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Aryl Derivatives of Thallium(III): Preparation and Use in Organic Synthesis

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The review presents new data on the preparation of aryl derivatives of thallium(III) and their application in organic synthesis, which is based on the possibility of the selective introduction of an organic group into an aromatic ring by replacing the thallium atom in arylthallium compounds. Processes involving the modification of aromatic compounds in the presence of thallium salts are also considered. The probable mechanisms of the reactions occurring in such processes are discussed. The bibliography includes 97 references.

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I. SYNTHESIS OF COMPOUNDS OF THE TYPE $ArTlX_2$

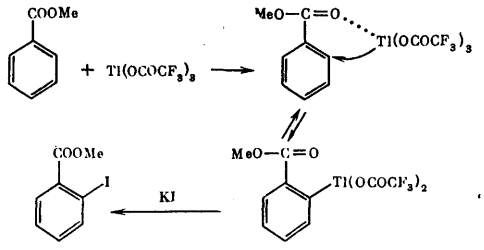
1. Reactions Involving Direction Thallation of Arenes

The commonest method of synthesis of compounds of the type $ArTlX_2$ and one which has been investigated in greatest detail is the direct thallation of arenes by trivalent thallium salts. The most convenient system for this purpose comprises thallium trifluoroacetate (TTFA) in trifluoroacetic acid (TFAA).[1-4]

In contrast to arenes activated by electron-donating substituents, which are thallated at room temperature in several minutes, the complete conversion of halogenobenzenes was attained in 48 h at room temperature or in 30 min in boiling TFAA. Substrates with a nucleus deactivated with respect to electrophilic substitution, such as benzoic acid and ααα-trifluorotoluene react with TTFA in boiling TFAA in 21 and 98 h respectively.

The reaction involving the substitution of the thallium atom by an iodine atom can be used to establish the position of substitution in the aromatic ring on thallation. The authors suggest the following methods of synthesis of aryl iodides from the arylthallium bis(trifluoroacetates) obtained depending on the properties of the latter: (a) treatment of the reaction mixture with an aqueous KI solution after the completion of thallation without isolating the products—for arylthallium bis(trifluoroacetates) soluble in CF_3COOH; (b) isolation, drying, and interaction with KI in an aqueous acetone solution—for products crystallising from the reaction mixture; (c) the addition of KI to the reaction mixture in acetonitrile—for aromatic systems sensitive to the action of acids.

The effect of the substituent in the aromatic nucleus on the isomeric composition of the thallation products has been investigated.[3] In the thallation of benzoic acid by treatment with TTFA in TFAA, it was established that substitution takes place mainly in the *ortho*-position in the aromatic ring. It was postulated initially that a mixed thallium(III) carboxylate is formed during the reaction and then donates the thallium atom to the *ortho*-position. However, the thallation of methyl benzoate also affords mainly the *ortho*-products. Bearing this finding in mind, the following reaction mechanism has been suggested:[3]



The isomeric composition of the products formed on thallation of aromatic compounds is presented in Table 1.

Analysis of the data in Table 1 for the thallation-iodination† of the homologous series of phenyl-containing carboxylic acids (compounds 4, 5, 10, and 11 in Table 1) shows that the degree of *ortho*-substitution depends appreciably on the chain length of the carboxyl-containing group, since the carboxy-group is a complex-forming agent in relation to TTFA. In fact, an intermediate is formed in the σ-complex formation stage in which the Tl atom is linked to a carbon atom of the arene and is coordinated to the carbonyl O atom in the side chain of the substitutuent. Such intermediate complexes have been called[3] "chelate intermediates". Thus, whereas benzoic and phenylacetic acids and the corresponding methyl esters afford exclusively *ortho*-derivatives via five- or six-membered "chelate" rings, the *ortho*-thallation of phenylpropionic acid can proceed only via the formation of a seven-membered "chelate" ring, which is less preferable and this in fact entails a decrease in the content of the *ortho*-thallation product (29%).

† By the term thallation-iodination, the authors denote the preliminary thallation of the substrate followed by the treatment of the compounds obtained with KI using one of the methods described by McKillop et al.[2]

The behaviour of a whole series of aromatic compounds containing substituents in the side chain, which are capable of forming complexes with TTFA, has been investigated[3] from the standpoint of the possible supply of the thallium atom to the ring via a "chelate intermediate" formed by the Lewis acid (TTFA) and an oxygen-containing Lewis base. Thus substrates capable of forming five- and six-membered intermediate chelates give rise almost exclusively to *ortho*-substitution products (compounds 15, 17, 22, and 23 in Table 1). The increase in the chain length of the intermediate chelate leads to a sharp fall of the yield of the *ortho*-isomer (compounds 10, 11, 18, and 20 in Table 1). The degree of *ortho*-substitution depends also on the nature of the Lewis base in the side chain of the substrate and decreases in the sequence ester, acid, ether, alcohol. Intramolecular thallation via a "chelate ring" is extremely sensitive to steric factors. Thus the replacement of one α-hydrogen atom in phenylacetic acid by the methyl group results in a decrease in the degree of *ortho*-substitution from 92 to 65%, while the replacement of the second α-hydrogen atom by the methyl group altogether inhibits *ortho*-substitution.

Table 1. The isomeric composition of the products of the thallation of the arenes C_6H_5R at room temperature.[3]

No.	R	Proportions of isomers, %		
		ortho	*meta*	*para*
1	CH_3	9	4	87
2	$CH_2CH_2CH_3$	3	6	91
3	$CH(CH_3)_2$	1	5	94
4	COOH	95	5	0
5	CH_2COOH	92	3	5
6	$CH(CH_3)COOH$	65	11	24
7	$C(CH_3)_2COOH$	0	37	63
8	CH_2CH_2COOH	29	13	58
9	$CH(CH_3)CH_2COOH$	37	14	49
10	$CH_2CH_2CH_2COOH$	6	10	84
11	$CH_2CH_2CH_2CH_2COOH$	5	9	86
12	$COOCH_3$	95	5	0
13	CH_2COOCH_3	92	3	5
14	$CH_2CH_2COOCH_3$	53	7	40
15	CH_2OH	99	—	—
16	CH_2OCOCH_3	50	21	29
17	CH_2CH_2OH	83	6	11
18	$CH_2CH_2OCOCH_3$	3	13	84
19	$CH_2CH_2CH_2OH$	10	10	80
20	$CH_2CH_2CH_2OCOCH_3$	5	12	83
21	OCH_3	7	0	93
22	CH_2OCH_3	99	—	—
23	$CH_2CH_2OCH_3$	85	3	12
24	$CH_2CH_2CH_2OCH_3$	27	6	67
25	CH_2OCOCF_3	49	24	27
26	$OCOCH_3$	21	0	79
27	—*	31% thallation in the 6-position		

*2-$CH_3C_6H_4CH_2COOH$.

The intermediate formation of a "chelate" ring is supported by the following results: firstly, the thallation of compounds containing in the side chain activated substituents incapable of forming "chelate complexes" with TTFA takes place in several minutes at room temperature, while the presence of a Lewis base in the side chain appreciably increases the thallation time regardless of the size of the ring which may be formed. Secondly, the degree of *meta*-substitution is highest when there is a possibility of the formation of an eight-membered "chelate" (compounds 8, 16, 18, and 25 in Table 1) and also in those cases where *ortho*-thallation via a "chelate complex" is hindered by steric factors (compounds 6 and 7 in Table 1). The thallation of cumene (compound 3 in Table 1), which has a bulky substitutuent incapable of forming a complex with thallium-(III), affords only 5% of the *meta*-isomer. The authors conclude that thallation is a process much more sensitive to steric factors than mercuration.

Thallation under the conditions of kinetic control leads to the initial preferential formation of *ortho*- and *para*-isomers. Since thallation is reversible, an increase in temperature to 73 °C (boiling CF_3COOH) increases the fraction of the *meta*-isomer, i.e. in this case thermodynamic control plays a significant role.

It is noteworthy that thallation of a substrate containing in the side chain substituents capable of complex formation requires additional time for the attainment of equilibrium. This finding imposes definite synthetic limitations on the *meta*-thallation process, since TTFA decomposes after prolonged heating in TFAA. Thallation of β-phenylethyl acetate (compound 18 in Table 1) under the conditions of kinetic control leads to substitution in the *para*-position of the aromatic ring (84%), which is associated with the increase in ring size in the *ortho*-thallation intermediate from six-membered for β-phenyl-ethanol (compound 17 in Table 1) to eight-membered in its acetate.

Thus variation of the thallation conditions (thermodynamic and kinetic control) makes it possible to introduce a thallium atom selectively in a specific position in the aromatic nucleus.

Thallium(III) acetate in acetic acid containing added $HClO_4$ has been used[5] as a thallating agent. In this case, thallation also proceeds smoothly, especially in the case of arenes activated with respect to electrophilic substitution. The products isolated were characterised as the monohydrates of mixed arylthallium acetate perchlorates. The highest yield of the arylthallium compounds is attained at room temperature. An increase in temperature entails a decrease in yield owing to the occurrence of side processes such as the coupling of aromatic radicals and the oxidation of the solvent with formation of a thallium(I) salt.

A series of kinetic studies of the influence of various additives on the course of thallation have been carried out. The thallation of arenes in various acids has been investigated.[6] Heating of thallium-(III) acetate with benzene in 1 M H_2SO_4 leads to the rapid precipitation of a deposit containing $PhTl(HSO_4)_2$, Ph_2TlHSO_4, and $Tl(HSO_4)_3$. Heating of benzene with a thallium(III) salt in perchloric acid affords a mixture of phenylthallium dichloride with diphenylthallium chloride.

It has been established[6] that the rate of thallation increases with increase in temperature to a greater extent for an activated aromatic compound (toluene) than for a non-activated one (benzoic acid). This fact can be associated both with the electronic effects of the substituents and with the possible formation of an intermediate chelate complex.[3] An approximate estimate of the rates of thallation and mercuration in aqueous $HClO_4$ demonstrated that the rate of mercuration under identical conditions is approximately 200–400 times higher than the rate of thallation.

The influence of catalytic strong acid additives on the rate of thallation has been investigated.[7,8] The authors showed that perchloric acid is a more active thallation catalyst than sulphuric acid. The mechanism of the catalysis consists in the formation of polar electrophilic species which are involved in an acid–base

equilibrium:

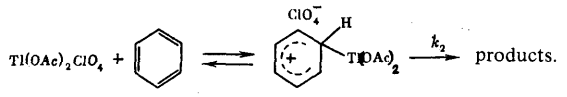
$$\begin{array}{l} Tl(OAc)_3 \rightleftarrows [Tl^{-}(OAc)_2^{-}OAc] \rightleftarrows Tl^{+}(OAc)_2 + OAc^{-}, \\ K_4\downarrow\uparrow \\ Tl(OAc)_2ClO_4 \rightleftarrows [Tl^{+}(OAc)_2ClO_4^{-}] \rightleftarrows Tl^{+}(OAc)_2 + ClO_4^{-}, \\ K_5\downarrow\uparrow \\ Tl(OAc)(ClO_4)_2 \rightleftarrows [Tl^{2+}(OAc)\,2ClO_4^{-}] \rightleftarrows Tl^{2+}(OAc) + 2ClO_4^{-}, \\ K_6\downarrow\uparrow \\ Tl(ClO_4)_3 \rightleftarrows [Tl^{3-}3ClO_4^{-}] \rightleftarrows Tl^{3+} + 3ClO_4^{-}. \end{array}$$

The values of K_1 were calculated for the *p*-nitroaniline–perchloric acid–thallium(III) acetate system. On the assumption that $Tl(OAc)_2ClO_4$ does not react with the indicator, $K_1 = 4.6-5.0$ litre mol^{-1}; on the other hand, if $Tl(OAc)_2ClO_4$ does react with the indicator, like $Tl(OAc)_3$, then the constants K_1 are between 6.0 and 8.4 litre mol^{-1}.

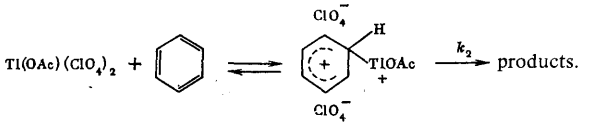
The data obtained show that the constants K_1 and K_2 are important for the determination of the character of the equilibrium in solution and hence of the thallation process itself, since at high catalyst concentrations the content of the $Tl(OAc)_2X$ species increases – the degree of conversion of $Tl(OAc)_3$ into $Tl(OAc)_2X$ is 92% for [HX] = 0.5 M. The data for the conductivities of the solutions permit the conclusion that in pure acetic acid, thallation is effected by the electrophile in the form of an ion pair, while in dilute solutions ionic species are active.

It follows from the activation parameters E_a and $\Delta S^{\neq}$ that more than one electrophilic species is involved in the thallation process. At low catalyst concentrations the process is characterised by high values of E_a and an appreciable positive entropy, while at high concentrations, where the catalyst is most effective, the values of E_a are comparatively low but $\Delta S^{\neq}$ also diminishes appreciably. According to the authors, the rate-limiting stage of the process is the decomposition of Wheland's intermediate, characterised by the constant k_2 (Schemes 1 and 2). The authors describe the process by Scheme 1 at low catalyst concentrations and by Scheme 2 at high concentrations:

Scheme 1



Scheme 2



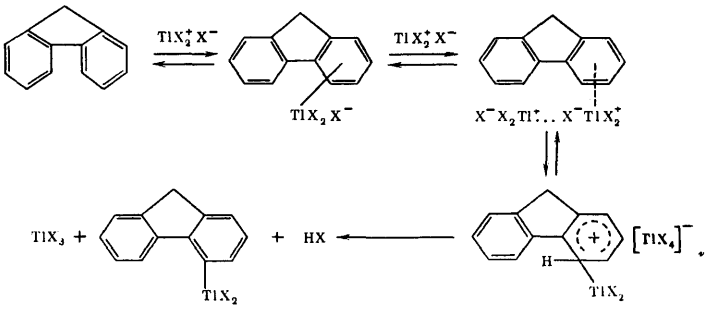
In their study of the variation of the isomeric composition of the toluene thallation products with time, the authors found that *para*-thallation initially predominates, its extent falling with time and with decrease in the catalyst concentration. Thus thallation for 24 h at an H_2SO_4 concentration of 2 M leads to the following proportions of the isomers: 18.7% *ortho*, 6.4% *meta*, and 75% *para*; when $[H_2SO_4]$ = 0.4 M, the proportions are 37.6, 3.4, and 59% respectively.

The kinetics of the thallation of fluorene by thallium(III) acetate in aqueous acetic acid have been investigated.[9] The authors observed that the reaction is of first order with respect to the substrate and of second with respect to thallium triacetate; its rate is described by the equation

$$v = k_3[Tl(III)]^2[\text{fluorene}].$$

The addition of strong protic acids sharply accelerates thallation; the reaction is of sixth order with respect to sulphuric acid. The reaction mechanism described by Scheme 3 was put forward:

Scheme 3



The second order with respect to the thallating agent agrees with the assumption of the participation of two and more electrophilic species in the thallation process,[8] but the influence of the second electrophile molecule may also be different than that suggested by Narasumnau et al.[9] In principle, there is a possibility of the formation of a dimeric species (Scheme 4) which is a stronger electrophile than the initial thallium(III) salt:

Scheme 4

$$2TlX_3 \rightleftarrows Tl_2X_6 \quad \text{or} \quad [TlX_2]^{+}[TlX_4]^{-}.$$

In a study of the thallation of activated arenes by TTFA in TFAA, the formation of the aromatic radical-cation Ar^{+} in the reaction mixture was detected by EPR.[10] According to the authors, the reaction proceeds via a one-electron transfer stage:

Scheme 5

$$Tl^{III} + ArH \rightleftarrows [ArH\cdot Tl^{III}];\ [ArH\cdot Tl^{III}] \rightleftarrows [ArH^{+\cdot}Tl^{II}],$$
$$[ArH^{+\cdot}Tl^{II}] \begin{cases} \longrightarrow Tl^{II} + ArH^{+} \\ \longrightarrow Ar^{+}{\diagup}{}^{H}{\diagdown}{}_{Tl^{III}} \xrightarrow[-H^{+}]{} ArTl^{III} \end{cases}$$

The authors suggest that the electron transfer stage is an obligatory process both for aromatic thallation and for the formation of Ar^{+}.

This concept was developed further in a study[11] where the interaction of the homologous series of methylbenzenes $C_6H_n(Me)_{6-n}$ with TTFA was investigated. It was shown that the active electrophilic species in this process is the cation $[Tl(OCOCF_3)_2]^{+}$, formed as a result of the reversible reaction

$$TTFA \rightleftarrows [Tl(OCOCF_3)_2]^{+} + CF_3COO^{-}\ (K).$$

The constant K at 25 °C in TFAA is 1×10^{-3} mol litre^{-1}. According to the authors,[11] further reactions are associated with the formation of a π-complex between the arene and $[Tl(OCOCF_3)_2]^{+}$, which decomposes in accordance with Scheme 5. Kinetic data characterising the electrophilic thallation and electron transfer pathways have been published.[11]

The relative rates of thallation of toluene and benzene (k_t/k_b) as well as the partial rates of formation of the isomers in the thallation of toluene with TTFA in TFAA have been determined.[12] The ratios k_t/k_b determined by Kwok et al.[12] and Olah et al.[13] are 43.5 and 33 respectively; the partial rate factors for the thallation of toluene at 25 °C were found to be 12.7, 4.5, and 226 by Kwok et al.[12] and 9.6, 5.7, and 168 by Olah et al.[13] for *ortho*-, *meta*-, and *para*-substitution respectively; this enabled Kwok et al.[12] to conclude that the aromatic thallation reaction proceeds via an aromatic electrophilic substitution mechanism, most probably via a Wheland intermediate, in contrast to the mechanism proposed by Kochi and coworkers.[10,11]

Roberts[14] investigated the kinetics of the thallation of arenes by NMR. He suggests that the data obtained by this method can describe the thallation process more accurately, since in this instance there is no need to treat the reaction mixture with KI and to determine the kinetic parameters of the reaction with respect to the iodoarene formed. It was found that k_t/k_b = 24. Roberts[14] explains the increase in k_t/k_b with increase in acid concentration, observed by Briody and Moore,[8] by the influence of the large positive charge on the thallium atom, i.e. in the first stage of the interaction of the electrophile and the substrate, the electrostatic interaction forces should play an appreciable role according to the author.

The kinetic isotope effect, obtained by Roberts, is 5.0 (3.7 according to Briody and Moore[8]). The authors suggest that the rate-limiting stage of the thallation process is proton transfer in a transition complex analogous to a Wheland intermediate.

The time variation of the isomeric composition of the products has also been investigated for toluene. Thus the *ortho*:*meta*:*para* ratios are 28:29:63 after 13 min and 31:38:31 after 5000 min.

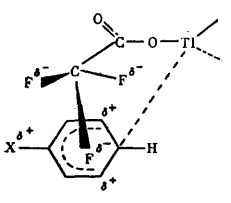
The kinetics of the thallation of a wide range of substrates by treatment with TTFA using both NMR and other methods for the detection of products were investigated in detail in a later study.[15] $Tl(OAc)_3.1.5H_2O$ was chosen as the thallating agent, since, according to the authors, it is more stable than TTFA. Furthermore, it was shown[15] that the rates of thallation of arenes by thallium(III) acetate sesquihydrate in TFAA agree with the rates of thallation of the same arenes by treatment with TTFA in TFAA.

The process mechanism was represented as follows:[15]

$$ArH + TlX_3 \overset{K_1}{\rightleftarrows} \pi\text{-complex} \overset{k_2}{\rightarrow} \text{products}.$$

The values of K_1 and k_2 found in the above study are listed in Table 2.

On the basis of the Hammett and Yukawa-Tsuno parameters, the authors concluded that there is an appreciable charge separation in each phase of the reaction, especially in the π-complex formation stage:



(A)

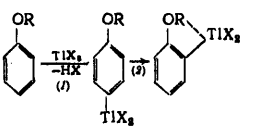
Analysis of the activation parameters for the reaction showed that, whereas the activation energies for mercuration and thallation are approximately equal, the activation entropy is much higher in absolute magnitude for thallation (−11.9 cal mol^{-1} K^{-1}) than for mercuration (−1.2 cal mol^{-1} K^{-1}). The appreciable, compared with mercuration, charge transfer in the intermediate (A) is responsible for this effect. Ultimately the stability of the complex (A) is higher than the stability of the analogous complex in the mercuration reaction and this contributes to the entropy factor.

Table 2. The values of K_1 and k_2 for the thallation of the arenes C_6H_5R.[15]

No.	R	10^2k_2, s^{-1}	K_1, litre mol^{-1}
1	H	1.04	1.9
2	Me	0.166	2.7
3	Et	10.1	10.7
4	t-Bu	12.3	12.9
5	F	0.176	1.18
6	Cl	0.0733	0.70
7	Br	0.0469	0.89

The thallation of a series of aromatic substrates by TTFA in TFAA, leading to a disubstituted product, has been investigated.[16] Dithalation takes place in the presence of an excess of $Tl(OCOCF_3)_3$; 2,4-bis[(trifluoroacetato)thallio]anisole and 2,4-bis-[(trifluoroacetato)thallio]phenetole were isolated in the case of anisole and phenetole in 70 and 50% yields respectively. The complete dithalation of thiophen has been achieved in acetonitrile; the occurrence of dithallation has been demonstrated by the formation of diiodothiophen. Partial dithallation of benzene, toluene, and *m*-xylene has been observed when they were treated with an excess of TTFA in boiling TFAA.

In the thallation of anisole with an equivalent amount of TTFA, Deacon et al.[16] observed that an appreciable amount of the *para*-substitution product is formed in the first stage of the reaction and that only then is there an increase in the content of the *o*-thallated anisole, which is apparently more stable by virtue of the intramolecular oxygen—thallium coordination with formation of a four-membered chelate ring:



The authors support their view that the thermodynamic stability of *o*-anisylthallium bis(trifluoroacetate) is higher than that of its *p*-isomer by the results of a study[17] in which the interaction of phenylthallium bis(trifluoroacetate) with anisole, leading to the formation of *o*-anisylthallium bis(trifluoroacetate), was described. It is suggested[16] that reaction (2) proceeds via a mechanism different from that of the rearrangement of the *p*-thallated product to the *m*-isomer or of the preferential *ortho*-thallation of substituted arenes via five- and six-membered chelate rings.[3]

It has been suggested that thallium(III) trichloroacetate in trichloroacetic acid be used to thallate benzene and toluene.[18] The reaction takes place smoothly at room temperature, the yields of the

products are about 70%, and the ratios of the isomers for toluene are *ortho : meta : para* = 9 : 5 : 86. However, the synthetic use of the thallium(III) trichloroacetate/trichloroacetic acid system is limited by the electronic influence of the substituents in the aromatic ring. Thus anisole, nitrobenzene, and methyl benzoate do not enter into the thallation reaction under the given conditions.

It has been noted[6,10,11] that the aromatic radicals are coupled to form biaryls in the interaction of arenes, activated by electron-donating substituents, with TTFA and that for many arenes of this kind the above reaction predominates over the electrophilic thallation process (see below). A method has been proposed[19] for the thallation of activated arenes. The suppression of oxidative dimerisation is achieved by using TTFA in an ether/TFAA mixture. The coloured ethereal solution of TTFA and the substrate is usually treated with TFAA before the formation of a colourless solution and the precipitation of a deposit (the thallated arene) or the substrate is added to TTFA in a 2/1 ether/TFAA mixture.

Whereas a whole series of thallating agents in different media can be used for the thallation of arenes activated by electron-donating substituents, the direct thallation of polyfluoroarenes is extremely difficult owing to the inactivity of the aromatic ring with respect to electrophilic substitution. Direct thallation of polyfluoroarenes has been achieved by using a new thalating agent—thallium(III) triflate:[20,21]

$$RH + Tl(O_3SCF_3)_3 \xrightarrow{CF_3COOH} RTl(O_3SCF_3)_2 + CF_3SO_3H,$$
$$R = p\text{-}MeOC_6F_4,\ p\text{-}MeC_6F_4,\ m\text{-}HC_6F_4,\ p\text{-}HC_6F_4,\ C_6F_5,\ 3,5\text{-}H_2C_6F_3,\ 3,6\text{-}H_2C_6F_3.$$

The authors established a qualitative reactivity series for the arenes investigated in the thallation reaction:

$$C_6H_6 > p\text{-}MeOC_6F_4H > 1,2,4\text{-}F_3C_6H_3 \cong 1,3,5\text{-}F_3C_6H_3 > m\text{-}H_2C_6F_4;$$
$$p\text{-}MeC_6F_4H > o\text{-}H_2C_6F_4 > C_6F_5H \geqslant p\text{-}H_2C_6H_4 > m\text{-}O_2NC_6F_4H.$$

They were unable to isolate polyfluorophenylthallium bis(trifluoromethanesulphonates) in a pure form because, after the removal of the solvent, the product remained contaminated by trifluoroacetate impurities and the attempt at crystallisation led to the symmetrisation of the product to bis(pentafluorophenyl)thallium salts. The direct thallation products are therefore characterised by NMR, conversion into the corresponding aryl iodides by treatment with KI, and symmetrisation to bis(pentafluorophenyl)thallium salts.

The highest yield of thallation products was attained in boiling TFAA, but under these conditions *m*-BrC_6F_4H and *m*-$O_2NC_6F_4H$ do not react. The use of trifluoromethanesulphonic acid as the solvent leads to the oxidation of the substrates by the thallium(III) salts to the corresponding phenols. Although, after the conversion of the thallation products by treatment with $Tl(O_3SCF_3)_3$ to aryl iodides the yields of the latter are high, presumably the degree of thallation of polyfluoroarenes is in fact higher still, since a reaction of polyfluorophenylthallium salts with I^-, in which iodine-containing products are not formed, is known.[22]

2. Substitution of the Anion in Arylthallium Bis(trifluoroacetates)

One of the known methods of synthesis of compounds of the type $ArTlX_2$ involves the substitution of the anion in arylthallium bis(trifluoroacetates). The stability of compounds of the type $ArTlX_2$ as a function of the nature of X has been investigated.[23] When X = I, arylthallium compounds are extremely unstable, which had been noted earlier (see, for example, McKillop et al.[2]), so that their decomposition is a preparative method of synthesis of aryl iodides and constitutes a test reaction for the thallation of the aromatic ring. However, one should note the relative stability of $C_6F_5TlI_2$. A stable compound containing the ArTlI fragment has been synthesised.[24] The Ar—Tl—I bond system is stabilised by introducing into the coordination sphere a complex-forming molecule—dibenzo-18-crown-6 ether (DBC):

$$PhTlO + HClO_4 + DBC \xrightarrow{H_2O} [PhTl(DBC)OH]ClO_4 \cdot H_2O \xrightarrow[MeCN]{Na(15\text{-crown-}5)I} [PhTl(DBC)I]ClO_4.$$

The properties of stabilised complexes of the type $[p\text{-}RC_6H_4Tl(L)X]^+$, where R = H or Me, X = Cl, Br, I, SPh, or OH, and L = dibenzo-18-crown-6 ether, have been investigated.[25] For R = H and X = I, the photolysis or pyrolysis of the initial complex leads mainly to iodobenzene, while in the case where X = Br and especially Cl only insignificant amounts of the corresponding halogenobenzenes are produced:

$$[PhTl(L)I]^+ \rightleftarrows [PhTl(L)]^+ \rightarrow PhTl^+$$
$$\downarrow \qquad\qquad \downarrow I^-$$
$$Ph^- \xrightarrow{I^-} PhI$$

The reduction of the complex in which R = Me and X = OH by treatment with $P(OMe)_3$, ascorbic acid, and *N*-benzyl-1,4-dihydronicotinamide affords toluene as the main product, while the analogous reduction of the cation $ArTlX^+$, unstabilised by L, leads to Ar_2TlX.

Arylthallium dibromides are also extremely unstable and readily decompose, affording aryl bromides and small amounts of diarylthallium bromides (15—20%), while arylthallium dichlorides are extremely stable.[23]

A convenient preparative method has been developed for the synthesis of arylthallium dihalides:[26]

$$ArTlCl_2 \xleftarrow{Me_3SiCl} ArTl(OCOMe)_2 \xrightarrow{R_2SnBr_2} ArTlBr_2.$$

The yields of the dihalides obtained by this method are quantitative; the target products, precipitated during the reaction, do not require additional purification.

A method has been proposed[27] for the synthesis of arylthallium diacetates from asymmetric organotin compounds:

$$Ar_2SnR_2 + Tl(OCOMe)_3 \rightarrow ArTl(OCOMe)_2.$$

The alkyl substituent is not split off from the tin atom, the more nucleophilic aryl group being transferred to the thallium atom.

By varying the reactant ratio, it is possible to obtain by this method the acylates of both mono- and di-phenylthallium. The target products crystallise from the reaction mixture and do not require additional purification, but the use of this method is limited by the availability of the organotin compound.

Compounds of the type $ArTlX_2$, where X is a halogen or an organic acid residue, can also be obtained from organomercury, organotin, and organoboron compounds. These methods of synthesis are generally accepted and have been described in detail in a monograph.[28]

II. SYNTHESIS OF COMPOUNDS OF THE TYPE AR_2TlX

1. Synthesis with the Aid of Organometallic Compounds

Compounds of the type Ar_2TlX are the most widely distributed class of organothallium compounds. There exists a whole series of methods of synthesis of these thallium(III) derivatives from organolithium, -magnesium, -zinc, -mercury, -boron, -aluminium, and -tin compounds, the procedures involved in the use of which have been described in detail in a monograph.[28] Methods in which organolithium, -magnesium, -boron, and -mercury compounds are used are the most convenient among them for the preparation of diarylthallium salts:

$$2ArM + TlX_3 \rightarrow Ar_2TlX + 2MX,$$
$$M = Li, MgX, B(OR)_2, HgAr.$$

In recent years, diarylthallium compounds have been synthesised via other organometallic derivatives not so much for the preparation of previously unknown diarlythallium salts as with the aim of creating model compounds for physicochemical studies, e.g. X-ray diffraction. Thus the X-ray diffraction analysis of the complexes of bis(pentafluorophenyl)thallium chlorides and bromides with triphenylphosphine oxide has been carried out.[29,30] Bis(pentafluorophenyl)thallium chlorides and bromides were obtained from thallium(III) salts and the pentafluorophenyl Grignard reagent. The complexes investigated are dimeric compounds with asymmetric chlorine bridges; the thallium atom in these compounds has a coordination number of 5.

The synthesis of diarylthallium trifluoroacetates from TTFA and arylmagnesium halide leads to the target products in satisfactory yields (50–70%), but it takes place in several stages owing to the difficulty of exchanging the Br^- anion for trifluoroacetate:[31]

$$ArMgBr \xrightarrow[Et_2O]{Tl(OCOCF_3)_3} Ar_2TlBr \xrightarrow[EtOH-H_2O]{KOH} Ar_2TlOH \xrightarrow{CF_3COOH} \rightarrow Ar_2Tl(OCOCF_3).$$

The symmetrisation of monoarylthallium derivatives is a more convenient method of synthesis of diarylthallium trifluoroacetates.

2. Symmetrisation of Monoarylthallium Salts

The spontaneous disproportionation of compounds of the type $ArTlX_2$ to Ar_2TlX is widely known,[28] but it had not been used previously as a preparative method. In many cases symmetrisation is a more convenient method than organometallic synthesis. Thus, in order to obtain diarylthallium trifluoroacetates via a Grignard reagent, a three-stage synthesis is required,[31] while refluxing of arylthallium bis(trifluoroacetate) in acetone for 30 min affords diarylthallium trifluoroacetates in 50–90% yields:[31]

$$2ArTlX_2 \rightarrow Ar_2TlX + TlX_3,$$
$$Ar = 4\text{-}MeC_6H_4, 3.4\text{-}Me_2C_6H_3, 2.4\text{-}Me_2C_6H_3, 2,5\text{-}Me_2C_6H_3; X = CF_3COO$$

It has been suggested that trimethyl phosphite, under the influence of which diarylthallium trifluoroacetate is formed from ArTl.$(OCOCF_3)_2$ in several minutes at room temperature in a nearly quantitative yield, be used as the symmetrising agent.[23]

An attempt was made later[32] to investigate the mechanism of the disproportionation of monoarylthallium compounds. It had been suggested earlier[23] that the role of trimethyl phosphite consists in reducing TlX_3 to a thallium(I) compound, which displaces an equilibrium of the type:

$$2ArTlX_2 \rightleftarrows Ar_2TlX + TlX_3.$$

According to the authors,[32] this reaction mechanism is unlikely, because they failed to observe spectroscopic evidence for the spontaneous disproportionation of the starting material. They therefore assumed that the complex $RTlX_2.P(OR)_3$ is formed in the first stage, as a result of which the electron density on the Tl atom increases and the reduction of thalium(III) to thallium(I) is promoted. It is suggested that in this complex the carbon–thallium bond becomes more accessible to electophilic attack by a proton or another thallium atom. However, it is not clear at which stage of the reaction such attack takes place—before reduction, synchronously with reduction, or after it. According to the authors, the electrophilic attack by a proton before the reduction of thallium(III) is unlikely, since the initial complex $RTlX_2.L$ should interact more readily with the electrophile than the product $R_2TlX.L$, and yet it is stable under the protolysis conditions.

The interaction of $RTl(OAc)_2$ with nucleophiles capable of coordination can also lead to the symmetrisation of the starting material instead of the expected nucleophilic substitution of thallium:[32]

$$RTl(OAc)_2 + NaSPh \rightarrow R_2TlX.$$

The authors were unable to determine the nature of X, but they suggest that it is a thiophenoxide.

It is noteworthy that phosphorous acid esters are not universal symmetrising agents for arylthallium compounds. Polyfluorophenylthallium bis(trifluoromethanesulphonates) are not symmetrised on refluxing in acetone and on treatment with $P(OR)_3$ but such symmetrisation can be readily achieved by treatment with sodium acetate in boiling water, affording bis(polyfluorophenyl)thallium acetate.[21] $(3,5\text{-}H_2C_6F_3)Tl(O_3SCF_3)_2$, which does not undergo symmetrisation but exchanges the anion and the metal atom, affording as a result the corresponding diacetate, is an exception.

3. Reactions Associated with the Exchange of an Anion at the Thallium Atom

The substitution of an anion at a thallium atom is an extremely convenient preparative method of synthesis of various diarylthallium salts. Of the relatively recent studies, mention should be made of the synthesis of various derivatives of bis(polychlorophenyl)-thallium:[33]

$$(C_6Cl_5)_2TlCl + AgX \rightarrow (C_6Cl_5)_2TlX + AgCl;$$
$$X = MeCOO, ClO_4, 1/2SO_4.$$

Bis(pentachlorophenyl)thallium perchlorate proved to be a convenient starting compound for the substitution of an anion, which cannot be achieved by treating $(C_6Cl_5)_2TlCl$ with silver salts:

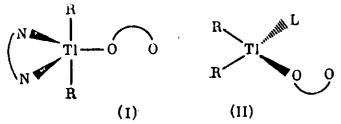
$$(C_6Cl_5)_2TlClO_4 + KX \rightarrow (C_6Cl_5)_2TlX + KClO_4;$$
$$X = I, Br, CN.$$

The substitution of an acetate residue by a halogen can be readily carried out by treating diarylthallium acylates with Me_3SiCl or R_2SnBr_2.[26] A new method of synthesis of such acylates has been proposed.[27]

Bis(pentafluorophenyl)thallium compounds $(C_6F_5)_2TlX$ (X = $CF_3COCHCOMe$, $CF_3COCHCOCF_3$, or PhCOCHCOMe) have been obtained by the reaction of $(C_6F_5)_2TlBr$ with the salts of diketones. They form stable complexes with αα-bipyridyl (bipy) and *o*-phenanthroline (phen).[34] The thallium salts of sulphinic acids, obtained as a result of ion exchange, also form stable complexes with bipy and phen:[35]

$$Ar_2TlBr + AgO_2SR \rightarrow Ar_2TlO_2SR + AgBr,$$
$$Ar = C_6H_5, C_6F_5;\ R = C_6H_5,\ 4\text{-}MeC_6H_4.$$
$$Ar_2TlO_2SR + L \rightarrow Ar_2Tl(L)O_2SR,$$
$$L = bipy,\ Ph_3PO,\ Ph_3AsO,\ phen.$$

The structure (I) with a 5-coordinated thallium atom for the complex with a bidentate ligand and the structure (II) for the complex with a monodentate ligand have been proposed from IR and NMR data:[35]



(I) (II)

The authors[35] also synthesised thallium(I) salts of sulphinic acids, but spectroscopic data do not provide a clear idea about their structure.

On heating, the thallium salts of sulphinic acid readily evolve SO_2, which has been used to synthesise bis(polyfluorophenyl)thallium acetates:[36]

$$2C_6F_nH_{5-n}SO_2Li + 3Tl(OCOCF_3)_3 \xrightarrow{MeCO_2H} (C_6F_nH_{5-n})_2TlO_2CMe +$$
$$+ CF_3COOH + 2SO_2 + 2LiOCOCF_3.$$

It has been found[35] that the highest yields of the target product are attained when the ratio of the initial reactants is Li : Tl = 2 : 3.

Later the reaction developed in the above study[36] was used to synthesise various dimesitylthallium salts.

Bis(polyfluorophenyl)thallium polyfluorobenzoates have been obtained by substituting an anion at the metal atom:[38]

$$R_2TlX + NaO_2CR \rightarrow R_2TlO_2CR + NaX;$$
$$R = C_6F_5, p\text{-}MeOC_6F_4, p\text{-}HC_6F_4, o\text{-}HC_6F_4, m\text{-}HC_6F_4.$$

4. The Synthesis of "Mixed" Diarylthallium Compounds Ar(Ar')TlX

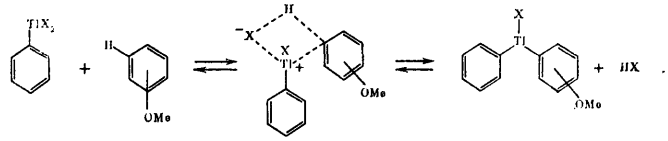
"Mixed" diarylthallium compounds Ar(Ar')TlX have been obtained by the reaction of monoarylthallium salts with aryl-boronic acids:[39,40]

$$ArTlX_2 + Ar'B(OH)_2 \rightarrow Ar(Ar')TlX.$$

They are less stable than Ar_2TlX and disproportionate after a time:

$$2Ar(Ar')TlX \rightarrow Ar_2TlX + Ar'_2TlX.$$

The thallation of anisole by phenylthallium bis(trifluoroacetate), leading to the formation of a mixed product—phenyl(anisyl)-thallium trifluoroacetate—has been investigated.[41] The formation of the target product was inferred from the amount of phenyl and anisyl iodides after treating the reaction mixture with the I_2/KI system. The authors propose the following process mechanism:



The use of chlorobenzene as the substrate does not lead to a "mixed" phenyl(chlorophenyl)thallium product and only the exchange of the aryl groups at the metal atom is observed:

$$PhCl + PhTlX_2 \rightleftarrows ClC_6H_4TlX_2 + PhH.$$

An analogous exchange of the aryl groups at the thallium atom had been noted earlier.[17]

"Mixed" aryl(*B*-carbaboranyl)thallium salts have been synthesised in accordance with the scheme[42]

$$RC{-}CR + PhMgBr \rightarrow RC{-}CR$$
$$B_{10}H_9Tl(OCOCF_3)_2 \qquad B_{10}H_9Tl(Br)Ph$$

III. SYNTHESIS OF TRIARYLTHALLIUM COMPOUNDS Ar_3Tl

Virtually no new methods of synthesis of compounds of the type Ar_3Tl have been proposed during the last 15 years. This is because the traditional methods of synthesis of such compounds,[28] especially via the organolithium, organosodium, and organomagnesium compounds, are sufficiently convenient and the use of triarylthallium derivatives in synthesis is insignificant. Nevertheless, several recent studies were devoted to the synthesis of compounds of the type Ar_3Tl.

Tris(polyfluorophenyl)thallium compounds have been obtained by the reaction of bis(polyfluorophenyl)thallium salts with metallic compounds:[43]

$$2R_2TlBr + 2Cu + C_4H_8O_2 \rightarrow 2R_3Tl \cdot C_4H_8O_2 + TlBr + 2CuBr.$$

The replacement of the complex-forming solvent (ether, dioxan) by toluene alters significantly the course of the reaction:

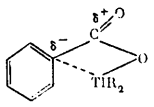
$$(C_6F_5)_2TlBr \xrightarrow[PhMe]{Cu} (C_6F_5)_2 + TlBr.$$

The attempts to symmetrise R_2TlBr, where R = *o*-HC_6F_4 or 2,5-$H_2C_6F_3$, were unsuccessful. The authors suggest that R_3Tl is formed via an intermediate organocopper compound. This hypothesis is supported by the formation of $(C_6F_5)_2$ in toluene, since it is known that bis(pentafluorophenyl)thallium bromide does not by itself decompose on refluxing in toluene.[44] In view of the dependence of the symmetrisation on the degree of substitution of the aromatic ring by fluorine atoms, the authors suggest the involvement of carbanionic species in the transition state. In their view, the reaction mechanism involves the coordination of thallium to copper atoms, the subsequent transfer of the polyfluorophenyl group to

copper, and electron transfer from thallium to copper:

$$R_2TlBr + Cu \rightarrow 2RCu + TlBr,$$
$$R_2TlBr + RCu \rightarrow R_3Tl + CuBr.$$

A convenient method of synthesis of tri(polyfluorophenyl)thallium involves the refluxing of bis(polyfluorophenyl)thallium benzoate in pyridine.[38] The rate of decarboxylation diminishes in the following sequence of groups R: $C_6F_5 \simeq p\text{-}MeOC_6F_4 > p\text{-}HC_6F_4 > m\text{-}HC_6F_4 \gg o\text{-}HC_6F_4$, i.e. with decrease in the -I effect of the group. This finding shows that the aryl residue in the transition state is carbanionic:



(III)

Another possible process mechanism involves the participation of the free carbanion, which captures the R_2Tl^+ species faster than it can decompose:

Scheme 6

$$R_2TlO_2CR \rightleftarrows R_2Tl^+ + RCO_2^-;\ RCO_2^- \rightarrow R^- + CO_2;$$
$$R^- + R_2Tl^+ \rightarrow R_3Tl;\ R^- + R_2TlO_2CR \rightarrow R_3Tl + RCO_2^-.$$

The rapid decarboxylation of pentafluorophenylbenzoic acid in pyridine, which apparently proceeds via pyridinium pentafluorophenylbenzoate, supports Scheme 6 according to the authors, although the formation of ion pairs may lead to a transition complex of type (III). Pyrolysis of R_2TlO_2Cr without a solvent leads to a significant yield of R_3Tl only for R = C_6S_5 (40%), while in the remaining cases the reaction products are polyarylenes.

The stability of tris(polychlorophenyl)thallium in air was unexpected.[45] The synthesis of stable compounds containing four pentafluorophenyl groups at the thallium atom has been described:[46]

$$Tl(C_6F_5)_2Br + 2C_6F_5Li \xrightarrow{QX} Q[Tl(C_6F_5)_4],$$
$$X = Cl, Br;\ Q = Et_4N,\ Ph_3PCH_2Ph.$$

The preparation of complexes of the type $R_3Tl(diox)$, where R = C_6F_5 or 2,4,6-$F_3C_6H_2$, has been described.[47] For R = C_6F_5, the reaction of RLi with $TlCl_3$ leads to a mixture of the products $Bu_4N[TlR_4]$ and $(Bu_4N)_3[TlR_6]$, while in the case where R = 2,4,6-$F_3C_6H_2$, the product is exclusively R_3Tl. The complexes $R_3Tl(diox)$ have been obtained either by adding dioxan to R_3Tl in ether (R = 2,4,6-$F_3C_6H_2$) or in accordance with the scheme

$$Bu_4NTl(C_6F_5)_4 + HBF_4 \xrightarrow{dioxan} Tl(C_6F_5)_3(diox) + Bu_4NBF_4 + C_6F_5H.$$

The reactions involving the substitution of the dioxan ligand lead to:

(a) neutral thallium(III) complexes:

$$R_3Tl(diox) + L \rightarrow R_3Tl(L) + diox;$$
$$L = Ph_3PO,\ Py,\ PPh_3,\ (Ph_2P)_2CH_2;$$

(b) anionic complexes:

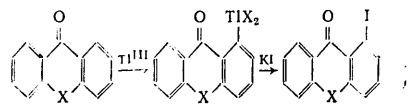
$$R_3Tl(diox) + QX \rightarrow Q[TlR_3(X)] + dioxan;$$
$$Q = Bu_4N,\ (PPh_3)_2N;\ X = Cl, CN;$$
$$Q[TlR_3(CN)] + AgX \xrightarrow{-AgCN} \begin{cases} \xrightarrow{X=Cl} QX + TlR_3 \\ \xrightarrow{X=CF_3COO} Q[TlR_3(X)] \end{cases},$$

(c) anionic complexes with a thallium–transition metal bond:

$$R_3Tl(diox) + QM^* \rightarrow Q[R_3Tl{-}M^*] + dioxan$$
$$R = 2,4,6\text{-}F_3C_6H_2,\ M^* = [MoCp(CO)_3]^-,\ [WCp(CO)_3]^-,\ [Mn(CO)_5]^-;$$
$$R = C_6F_5,\ M^* = [MoCp(CO)_3]^-,\ [WCp(CO)_3]^-.$$
$$Tl(C_6F_5)_3 + QM^* \rightarrow Q[(C_6F_5)_3Tl{-}M^*],$$
$$M^* = [Co(CO)_4]^-.$$

IV. APPLICATIONS OF ARYLTHALLIUM(III) COMPOUNDS IN ORGANIC SYNTHESIS

The possibility of substituting the thallium atom in arylthallium derivatives by an organic group has opened a pathway to the selective introduction of a substituent into the aromatic ring, since thallation itself is a selective process. McKillop, Taylor, and coworkers[1] have shown that, when arylthallium bis(trifluoroacetates) are treated with KI, the iodine atom replaces thallium in the aromatic ring. The thallation-iodination reaction has been used successfully for the selective introduction of iodine into the aromatic ring of diaryl ketones:[48]



X=CMe_2, $(CH_2)_2$, S.

The intermediate arylthallium compound formed when an organic substituent is introduced into the aromatic ring is not always isolated. Thus, in the synthesis of phenols,[49] the authors began with the corresponding arenes and TTFA:

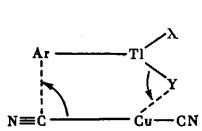
$$PhH \xrightarrow[CF_3COOH]{Tl(OCOCF_3)_3} PhTl(OCOCF_3)_2 \xrightarrow[PPh_3]{Pb(OAc)_4} PhOCOCF_3 \xrightarrow{NaOH} PhOH.$$

The yields of the phenols were 50–80%.

The attempt to obtain aromatic nitriles by the pyrolysis of $[ArTl.(CN)_3]K$ or $ArTl(CN)_2$ ws unsuccessful but the photolysis of a 1% aqueous solution of arylthallium bis(trifluoroacetate) in the presence of 25 equivalents of KCN led to the formation of aromatic nitriles in 50–80% yields. Traces of benzene, cyanobiphenyl, and phenol were detected as side products in the reaction mixture.[49] In order to obtain cyanoarenes, the reaction of $ArTl(OAc)ClO_4H_2O$ with bivalent or monovalent copper cyanides was also used[50] (Scheme 7, see below):

$$ArTlX_2 \xrightarrow[MeCN(pyridine)]{CuCN(Cu(CN)_2)} ArCN.$$

The highest yields of aryl cyanides are obtained when pyridine is used as the solvent. A free radical pathway to the formation of aryl cyanides is thought[50] to be unlikely since neither biphenyl nor benzene were detected in the reaction mixture. Nor were the transfer of the aryl group to acrylonitrile and the polymerisation of acrylonitrile observed. According to the authors, the interaction of the substrate with $Cu(CN)_2$ proceeds via the cyclic transition state

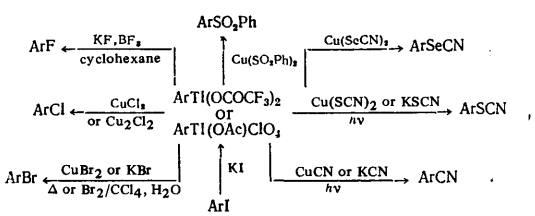


In contrast to the method of Uemura et al.,[50] which is limited by the relatively weak thallating capacity of $Tl(OAc)_2ClO_4$, Taylor et al.[51] obtained the nitriles over a wide range of arenes, both electron-deficient and electron-saturated. An increase in the types of aromatic substrates has been achieved[51] by using a more universal thallating agent—TTFA. The essential feature of the method consists in the refluxing of the thallated substrate with CuCN in acetonitrile for 2–17 h. The proposed reaction mechanism is

$$PhTlX_2 \xrightarrow[-[Cu^{II}CN]^+]{CuCN} [PhTlX \xrightarrow[-TlX]{} Ph^{\cdot}] \xrightarrow[-Cu^+]{^{\cdot}CuCN} PhCN.$$

The intermediate formation of an aryl complex of thallium(II) is postulated; the homolysis of the C–Tl bond in the complex leads to the formation of Ar·—an intermediate in the Rosenmund–von Braun reaction. In those cases where thallation in acetonitrile is impossible, the reaction was carried out in two stages: (1) thallation by treatment with TTFA in TFAA and isolation of the thallated products; (2) reaction with CuCN in acetonitrile; if the thallation is carried out in acetonitrile, the isolation stage is not required and the interaction with CuCN takes place *in situ*. The yields of the nitriles are 60–90% (Scheme 7):

Scheme 7



Aryl thiocyanates have been obtained by the photolysis of a solution of arylthallium bis(trifluoroacetates) in the presence of potassium thiocyanate[52] and on refluxing $ArTl(OAc)ClO_4$ with $Cu(SCN)_2$ in dioxan:[53]

$$\left.\begin{array}{l} ArTl(OCOCF_3)_2 \xrightarrow{h\nu, KSCN} \\ ArTl(OAc)ClO_4 \xrightarrow{Cu(SCN)_2} \end{array}\right\} \rightarrow ArSCN.$$

The yields of aryl thiocyantes are 50–80%.

Phenyl and tolyl selenocyanates have been obtained from phenyl- and tolyl-thallium bis(trifluoroacetates) by treatment with Cu(SeCN) in dioxan.[18]

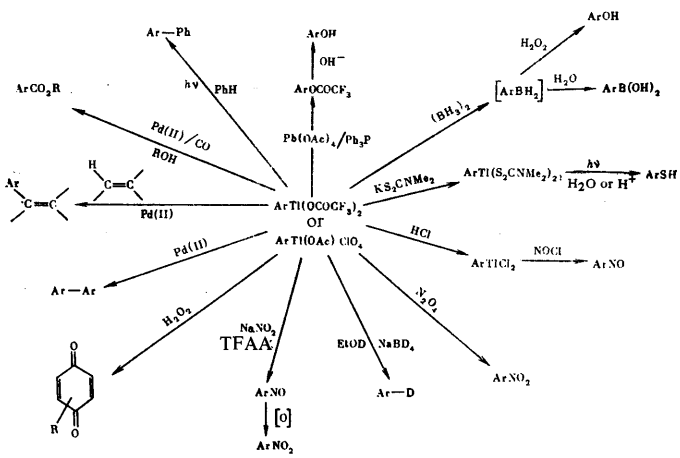
Arylthallium bis(trifluoroacetates) proved to be convenient initial compounds for the preparation of nitrosoarenes:[54]

$$ArTl(OCOCF_3)_2 \xrightarrow{HCl} ArTlCl_2 \xrightarrow[CHCl_3]{NOCl} ArNO.$$

Since the thallium derivatives of substituted arenes can be isolated comparatively readily in an isomerically pure form, this method is very much more selective than the direct nitrosation of arenes.

Nitroarenes have been obtained for the reaction of arylthallium bis(trifluoroacetates) with NO_2 [55] (yields 50–90%) (Scheme 8, see below). It has been shown in relation to tolylthallium bis(trifluoroacetates) that the main reaction product is *p*-nitrotoluene, but the refluxing of a solution of the thallated substrates before nitration entails some increase in the fraction of the *meta*-isomer. Treatment of the reaction mixture with NO_2 without isolating arylthallium bis(trifluoroacetate) also led to a satisfactory yield of the corresponding nitroarenes in which the *para*-product preominated. Direct nitration of arenes does not involve a selectivity as high as that which can be achieved using arylthallium compounds. Treatment of the products of the thallation of ethylbenzene with NO_2 affords nitroethylbenzenes with the isomers in the proportions $o:m:p$ = 5.3:1.7:93 for an overall yield of 76%, while the direct nitration of ethylbenzene by treatment with NO_2 in CF_3COOH leads to the isomer ratios $o:m:p$ = 42.5:2.0:55.5 for an overall yield of 11%.[55]

Scheme 8



Aromatic nitro-compounds have been obtained by the reaction of an arylthallium substrate with $NaNO_3$, KNO_2, or $AgNO_2$ in trifluoroacetic acid[56,57] (Scheme 8):

$$ArTl(OAc)ClO_4 \xrightarrow[CF_3COOH]{NaNO_2} ArNO_2.$$

It has been established for Ar-*p*-$CH_3C_6H_4$ that the nitro-group replaces the thallium atom and traces of *o*- and *m*-nitrotoluenes were not observed. In contrast to the halogenodethallation[58] and pseudohalogenodethallation[50,53] reactions (Scheme 7), the replacement of thallium by the nitro-group does not occur in organic solvents such as pyridine, dioxan, and dimethylformamide (DMF) even on refluxing. In the case of anisylthallium derivatives, the corresponding nitroarenes were obtained, but the formation of significant amounts of nitroso-derivatives was also noted. The addition of potassium dichromate to the reaction mixture makes it possible to obtain only the nitro-derivatives of anisole. The authors suggest that the action of potassium dichromate does not reduce to simple oxidation of the nitroso-group to the nitro-group; $K_2Cr_2O_7$ probably oxidises the C–Tl bond and then follows attack by NO_2^- in accordance with the scheme proposed for arylpalladium derivatives.[59]

The reaction of arylthallium diacetate with $Me_2CNO_2^-$ on irradiation by the light of a xenon lamp with ordinary glass leads to the formation of 2-arylnitropropanes:[60]

$$ArTl(OAc)_2 + Me_2CNO_2^- \rightarrow ArCMe_2NO_2.$$

The formation of the radical $C_6HMe_4NO^{\cdot}$ has been detected by EPR in the presence of nitrosodurene, which indicates a radical process mechanism:

$$ArTl(OAc)_2 + R_2CNO_2^- \rightarrow ArTlOAc + OAc^- + R_2CNO_2^{\cdot},$$
$$ArTlOAc \rightarrow Ar^{\cdot} + TlOAc,$$
$$Ar^{\cdot} + R_2CNO_2^{\cdot} \rightarrow ArCMe_2NO_2.$$

The product yields are 60–70%. In the absence of irradiation, up to 20% of arylthallium diacetate is formed.

The radical cleavage of the C–Tl bond on UV irradiation is a characteristic feature of arylthallium compounds. Thus irradiation of a suspension of arylthallium bis(trifluoroacetates) in aqueous ammonia results in the formation of aromatic amines.[61] A method of synthesis of aniline and phenol has been proposed.[62] Its essential feature consists in the reaction of the thallated arene in an aqueous or organic medium with a nucleophile (NH_3, H_2O), which results in the formation of the products of the nucleophilic substitution of thallium. The reaction was carried out at relatively low temperatures (200 °C) in steel reactors in the presence of promoting additives such as CuCl, $FeCl_2.4H_2O$, etc. When the reaction is carried out in an aqueous medium, the main products are phenols, while in methane or benzene, in the presence of a suitable promoting agent, for example, $CuCl_2$, the main product proved to be aniline.

The photolysis of arylthallium bis(*NN*-dimethyldithiocarbamates)[61] leads to thiophenols, while arylthallium difluorides are stable under the photolysis and pyrolysis conditions.[63] Fluoroarenes have been synthesised (in 40–90% yield) by refluxing arylthallium difluorides with dry BF_3 in cyclohexane (Scheme 7):[63]

$$ArTlF_2 \xrightarrow{BF_3} ArF.$$

The reaction of arylthallium substrates with palladium salts has come to be widely used in organic synthesis recently.

The interaction of monoarylthallium salts with palladium(II) chloride leads to the formation of biaryls in 40–60% yields:

$$ArTlX_2 \xrightarrow[NaOAc,AcOH]{PdCl_2} Ar{-}Ar + Pd^0 + Tl^I.$$

Apart from biaryls, ArH and ArX were detected as side products.

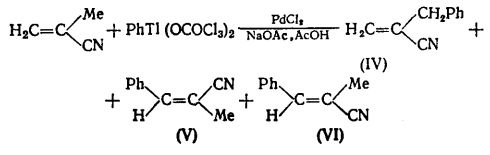
The authors showed that the nature of X does not have a significant influence on the yield of biaryls except in the case where X = Cl and Ar = Ph, where the yield of chlorobenzene is 30%.

The aryl group is transferred from arylthallium salts of olefins:[65]

$$ArTlX_2 + RCH{=}CHR' \xrightarrow[CuCl]{Li_2PdCl_4} ArCR{=}CHR';$$
Ar = Ph, *n*-MeC_6H_4, 1,3,5-$Me_3C_6H_2$; R = H, Ph;
R′ = CO_2Me, H; X = O_2CCF_3, O_2CMe, Cl, CN.

The authors showed that palladium(II) can be used in both catalytic and equimolecular amounts in relation to $ArTlX_2$. The olefins obtained have the *trans*-configuration.

The reaction of phenylthallium bis(trichloroacetates) with $PdCl_2$ in acetic acid in the presence of styrene affords exclusively *trans*-stilbene, while the analogous reaction with methacrylonitrile is not so selective:[18]



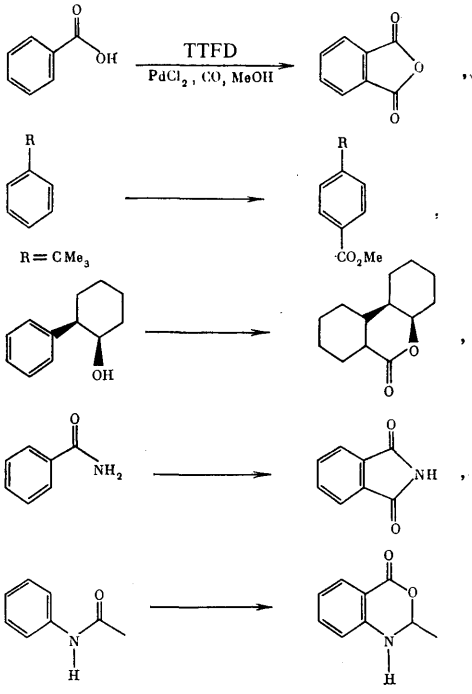
The ratios (IV):(V):(VI) = 55:26:19 are obtained. Analogous products have been prepared using metallic palladium as the catalyst.

The high selectivity of aromatic thallation and the ease of the exchange of thallium for palladium lead to extensive synthetic prospects for the use of the thallium(III)–palladium(II) system. A method has been proposed[66] for the synthesis of arenecarboxylic acids, consisting in the interaction of the arene with thallium(III) trifluoroacetate in the presence of catalytic amounts of palladium acetate under a CO pressure of 4–7 atm, but the selectivity of the method is low. The use of the analogous reaction under a CO pressure of 1 atm[67,68] made it possible to obtain a series of esters, lactones, and heterocyclic compounds, the reactions exhibiting high regio- and stereo-selectivities in many cases. In contrast to the study of Spencer and Thorpe,[65] the authors do not introduce an oxidant into the reaction mixture assuming that the zero-valent palladium formed is oxidised by the thallium(III) salt generated during the transmetallation of arylthallium bis(trifluoroacetate):

$$ArTlX_2 + PdX_4^{-2} \rightarrow ArPdX_3^{-2} + TlX_3,$$
$$ArPdX_3^{-2} + CO \rightarrow ArC(O)PdX_3^{-2},$$
$$ArC(O)PdX_3^{-2} + ROH \rightarrow ArC(O)OR + HX + Pd^0 + 2X^-,$$
$$Pd^0 + TlX_3 \rightarrow PdX_2 + TlX.$$

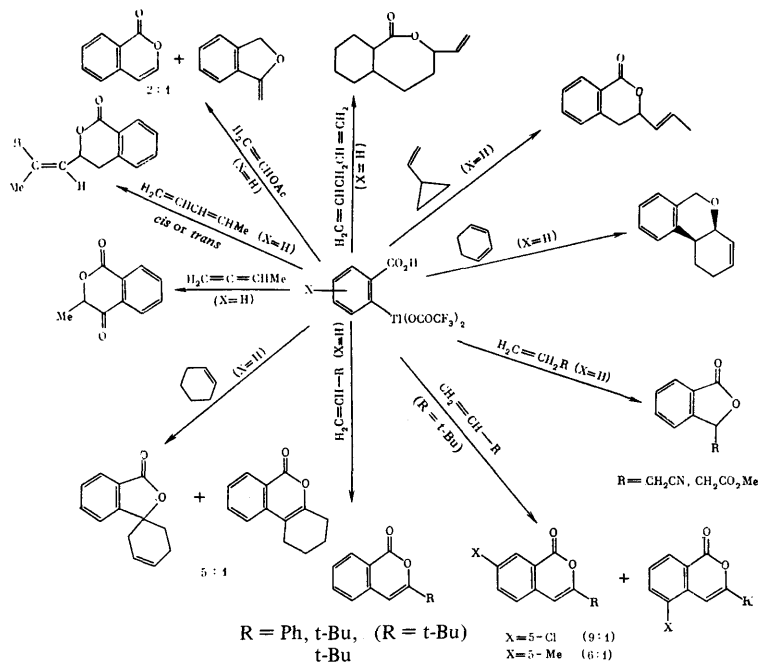
Biphenyl is a side product in this reaction, its formation being suppressed by the addition of LiCl and MgO. It has been found that the use of 0.1 of an equivalent of $PdCl_2$, 2 equivalents of LiCl, and one equivalent of MgO ensures product yields in excess of 90% (Scheme 9).

Scheme 9



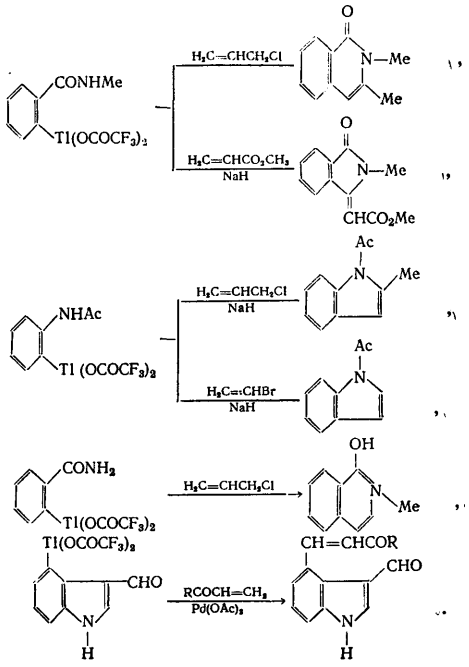
A method has also been developed for the synthesis of isocoumarins and 3,4-dihydrocoumarins from thallated benzoic acid, palladium(II) salts, and substituted olefins or cyclopropanes[69] (Scheme 10):

Scheme 10



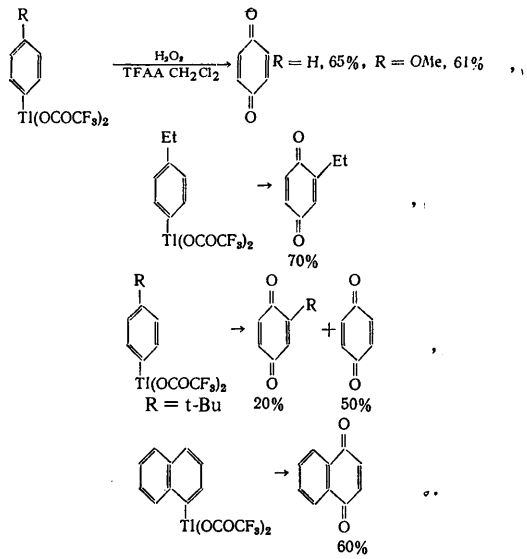
The reactions were usually carried out in acetonitrile with the ratio substrate: Li_2PdCl_4 = 1 : 1. In the successful synthetic procedure, the addition of 2 equivalents of Et_3N and Na_2CO_3 to the reaction mixture after the start of the reaction between the thallated substrate and the olefin makes it possible to cyclise the *o*-vinylbenzoic acids formed as side products to isocoumarin (Scheme 10). using an analogous method, isoquinolines and indoles have been obtained[70] (Scheme 11); the synthesis of substituted indoles containing a carbonyl group linked to the heterocyclic fragment has been described.[71]

Scheme 11



The oxidation of thallated arenes by H_2O_2 [72] is a fairly convenient method of synthesis of *p*-benzoquinones and in the course of the oxidation the alkyl substituent is either eliminated or migrates (Scheme 12).

Scheme 12



The presence of TTFA is known to ensure the selective bromination of aromatic compounds, while the oxidation of phenols by TTFA makes it possible to obtain a wide range of quinones. However, it has been shown that arylthallium derivatives were not formed in the course of these processes. The data on the bromination of arenes and the oxidation of phenols with particiption of TTFA have been surveyed.[4,73]

Ryabov et al.[74] were able to synthesise 4,4′-substituted biaryls by adding catalytic amounts of palladium(II) in the interaction of substituted arenes with TTFA:

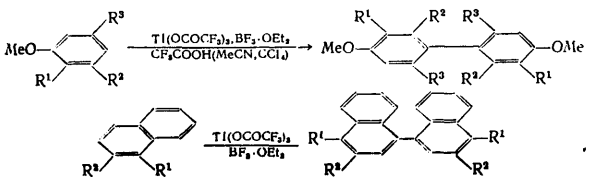
$$PhX + Tl(OCOCF_3)_3 \xrightarrow{10\%Pd(OAc)_2} XC_6H_4C_6H_4X,$$
$$X = Me, MeO, Cl, F, H.$$

The reaction takes place under mild conditions and the initial arene is used as the solvent. The proportions of the isomers in the arene coupling reaction under the influence of the TTFA/$Pd(OAc)_2$ system were investigated later[75,76] and the partial rate factors f_o, f_m, and f_p were determined in relation to the formation of bitolyl. The yield of 4,4′-bitolyl in the coupling of toluene on treatment with the Tl(III)/Pd(II) system is higher than in the presence of palladium(II) acetate or thallium(III) trifluoroacetate alone. It has been shown[76] that rapid thallation of the aromatic substrate takes place in the first stage, this being followed by the rate-limiting stage—the interaction of $ArTl(OCOCF_3)_2$ with the monomeric palladium diacetate [the $Pd_3(OAc)_6$ depolymerisation product]. The subsequent reactions of the arylpalladium intermediate lead to the observed reaction products. The thallation and transmetallation stages are characterised by rate constants which are respectively $-5.6(\sigma^+)$ and $-3.0(\sigma)$:

$$ArH + TlX_3 \rightarrow ArTlX_2 + HX,$$
$$Pd_3(OAc)_6 \rightleftarrows 3Pd(OAc)_2,$$
$$ArTlX_2 + Pd(OAc)_2 \xrightarrow{slow} ArPd(OAc) + TlX_2(OAc),$$
$$2ArPd(OAc) \xrightarrow{fast} Ar-Ar + Pd^0 + Pd(OAc)_2,$$
$$Pd^0 + Tl^{III} \xrightarrow{fast} Pd^{II} + Tl^{I}.$$

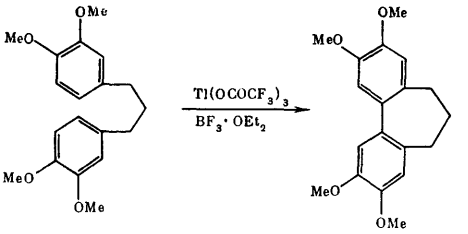
A whole series of studies have been devoted to the coupling of arenes to biaryls on treatment with arylthallium or thallium(III) salts. Thus the photolysis of arylthallium bis(trifluoroacetate) in benzene leads to asymmetric biaryls in 50–98% yields.[77] The reaction of an aromatic Grignard reagent with thallium monobromide in the tetrahydrofuran (THF)–benzene mixture affords biaryls in 70–90% yields.[78] The best reaction condition involves the addition of ArMgBr to a suspension of TlBr in the boiling solvent with the ratio ArMgBr : TlBr = 1 : 1.15. The reaction is complicated when an *o*-substituted organomagnesium compound is used; in this case, dehalogenation or the formation of diarylthallium bromide are observed. The cross-coupling of aryl groups can be achieved by this method. Thus the interaction of a mixture of phenyl- and *p*-anisyl-magnesium bromides with TlBr leads to a mixture of all the possible biaryls: 4-$MeOC_6H_4Ph$ (46%), PhPh (36%), and $(4\text{-}MeOC_6H_4)_2$ (18%).

It has been noted[6] that, when toluene is refluxed with thallium(III) acetate, a small amount of coupling products—isomeric bitolyls—is formed together with the main product—*p*-tolylthallium diacetate. The reaction of arenes containing strong electron-donating substituents with TTFA in TFAA, CCl_4, or acetonitrile with added boron trifluoride etherate leads to arene coupling products in 80–100% yields:[79]



The authors showed that the presence of electron-accepting substituents in the aromatic ring (COOR, CN, NO_2) fully suppresses the coupling reaction.

The possibility of the intramolecular coupling of aryl radicals has also been observed:

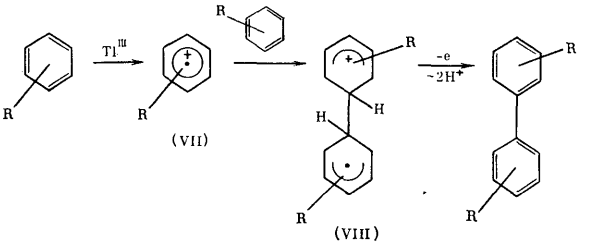


The authors put forward the hypothesis that the coupling of the aryl fragments proceeds via the intermediate formation of an aromatic radical-cation Ar^+. Data[10,11] indicating the intermediate formation of radical-cations in aromatic thallation reactions and also the formation of heptamethyldiphenylmethane (15%) in the interaction of TTFA with durene were quoted in support of this hypothesis. It is known that heptamethyldiphenylmethane is the product of the electrochemical oxidation of durene which proceeds via the intermediate formation of an aromatic radical-cation.[80]

The mechanism of the coupling of arenes on treatment with TTFA and the subsequent synthetic use of this method have been investigated in a study[81] in which five main procedures for the coupling of arenes are proposed: (1) $Tl(OCOCF_3)_3$, CCl_4, $BF_3.OEt_2$, room temperature; (2) $Tl(OCOCF_3)_3$, CCl_4, $BF_3.OEt_2$, −40–60 °C; (3) $Tl(OCOCF_3)_3$, CH_3CN, $BF_3.OEt_2$, room temperature; (4) $Tl(OCOCF_3)_3$, CF_3COOH, room temperature; (5) Tl.$(OCOCF_3)_3$, CF_3COOH, $BF_3.OEt$, room temperature. The addition of boron trifluoride etherate influences significantly the reactions in organic solvents such as CCl_4 and acetonitrile, since in their absence the coupling cannot be achieved in solvents of this kind.

The authors propose the following reaction mechanism: in the first stage an electron is transferred from the arene to TTFA with formation of the aromatic radical-cation (VII), which is followed by the electrophilic attack on the aromatic substrate by the radical-cation with formation of the intermediate (VIII), the oxidative aromatisation of which affords the biaryl (Scheme 13):

Scheme 13

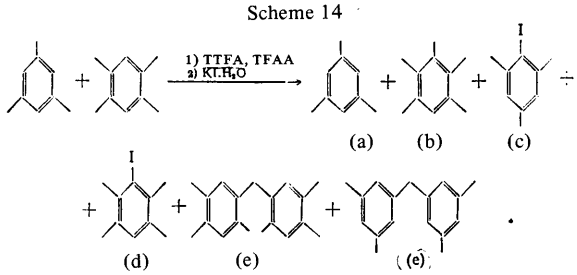


An an alternative, one can postulate that the coupling proceeds via the intermediate formation of an arylthallium compound.

The authors quote the following convincing arguments in support of the proposed mechanism:[81] (1) mesitylene and durene interact with TTFA in CF_3COOH both in the presence of added $BF_3.OEt_2$

and in its absence, but in the former case the aromatic ring is thallated while in the latter coupling leading to biaryl occurs; (2) if the biarylthallium bis(trifluoroacetate) is an intermediate in the biaryl formation reaction, one would expect that the reactivity of the arene in relation to $Tl(OCOCF_3)_3$ is determined by its basicity, whereas if the formation of the biaryl involves a one-electron transfer stage, then the factor determining the interaction of the substrate with the metal salt should be its ionisation potential. Mesitylene is a 200 times stronger base than durene but, in the competitive interaction of mesitylene and durene with TTFA, mainly the durene coupling products are formed (Scheme 14). The data in Scheme 14 are consistent with the difference between the ionisation potentials (8.4 and 8.03 eV) and also between the half-wave polarographic reduction potentials (1.85 and 1.59 eV) for durene and mesitylene respectively.

Scheme 14



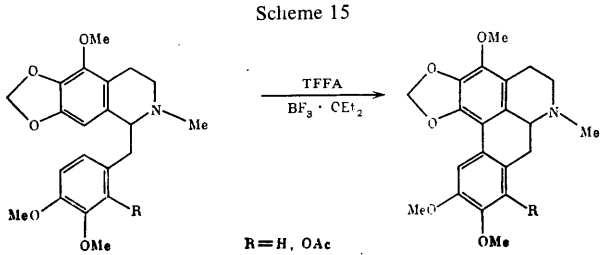
Reaction time	Yield of products, % a	b	c	d	e	f
1 h*	25.0	33.5	19.0	8.4	13.5	0.3
1 min**	38.1	52.0	0.3	0	8.5	0.1
1 h**	36.1	52.0	0	0	11.5	0.1

*Without $BF_3.OEt$. **With added $BF_3.OEt_2$.

The salts of other metals capable of accepting an electron, such as mercury(II) trifluoroacetate, iron(III) chloride, lead tetra-acetate, and $CoCF_3$, have been investigated in arene coupling reactions,[81] but the yields of biaryls obtained using them are lower than in the case where thallium(III) trifluoroacetate is employed.

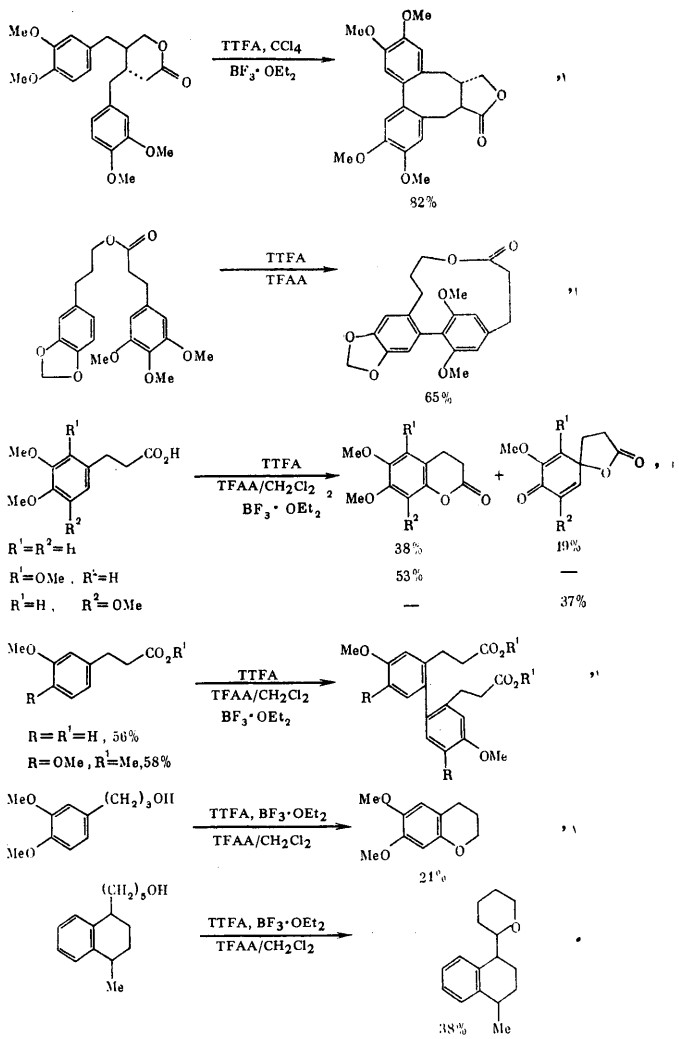
Although a C–Tl bond is in all probability not formed in the reactions involving the coupling of aryl groups on treatment with TTFA in the presence of boron trifluoride etherate, we believe it is essential to consider them briefly bearing in mind the extensive synthetic possibilities arising when this system is used. Thus, a whole series of alkaloids of the aporphine and homoaporphine series have been synthesised using the method developed by McKillop et al.:[79] (±)-ocoteine, (±)-*N*-acetyl-3-methoxynornantenine, (±)-kreysigine, (±)-*O*-methylkreysigine, and (±)-multifloramine.[82] The reactions were carried out in CH_2Cl_2 containing added $BF_3.OEt_2$: the product yields were about 50%. Scheme 15 illustrates the synthesis of (±)-ocoteine (R = H) and (±)-acetoxyocoxylonine (R = OAc) in 46 and 35% yields respectively.

Scheme 15



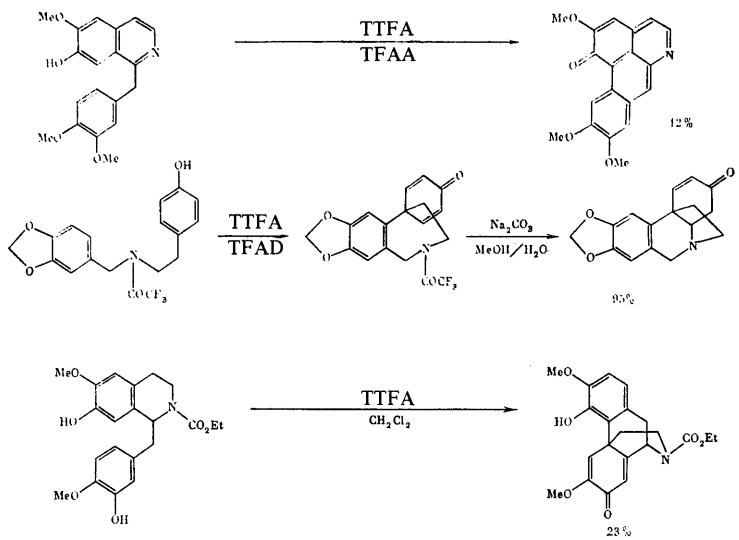
The single step synthesis of (±)-ocoteine developed by Taylor et al.[82] is simpler and the product yields are higher than in the method used previously.[83] Intramolecular cyclisation on treatment with TTFA has been used successfully for the synthesis of tetracyclic dibenzocyclo-octadiene systems[84] and also 11-and 13-membered cyclic lactones[85] (Scheme 16).

Scheme 16

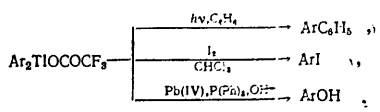


In those cases where the intramolecular coupling of the aryl fragments is impossible, the radical-cation intermediate is stabilised by the side chain or as a result of the reaction with another substrate molecule (Scheme 16). The intramolecular coupling of aromatic substrates on treatment with TTFA makes it possible to synthesise a whole series of polyarylene and spirocyclic compounds,[88–92] including certain alkaloids of the morphine series[93–95] (Scheme 17).

Scheme 17



Diarylthallium compounds can be used in organic synthesis for the preparation of asymmetric biaryls, aryl iodides, and phenols:[31]



The yields of the products are high, but the use of monoarylthallium compounds for the synthesis of biaryls, aryl iodides, and phenols appears more convenient.

Derivatives of monoarylthallium $ArTlX_2$ are the most promising and convenient starting compounds for organic synthesis. The use of diaryl- and triaryl-thallium compounds is evidently more useful in organometallic synthesis, as has been described, for example, in a monograph[28] and in two communications.[96,97]

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