THALLIUM; ANNUAL SURVEY COVERING THE YEAR 1978 *

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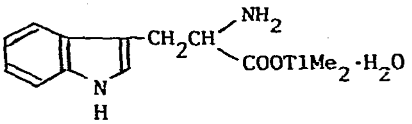
The number of papers dealing with organothallium compounds during the year 1978 remained almost the same as those in the previous years, but studies bearing on more or less biological interests have increased gradually. This survey will deal with 1) reviews, 2) synthesis, structure and spectroscopy of organothallium(III) compounds, 3) thallium-metal bonded compounds, 4) reactions and kinetics, 5) organic synthesis with thallium(III) and thallium(I) compounds and 6) organothallium(I) compounds.

1. Reviews

Papers on the aqueous chemistry of organolead and organothallium compounds in the presence of microorganisms were reviewed in the book "Organometals and Organometalloids: Occurrence and Fate in the Environment," (1). In other chapters of this book is often mentioned the behavior of organothallium compounds with regard to biological methylation or alkyl transfer reactions.

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

The structure of dimethylthallium DL-tryptophanate, I, was determined by X-ray crystallography (Fig. 1) (2). The complex exists as a discrete dimer



I

in which the Me_2Tl unit is bonded to one N and two O atoms. It is a distorted octahedral complex with a vacant coordination site. The C-Tl-C angle is 165.7°. The structure of the related dimethylthallium complex of L-phenylalanine, $Me_2Tl[O_2CCH(NH_2)CH_2Ph]$, II, was also determined (3). The complex consists of two independent polymeric chains where each Tl atom is linked via the carboxyl bridge, and these chains are held together by weak Tl-O interac-

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*Thallium; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 158(1978)p.221-233.

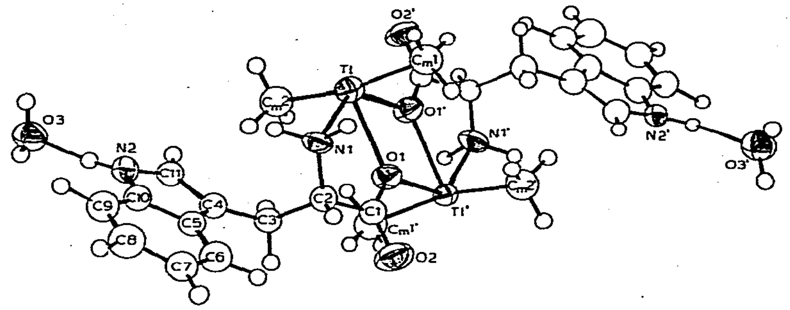
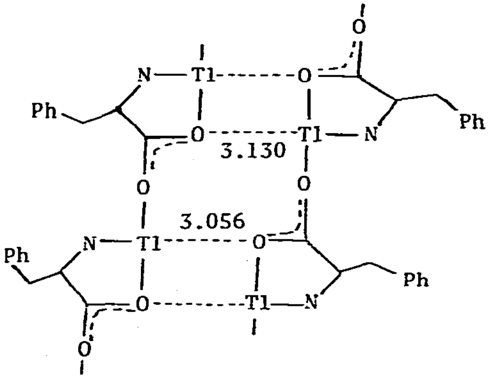


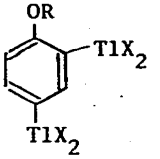
Fig. 1 Structure of I [Reproduced from Acta Cryst., B34 (1978) 935]



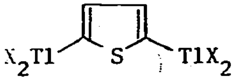
II (Methyl is not shown for clarity)

tions. Each Tl atom is 6-coordinate with C-Tl-C angles of 163.7° and 165.6°. The crystal structural determination of $Tl[N(SiMe_3)_2]_3$ revealed the presence of trigonal planar TlN_3, with a propeller-twist of the Si_2N groups versus the metal coordination plane (twist angle= 49.1°), similar to the structure of $M[N(SiMe_3)_2]_3$ (M= Fe, Al) (4). The Tl-N bond length was 2.089 A.

A full paper on dithallation of aromatic compounds was published (5). In contrast to the isolation of the para-thallated product when anisole or phenetole was reacted with an equimolar amount of $Tl(OOCCF_3)_3$ using short reaction times, or ortho-thallated product using long reaction times, dithallation occurred to give III when an excess of $Tl(OOCCF_3)_3$ was used. Similarly, thiophene gave IV. Use of an excess of $Tl(OOCCF_3)_3$ in refluxing CF_3COOH caused partial dithallation of toluene, m-xylene and benzene. These reactions may provide a satisfactory route to the corresponding diiodoaromatic compounds when the thallium compounds are treated with I^- ion. Reaction of D-galactal triacetate with $Tl(OAc)_3$ in methanol at room temperature gave (diacetoxythallio)talopyranoside,

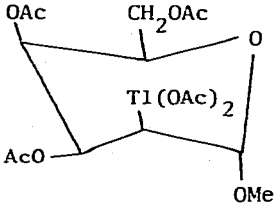


III X= $OOCCF_3$; R= Me, Et

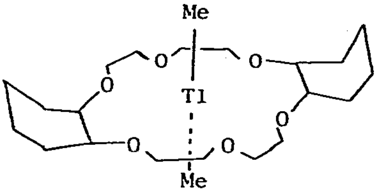


IV

V, in 75 % yield (6). ^1H NMR data for V were given. Some organothallium compounds, R_2TlX (X= Cl, Br) and $RTl(OOC^iPr)_2$ containing bulky R groups such as Me_3SiCH_2, Me_3CCH_2 or Me_2CHCH_2, were prepared (7). Unique stabilities and structural aspects of this class of compounds compared with those of ordinary, simple alkyl analogs were discussed in terms of the steric bulk of the thallium-bound alkyl ligand. Dimethylthallium complexes of dicyclohexyl-18-crown-6, $[Me_2Tl(crown)]$pic (pic= picrate) were prepared (8). A linear C-Tl-C moiety was held strongly and perpendicularly in the quasi-planar ring of six oxygen atoms, and the magnetic non-equivalence of the two methyl groups in the syn isomer, VI was observed in NMR spectra. Exchange of the crown ligand shown in eq. 1 was found to be slow on the NMR time scale.



V

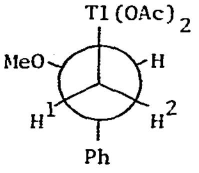


VI

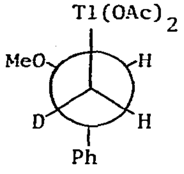
$$[Me_2Tl(crown)]pic \; + \; crown^* \rightleftharpoons [Me_2Tl(crown^*)]pic \; + \; crown \qquad (1)$$

The compounds, R_nTlCl_{3-n} (n= 1, R= Ph, p-tolyl, p-ClC_6H_4; n= 2, R= Ph) (9), R_2TlOR' (R= Ph, o-, m-, p-tolyl, R'= Ph, $C_{10}H_7$) (10) and R_2TlX (R= C_5H_5, indenyl, X= NO_2, ONO, NO_3) (11) were prepared by metathetical reactions using Me_3SiCl (with $R_nTl(OAc)_{3-n}$), NaOR' and AgX, respectively. Biomethylation of Tl(I) compounds was found by Huber and Kirchmann (12). Thus, they incubated bacteria from the anaerobic sediment of a natural small lake with added nutrient for 10 days at 30°C under N_2 and in the dark, during which period TlOAc was added in portions. After 21 days ca 3 % conversion of Tl^+ to Me_2Tl^+ was detected. Details about the way in which the Me_2Tl^+ species were formed were not clarified. Russian workers prepared o- and m-carborane derivatives of thallium, $(RCB_{10}H_{10}C)_2TlCl$ and $(RCB_{10}H_{10}C)(Bu)TlCl$ (R= H, Ph), from, e.g., $RCB_{10}H_{10}CLi$ and $TlCl_3$ (13).

A full account of the configurational study of oxythallated adducts of styrene appeared (14). After unequivocal assignment of the H^1 and H^2 resonances in the most stable configuration, VII was made on the basis of $^3J_{HH}$ and $^2J_{TlH}$ values, the stereochemistry of the oxythallation of styrene was shown to be specifically trans with VII-d being formed from trans-PhCH=CHD. During this study a new method was found to trap effectively the rather unstable oxythallated adducts of some olefins (e.g. of propylene or octene-1) by forming more stable $RTl(SSCNMe_2)_2$ with $NaSSCNMe_2$ or R(Me)TlOAc with tetramethyltin. The assignment of ^{13}C NMR spectra of several organothallium compounds such as acetoxythallated adducts of norbornene, norbornadiene or benzonorbornadiene, which exhibit many splittings due to the ^{13}C-Tl spin coupling, was facilitated by the use of di-tertiary-butyl nitroxide radical as a spin decoupling reagent in $CDCl_3$ (15). The radical showed signal broadening effects on the carbons having large ^{13}C-Tl coupling constants, and decoupling effects on the carbons having rather small coupling constants.

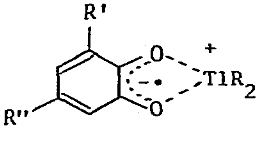


VII



VII-d

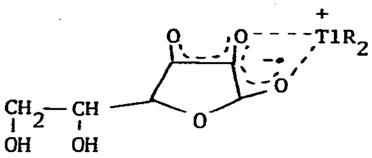
Continuing their previous studies on paramagnetic organothallium complexes, Ulmschneider et al. prepared ion-pairs of diorganothallium cations and semiquinones, VIII (16). ESR measurements indicated a strong dependence of the



VIII

R'= R''= H; R'= CPh_3, R''= CMe_3
R= Ph, $4\text{-}XC_6H_4$ (X= F, Cl, Me), $3,4\text{-}Me_2C_6H_3$, $2,4\text{-}Me_2C_6H_3$, $2,5\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, C_6F_5, Me, Et, ^nBu, vinyl

thallium coupling constant on the nature of the metal-substituents. The half-lives of paramagnetic anions of L-(+)-ascorbic acid were found to be considerably extended by complexation to R_2Tl^+ ions (17). Thus, equimolar mixtures of R_2TlOH (R= Ph, $2,5\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, C_6F_5) and ascorbic acid in pyridine at room temperature showed, immediately after mixing, distinct ESR signals due to the radicals, IX, formed by autoxidation, with the half-life of IX (R= Ph) being of the order of days. The value, a_{Tl} varied considerably



IX

from 5.19 G (R= 2,5-$Me_2C_6H_3$) through 61.75 G (R= C_6F_5). A linear dependence of the signal intensity upon the concentration of the acid was observed, suggesting that such spectroscopy may permit quantitative determination of L-(+)-ascorbic acid. A previous ESR study of the oxidation of anthracene with $Tl(OOCCF_3)_3$ in CF_3COOH [J. Eloranta and A. Sippula, Finn. Chem. Lett., (1975) 170] was reexamined (18). The observed spectra were interpreted in terms of cation radicals of 9-trifluoroacetoxyanthracene and 9,10-bis(trifluoroacetoxy)-anthracene, but not the cation radical of anthracene itself with its 9 and 10 protons hydrogen-bonded to fluorines, as previously suggested.

Raman spectra of several carboranyl derivatives of non-transition metals including Tl were measured, and the lines at around 150 cm^{-1} were assigned to metal-carborane ring stretcing vibrations (19).

3. Thallium-metal bonded Compounds

Carboranes having Tl-B bonds, 9-$(CF_3COO)_2Tl$-o-$B_{10}H_9C_2H_2$ and 9-$(CF_3COO)_2Tl$-m-$B_{10}H_9C_2H_2$, were prepared either by the reaction of $Tl(OOCCF_3)_3$ with (o- or m-carboranyl)mercury derivatives or direct thallation of ortho- or meta-carboranes with $Tl(OOCCF_3)_3$ (20, 21).

Dialkylthallium-transition metal bonded complexes of general formula, $R_2Tl\text{-}ML_n$ where R= Me, Et, Ph and ML_n= $M(CO)_2L(C_5H_5)$ (M= Mo, W; L= CO, PPh_3) were prepared by three methods (eq. 2-4) (22).

$$R_2TlR' + HML_n \longrightarrow R_2Tl\text{-}ML_n + R'H \quad (R'= R \text{ or } NMe_2) \qquad (2)$$

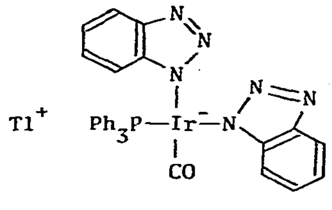
$$Ph_2TlBr + NaML_n \longrightarrow Ph_2Tl\text{-}ML_n + NaBr \qquad (3)$$

$$Tl[W(CO)_3(C_5H_5)]_3 + 2Me_3Tl \longrightarrow 3Me_2Tl\text{-}W(CO)_3(C_5H_5) \qquad (4)$$

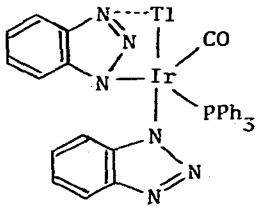
Temperature-dependent ^1H NMR spectra of $Me_2Tl\text{-}M(CO)_3(C_5H_5)$ (M= Mo, W) in CH_2Cl_2 showed that an equilibrium (eq. 5) exists, with the right-hand species becoming more dominant at higher temperatures. Attempts to prepare $R_2Tl\text{-}ML_n$ [ML_n=

$$3Me_2Tl\text{-}M(CO)_3(C_5H_5) \rightleftharpoons 2Me_3Tl + Tl[M(CO)_3(C_5H_5)]_3 \qquad (5)$$

$Cr(CO)_3(C_5H_5)$, $Fe(CO)_2(C_5H_5)$, $Co(CO)_4]$ always led to formation of R_3Tl and $Tl[ML_n]_3$. ^1H NMR data and reactivities of $R_2Tl\text{-}M(CO)_3(C_5H_5)$ with halogens, alkyl halides and metallic halides were explained in terms of the bond polarity, $Tl^{\delta+}\cdots M^{\delta-}$. The reaction of Tl·BTA (BTA= benzotriazenide) with $IrCl(CO)(PPh_3)_2$ in benzene-acetone afforded $Ir(BTA)_2(CO)(PPh_3)Tl\cdot C_6H_6$ as violet microcrystals (23). Two possible structures, X and XI, were suggested for this complex.



X



XI

4. Reactions and Kinetics

Redistribution of monoorganothallium diacetates (eq. 6) was induced by adding $P(OMe)_3$ in order to remove $Tl(OAc)_3$ from the equilibrium (24). Reduction of $Tl(OAc)_3$ occurs according to eq. 7. Such redistribution for R= Me was accomplished for the first time.

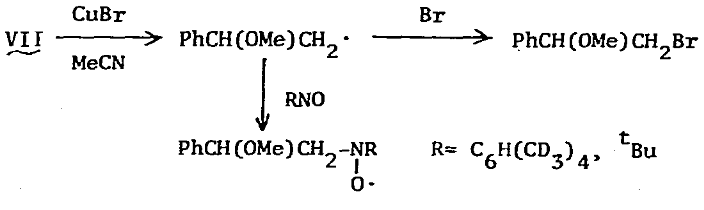
$$2RTl(OAc)_2 \longrightarrow R_2TlOAc + Tl(OAc)_3 \quad (R= Me,\ Ph) \tag{6}$$

$$Tl(OAc)_3 + P(OMe)_3 + MeOH \longrightarrow TlOAc + (MeO)_3PO + MeCOOH + MeCOOMe \tag{7}$$

Thermolysis of $R_2TlOOCR$ (R= C_6F_5, p-$MeOC_6F_4$, p-HC_6F_4, m-HC_6F_4) in boiling pyridine resulted in decarboxylation and formation of the corresponding tris-(polyfluorophenyl)thallium compounds (25). No decomposition was observed when R= o-HC_6F_4. Similar treatment in the absence of a solvent at 310°C also gave R_3Tl, together with TlF, polyfluorobiphenyls, polyfluoropolyphenyls, decafluorobenzophenone (R= C_6F_5), methyl fluoride (R= p-$MeOC_6F_4$) and $C_6H_2F_4$.

The alkyl radical, $PhCH(OMe)CH_2\cdot$, was detected by a spin trapping technique in the bromodethallation of the oxythallated adduct of styrene, VII with CuBr (see Scheme 1) (26). The radical was suggested to be involved in the main course of this transformation.

Scheme 1



$$\begin{tikzcd} \text{VII} \arrow[r, "CuBr", "MeCN"'] & PhCH(OMe)CH_2\cdot \arrow[r, "Br"] \arrow[d, "RNO"] & PhCH(OMe)CH_2Br \\ & PhCH(OMe)CH_2\text{-}\underset{\displaystyle O\cdot}{\underset{|}{N}}R & \end{tikzcd}$$

$R= C_6H(CD_3)_4,\ {}^tBu$

In another study on the decomposition of alkylthallium compounds, the homolytic Tl-C bond cleavage was suggested to be induced by one-electron reduction of $RTl(OAc)_2$ compounds with such reductants as ascorbic acid, hydrazine or $NaBH_4$ (eq. 8) (27). The basis on which the occurrence of such homolysis was deduced

$$RTl^{III} \xrightarrow{e^-} RTl^{II} \longrightarrow R\cdot + Tl^{I} \qquad (8)$$

includes stereochemical examination of the products, R_2TlOAc from VII-d, and effective trapping of the alkyl radical by nitrosodurene or oxygen. The reaction with ascorbic acid under oxygen was particularly effective in converting $RTl(OAc)_2$ compounds into ROH. Nitrosodethallation of arylthallium compounds, [Bull. Chem. Soc. Japan, 49 (1976) 2582] (eq. 9) was compared with similar reactions of other arylmetallic compounds (Hg, Si, Sn, Pb, Bi), and with

$$ArTlOAc\cdot ClO_4 \xrightarrow[CF_3COOH]{NaNO_2} Ar\text{-}NO \qquad (9)$$

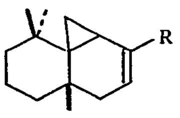
nitration of aromatic hydrocarbons using $NaNO_2/CF_3COOH$ (28). The nitrosodethallation was re-confirmed to proceed through attack of NO^+.

Bis(pentachlorophenyl)thallium chloride, R_2TlCl (R= C_6Cl_5), was used as an arylating reagent for several transition metal complexes in low oxidation state (29). The complexes thus prepared are (starting material in parenthesis): R_2Hg (Hg_2Cl_2), $R_2Ni(diphos)$ ($Ni(CO)_2(diphos)$), $RClNi(PPh_3)_2$ ($ClNi(PPh_3)_3$), $RRh(CO)(PPh_3)_2$ ($ClRh(CO)(PPh_3)_2$), $R_2ClAu(PPh_3)$ and $RAuPPh_3$ ($ClAuPPh_3$). In a related paper, $(C_6F_5)_2TlBr$ was used to oxidize ClAu(CNPh) to $(C_6F_5)_2ClAu(CNPh)$ (30).

A good correlation was observed between the rate constants for oxythallation of various alkenes in aqueous sulfuric acid and experimental or calculated ionization potentials of the alkenes (31). It was suggested that inductive effects are the most important in the oxythallation of $RCH{=}CH_2$ and $RR'C{=}CH_2$.

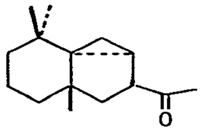
5. Organic Synthesis with Thallium(III) and Thallium(I) Compounds

Oxidation of thujopsene, XII with $Tl(OAc)_3$ gave a ring-contracted ketone, XIII, at room temperature, and XIV at 50°C (32).



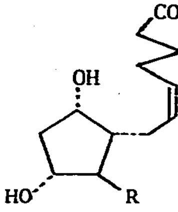
XII R= Me

XIV R= CH_2OAc

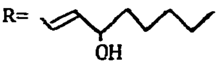


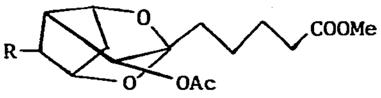
XIII

Action of 3 equivalents of $Tl(OAc)_3$ in acetic acid on $PGF_{2\alpha}$ methyl ester, XV, gave XVI and XVII in 1 : 2.5 ratio (33). The intermediacy of XVIII was postulated.

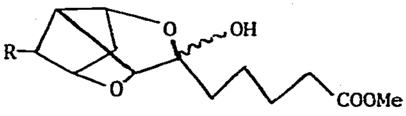


XV

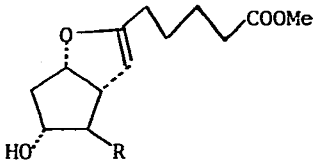




XVI

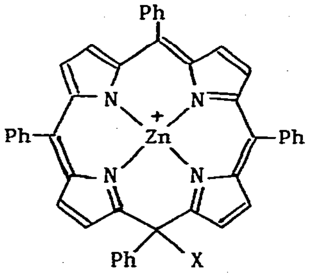


XVII

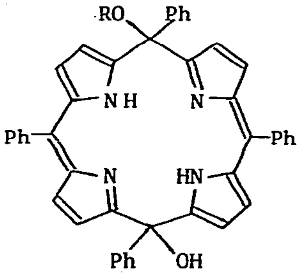


XVIII

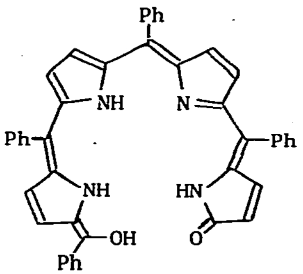
Evans and co-workers described oxidation of zinc(II) complexes of meso-tetraphenylporphyrin with $Tl(OOCCF_3)_3$ or $Tl(NO_3)_3$ (34). The initial product, XIX, gave, after acidic demetallation, XX, XXI and XXII. Nitration of zinc(II) octa-alkylporphyrins with $Tl(NO_3)_3$ was shown to be a general reaction which can be controlled to give mono- or di-nitration at the meso-positions.



XIX X= $OOCCF_3$, ONO_2



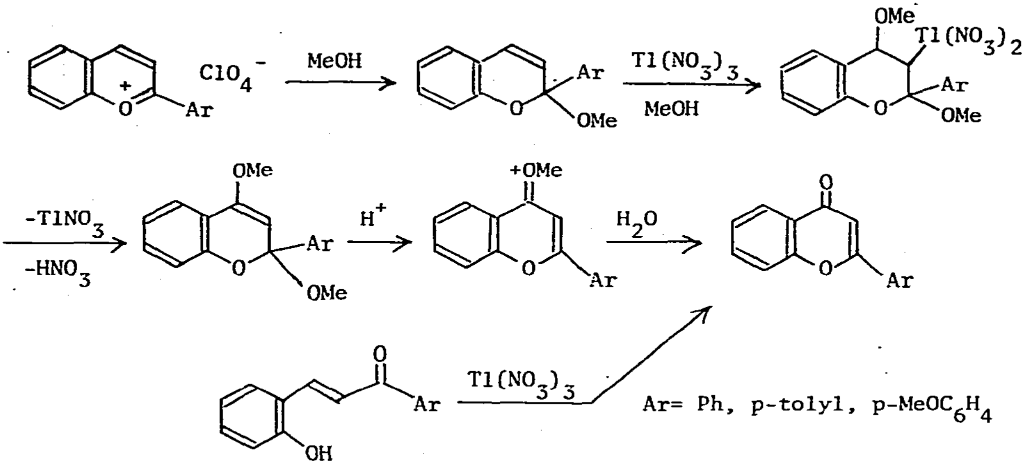
XX R= H
XXI R= Me



XXII

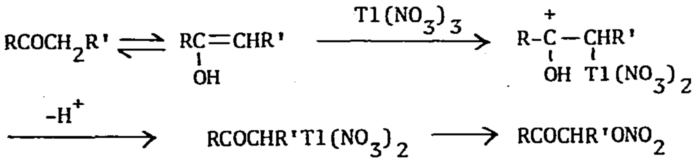
Oxidation of flavylium salts with $Tl(NO_3)_3$ in methanol gave the corresponding flavones (Scheme 2) (35). The same flavones were obtained from oxidation of 2-hydroxychalcones with $Tl(NO_3)_3$, in contrast to the known aryl migration in $Tl(NO_3)_3$-oxidation of non-hydroxychalcones.

Scheme 2



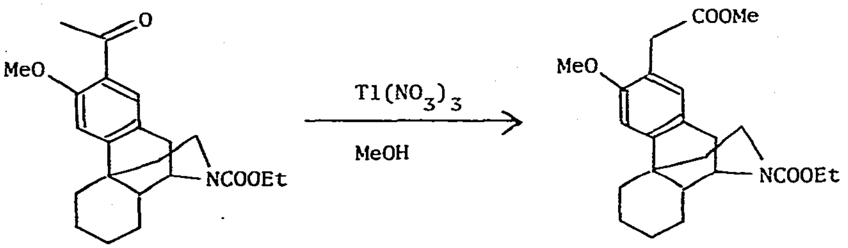
Oxidation of ketones with $Tl(NO_3)_3$ in non-nucleophilic solvents such as acetonitrile or diethyl carbonate gave good yields of α-nitrato ketones instead of skeletal rearrangements (Scheme 3) (36). Ketones examined include substituted acetophenones, propiophenone and some aliphatic ketones. During a study of synthesis of an acidic morphinan derivative, $Tl(NO_3)_3$-mediated rearrangement of aryl methyl ketones into acid derivatives was successfully employed as shown in eq. 10 (37).

Scheme 3



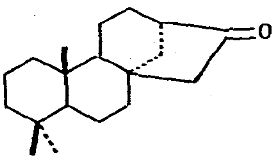
$$RCOCH_2R' \rightleftharpoons \underset{OH}{RC}{=}CHR' \xrightarrow{Tl(NO_3)_3} R\text{-}\overset{+}{\underset{OH}{C}}-\underset{Tl(NO_3)_2}{CHR'}$$

$$\xrightarrow{-H^+} RCOCHR'Tl(NO_3)_2 \longrightarrow RCOCHR'ONO_2$$

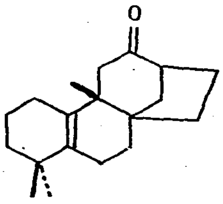


(10)

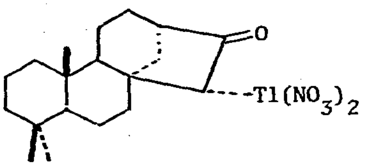
Treatment of 17-nor-13β-kauran-16-one, XXIII with $Tl(NO_3)_3$ in acetic acid at room temperature for 4 days gave XXIV in 81 % yield through initial formation of an organothallium intermediate, XXV, and several subsequent skeletal rearrangements (38).



XXIII



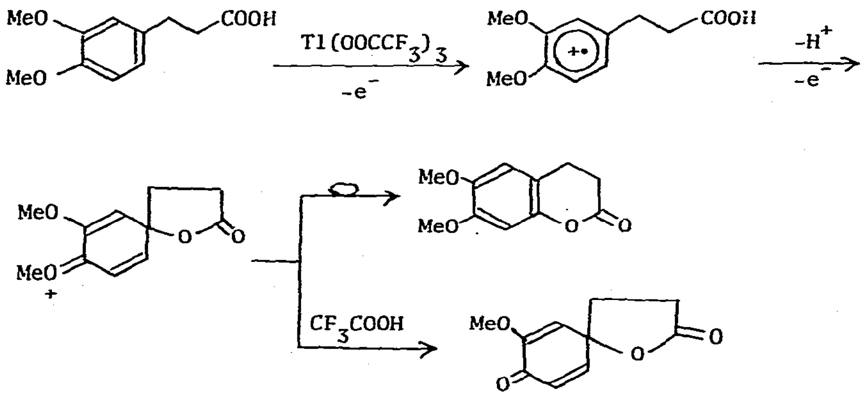
XXIV



XXV

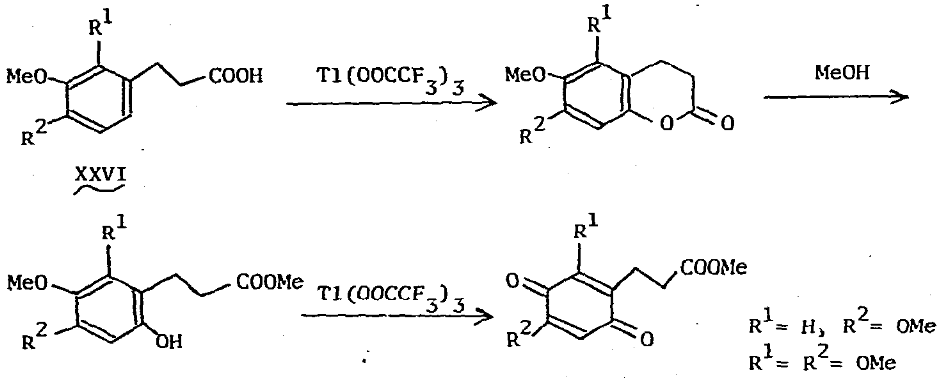
Taylor and co-workers previously suggested the intermediacy of an aromatic radical cation in $Tl(OOCCF_3)_3$-mediated biaryl formation from aromatic compounds [A.S. for 1977]. These authors now have carried out intramolecular trapping of aromatic radical cations by a suitably positioned carboxyl group, as shown in Scheme 4 (39). In accordance with this scheme, the corresponding methyl ester of 3-(3,4-dimethoxyphenyl)propionic acid gave, under similar conditions, the biaryl, because intramolecular trapping of the radical cation is impossible in this case. Oxidation of 3-(3-methoxyphenyl)propionic acid also gave only the biaryl, possibly due to the absence of mesomeric stabilization by the methoxy group. Treatment of XXVI with 2 equivalents of $Tl(OOCCF_3)_3$ and quenching of the reaction mixture with MeOH gave the p-benzoquinones directly (Scheme 5). In a closely related study, 4-alkoxycinnamic acids were converted to the corresponding fused bis-lactones with $Tl(OOCCF_3)_3$ in CF_3COOH/CH_2Cl_2 at room temperature in the presence of $BF_3 \cdot OEt_2$ (Scheme 6) (40). Consistent with this scheme are the observations that non-substituted cinnamic acid failed to undergo the above dimerization, and that methyl p-methoxycinnamate gave XXVII by deprotonation of the initially formed product of radical dimerization.

Scheme 4

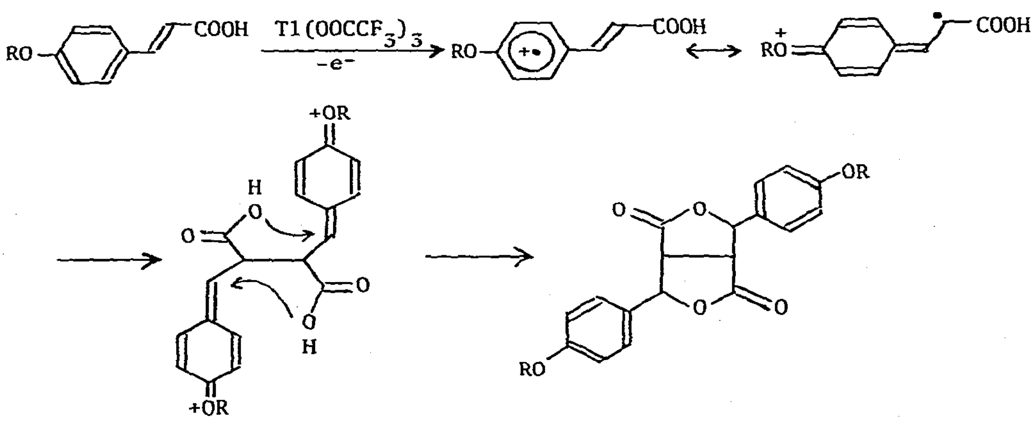


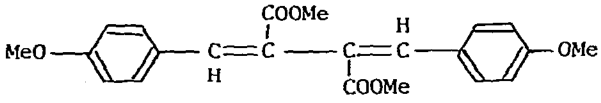
Conversion of hydroquinone monoalkyl ethers to p-benzoquinone monoketals was accomplished by using $Tl(NO_3)_3$ in MeOH in the presence of suspended $KHCO_3$

Scheme 5



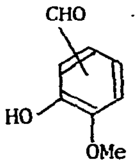
Scheme 6



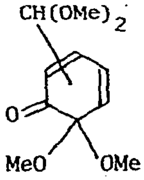


XXVII

[see also J. Org. Chem., 41 (1976) 282] (41). Oxidation of vanillins, XXVIII, with $Tl(NO_3)_3$ in MeOH gave the dimethyl acetals of 6,6-dimethoxy-2,4-cyclohexadien-1-one aldehydes, XXIX which dimerized rapidly at room temperature (42).



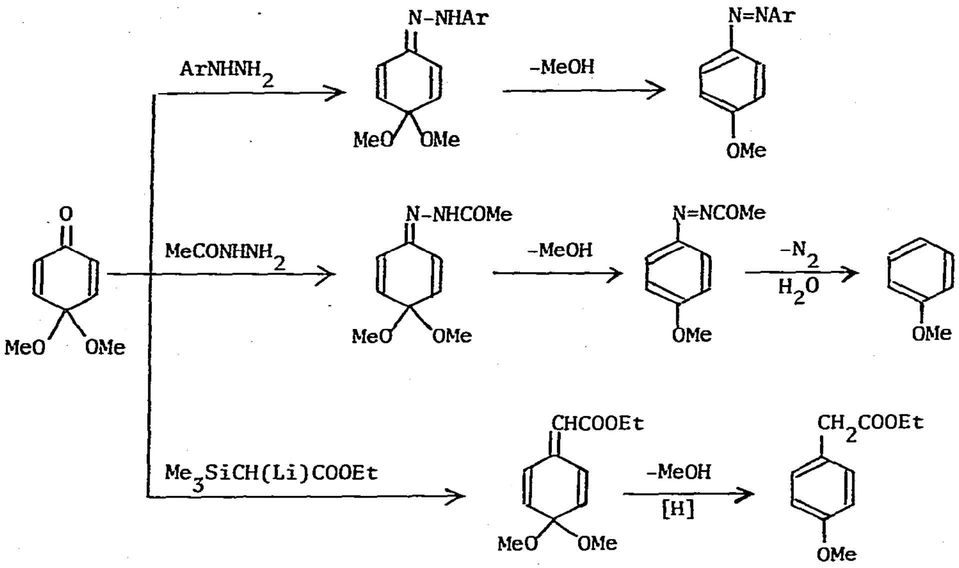
XXVIII



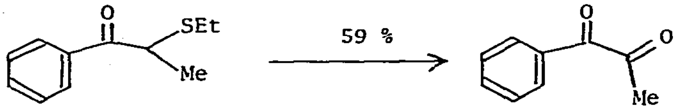
XXIX [$CH(OMe)_2$ is at position 2, 3 or 4]

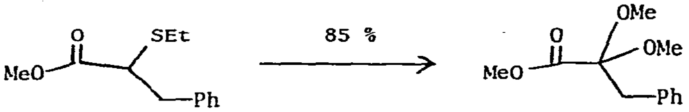
Simple procedures for the replacement of a phenolic OH group by N=NAr, N=O, H, NH_2 and even C-substituents were developed using $Tl(NO_3)_3$-mediated formation of cyclohexadienones from phenols (43). Typical examples are shown in Scheme 7.

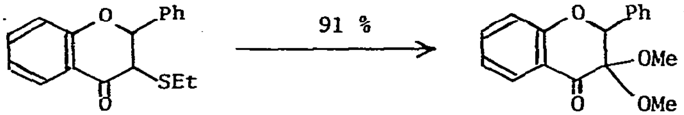
Scheme 7

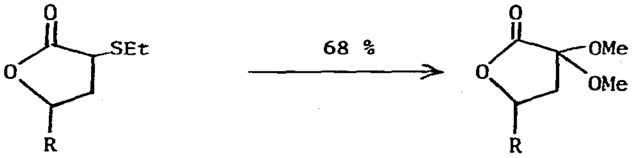


Oxidation of β-oxosufides to the corresponding α-oxodimethyl acetals with $Tl(NO_3)_3$ in MeOH [Tetrahedron Lett., (1977) 1345] was now extended to a general synthesis of α-oxodimethyl ketals (44). The reactions examined include:



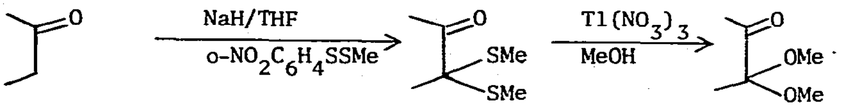






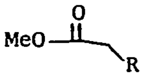
R= Bu, ^{n}Octyl

The same authors also described a new general synthesis of α-oxodimethyl ketals as outlined in eq. 11 (45). The ketones or esters subjected to this trans-



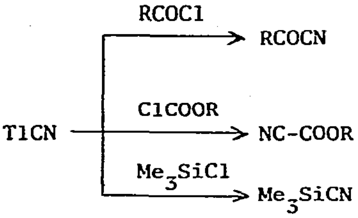
(11)

formation are estrone 3-methyl ether, epiandrosterone, dihydrolanosterone, and XXX.



XXX R= CH_2Ph, $CH_2C_6H_4OMe$-p, ${}^{i}Bu$

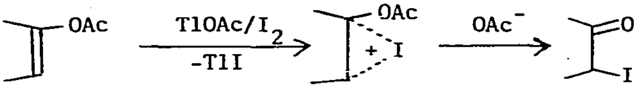
A modified method of preparing TlCN from TlOPh and HCN was described (46). Utility of TlCN in synthetic reaction also was examined, e.g.,



R= Ph, m- or p-tolyl, p-anisyl, o-ClC_6H_4, m- or p-$NO_2C_6H_4$, 2-furyl, 2-thienyl, cyc-C_3H_5, ${}^{t}Bu$

R= Me, Et, ${}^{i}Bu$

The action of TlOAc and iodine on several enol acetates was examined as a general method for the formation of α-iodo-ketones (47).

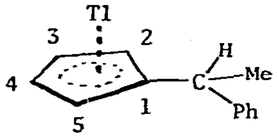


6. Organothallium(I) Compounds

The reaction of TlCl and alkali metal borinates in acetonitrile gave $Tl[C_5H_5BR]$ (R= Me, Ph), the first borabenzene derivatives of a main-group metal to be isolated in pure form (48). The mass spectral and ^{1}H, ^{11}B and ^{13}C NMR data were discussed in terms of the structure and the nature of bonding. A new, convenient method of preparing TlC_5D_5 was described which involves shaking a D_2O solution of NaOD and cyclopentadiene, followed by addition of Tl_2SO_4 (49).

An SCF calculation based on the theory of effective potentials for gaseous TlC_5H_5 in its experimental equilibrium conformation indicated that the thallium atom is nearly neutral with an overall electron distribution of $s^{1.75}p^{0.45}d^{0.71}$ as obtained from a Mulliken population analysis (50). The overlap population of 0.47 electron between Tl and the C_5H_5 ring is about half of each C-C overlap. Bonding was principally due to the highest filled m.o. pairs of E_1

symmetry based primarily on $\underline{pd^2}$ of Tl and $\underline{p}$ of carbons, constituting π-interaction with respect to the Tl-ring bond. The nature of bonding in $TlC_5H_4C_6H_4F$-m, $TlC_5H_4C_6H_4F$-p and XXXI was also examined by ^{19}F and ^{13}C NMR spectroscopy (51). ^{13}C NMR spectra of XXXI in benzene, CH_2Cl_2 or THF at 34°C showed only one signal for a formally diastereotopic pair of carbons, 2 and 5, or 3 and 4. This result, together with comparison of the ^{19}F and ^{13}C shifts of the thallium compounds with those of alkali metals and Fe(II) analogs, led the authors to suggest the absence of a stable covalent thallium-ring bond. In a related study, ^{13}C chemical shifts of some methylcyclopentadienyl derivatives of Ge(II), Sn(II), Pb(II), Tl(I), Li(I) and K(I) were measured and discussed in terms of bonding and electronegativity effects (52). A somewhat lower ^{13}C shift of the Tl(I) compound than those of the alkali metals was said to be consistent with some degree of covalent character for the Tl(I) compound.



XXXI

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