THALLIUM ; ANNUAL SURVEY COVERING THE YEAR 1977

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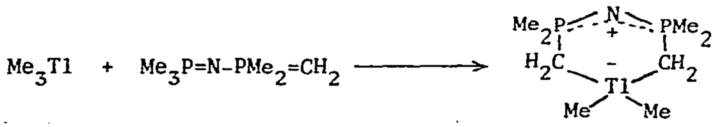
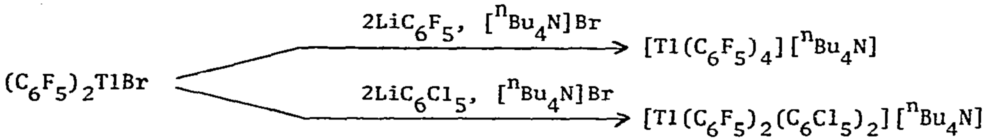
This survey will deal with 1) synthesis, structure and spectroscopy of organothallium(III) compounds, 2) thallium-metal bonded compounds, 3) reactions and kinetics, 4) organic synthesis with thallium(III) and thallium(I) compounds and 5) organothallium(I) compounds.

1. Synthesis, Structure and Spectroscopy of Organothallium(III) Compounds

A six-membered heterocycle containing a formal tetraalkylthallate moiety, I was prepared from Me_3Tl and a conjugated double ylide (1). ^1H and ^{31}P NMR data of I are described. Some pentahalophenylthallate anions have been isolated as the ammonium salts (2). Treatment of $[Tl(C_6F_5)_4][^nBu_4N]$ with $TlCl_3$ gave $[\{Tl(C_6F_5)_2Cl\}_2Cl][^nBu_4N]$ and $[Tl(C_6F_5)_3Cl][^nBu_4N]$. Bis(pentachlorophenyl)thallium derivatives, $(C_6Cl_5)_2TlX$ (X= Cl, OAc, ClO_4, 1/2 SO_4, Br, I, CN) have been prepared from C_6Cl_5Li and $TlCl_3$ and subsequent metathetical procedures (3). The cis-1,2-dicyanoethylenedithiolate complex of the dimethylthallium ion, $[Me_2Tl\{S_2C_2(CN)_2\}][Ph_4As]$, was prepared, and a preliminary IR and ^1H NMR study of this complex was reported (4). Dimethylthallium silylamide, $Me_2TlN(SiMe_3)_2$ was prepared from Me_2TlCl and $NaN(SiMe_3)_2$ in toluene (5).



I



$$(C_6F_5)_2TlBr \xrightarrow{2LiC_6F_5,\ [^nBu_4N]Br} [Tl(C_6F_5)_4][^nBu_4N]$$

$$(C_6F_5)_2TlBr \xrightarrow{2LiC_6Cl_5,\ [^nBu_4N]Br} [Tl(C_6F_5)_2(C_6Cl_5)_2][^nBu_4N]$$

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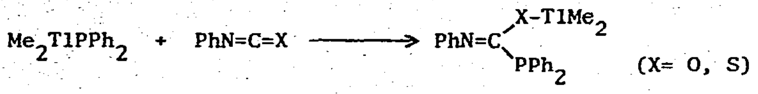
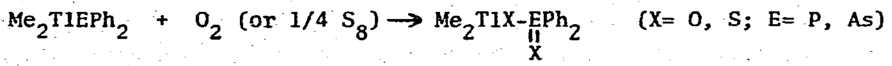
*Thallium: Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 147(1978)p.193-204.

The ^1H NMR spectrum in concentrated solution showed fast thallium-methyl exchange. The preparation and mass spectrum of $Tl[N(SiMe_3)_2]_3$ also were described. This compound reacted with HN_3 and cyclopentadiene to give $H_3[Tl(N_3)_6]$ and C_5H_5Tl, respectively. Dialkylthallium phosphides and arsenides, $R_2TlEPhR'$ (R= Me, Et; R'= Ph, H; E= P, As) were prepared from HEPhR' and R_3Tl or R_2TlNMe_2 (6). They were characterized by mass and ^1H and ^{31}P NMR spectra. Reactions of these compounds with heterocumulenes, oxygen or sulfur gave insertion products.



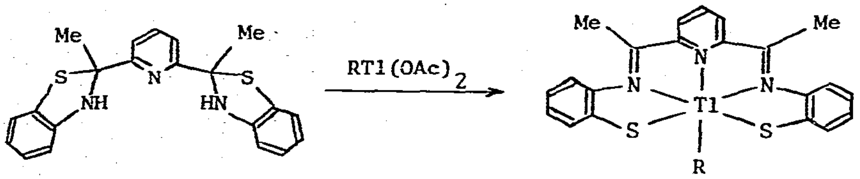
$$Me_2TlPPh_2 + PhN{=}C{=}X \longrightarrow PhN{=}C(X\text{-}TlMe_2)(PPh_2) \qquad (X= O,\ S)$$



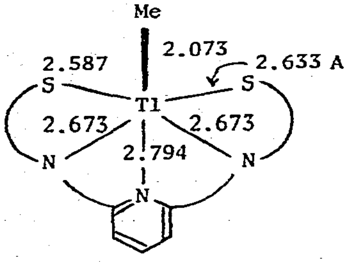
$$Me_2TlEPh_2 + O_2\ (\text{or } 1/4\ S_8) \longrightarrow Me_2TlX\text{-}\underset{\overset{\|}{X}}{E}Ph_2 \qquad (X= O,\ S;\ E= P,\ As)$$

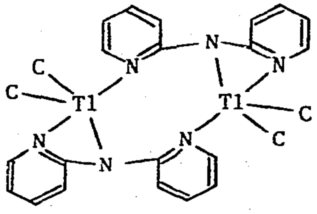
Preparation of $RTlX_2$ and R_2TlX (R= Ph, p-MeC_6H_4, p-ClC_6H_4; X= OAc, OOCPr, caproate) using aryltin compounds and TlX_3 has been described (7).

Rearrangement and deprotonation of 2,6-bis(2-methyl-2-benzothiazolinyl)-pyridine occurred upon reaction with $RTl(OAc)_2$ (R= Me, Et) to give II (8). X-ray crystallographic study of II (R= Me) showed that this complex has a highly distorted pentagonal pyramidal geometry with the methyl group occupying the axial position.



II





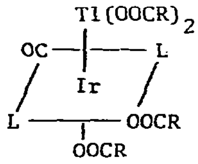
II (R= Me) III

2,2'-Dipyridylamine reacted with $(C_6F_5)_3Tl$ to give a dimeric compound, $[(C_6F_5)_2Tl\{N(C_5H_4N)_2\}]_2$ III, whose X-ray study revealed the presence of a 5-coordinate thallium atom with very distorted trigonal bipyramidal geometry (9). X-ray structural determination of $[Me_2TlX]_2$ (X= OPh, OC_6H_4Cl-o, SPh) confirmed their formulation as discrete dimers (10). No apparent correlation between the C-Tl-C angle (less than 17° deviation from 180°) and the $^{1}J_{Tl-C}$ or $^{2}J_{Tl-H}$ coupling constants in these dimethylthallium derivatives was found.

^{205}Tl, ^{13}C and ^{1}H NMR spectra were measured for $MeTl(OAc)_2$ and MeTl(CN)OAc, permitting comparison of NMR parameters in the series, $MeTlX_2$, Me_2TlX and Me_3Tl (11). ^{13}C NMR spectra of some oxythallated adducts of norbornene, norbornadiene and norborn-2-ene-5-endo carboxylic acid have been obtained and assigned (12). The substituent induced shifts (α, β, γ effects) at various carbons have been calculated and compared with those for the analogous mercury(II) compounds. A dihedral angle dependence of $^{3}J_{Tl-C}$ coupling constants was demonstrated.

2. Thallium-metal Bonded Compounds

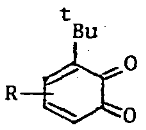
Reaction of $L_2(CO)IrX$ with $Tl(OOCR)_3$ afforded Ir-Tl bonded complexes, $L_2(CO)X(OOCR)Ir\text{-}Tl(OOCR)_2$ (L= PPh_3, $PPhMe_2$, $AsPh_3$; X= Cl, OOCR; R= Me, Et, ^{i}Pr, CF_3) (13). The proposed structure (on the basis of ^{31}P NMR and IR spectroscopy) is shown in IV. The Ir-Tl bond in these complexes was stable to H_2O, HCl, RCOOH, NH_3 and NEt_3. A catalytic reduction of $Tl(OOCR)_3$ to TlOOCR and CO_2 occurred in the presence of $L_2(CO)Rh(OOCR)$. In connection with the inhibitory effect of Tl(I) ion on hydrogen uptake by $[Co(CN)_5]^{3-}$, the presence of a Co-Tl-Co bonded complex, $[\{(CN)_5Co\}_2Tl]^{5-}$ was detected by a rapid-scan spectroscopic method (14). Attempts also were made to prepare this complex as an isolable solid.



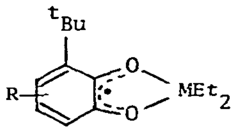
IV

3. Reactions and Kinetics

Reaction of the quinone V (R= 5-^{t}Bu, 6-^{t}Bu) with Et_3M (M= Al, Ga, In, Tl) proceeded by a one-electron transfer mechanism via a paramagnetic chelate intermediate VI (15). Thus, treating V (R= 5-^{t}Bu) with Et_3M (M= Tl, Al) gave, after hydrolysis, 86 % of a mixture of 2,4,6-$(^{t}Bu)_2(EtO)C_6H_2OH$ and 2,3,5-EtO-$(^{t}Bu)_2C_6H_2OH$. Similarly, reaction of V (R= 6-^{t}Bu) with Et_3Tl gave 2,3,6-EtO-$(^{t}Bu)_2C_6H_2OH$. Tris(tetrachlorophenyl)thallium has been used to prepare a

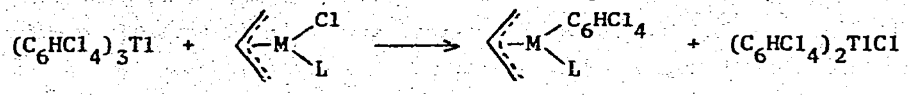


V



VI

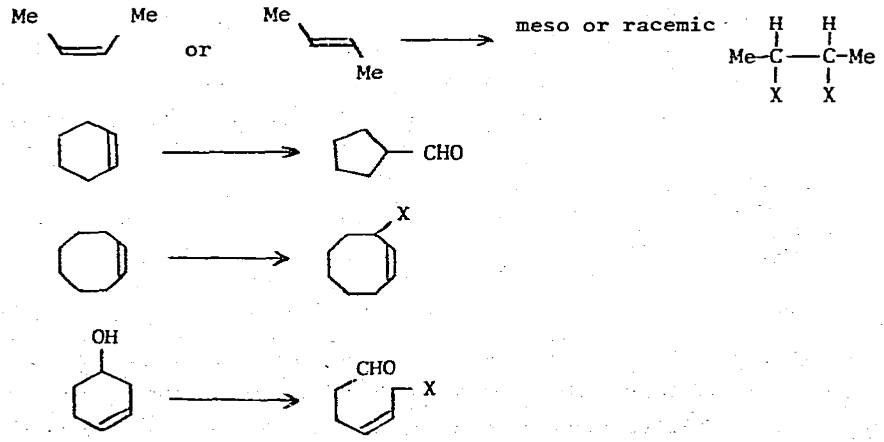
series of π-allylpalladium(II) and platinum(II) complexes, M(π-allyl)(C_6HCl_4)L (M= Pd, Pt; L= PPh_3, $SbPh_3$), model intermediates for allylic coupling by means of transition-metal complexes (16, 17).

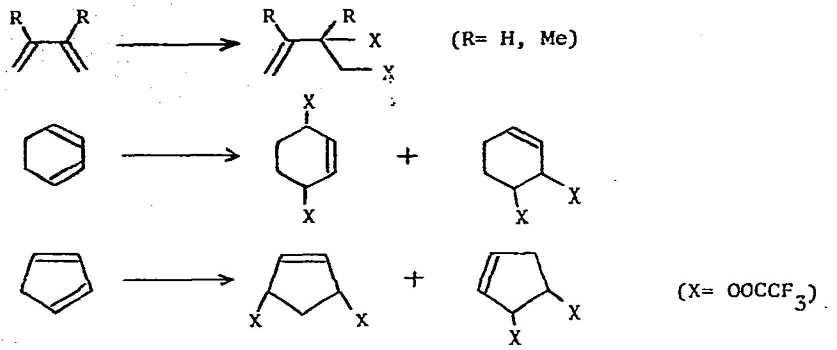


The kinetics of the decomposition of MeTl$(OAc)_2$ in pyridine or methanol containing equimolar amounts of pyridine have been studied (18). In methanol more than 90 % of N-methylpyridinium acetate and less than 10 % of methyl acetate were obtained. A bimolecular mechanism involving an S_N2 attack of pyridine and OAc^- at the methyl group of the $MeTlOAc^+$ intermediate was suggested. Nadon and Zador studied the effect of coordination around the thallium atom on the rate of decomposition of $PhCH(OMe)CH_2TlX_2$ in aqueous methanol (19). At low Cl^- concentration, the rate of oxidative decomposition decreased because of the formation of $PhCH(OMe)CH_2TlCl^+$ and $PhCH(OMe)CH_2TlCl(OH)$. At high Cl^- concentration, $PhCH(OMe)CH_2TlCl_2$ or $PhCH(OMe)CH_2TlCl_3^-$ are formed, and deoxythallation was observed. The determination of polar, steric and resonance effects in the oxidation of 32 different olefins by $Tl_2(SO_4)_3$ in water was carried out using the linear free energy relationship for the chosen set of $RCH{=}CH_2$, $RR'C{=}CH_2$ and internal olefins (20). Polar effects were the most important for the $RCH{=}CH_2$ and $RR'C{=}CH_2$ series, while both steric and resonance effects were important for the internal olefins. An aqueous medium was advantageous for the preparation of the carbonyl compounds from olefins with electron-releasing substituents.

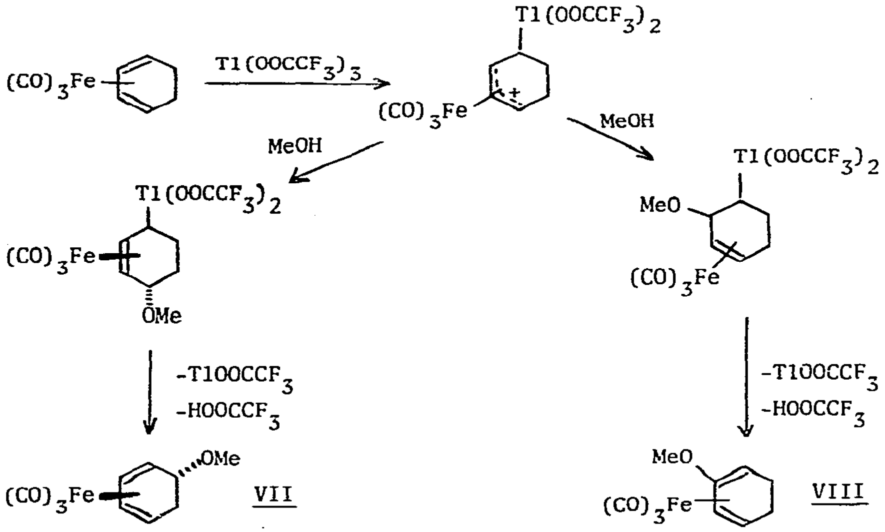
4. Organic Synthesis with Thallium(III) and Thallium(I) Compounds

Oxidation of several mono- and diolefins with $Tl(OOCCF_3)_3$ was investigated (21). Transformations examined include:





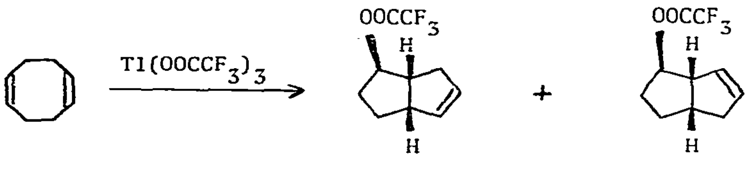
When cyclohexa-1,3-diene is coordinated to iron, oxidation with Tl$(OOCCF_3)_3$, Tl$(NO_3)_3$ or Tl$(OAc)_3$ in methanol proceeds as shown below to give VII and VIII (22).



VII

VIII

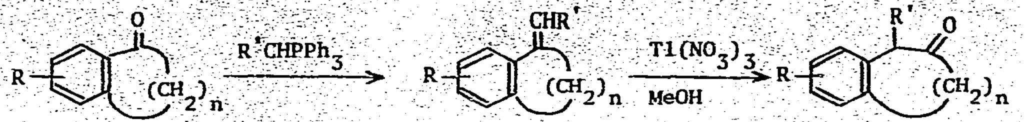
Cyclooctadiene reacted with Tl$(OOCCF_3)_3$ in CH_2Cl_2 to give transannular cyclization products, IX and X (23). A general method for regioselective



IX

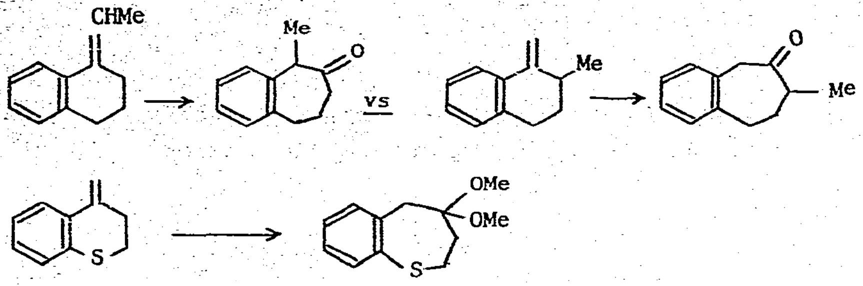
X

ring expansion of cyclic aralkyl ketones by means of the Wittig reagents and Tl$(NO_3)_3$ was described (24).

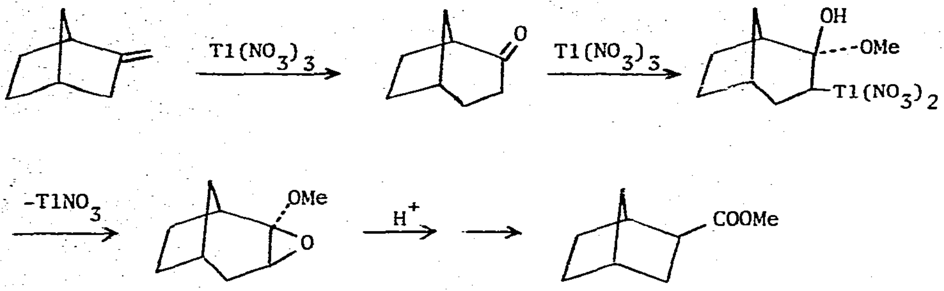


R= H, MeO; R' = H, Me, Et; n= 2, 3, 4

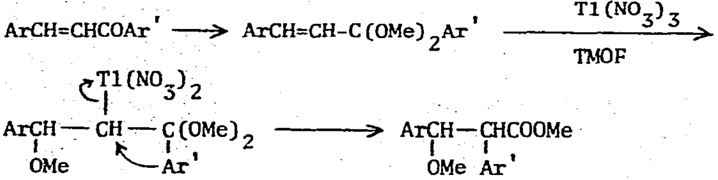
Particularly notable examples include:



2-Methylenenorbornane and $Tl(NO_3)_3$ in methanol gave a ketone which further reacted with $Tl(NO_3)_3$ to result in a stereospecific ring contraction (25).



Dimethylketals of chalcones reacted with $Tl(NO_3)_3$ in trimethyl orthoformate (TMOF) to afford XI, provided that the migratory aptitude of Ar' is moderate to good (26).

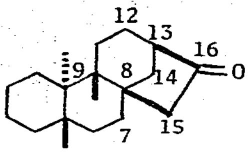


$$ArCH{=}CHCOAr' \longrightarrow ArCH{=}CH{-}C(OMe)_2Ar' \xrightarrow[TMOF]{Tl(NO_3)_3} ArCH(OMe){-}CH(Tl(NO_3)_2){-}C(OMe)_2Ar' \longrightarrow ArCH(OMe){-}CH(Ar')COOMe$$

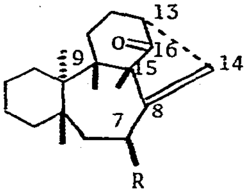
XI

Ar= Ph, Ar'= Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$;
Ar= 4-ClC_6H_4, Ar'= 4-MeC_6H_4;
Ar= 4-$NO_2C_6H_4$, Ar'= Ph, 4-$MeOC_6H_4$

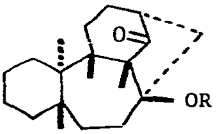
Oxidative rearrangement of ent-17-norkauran-16-one XII with $Tl(NO_3)_3$ in acetic acid gave XIII as the major product, together with XIV~XVI (27).



XII

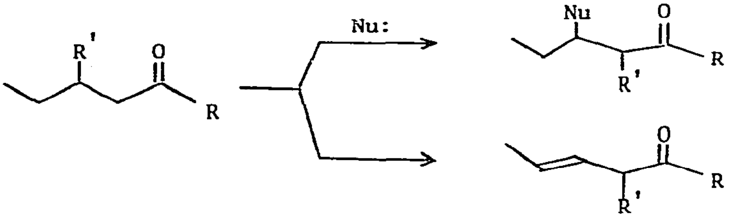


XIII (R= H)
XIV (R= OAc)

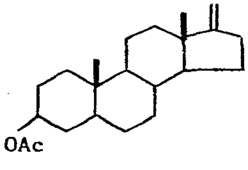


XV (R= H)
XVI (R= Ac)

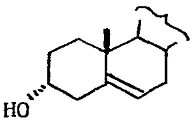
Formation of these compounds formally corresponds to a new type of rearrangement shown below.



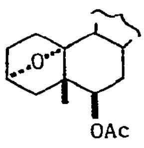
The same authors also reported oxidation of ent-kaurenes or 13β-kaurenes with $Tl(NO_3)_3$ in 1,2-dimethoxyethane where the primary products were derived by replacement of the allylic hydrogens in the parent olefins by OH or ONO_2 (28). In a comparative study of the oxidation of XVII with Hg(II), Tl(III) and Pb(IV) acetates, the methyl ethers of the allylic alcohols were the major products from the thallium oxidation (29). Among several steroidal 5-enes which were allowed to react with $Tl(OAc)_3$, XVIII gave, as the major product, XIX which may have been formed through a Westphalen-type rearrangement of the organothallium intermediate, XX, involving migration of the 10-methyl group, followed by internal nucleophilic attack of the 3α-hydroxyl group (30).



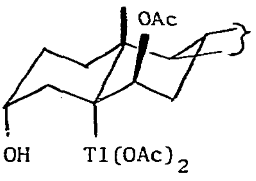
XVII



XVIII

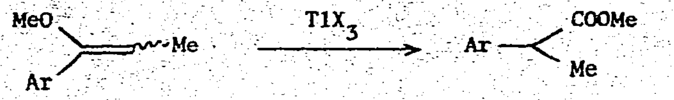


XIX



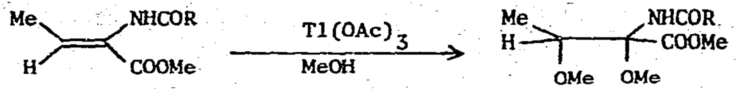
XX

In connection with the intermediacy of enol ethers in the oxidation of propiophenone with $Tl(NO_3)_3$ in TMOF [J. Am. Chem. Soc., 98 (1976) 3037], Walker and Pillai examined the reaction of α-methoxystyrene derivatives with Tl(III) salts to find selective formation of 2-aryl alkanoates even in the absence of TMOF or a solid support (31). Further, this transformation can be carried out under aqueous conditions or less acidic conditions.



Ar= p-$^{i}BuC_6H_4$; X= NO_3, ClO_4, OAc, 1/2 SO_4

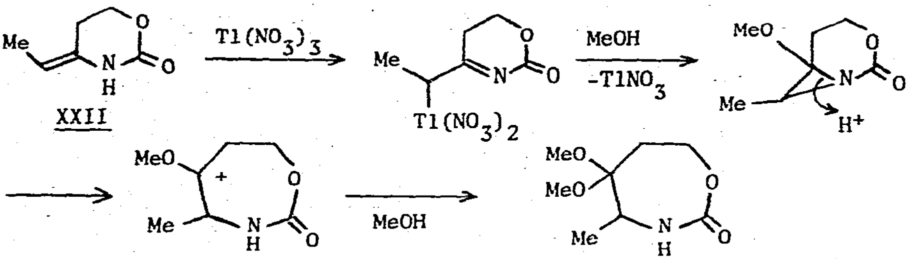
Oxidation of the enamine XXI with $Tl(OAc)_3$ in methanol gave a diastereomeric mixture of α,β-dimethoxy derivatives (32). In another reaction of enamines,



XXI

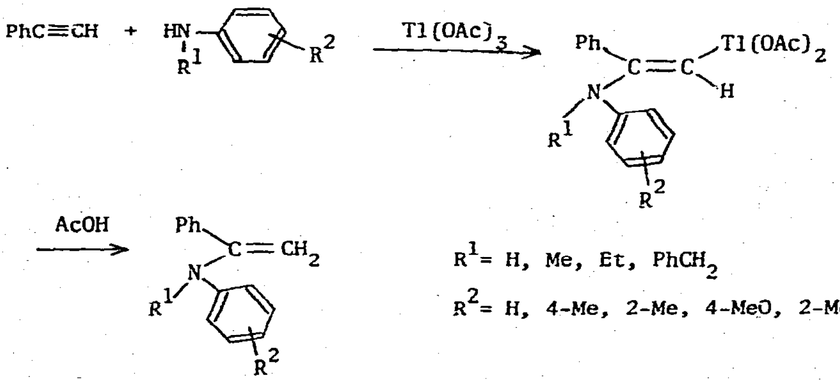
(R= Me, $PhCH_2$, Ph)

Back et. al obtained a ring-expanded product from XXII as shown below (33).



XXII

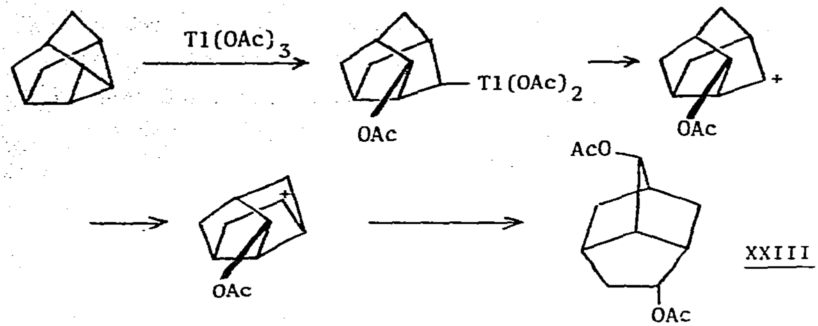
Addition of aromatic amines to phenylacetylene was catalyzed by $Tl(OAc)_3$ in which intermediate formation of organothallium compound was postulated (34).



R^1= H, Me, Et, $PhCH_2$

R^2= H, 4-Me, 2-Me, 4-MeO, 2-MeO, 4-Cl

Treatment of triaxane with $Tl(OAc)_3$ in acetic acid gave XXIII, providing a simple, stereospecific route to a C-4, C-8 difunctionalized brendane (35).



XXIII

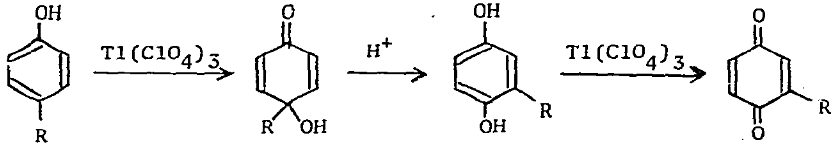
Simple synthesis of aromatic fluorides by means of $Tl(OOCCF_3)_3$ was described (36). The method is limited to aromatic substrates which contain neither powerful electron-withdrawing groups nor oxygen or amino substituents.

$$ArH \xrightarrow{Tl(OOCCF_3)_3} ArTl(OOCCF_3)_2 \xrightarrow[BF_3]{KF} ArF$$

Ar= 4-MeC_6H_4, 4-EtC_6H_4, 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 4-PhC_6H_4

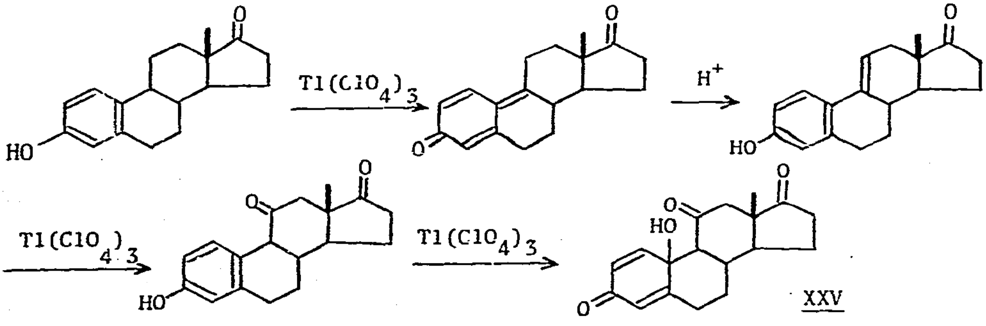
Thallation of 2,3,5,6-tetrafluoroanisole, XXIV, was examined (37). Thus, while XXIV was not thallated by $Tl(OOCCF_3)_3$ in CF_3COOH, the same reaction mixture containing CF_3SO_3H gave, after treatment with NaI, 39 % p-IC_6F_4OMe. $Tl(O_3SCF_3)_3$, however, did not give as good results as the above system due to solubility problems.

The reaction of p-alkylphenols with $Tl(ClO_4)_3$ in aqueous perchloric acid afforded 65-70 % of alkyl-substituted p-benzoquinones via acid catalyzed dienone-phenol rearrangement (38).

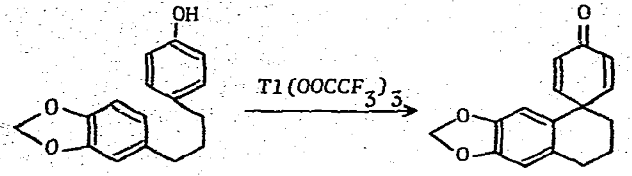


R= Me, CH_2CH_2OAc, $CH_2CH_2OCOCH_2Cl$

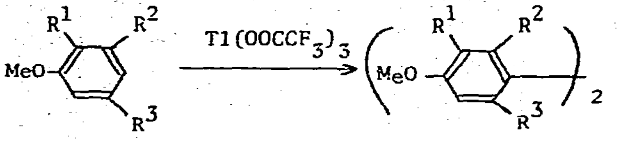
A major product from oxidation of estrone with $Tl(ClO_4)_3$ was found to be XXV, a possible route to which is shown below (39).



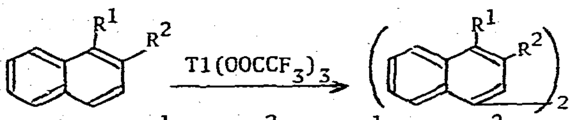
Intramolecular coupling of phenolic diarylalkanes using $Tl(OOCCF_3)_3$ has previously been reported [J. Am. Chem. Soc., 95 (1973) 612; 97 (1975) 1239; 98 (1976) 2571]. Schwartz and co-workers now compared such coupling of diphenolic, monophenolic and non-phenolic substrates using $Tl(OOCCF_3)_3$, $VOCl_3$ and $Ag(OOCCF_3)_2$ (40), and found that $Tl(OOCCF_3)_3$ is suited for monophenolic coupling, e.g.



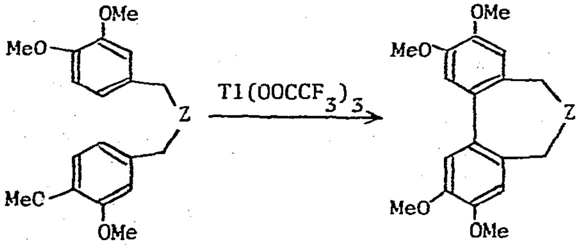
These authors suggested an O-thallated intermediate, in contrast to ring-thallated intermediates in the *oxidation of phenols by Tl(III) compounds* [J. Org. Chem., 41 (1976) 282]. Oxidative coupling of aromatic compounds using $Tl(OOCCF_3)_3$ in CF_3COOH, carbon tetrachloride or CH_3CN was described (41).



R^1	R^2	R^3
MeO	H	Br
		I
		Me
	Me	Br
Me	H	Me
Me	Me	Me



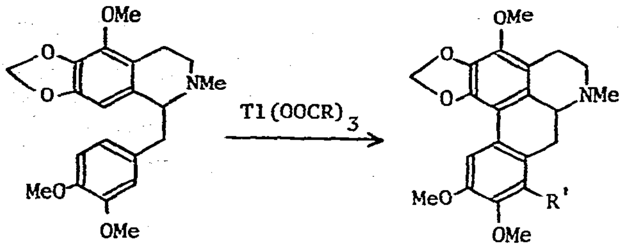
R^1= Me, R^2= H; R^1= MeO, R^2= H, Me, Cl, Br;
R^1= Br, R^2= H; R^1= I, R^2= H



XXVI

[Z= CH_2 (ref. 41); Z= O (ref. 42)]

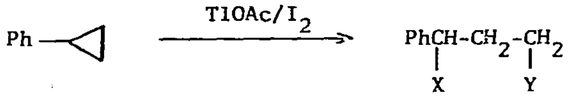
Aromatics which contain powerful electron-withdrawing groups (COOR, CN, NO_2) failed to couple. The same authors also described similar coupling of XXVI (Z= O) and XXVII (42). Treatment of XXVII with $Tl(OAc)_3$, however, led to aromatic acetoxylation to give XXVIII (R'= OAc).



XXVII XXVIII

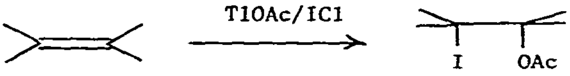
(R' = H when R = CF_3; R' = OAc when R = Me)

Several thallium compounds including C_5H_5Tl, 2,4-dimethylphenylthallium compounds and oxythallated adducts of *o*-allylphenol, styrene and norbornadiene were found to be effective catalysts for the transesterification of alkyl esters of di-, tri- and tetracarboxylic acids such as methyl terephthalate, phthalate or isophthalate with 2,3-epoxypropanol (43). Treatment of phenylcyclopropane with $TlOAc/I_2$ gave, as the major products, 1,3-disubstituted phenylpropanes, possibly via electrophilic attack of iodine at the ring (44).



X,Y= OAc, OH, I

The same authors extended their previous reaction of olefins with $TlOAc/I_2$ to TlOAc/ICl, *e.g.* as shown below (45).



5. Organothallium(I) Compounds

Pyrolysis at 200-300°C of $Tl_2R^1R^2C_2B_9H_9$ (R^1, R^2 = H, Me) gave thallium metal and $TlR^1R^2C_2B_9H_{10}$ as the major product (46). The structure of the thallacarboranes thus prepared was discussed on the basis of mass and ^1H and ^{11}B NMR spectra. Reaction of C_5H_5Tl with tetracyanoethylene proceeded almost quantitatively to give XXIX (47). A low temperature X-ray investigation

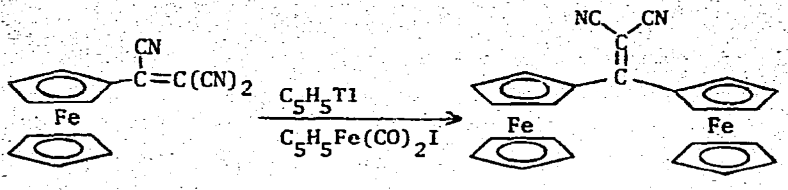
$$C_5H_5Tl + (CN)_2C{=}C(CN)_2 \longrightarrow \underset{\underline{XXIX}}{Tl[C_5H_4C(CN){=}C(CN)_2]} + HCN$$

confirmed the structure of XXIX to be similar to that of C_5H_5Tl. XXIX was found to be useful for making tricyanovinyl-substituted metallocenes, *e.g.*

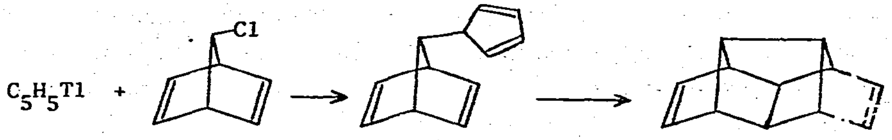
$$\underline{XXIX} \xrightarrow{m-X} m'-C_5H_4C(CN){=}C(CN)_2$$

m= $Mn(CO)_5$, m'= $Mn(CO)_3$; m= m'= $CuPPh_3$; m= $Fe(C_5H_5)(CO)_2$, m'= $Fe(C_5H_5)$

In the presence of additional C_5H_5Tl, $Fe(C_5H_5)[C_5H_4C(CN)=C(CN)_2]$ gave a dinuclear complex.



Reaction of C_5H_5Tl with 7-norbornadienyl chloride in diglyme at 150°C is reported to constitute a convenient one-step synthesis of XXX (48).



XXX

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