisole and -phenetole respectively (Tables 1 and 2), indicative of dithallation of the ethers [reactions (3) and (4)].



(R = Me or Et)

II (R = Me); III (R = Et). X = CF_3CO_2

The diiodoarenes were identified by PMR spectroscopy, and the compounds were independently synthesized by routes (5) (R = Me) and (6) (R = Me or Et).



X = CF_3CO_2

Control experiments showed that fortuitous iododeprotonation does not occur in the mixture obtained by addition of aqueous sodium iodide to the thallation reaction mixture, since addition of the highly reactive substrates anisole and phenetole to such mixtures did not result in iodination.

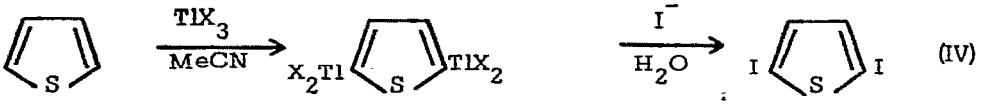
2,4-Bis[bis(trifluoroacetato)thallio]-anisole (II) and -phenetole (III) were successfully isolated by evaporation of typical reaction mixtures to crystallization. Both were obtained analytically pure on recrystallization from aqueous trifluoroacetic acid. Treatment of each compound with aqueous iodide ions gave the corresponding 1-alkoxy-2,4-diiodobenzene as the sole organic product [reaction (4)], establishing the positions of the thallium substituents. The PMR spectra of II and III in $(CD_3)_2SO$ (Experimental Section) were poorly resolved owing to very low solubility and meaningful integrations could not be obtained. However, both spectra showed a triplet [^3J(Tl–H) ≈ 1000 Hz] attributable to H3 coupled to two ortho thallium atoms, together with poorly resolved features, which could be rationalised as arising from overlap of a doublet of doublets (H5) and a

triplet (H6) with $^{n}J(Tl-H)$ values of similar magnitude to those [6] of monothallated arenes.

The para ⟶ ortho rearrangement (2) may play a vital role in dithallation, since migration of the first thallium substituent frees the kinetically (and sterically) favoured para position for further substitution. The most successful dithallations were achieved at room temperature. Reaction of anisole with an excess of thallic trifluoroacetate in refluxing trifluoroacetic acid gave a low total yield of iodoanisoles (Table 1), probably due to competition from oxidation.

2. Dithallation of Thiophen

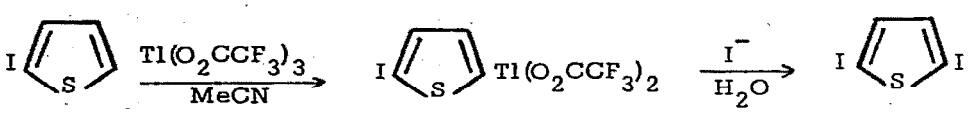
Thallation of thiophen with thallic trifluoroacetate (mol. ratio 1:5) in acetonitrile (used [3] for acid-sensitive substrates) for 6 days at 25° followed by treatment with aqueous iodide ions gave a quantitative yield of a symmetrically substituted diiodothiophen, indicative of complete dithallation of thiophen. Since monothallation of thiophen is known [3] to occur in the 2-position, the product is presumably 2,5-diiodothiophen (IV), which is formed by reactions (7) and (8).



(7) (8)

$X = CF_3CO_2$

The identity of IV was confirmed in an independent synthesis by thallation (9) and iodide induced dethallation (10) of 2-iodothiophen.



(9) (10)

3. Dithallation of Toluene, m-Xylene, and Benzene

Details of the thallation of toluene, m-xylene, and benzene are given in Table 3. Partial dithallation of these substrates was achieved using an excess of thallic trifluoroacetate in boiling trifluoroacetic acid, as indicated

by the formation of 2,4-diiodotoluene, 1,5-diiodo-2,4-dimethylbenzene, and m-diiodobenzene respectively in low yield on treatment of the reaction mixtures with aqueous sodium iodide. Extended reaction times could not be used with m-xylene owing to intervention of gross decomposition. No dithallation of toluene was observed at room temperature, and no appreciable dithallation of benzene could be induced in acetonitrile. Exclusive meta-dithallation of benzene is consistent with strong electron withdrawing

TABLE 3

THALLATION OF TOLUENE, m-XYLENE, and BENZENE IN TRIFLUORO-ACETIC ACID[a]

Substrate	Time (hr.)	Temp. (°C)	Products (% yield)[b]	Total[b] Yield (%)
toluene	168	25	A (11) B (0) C (88) D (0)	92
toluene	22	73	A (13) B (19) C (11) D (14)	57
m-xylene	0.5	73	E (60) F (12) G (8)	80
m-xylene	5.0	73	tar	
benzene	75	73	PhI (47) m-$I_2C_6H_4$ (14)	61
benzene[c]	72	81	PhI (15) m-$I_2C_6H_4$ (1)	16
benzene[c]	168	25	PhI (28)	

[a] Using a mol. ratio, $Tl(O_2CCF_3)_3$:arene = 3:1. [b] Yields of iodoarenes based on the reactant arene, after treatment of the product with iodide ions. [c] In MeCN.

Products: A = 2-iodotoluene, B = 3-iodotoluene, C = 4-iodotoluene, D = 2,4-diiodotoluene, E = 1-iodo-2,4-dimethylbenzene, F = 1-iodo-3,5-dimethylbenzene, G = 1,5-diiodo-2,4-dimethylbenzene.

character for the $-Tl(O_2CCF_3)_2$ substituent. Preparations of authentic 2,4-diiodotoluene and 1,5-diiodo-2,4-dimethylbenzene, required as PMR standards, were readily achieved by iodination of p-iodotoluene and m-xylene with iodine and thallic trifluoroacetate in trifluoroacetic acid. Iodination using this reagent is considered [18] to involve monothallation followed by iododethallation, the sequence being repeated for diiodination or polyiodination, but it is also possible that direct iodination by an intermediate of the type $\overset{\delta+}{I} \ldots I \ldots \overset{\delta-}{Tl}(O_2CCF_3)_3$ may occur. A species of the type $CF_3\overset{\delta-}{C}O_2\overset{\delta+}{I}$ has been proposed [19] to explain iodination by I_2/AgO_2CCF_3 [18, 19]. Certainly, bromination using $Br_2/Tl(O_2CCH_3)_3$ [20] cannot involve thallation, as thallic acetate is too ineffective a thallating agent [21]

to account for the observed reactions, and the reactive species is considered to be the complex Br - Br ... $Tl(O_2CCH_3)_3$ [20].

4. General Remarks

The present study has shown that, despite the deactivating effect of the $-Tl(O_2CCF_3)_2$ substituent, substantial dithallation of some activated monocyclic aromatic compounds can be achieved [reactions (3) and (7)], providing a satisfactory route to the corresponding diiodoaromatics [reactions (4) and (8)] and presumably to other disubstituted derivatives by use of appropriate known dethallation procedures [9, 22, 23]. With less activated substrates, dithallation is highly incomplete and does not provide a viable path to the diiodoarenes. However, in these cases, use of $I_2/Tl(O_2CCF_3)_3$ in trifluoroacetic acid may provide a satisfactory alternative route, as illustrated by the synthesis of 1,5-diiodo-2,4-dimethylbenzene [section 3]. It seems unlikely that more than two thallium substituents per ring could be introduced even into highly reactive aromatic compounds, e.g. significant trithallation of thiophen and phenetole could not be achieved with a $Tl(O_2CCF_3)_3$: substrate mol.ratio of 5:1 and 6:1 respectively and a large reaction time.

Experimental

Microanalyses were by the Australian Microanalytical Service, Melbourne. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E or a Hitachi RM-50 spectrometer. PMR spectra were recorded with a Varian A56/60A or a Bruker WH 90 spectrometer. Chemical shifts are in p.p.m. downfield from internal tetramethylsilane, the solvent being $CDCl_3$ or carbon tetrachloride unless stated otherwise. Infrared spectra (4000-500 cm^{-1}) of dithallated anisole and phenetole as Nujol mulls were recorded with a Perkin-Elmer 180 spectrometer, silver chloride plates being used to avoid the possibility of exchange between coordinated trifluoroacetate groups and alkali metal halide plates. Other spectra (2000-625 cm^{-1}) were obtained with a Perkin-Elmer 257 instrument.

Reagents

Trifluoroacetic acid was from Bristol Organics, thallic oxide from Fluka or ROC/RIC, and thallic trifluoroacetate was from ROC/RIC. Solutions of thallic trifluoroacetate (ca. 1 M) in trifluoroacetic acid containing 10-20% water were prepared either from the commercial product or from thallic oxide and trifluoroacetic acid as reported [3]. The

concentrations of representative solutions were determined by reduction to the thallous state with sulphur dioxide and titration with potassium iodate using Andrews conditions [24]. Blank titrations before reduction showed that ca. 5% of the thallium in all solutions was in the thallous state. Thallations in acetonitrile were effected using commerical thallic trifluoroacetate in redistilled (from P_2O_5) acetonitrile. Anisole, phenetole, thiophen, toluene, m-xylene, benzene, 2- and 4-iodotoluene, 2- and 3-methoxyaniline, 2-, 3-, and 4-ethoxyaniline, and 3,5-dimethylaniline were from standard commercial sources and were used without purification.

Authentic Iodoarenes

2-Iodo- and 3-iodo-anisole were prepared from the appropriate methoxyanilines by the Sandmeyer reaction, and 4-iodoanisole was provided by Dr. G. Jackman of this Department. The compounds were identified by their infrared [25] and mass spectra [mol. wt., 234. C_7H_7IO calcd.: 234]. The PMR spectra of 3-iodo- and 4-iodo-anisole were in agreement with those reported [26, 27a]. 2-Iodoanisole: PMR spectrum: 3.82s, 3H, CH_3; 6.5-6.9m, 2H, H4,6; 7.1-7.4m, 1H, H5; 7.6-7.8m, 1H, H3 p.p.m. The iodophenetoles were also prepared by the Sandmeyer method [mol. wt. (mass spectrometry), 248 (all isomers). C_8H_9IO calcd.: 248]. The PMR spectrum of 4-iodophenetole agreed with that reported [28]. 2-Iodophenetole: PMR spectrum: 1.40t, J 7 Hz, 3H, CH_3; 3.99q, J 7 Hz, 2H, CH_2; 6.5-6.8m, 2H, H4,6; 7.1-7.4m, 1H, H5; 7.7-7.8m, 1H, H3 p.p.m. 3-Iodophenetole: PMR spectrum: 1.35t, J 7 Hz, 3H CH_3; 3.95q, J 7 Hz, 2H, CH_2; 6.8-7.4m, 4H, H2,4,5,6 p.p.m.

2,4-Diiodoanisole.- (a) 2-Iodoanisole (20 mmol) was added to a stirred solution of thallic trifluoroacetate (44 mmol) in trifluoroacetic acid (40 ml.) at room temperature. After 10 hr., the mixture was treated with aqueous sodium iodide, and was worked up as in procedure A of ref. [3] giving the required compound (98%), which was recrystallized from aqueous methanol m.p. 68°, lit. [29a], 68°. The infrared and PMR spectra were in agreement with those reported [30]. (b) 4-Iodoanisole (10 mmol) was treated with thallic trifluoroacetate (10 mmol) in refluxing trifluoroacetic acid (20 ml) for 5 hr. Isolation as in (a) gave 2,4-diiodoanisole (74%) - PMR identification.

2,4-Diiodophenetole.- Thallation of 2-iodophenetole at room temperature for 96 hr. as for 2-iodoanisole gave 2,4-diiodophenetole (77%), which on recrystallization from ligroin, had m.p. 53.5-55°, lit. [29a], 46 or 51°, and PMR and infrared spectra in agreement with those reported [30].

2-Iodothiophen was prepared as reported [3], and had the correct PMR spectrum [31].

2,5-Diiodothiophen.- 2-Iodothiophen (13 mmol) and thallic trifluoroacetate (13.3 mmol) in acetonitrile (10 ml) were stirred for 1 hr. at room temperature. After work up as in procedure C of Ref. [3], and recrystallization of the product from methanol/diethyl ether, 2,5-diiodothiophen was obtained (yield, 44%), m.p. 41-42°, lit. [32], 40.5-41.5°, having PMR [33] and mass spectra [34] in agreement with those reported.

3-Iodotoluene was obtained by the Sandmeyer method, and was identified by the PMR spectrum [27b].

2,4-Diiodotoluene.- 4-Iodotoluene (10 mmol), iodine (5.9 mmol), and thallic trifluoroacetate (6.5 mmol) in trifluoroacetic acid (8.5 ml.) were kept at room temperature for 20 hr. The trifluoroacetic acid was removed under vacuum, and the excess of iodine was decomposed with sodium sulphite. After making the solution alkaline with sodium hydroxide, ether extraction and evaporation with a stream of dry nitrogen at room temperature gave the diiodotoluene, which was distilled under reduced pressure (yield 58%), (Found: C, 24.6; H, 2.0. $C_7H_6I_2$ calcd.: C, 24.5; H, 1.8%). The PMR spectrum agreed with that reported [35], but slight impurity resonances (2.22s and 7.75br p.p.m.) were also observed.

1-Iodo-2,4-dimethylbenzene was prepared as reported [3] and was identified by the PMR spectrum [36].

1-Iodo-3,5-dimethylbenzene was obtained from the corresponding aniline by the Sandmeyer reaction, and was identified by the PMR spectrum [37].

1,5-Diiodo-2,4-dimethylbenzene.- m-Xylene, iodine, and thallic trifluoroacetate (each 10 mmol) in trifluoroacetic acid (10 ml.) at room temperature for 1 hr gave, on isolation as for 2,4-diiodotoluene, the required diiodoarene (yield, 93%), which was recrystallized from diethyl ether/ethanol, m.p. 71-72°, lit. [29b], 72°, the infrared spectrum being identical with that reported [38]. PMR spectrum: 2.34s, 6H, CH_3; 7.16s, 1H, H3; 8.25s, 1H, H6 p.p.m.

1,3-Diiodobenzene.- 1,3-Di(chloromercuri)benzene (1.7 g; synthesis [39]) was treated with iodine (2.0 g) in dimethylformamide (10 ml) for 5 hr. at room temperature. Dilution with water, addition of aqueous sodium sulphite, ether extraction, and evaporation gave 1,3-diiodobenzene (0.33 g, 30%), identified by the PMR spectrum [40].

Thallation of Anisole, Phenetole, Thiophen, Toluene, m-Xylene, and Benzene

The reaction conditions for all compounds except thiophen are given in Tables 1-3. Thiophen (10 mmol) was treated with thallic trifluoroacetate (50 mmol) in acetonitrile (50 ml) for 6 days at room temperature. Cleavage with sodium iodide (reaction time ≤ 5 min. before addition of sodium metabisulphite) and subsequent work up were by reported procedures [3]. Ether extracts were evaporated with a stream of dry nitrogen at room temperature to avoid loss of products. Yields and compositions of the mixtures of iodoarenes were determined by comparison of their PMR spectra with those of authentic samples of the appropriate iodoarenes.

Preparation of 2,4-bis[bis(trifluoroacetato)thallio] anisole.- Anisole (10 mmol) was treated with thallic trifluoroacetate (30 mmol) in trifluoroacetic acid (30 ml) at room temperature for 65 hr. Evaporation to crystallization under vacuum at room temperature gave the dithallated anisole in 70% yield. Recrystallization from aqueous trifluoroacetic acid and drying in vacuo over phosphorus pentoxide gave an analytically pure sample, dec. temp. 195° (Found: C, 18.3; H, 0.8. $C_{15}H_6F_{12}O_9Tl_2$ calcd.: C, 18.6; H, 0.6%). Infrared absorption: 3090vw [ν(CH)], 1760w (br), 1690, 1650, and 1612vs (br) [ν_{as} (CO_2)], 1573m (sh) [ν(CC)], 1444s, 1420m, 1404m, 1291s, 1251s, ca. 1200vs (vbr) [ν(CF)], 1038m, 1010w, 870 and 865s, 818m, 803m (sh), 793 and 788s, 740 and 735vs, 726s (sh), 700w, 666w, 615w (sh), 601m, and 524m (br) cm^{-1}. PMR spectrum [in $(CD_3)_2SO$]: 7.44br,t, ^4J(Tl-H) 430 Hz, H6; 7.45br,dd, ^3J(Tl-H) 980 Hz, ^5J(Tl-H) 67 Hz, H5; 7.81t, ^3J(Tl-H) 999 Hz, H3 p.p.m. The methoxy resonance was coincident with that of a water impurity in the solvent. Treatment of both the crude and the recrystallized products with aqueous sodium iodide as described above gave 2,4-diiodoanisole as the sole organic product (PMR identification).

Preparation of 2,4-bis[bis(trifluoroacetato)thallio] phenetole.- By the preceding method, phenetole (10 mmol) and thallic trifluoroacetate (30 mmol) in trifluoroacetic acid (30 ml) at room temperature for 3 days gave the dithallated phenetole in 51% yield. After recrystallization from aqueous trifluoroacetic acid and drying in vacuo over phosphorus pentoxide, the compound had dec. temp. 212°[Found: C, 19.1; H, 0.9. $C_{16}H_8F_{12}O_9Tl_2$ calcd.: C, 19.6; H, 0.8%]. Infrared absorption: 3100vw [ν(CH)], 1756m, 1687w, 1605vs (br) [ν_{as}(CO_2)], 1570sh [ν(CC)], 1553w, 1409w, 1390sh, 1287m, 1255sh, 1215, 1186, and 1160vs (vbr) [ν(CF)],

1040m, 922w, 898w, 868s, 801m, 787s, 739, 734, and 730s, 695m, 624w, 579vw, 547w, 519m cm^{-1}. PMR spectrum [in $(CD_3)_2SO$]: 1.32br, CH_3; ca. 4.1br, CH_2; 7.26br,t, ^4J(Tl-H) 420 Hz, H6; ca. 7.7br,dd, ^3J(Tl-H) 915 Hz, ^5J(Tl-H) 67 Hz, H5; 7.70t, ^3J(Tl-H) 992 Hz, H3 p.p.m. Cleavage of the crude or recrystallized compound with aqueous sodium iodide gave 2,4-diiodophenetole as the sole organic product.

Control Experiments: Aqueous sodium iodide was added to thallic trifluoroacetate (mol. ratio ≃ 3:1 respectively) in trifluoroacetic acid, followed immediately by anisole [0.33 or 1 mol/mol. of $Tl(O_2CCF_3)_3$], o-iodoanisole [0.5 mol/mol. of $Tl(O_2CCF_3)_3$], or phenetole [equimolar with $Tl(O_2CCF_3)_3$]. After stirring for 5 min (also 15 min for anisole), the reaction mixtures were worked up in the usual way, and the arenes were recovered unchanged (infrared or PMR identification).

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