THALLIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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This survey will deal with 1) reviews, 2) synthesis, structure and spectroscopy of organothallium(III) compounds, 3) compounds containing thallium-metal bonds, 4) reactions of organothallium(III) compounds and 5) thallium(I) compounds

1. Reviews

Review articles on O-organometal hydroxylamines and oximes (1) and on the biological aspects and effects displayed by organometallic compounds (2) included surveys on organothallium compounds of related interest.

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

The reaction of TlSCN with trimethylaluminum in toluene has been found (3) to yield $[Me_2Tl][Me_3AlNCS]$ according to eq. 1.

$$3TlSCN + 3Me_3Al \longrightarrow [Me_2Tl][Me_3AlNCS] + 2Tl + 2Me_2AlSCN \quad (1)$$

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* Thallium, Annual Survey covering the year 1973 see J. Organometal. Chem., 79 (1974)1-16.

The crystal structural determination of the compound revealed the presence of the Al-N bond in the anion which was believed to be a consequence of the coordination requirements of the thallium atom. The environment of the thallium atom in the cation was essentially octahedral (Fig. 1) with a linear C-Tl-C unit (Tl-C distance 2.15 Å), two sulfur atoms interacting with thallium, though largely electrostatic in character, at 3.13 Å from thalliu and two Al-methyl carbon atoms lying at 3.15 Å from thallium.

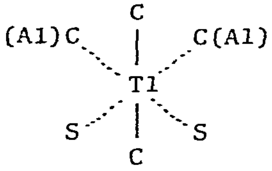
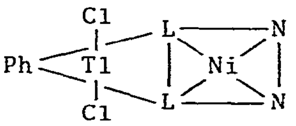


Fig. 1

The crystal structure of dimethylthallium chloride (see Z. Kristallogr., 87 (1934) 370) has been refined (4); the observed Tl-C and Tl-Cl distances are 2.139 and 3.029 Å, respectively.

The reaction of Me_3Tl with SO_3 afforded dimethylthallium methylsulfonate, $Me_2TlO(O)_2SMe$ (5). The same compound was also obtained from the reaction of Me_3Tl and methylsulfonic acid. The compound is ionic in nature and the IR and Raman spectra have been reported. Me_3Tl reacted with an equimolar quantity of $HO(O)PF_2$ to afford $Me_2TlO(O)PF_2$ I (6). The NMR (^1H, ^{19}F, ^{31}P) spectra of I were discussed and compared with corresponding data for the other Group IIIb organometallic derivatives of phosphoric acid. The vibrational spectra (IR and Raman) of I and other Group IIIb analogs were measured and assigned (7). Unlike the latter compounds, I was suggested to be ionic in nature. In another study, Et_3Tl was reported to react with H_2NCN in 1/1 and 2/1 ratio to give $Et_2TlNHCN$ and $(Et_2Tl)_2NCN$, respectively (8). Ehemann and Dehnicke obtained organothallate compounds $[Me_4N][Me_3TlCN]$ and $[Me_4N][(Me_3Tl)_2F]$ from the reaction of Me_3Tl with $[Me_4N]CN$ and $[Me_4N]F$ in hot toluene (9). On the basis of the vibrational spectra of these compounds, a C_{3v} point-group could be assigned to the former and a linear Tl-F-Tl bridged system of D_{3h} symmetry was assumed in the latter compound. Another IR spectroscopic study of the thiocyanate derivatives, R_2TlNCS (R= Me, Ph), $[Ph_4As][Me_2Tl(NCS)_2]$ and $PhTl(NCS)_2$, was reported (10). From the frequencies of the NCS group vibrations in the solid state, and the integrated intensity of the $\nu(C\equiv N)$ band in solution, it was suggested that the diorganothallium derivatives are isothiocyanates with a certain amount of ionic character in the Tl-NCS bond, whereas $PhTl(NCS)_2$ is essentially a Tl-SCN bonded compound. Possible configurations of the dimethylthallium moiety were also discussed.

1/1 Adducts of $PhTlCl_2$ with the complexes N,N'-ethylenebis(salicylideneiminato)nickel(II) (Nisalen) and bis(β-mercaptoethylamine)nickel(II) ($NiMEA_2$) have been synthesized by a research group in Italy (11). A possible structure of these new compounds in the solid state has been suggested on the basis of IR and electronic spectra as well as magnetic measurements (Fig. 2).



L= O for $PhTlCl_2 \cdot Nisalen$
L= S for $PhTlCl_2 \cdot NiMEA_2$

Fig. 2

These Italian authors also reported (12) that the 1/1 adduct formed from $PhTlCl_2$ and N,N'-ethylenebis(acetylacetoneimine) dissociates into the parent components in methanol, as suggested by examining the IR, electronic and PMR spectra as well as the conductivity.

Bis(trimethylsilylmethyl)thallium halides, $(Me_3SiCH_2)_2TlX$ (II, X= Cl; III, X= Br) have been prepared from Me_3SiCH_2Li and $TlCl_3$ or TlBr (13). Several other trimethylsilylmethyl derivatives of Tl(III) were synthesized starting from II as shown in Scheme 1.

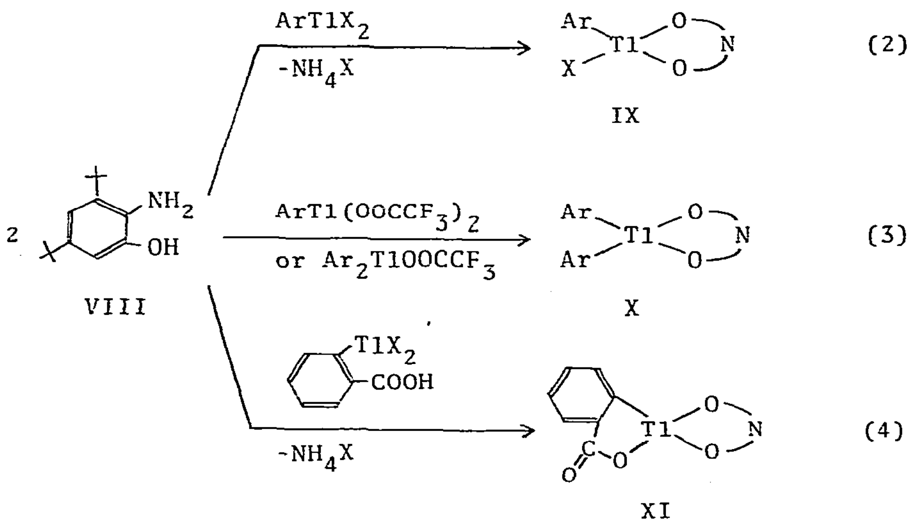
Scheme 1

$$\begin{tikzcd}
\underset{\mathrm{II}}{R_2TlCl} \arrow[r, "TlOOC^iPr"] \arrow[d, "Br_2Py"] & \underset{\mathrm{V}}{R_2TlOOC^iPr} \arrow[d, "Hg(OOC^iPr)_2"] \\
{[RTClBr]} \arrow[r, "TlOOC^iPr"] \arrow[d, "Me_4Sn"] & \underset{\mathrm{VI}}{RTl(OOC^iPr)_2} \arrow[d, "Me_4Sn"] \\
\underset{\mathrm{IV}}{MeRTlBr} \arrow[r, "TlOOC^iPr"] & \underset{\mathrm{VII}}{MeRTlOOC^iPr}
\end{tikzcd}$$

$(R= Me_3SiCH_2)$

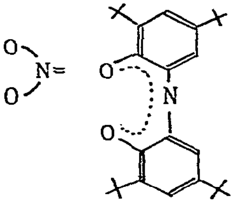
Compounds II, III and IV were found to be dimeric in chloroform, in marked contrast to the polymeric dimethylthallium halides. This has been attributed to the bulkiness of the Me_3SiCH_2 group. Comparison of the J(Tl-H) values in III and IV as well as in V, VII and Me_2TlOOC^iPr suggested that the electronic effect of the Me_3SiCH_2 is very similar to that of the methyl group. That VI is much more stable toward reductive decomposition than its methyl or ethyl analogs also was interpreted in terms of the steric effect.

Mono- and diarylthallium compounds reacted with 2-amino-4,6-di-t-butylphenol VIII in polar solvents to yield diamagnetic, stable compounds IX-XI (14) as shown in eq. 2-4.

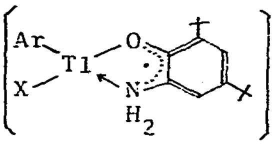


Ar= Ph, p-tolyl, 2,4,6-$Me_3C_6H_2$, p-ClC_6H_4

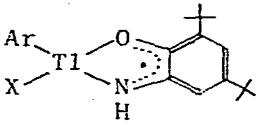
X= Cl, Br



On the basis of the ESR measurements of the reaction mixture from $PhTl(OOCCF_3)_2$ and VIII, the existence of paramagnetic intermediates such as XII and XIII was suggested.



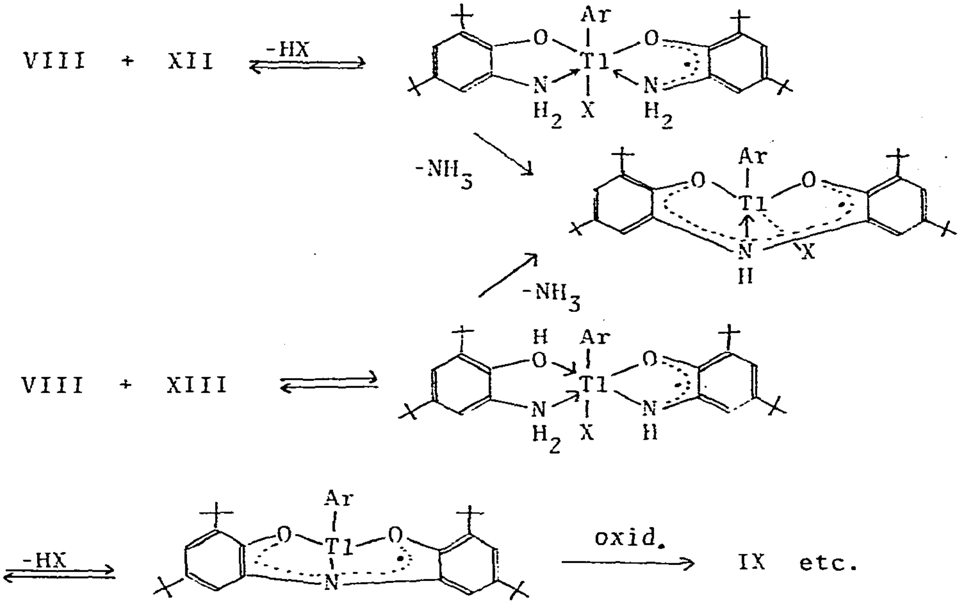
XII



XIII

XII and XIII further reacted with VIII to form the eight-membered chelate compounds as shown in Scheme 2.

Scheme 2



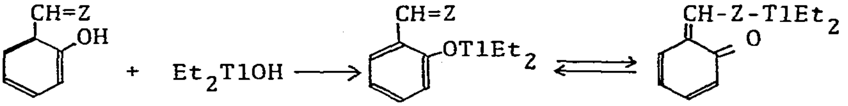
The IR and proton NMR spectral data of IX-XI were discussed in terms of their structure.

Kumar et al. extended the chemistry of cyclopentadienyl- and indenylthallium derivatives. Thus, treatment of R_2TlCl (R= C_5H_5, C_9H_7) with KX (X= CN, NCO, NCS, N_3) afforded the corresponding organothallium pseudohalides (15). IR studies indicated these compounds to be ionic. Organothallium hydride species, R_2TlH (R= C_5H_5, C_9H_7) has been claimed to be prepared (16) from the reaction of R_2TlBH_4 with Et_3N or that of R_2TlCl with NaH in THF. ν(Tl-H) values of 2105 cm^{-1} for R= C_5H_5 and 2200 cm^{-1} for R= C_9H_7 were reported. These authors also reported (17) that reduction of cyclooctatetraene thallium(III) chloride with potassium metal in THF resulted in the formation of the potassium salt of cyclooctatetraene thallium(I), $K(C_8H_8)Tl(I)$, while the product formed by the reduction of C_8H_8TlCl with the sodium salt of naphthalene was identified as $(C_8H_8)_2Tl_2$, in which two thallium atoms are in +3 and +1 oxidation states (eq. 5).

$$C_8H_8TlCl + NaC_{10}H_8 \xrightarrow{THF} 1/2(C_8H_8)_2Tl_2 + NaCl + C_{10}H_8 \qquad (5)$$

The reaction of $(C_5H_6N)_2TlCl_5$ with cycloheptatriene in dichloromethane in the presence of triethylamine afforded cycloheptatrienylthallium dichloride, $C_7H_7TlCl_2$ (18).

The compounds o-$Et_2TlOC_6H_4CH{=}Z$ (Z= NMe, NC_6H_4OMe-p, O) were prepared by boiling the aldehyde or aldimines with Et_2TlOH (19) as shown in eq. 6. The presence of the quinonoid tautomer in solution was shown by the electronic spectra.



(6)

The structural study of diethylthallium salts of polynitroalkanes,

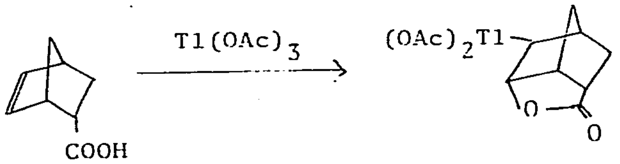
$CH(NO_2)_3$, $CH_2(NO_2)_2$ and $MeCH(NO_2)_2$ was reported (20). Diorganothallium iodides R_2TlI (R= CH_2CH_2CN, Me, Et) were prepared by electrolyzing β-cyanoethyl, methyl and ethyl iodides in aqueous solutions of K_2HPO_4 using a Tl cathode and a Pt-wire anode separated with a ceramic diaphragram (21).

Various arylthallium bistrifluoroacetates, some of which could not be readily obtained by the previously reported thallation method, have now been synthesized (22) using aryltrimethylsilanes as in eq. 7.

$$Me_3SiC_6H_4X + Tl(OOCCF_3)_3 \xrightarrow{CF_3COOH} XC_6H_4Tl(OOCCF_3)_2 + Me_3SiOOCCF_3 \qquad (7)$$

X= H, 3-Me, 3-F, 3-Cl, 3-Br, 3-CF_3, 3-OMe, 2-F, 2-Cl, 2-Me, 4-CF_3, 4-Ph

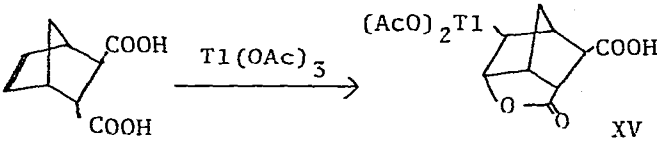
$Tl(OOCCF_3)_3$ was also found to react with Me_4Si to form $Me_3SiOOCCF_3$ and CF_3COOMe, probably <u>via</u> the formation of $MeTl(OOCCF_3)_2$. The proton NMR data for the arylthallium compounds obtained above were reported. A reexamination of the report (Tetrahedron Letters, (1966) 4363) on the reaction of 5-norbornene-2-<u>endo</u>-carboxylic acid and $Tl(OAc)_3$ now has confirmed (23) that the oxythallated adduct XIV, which could not be isolated in the former work, does exist as a well-characterizable material.



XIV

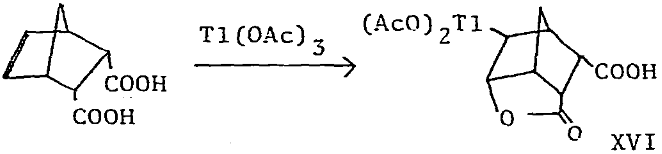
(8)

XV and XVI were obtained similarly (eq. 9,10).



XV

(9)



XVI

(10)

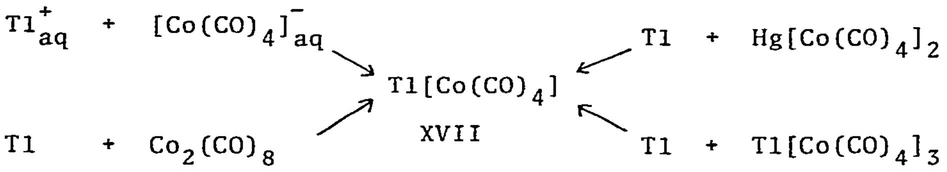
^{13}C NMR data for a series of arylthallium compounds were reported by two groups. The range of ^{13}C-$^{203,\,205}$Tl couplings to be expected, the dependence on the disposition of coupled nuclei and chemical shift effects were discussed by Kitching and coworkers (24). On the basis of both the ^{13}C data and ^{19}F chemical shifts of the p-fluorophenyl derivatives, these authors suggested that the Tl(OOCCF$_3$)$_2$ group is a powerful electron-withdrawing group. In a related study on alkyl-substituted arylthallium trifluoroacetates by Ernst (25), substituent effects on chemical shifts and coupling constants were derived after a detailed description of the method of signal assignment was given. The dependence of $^6J(^{13}C-^{205}Tl)$ on the conformation of alkyl side-chains para to the Tl(OOCCF$_3$)$_2$ group was shown. The ^{13}C NMR spectra of the Tl(III) coproporphyrin tetramethyl ester chelates were reported and assigned (26). The pattern of ^{13}C-Tl couplings was interpreted in terms of the Fermi contact mechanism.

3. Compounds Containing Thallium-metal Bonds

A comparative study on the stability of transition-metal carbonyl derivatives of both Tl(I) and Tl(III) was reported (27).

$Tl[Co(CO)_4]$ XVII was prepared by several methods as shown in Scheme 3.

Scheme 3



The new compounds $Tl[M(CO)_3Cp]$ (XVIII, M= Cr; XIX, M= Mo, XX, M= W) have been synthesized by metathetical reactions of $Na[M(CO)_3Cp]$ with $TlNO_3$ or Tl_2SO_4 in water. The existence of $Tl[Co(CO)_3PPh_3]$ and $Tl[Mn(CO)_5]$ has been inferred by examining the IR spectra where the formation of the latter was accomplished through the following reaction.

$$[Tl(OEt)]_4 + 4HMn(CO)_5 \longrightarrow 4Tl[Mn(CO)_5] + 4EtOH \quad (11)$$

The stability of these Tl(I) compounds toward disproportionation (eq. 12) was found to decrease in the order X= $Co(CO)_4 \gg M(CO)_3Cp$ (W>Mo>Cr)$>Co(CO)_3PPh_3 \approx Mn(CO)_5 \gg Fe(CO)_2Cp$.

$$3TlX \longrightarrow TlX_3 + 2Tl \quad (12)$$

The corresponding TlX_3 compounds were characterized, and found to undergo a reversible reductive elimination process (eq.13) to a greater or lesser degree depending on the reaction conditions and the stability of the TlX compounds, such elimination being particularly promoted by light.

$$TlX_3 \rightleftharpoons TlX + X\text{-}X \qquad (13)$$

The reversibility of this reaction enabled the mixed complex $Tl[Co(CO)_4]_2[W(CO)_3Cp]$ to be prepared from $Tl[W(CO)_3Cp]$ and $Co_2(CO)_8$. Closely related work appeared (28) in which the stability of Tl(I) transition-metal carbonyls was shown to be a function of the base strength of such metal-carbonyl anions, X^- Thus, when the pK_a of $HCo(CO)_3L$ is less than 5 ($L= P(OPh)_3$ and $P(\underline{p}\text{-}OC_6H_4Cl)_3$], stable compounds $Tl[Co(CO)_3L]$ were obtained from the reaction of XVII and L, while those L which give $HCo(CO)_3L$ of $pK_a>5$ did not form the Tl(I) derivatives but $Tl[Co(CO)_3L]_3$ ($L= PPh_3$, $P(OMe)_3$, $P(OEt)_3$, $AsPh_3$, $SbPh_3$, P^nBu_3) resulted according to eq. 12. Similarly obtained were $Tl[Fe(CO)_4R]$ ($R= CH_2CN$, COPh, $SnPh_3$), $Tl[Fe(CO)_3NO]$ and $Tl[V(CO)_6]$. In related work, Behrens and coworkers obtained $Tl[M(CO)_3Cp]_3$ (XXI, M= Cr; XXII, M= Mo) from thallium metal and $[M(CO)_3Cp]_2$ (29) (eq. 14).

$$3[M(CO)_3Cp]_2 + 2Tl \xrightarrow[THF]{20^\circ} 2Tl[M(CO)_3Cp]_3 \qquad (14)$$

M= Cr, Mo

The reaction of $[Cr(CO)_3Cp]_2$ with excess thallium afforded XVIII. XVIII reacted with solid KBr to give $K[Cr(CO)_3Cp]$ and TlBr. Treatment of XVIII with $[Cr(CO)_3Cp]_2$ gave XXI according to eq. 13. Addition of iodine to XVIII also afforded XXI (eq. 15).

$$3Tl[Cr(CO)_3Cp] + I_2 \xrightarrow[THF]{20^\circ} Tl[Cr(CO)_3Cp]_3 + 2TlI \qquad (15)$$

Structure and some reactivities of $Tl[Co(CO)_4]$ XVII were studied in some detail by Schussler *et al*. (30). The X-ray crystal structural determination showed that XVII is an essentiall ionic solid composed of Tl^+ and $Co(CO)_4^-$ ions. There are no discrete $Tl[Co(CO)_4]$ moieties in the solid state, nor are there any particular close distances between Tl and other atoms which are consistent with the existence of strong covalent bonds. In solvents of high dielectric constant and good coordinating ability (water, DMSO, DMF), the compound dissociates into Tl^+ and $Co(CO)_4^-$, while in solvents of low dielectric constant and weak coordinating ability (THF, CH_2Cl_2), IR spectra consistent with the presence of tight ion-pairs or triple ions with significant amounts of covalent Tl-Co bonding were observed. XVII was found to react with $[(PhCH_2)Ph_3P][Co(CO)_4]$ in CH_2Cl_2 to afford very air-sensitive crystalline $[(PhCH_2)Ph_3P]\{Tl[Co(CO)_4]_2\}$ which is extensively dissociated in solution (eq. 16).

$$Tl[Co(CO)_4] + Co(CO)_4^- \rightleftharpoons Tl[Co(CO)_4]_2^- \qquad (16)$$

The reactions of $Co_2(CO)_8$ with halides of the Group IIIb metals were investigated (31). Unlike the other MX_3 compounds which formed adducts (BX_3, AlX_3) or clusters of type $MCo_2Br_4(CO)_6$ ($GaBr_3$, $InBr_3$), $TlCl_3$ merely chlorinated the cobalt carbonyl to $CoCl_2$. The study on the Group IIIb metal-tin bonded compounds was extended by Weibel and Oliver (32). In this work, $Li[TlMe_4]$ was synthesized from lithium metal and Me_3Tl (eq. 17).

$$3Li + 4Me_3Tl \longrightarrow Tl + 3Li[TlMe_4] \qquad (17)$$

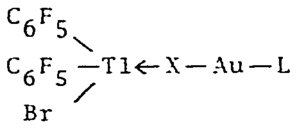
The reaction of this compound with varying amounts of Me_6Sn_2 allowed the formation of $Li[Tl(Me_3Sn)_nMe_{4-n}]$ (n= 1-4) (eq. 18).

$$\mathrm{Li[TlMe_4]} \;+\; \mathrm{nMe_6Sn_2} \longrightarrow \mathrm{Li[Tl(Me_3Sn)_nMe_{4-n}]} \;+\; \mathrm{nMe_4Sn} \qquad (18)$$

Proton NMR data for such tallium-tin compounds as well as for analogous $\mathrm{Li[M(Me_3Sn)Me_3]}$ (M= Al, Ga, In) have been reported. The variation in the values of ^2J(Sn-H), ^3J(Sn-H), ^2J(Tl-H) and ^3J(Tl-H) was discussed as a function of both M and n. The factors governing the changes in the couplings and the chemical shifts were proposed.

4. Reactions of Organothallium(III) Compounds

The reactions of $(C_6F_5)_2TlX$ (X= Br, I) with XAuL (L= PPh_3, $AsPh_3$) afforded $XAu(C_6F_5)_2L$ and TlX (33). Analogous reactions of $(C_6F_5)_2TlBr$ with $YAuPPh_3$ (Y= C_6F_5, Ph, NO_3, OAc, SCN, PPh_3^+) resulted in no oxidation of Au(I) to Au(III) but ligand substitution was observed. A possible intermediate for the reactions with X= halogen was postulated as shown below.



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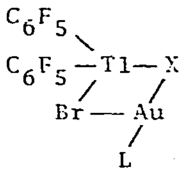
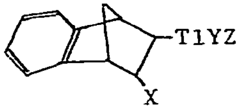


$(C_6F_5)_2TlBr$ also reacted with $PtCl_2(PEt_3)_2$ or $PtCl(C_6F_5)(PEt_3)_2$ to afford $PtCl_2(PEt_3)_2.Tl(C_6F_5)_2Br$ or $PtCl(C_6F_5)(PEt_3)_2.Tl(C_6F_5)_2Br$, respectively (34). The galvanostatic method has been employed to study the interaction of Et_2Tl^+ ion with mercury metal (35). In this study Et_2Hg_2 was shown to be formed on the mercury surface, probably <u>via</u> the formation of an intermediate $[EtHgTlEt]^+$ ion (eq. 19).

$$Et_2Tl^+ + Hg \rightleftharpoons [EtHgTlEt]^+ \xrightleftharpoons{Hg} Tl^+ + Et_2Hg_2 \qquad (19)$$

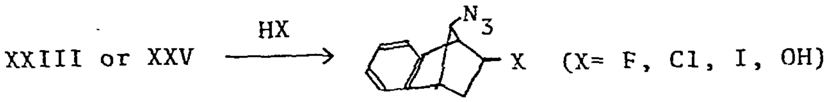
The formation constants of $PhTl(NCS)_n^{2-n}$ (n= 1-4) and $Ph_2Tl(NCS)_n^{1-n}$ (n= 1, 2) were determined at 25° from the distribution coefficients of $PhTl^{2+}$ and Ph_2Tl^+ between Sephadex A 25 anion exchanger and aqueous KSCN containing $PhTl(NCS)_2$ or Ph_2TlNCS (36). For $PhTl(NCS)_n^{2-n}$, log β_n= 2.3, 3.9, 4.7 and 4.8 for n= 1-4, respectively, were obtained; for $Ph_2Tl(NCS)_n^{1-n}$, log β_n= 0.1 and 0.6 for n= 1,2 respectively. From studies of the specific OH^- catalyzed decomposition of diacetone alcohol by Me_2TlOH at 25°, it was concluded that both ion pairs (dissociation constant 0.090 M) and dimers (dimerization constant 1.5 M^{-1}) of Me_2TlOH exist in aqueous solution (37).

The reaction of olefins with the system $Tl(OAc)_{3-n}(N_3)_n$ (n= 0-3), which can be generated by mixing varying amounts of $Tl(OAc)_3$ and Me_3SiN_3, has been investigated (38). With benzonorbornadiene, adducts XXIII-XXV were isolated and characterized. XXIV and XXV were further converted to XXVI and XXVII by Me_3SiN_3 and Me_3SiNCO, respectively.



XXIII	$X=Y=Z=N_3$
XXIV	$X=Y=Z=OAc$
XXV	$X=N_3$, $Y=Z=OAc$
XXVI	$X=Y=OAc$, $Z=N_3$
XXVII	$X=N_3$, $Y=OAc$, $Z=NCO$

Dethallation from such oxythallated adducts was performed under several conditions affording various compounds as shown in eq. 20-22.



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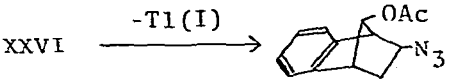

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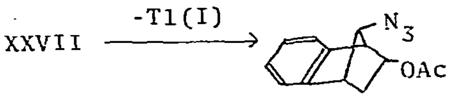
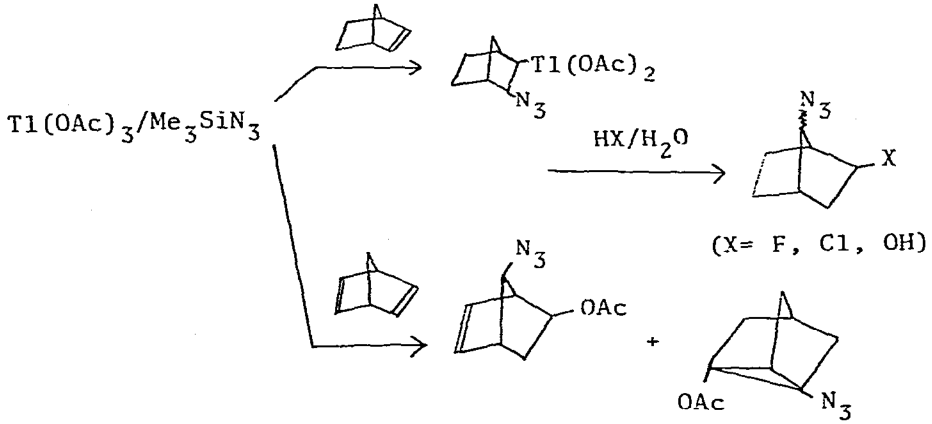


(22)

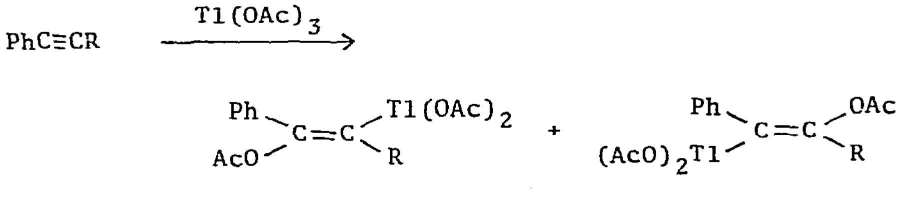
The reaction of $Tl(OAc)_3/Me_3SiN_3$ with norbornene or norbornadiene proceeded according to eq. 23 and 24.



(23)

(24)

A full account of the study by Uemura et al. on the acetoxythallation of acetylenes appeared (39). Treatment of alkylphenylacetylenes with $Tl(OAc)_3$ in acetic acid yielded two isomeric trans-acetoxythallated products (eq. 25).



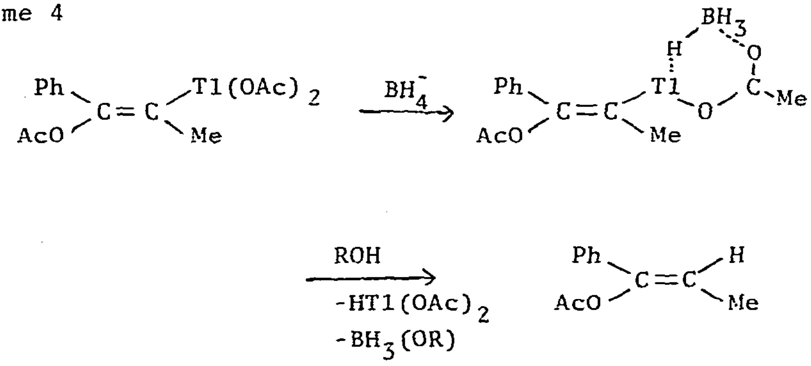
(25)

XXVIII XXIX

R= Me, Et, ^{n}Pr, ^{n}Bu

Heating XXVIII and XXIX in acetic acid resulted in the formation of PhC(OAc)=CHR and PhCH=C(OAc)R with retention of configuration. The same compounds also were the principal products from hydrogenolysis of XXVIII and XXIX with $NaBH_4$ in protic solvents at pH 6-7. In this reaction, deuterium labelling experiments showed that the hydrogen for replacement of the $Tl(OAc)_2$ group came from the solvent, not from $NaBH_4$, suggesting the following sequence (Scheme 4).

Scheme 4



Treating XXVIII with CuX or CuX_2 gave PhC(OAc)=CRX (X= Cl, Br, I, CN, SCN) with retention of configuration. These authors also prepared some oxythallated adducts of styrene and α-methylstyrene, and investigated the reactivities of these adducts (40). The adducts reacted with copper(I) halides and pseudohalides to afford the corresponding alkyl halides and pseudohalides in moderate to good yields (eq. 26, 27).

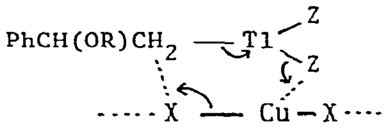
$$PhCR^1{=}CH_2 \xrightarrow[R^3OH]{Tl(OOCR^2)_3} PhCR^1(OR^3)CH_2Tl(OOCR^2)_2 \qquad (26)$$

R^1= H, Me; R^2= Me, ${}^iPr$; R^3= Me, Et, ${}^nPr$ ${}^iPr$, ${}^nBu$, ${}^iBu$

$$PhCH(OR^3)CH_2Tl(OAc)_2 \xrightarrow{CuX} PhCH(OR^3)CH_2X \qquad (27)$$

X= Cl, Br, I, CN, SCN;
R^3= Me, Et, ^{n}Pr, ^{n}Bu

The effects of both the nature of solvents and the addition of KX were examined. A possible intermediate proposed for such halogenodethallation reaction is



The kinetics of decomposition of the oxythallated adduct from $Tl(OAc)_3$ and styrene, $PhCH(OMe)CH_2Tl(OAc)_2$ XXX has been studied in H_2O/MeOH (41). The products identified were phenylacetaldehyde and its dimethylacetal. The reaction follows a first order rate law. Analysis of the kinetic parameters indicated that XXX dissociates into a reactive species $RTlOH^+$ and a more reactive RTl^{2+} (eq. 28).

$$RTl(OAc)_2 \rightleftharpoons RTlOAc^+ + OAc^- \overset{H_2O}{\rightleftharpoons} RTlOH^+ \overset{H^+}{\rightleftharpoons} RTl^{2+} \qquad (28)$$

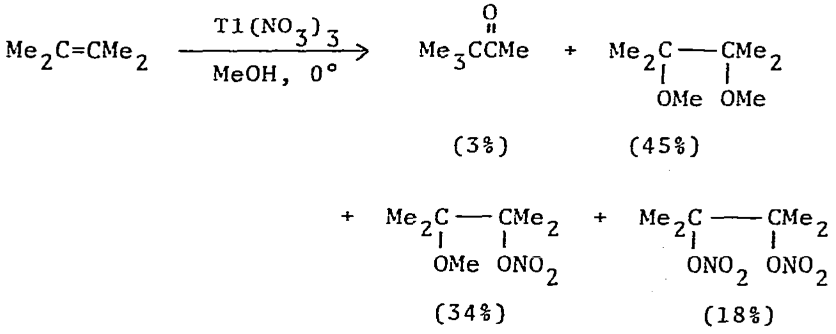
R= $PhCH(OMe)CH_2$

The implication of this study is that the nature of the rate-determining step in the overall oxidation of styrene by Tl(III) largely depends on experimental conditions.

The distribution of products formed in the oxidation by $Tl(NO_3)_3$ of the olefins $RCH{=}CH_2$ and $R^1R^2C{=}CH_2$ in methanol has been studied (42). Both $RCH(OMe)CH_2OMe$ and RCOMe were formed from the former olefins. When R= CH_2Cl only the diether was formed. With $R^1R^2C{=}CH_2$, the ratio of the rate constants for the formation of the $R^2COCH_2R^1$ (k_1) *versus* that of the $R^1COCH_2R^2$ (k_2) was related to the polar Taft constants by the equation,

$$\log k_1/k_2 = \rho^*(\alpha_2^* - \alpha_1^*) \text{ with } \rho^* = -4.$$

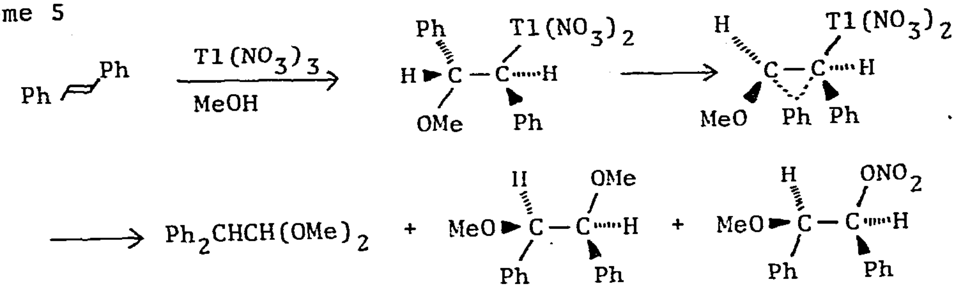
This result led the authors to suggest that the migration of the better electron donor occurs preferentially. A possible reaction sequence involving $R^1R^2C(OMe)CH_2TlX_2$ and its dethallation step was discussed. In a related study by Bertsch and Ouellette (43), a careful examination of the oxidation of 1-decene, 2,3-dimethyl-2-butene and *cis*- and *trans*-stilbene with $Tl(NO_3)_3$ in methanol has confirmed the formation of not only the carbonyl and dimethoxy compounds but mono- and dinitrate esters of the corresponding diols, *e.g.*



$$Me_2C{=}CMe_2 \xrightarrow[\text{MeOH, 0°}]{Tl(NO_3)_3} \underset{(3\%)}{Me_3C\overset{O}{\overset{\|}{C}}Me} + \underset{(45\%)}{Me_2\underset{OMe}{C}-\underset{OMe}{C}Me_2} + \underset{(34\%)}{Me_2\underset{OMe}{C}-\underset{ONO_2}{C}Me_2} + \underset{(18\%)}{Me_2\underset{ONO_2}{C}-\underset{ONO_2}{C}Me_2} \qquad (29)$$

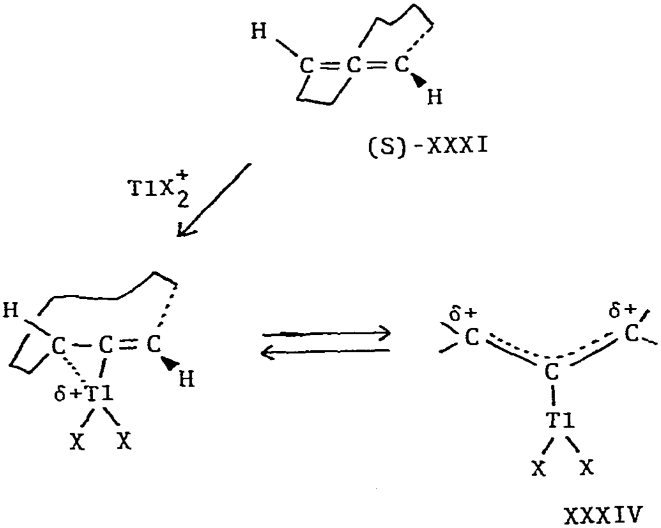
Stereochemical analyses of the products from *cis*- and *trans*-stilbene led the authors to believe that the initial oxythallation proceeds in a trans fashion, *e.g.* in Scheme 5.

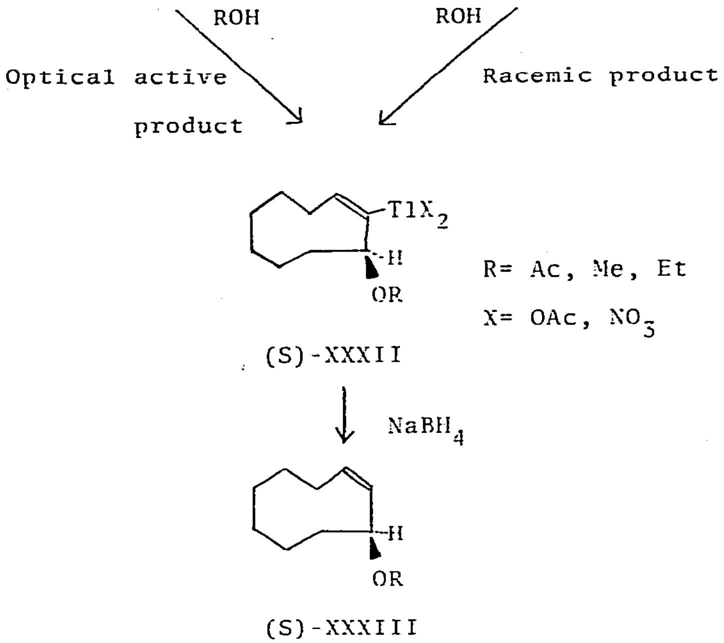
Scheme 5



Stereochemical problems in oxythallation also were the subjects of work by other groups. Bach and Holubka reported (44) that acetoxythallation of optically active 1,2-cyclononadiene XXXI ($[\alpha]_D^{25}$ -15.6°) affords XXXII ($[\alpha]_D^{25}$ ca. -0.5°), which on reduction with $NaBH_4$ gives XXXIII (R= Ac) ($[\alpha]_D^{25}$ +0.6°) (Scheme 6).

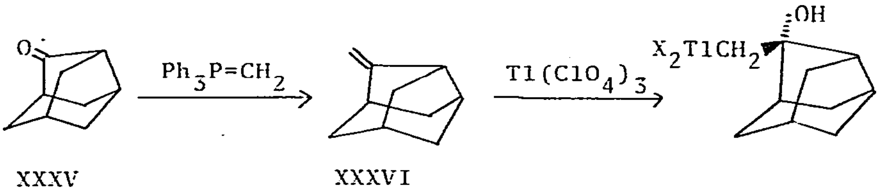
Scheme 6

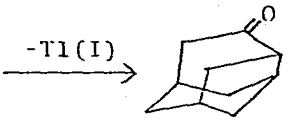




Similarly, methoxy- and ethoxythallation-dethallation of XXXI also gave optically active allylic ethers XXXIII (R= Me, Et). These facts led the authors to suggest that the planar allylic cation XXXIV cannot be the sole precursor to XXXII and that the oxythallation process involves an anti mode of addition. The optical purity of XXXIII (R= Me, Et) was reduced when X= NO_3. In other work (45), $Tl(ClO_4)_3$ was treated with 2-methylene-noradamantane XXXVI, which had been prepared from 2-noradamantanone XXXV and Ph_3PCH_2, to give a 60% yield of 4-protoadamantanone XXXVII (Scheme 7).

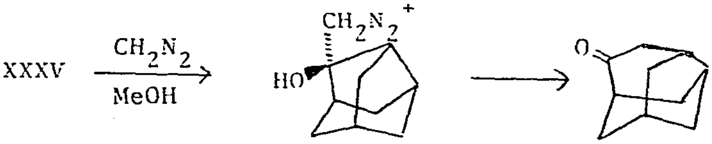
Scheme 7





XXXVII

The formation of XXXVII was assumed to be a consequence of an intermediate involving a cationoidic methylene group in an axial position resulting from the exo attack of H_2O in oxythallation and a subsequent dethallation. These sequences were compared with the fact that the isomer of XXXVII is formed selectively when XXXV is treated with diazomethane in MeOH owing to an intermediate of different conformation bearing an exo cationoidic methylene as in eq. 30.



(30)

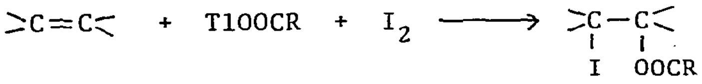
A comparative study has been made of the oxidation by Hg(II), Tl(III) and Pb(IV) acetates of 1-octene in methanol (46). The products identified from the Tl(III) and Pb(IV) oxidations include RCOMe, $RCH(OMe)CH_2OMe$, $RCH(OMe)CH_2OAc$, $RCH(OAc)CH_2OMe$ and $RCH(OMe)CH_2Cl$ ($R= C_6H_{13}$). Chlorine in the last compound came from Cl^- impurity in the metal oxidant. The product distribution was discussed in terms of the relative importance of several ways of decomposition of the oxymetallated adducts.

Some other studies of the application of Tl(III) compounds to organic synthesis include the synthesis of isoflavonoids through the oxidative rearrangement of chalcones with $Tl(NO_3)_3$ (47), an effective synthesis of p-quinols by oxidation of p-alkylphenols with $Tl(ClO_4)_3$ (48), iodination of benzene and mesitylene with I_2 in the presence of $Tl(OOCCF_3)_3$ (49), and iodination by KI of arylthallium bistrifluoroacetates derived from $Tl(OOCCF_3)_3$ and aromatic acids (50).

Thallium(I) Compounds

m- and p-Fluorophenylcyclopentadienylthallium(I) have been synthesized and ^{19}F NMR spectra were measured in THF (51). The chemical shifts and α_I and α_R^o values calculated thereof were compared with the respective values for $MC_5H_4C_6H_4F$-m(p) (M= alkali metal) and $C_5H_5FeC_5H_4C_6H_4F$-m(p). The thallium-cyclopentadienyl bond ionicity has been estimated to be 40-50% in THF. The thallium(I) salt of 7,8-$C_2B_9H_{11}^{2-}$, $Tl_2C_2B_9H_{11}$ which was obtained previously (Chem. Commun., (1972) 1178) has been utilized for synthesizing several arsacarboranes (52). Thus, the reaction of $Tl_2C_2B_9H_{11}$ with $RAsX_2$ (R= Me, X= Br; R= Ph, ^nBu, X= Cl) produced 3-R-3-As-1,2-$C_2B_9H_{11}$; the reaction with Me_2AsBr in a 2/1 ratio afforded $(Me_2As)_2C_2B_9H_{11}$.

Cambie and coworkers extended their study of the use of $TlOOCR/I_2$ system in organic synthesis. Thus, treatment of alkenes with TlOOCR and I_2 gave the corresponding vic-iodocarboxylates in high yield (53, 54).



$$>C{=}C< \; + \; TlOOCR \; + \; I_2 \longrightarrow \underset{I}{>C}-\underset{OOCR}{C<} \qquad (31)$$

(R= Me, CF_3, Ph)

The reactions are regiospecific and in conjunction with solvolysis of the products, offer an alternative to the Prevost reaction. A possible mechanism involving an iodine-alkene π-complex, an iodonium ion type intermediate and a Tl(I) species rather than a

Tl(III)-olefin interaction has been discussed. A similar reaction of unsaturated thallium(I) carboxylates *e.g.* $\mathrm{TlOOC(CH_2)_n\overset{|}{C}=C<}$ with I_2 gave a convenient procedure for iodolactonization under neutral conditions (55).

Complementary to the Survey Covering the Year 1973

Solutions of the 5-bromo- or 5-chlorocyclopentadienes were prepared by treatment of CpTl with the N-halosuccinimide in various solvents (56). These 5-halocyclopentadienes were converted to the unsubstituted cyclopentadienyl cation on treatment with SbF_5.

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