THALLIUM

ANNUAL SURVEY COVERING THE YEAR 1973

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The synthesis and structure of new organo-thallium compounds have seen very little progress during the year 1973, while a modest number of papers concerning the reactivity of organothallium derivatives and their application to organic synthesis continued to appear. This survey will deal with 1) reviews, 2) synthesis of new organothallium compounds, 3) compounds containing thallium-metal bonds, 4) kinetic studies, 5) reactions of organothallium(III) compounds and 6) reactions of Tl(I) compounds.

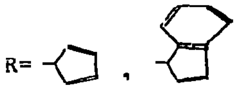
Reviews

Two reviews by McKillop and Taylor have appeared (1,2) which are mainly concerned with the applications of organothallium compounds to organic chemistry. Other review articles on organometallic eight-membered ring compounds (3) and on the stability of organometallic complexes with anionic and neutral ligands (4) included surveys on organothallium compounds of related interest.

Synthesis of new organothallium compounds

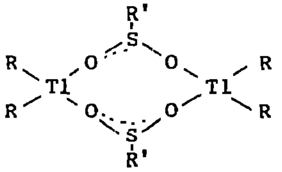
A research group in India reported the preparation of a series of cyclopentadienyl, indenyl and fluorenyl derivatives of Tl(III) (5-9). Treatment of $(C_5H_5NH)_2TlCl_5$ with cyclopentadienyl- (5), indenyl- (5), and fluorenylsodium (5) gave tricyclopentadienyl-, triindenyl- and trifluorenylthallium, respectively The former two compounds could also be obtained by refluxing Tl_2O_3 with cyclopentadiene or indene in THF solution (7). The reaction of $(C_5H_5NH)_2TlCl_5$ with two equivalents of cyclopentadienyl- and indenylsodium gave dicyclopentadienylthallium chloride and diindenylthallium chloride, respectively (8). The chlorides could be converted to the corresponding borohydrides by treatment with sodium borohydride (9).

$$R_2TlCl + NaBH_4 \longrightarrow \underset{I}{R_2TlBH_4} + NaCl \qquad (1)$$



IR studies suggested that thallium-to-boron bonding through bridging hydrogen atoms occurs in I. Preparation of cyclooctatetraenethallium(III) chloride and potassium salt of cyclooctatetraenethallium(I) was reported (10).

Deacon et al. synthesized several diorganothallium arenesulfinates R_2TlO_2SR (R= Me, Et, Ph, C_6F_5; R'= Ph, p-MeC_6H_4) from R_2TlX (X= halogen) and AgO_2SR' (10) Molecular weight determinations and IR spectra of II indicated the structure in solution to be dimeric with bridging O-sulfinato groups, while weak association the dimeric units occurs in the solid state. II forms some 1:1 adducts with 1,1' phenanthroline (phen), 2,2'-bipyridyl (bipy), pyridine, Ph_3PO or Ph_3AsO. For th monomeric pyridine, Ph_3PO and Ph_3AsO complexes, the sulfinato groups are unident with 4-coordinate Tl atom, while the phen and bipy analogs may contain either unidentate or bidentate sulfinato groups with 5- or 6-coordinate Tl atoms. Deac et al. also reported the preparation of $(C_6F_5)_2TlOAc$ from $LiO_2SC_6F_5$ and Tl(III) salts through SO_2 elimination of S-sulfinatothallium(III) compounds (12).



II

Some organothallium dithiophosphates were investigated by Walther (13). Phenylthallium(III) derivatives of the type, $PhTl(S_2PRR')_2$ III (R= R'= OMe; R= R'= OPh; R= R'= Ph; R= Ph, R'= OEt) were prepared from $PhTlCl_2$ and the corresponding alkali metal dithiophosphates. Ph_2TlS_2PRR' IV (R= R'= OMe; R= R'= OEt; R= R'= OPh; R= Ph, R'= OEt) were obtained similarly. An analogous reaction of $EtTl(OOC^iPr)_2$ with $KS_2P(OR)_2$ resulted in the formation of $TlS_2P(OR)_2$ as shown in eq. 2. Both III and IV were found to be monomeric in benzene.

$$EtTl(OOC^iPr)_2 + 2KS_2P(OR)_2 \longrightarrow TlS_2P(OR)_2 + 2KOOC^iPr + (RO)_2PS_2Et \quad (2)$$

R= Me, Et, Ph

The following order of stability of dithiophosphate derivatives of Tl was suggested.

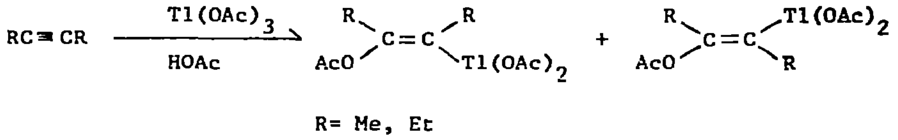
$$Tl(I) > Ph_2Tl(III) > PhTl(III) \gg alkylTl(III),\ Tl(III)$$

The results of IR, mass and proton NMR spectral studies of III and IV were discussed in terms of structure and stability.

Synthesis of organothallium(III) derivatives of aminopolycarboxylates and bases of biological interest was reported by Stocco et al. (14). Thus $PhTlCl_2$ forms 1:2 complexes with phenylglycine and phenylalanine, and 1:1 complexes with iminodiacetic acid, NTA and EDTA. The IR spectra of these compounds were reported. Cumylperoxydiphenylthallium, $Ph_2TlOOCMe_2Ph$, was prepared from Ph_2TlBr and $PhMe_2COONa$ and was found to be stable for a short time at 0-5°. It was cleaved rapidly by atmospheric moisture (15). Preparation and IR spectra of R_2TlCN (R= o-, m-, and p-MeC_6H_4, Ph) were reported (16).

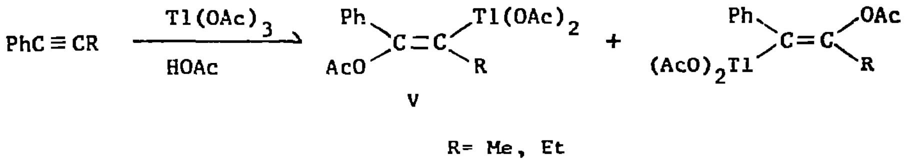
Olapinski and Weidlein prepared $(Me_2Tl)_2SO_4$ from Me_3Tl and H_2SO_4 (17) (see also the chapter on Ga and In). Raman and IR study of this compound gave evidence which suggested the presence of a linear Me_2Tl^+ cation and $SO_4^=$ anion in water solution.

Two independent groups reported on the preparation of vinylic derivatives of Tl(III) by oxythallation. Treatment of dialkylacetylenes with $Tl(OAc)_3$ in acetic acid gave stable acetoxythallated compounds (18) as shown in eq. 3.

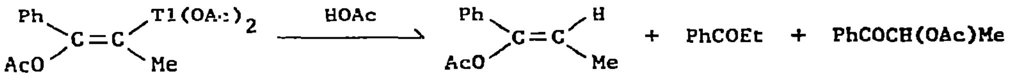


(3)

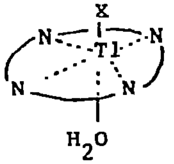
Assignments of the proton NMR spectra for cis and trans isomers above were made the basis of the magnitude of J(Tl-H). Uemura et al. reported a similar acetoxy thallation reaction using alkylphenylacetylenes (19).



Treatment of V (R= Me) with boiling acetic acid gave the dethallation product wil complete retention (eq. 5).



Abraham et al. reported the preparation and spectroscopic studies of some thallium(III) porphyrin (20) and coproporphyrin (21) chelate compounds. Visible absorption and proton NMR spectral evidence suggested that the Tl atom is situat out of the plane of the porphyrin ring with the anionic ligand (OH, OAc, $OOCCF_3$, CN) in the axial position (VI). A pronounced concentration dependence in the proton NMR spectra of thallium(III) coproporphyrins were interpreted in terms of a monomer-dimer equilibrium.



VI

Compounds containing thallium-metal bonds

Haupt and Neumann prepared $Ph_2TlMn(CO)_5$ from Ph_2TlCl and $NaMn(CO)_5$ in ether (22). Analogous reactions of R_2TlX (R= Me, ^{n}Pr and Ph; X= halogen) with $NaMn(CO)_5$ in THF resulted in the formation of $Tl[Mn(CO)_5]_3$. They also obtained $ClTl[Mn(CO)_5]_2$ according to the following scheme.

$$PhTlCl_2 + 2NaMn(CO)_5 \longrightarrow PhTl[Mn(CO)_5]_2 + 2NaCl \quad (6)$$

$$PhTl[Mn(CO)_5]_2 + PhTlCl_2 \longrightarrow Ph_2TlCl + ClTl[Mn(CO)_5]_2 \quad (7)$$

The IR spectra of these new metal-metal compounds were reported.

A Russian group synthesized a thallium-tin bonded compound, $Tl[Sn(CH_2SiMe_3)_3]_3$ VII by the reaction of Et_3Tl with 3 moles of $(Me_3SiCH_2)_3SnH$ at -10 to 20° (23). VII reacted with metallic mercury at 20° to give elemental thallium and $Hg[Sn(CH_2SiMe_3)_3]_2$, whereas the reaction of VII with $BrCH_2CH_2Br$ gave C_2H_4 and $(Me_3SiCH_2)_3SnBr$ (95%).

The crystal and molecular structure of $Tl[MoCp(CO)_3]_3$ was determined by Rajaram and Ibers (24). An overall view of the molecule is shown in Fig 1. The coordination around the central Tl atom was found to be trigonal pyramidal with the Tl atom being 0.586 Å out of the plane of the three Mo atoms. An average Tl-Mo bond distance is 2.965 Å and an average Mo-Tl-Mo bond angle 119.7°, where individual Tl-Mo distances and Mo-Tl-Mo bond angles differ significantly from these average values. No other metal-metal interactions were observed, which fails to explain the dichroism observed in that compound (Inorg. Chem., 9 (1970) 1936).

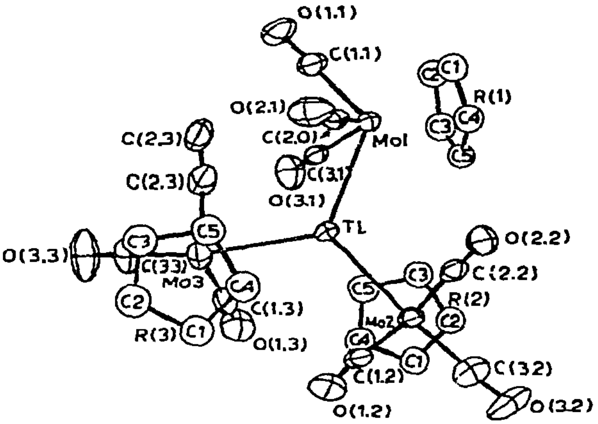


Fig. 1

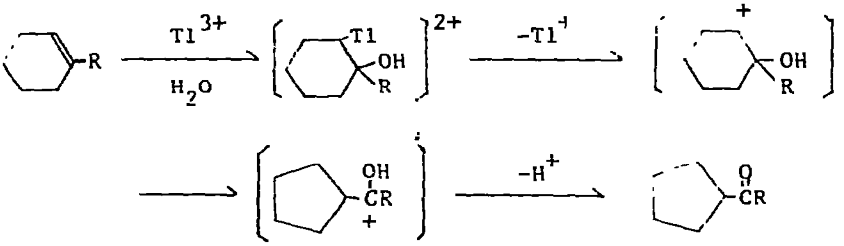
Kinetic studies

Price et al. investigated the pyrolysis of Me_3Tl in a mercury-free toluene carrier flow system (452-536°K, total pressure 6.7-39.3 mm, contact time 0.9-5.1 sec, 5.4-90.2% decomposition) (25). In a vessel cleaned with boiling concentrat HNO_3 and coated by decomposing 0.1 g Me_3Tl no heterogeneous reaction could be detected. The authors claim that the activation energy (36.4 Kcal/mole) obtaine by least square analysis of the first order rate constants should be a good approximation to $D[Me_2Tl\text{-}Me]$.

Kinetic studies on the oxidation of olefins by Tl(III) salts have been report by several research groups. Halpern et al. examined the kinetics of the reaction between $Tl(ClO_4)_3$ and several alkenols in aqueous perchloric acid (26). Substra studied include 1-propen-3-ol, 1-buten-4-ol, 1-penten-4-ol, 1-penten-5-ol and 1-hexen-6-ol which were converted to hydroxy-acetone and 1,2,3-propanetriol, 3-hydroxytetrahydrofuran, 2-methyl-4-hydroxytetrahydrofuran, 5-hydroxy-2-pentanon and 6-hydroxy-2-hexanone, respectively. The reactivity patterns for the initial rate of hydroxythallation step were found to be very similar to those for the corresponding hydroxymercuration over a wide range of olefin structures. The direct spectral detection of some of the intermediate hydroxythallated adducts also was described. These findings led the authors to propose the oxythallation dethallation mechanism:

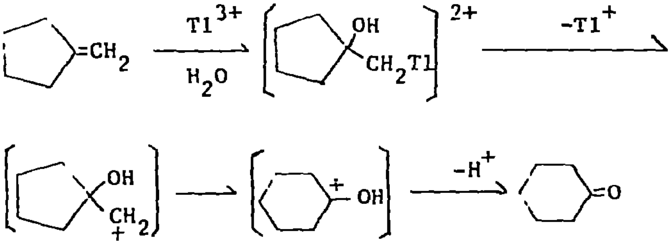
$$Tl^{3+} + CH_2{=}CHR \xrightarrow{H_2O} [TlCH_2CH(R)OH]^{2+} + H^+ \longrightarrow Tl^+ + \text{oxidation products} \qquad (8)$$

Halpern et al. suggested a similar mechanistic sequence for the oxidation of cycloalkenes, 1-methylcycloalkenes and methylenecycloalkanes by $Tl(ClO_4)_3$ on the basis of a kinetic study (27). The carbonyl products of the oxidation of the cycloalkenes and 1-methylcycloalkenes were typically ring-contracted aldehydes or ketones (eq. 9) and of the methylenecycloalkanes, ring-expanded cyclic ketones (eq. 10).



(9)

R= H, Me



(10)

A kinetic study of the oxidation of phenylethylenes by $Tl(NO_3)_3$ in methanol was reported by Nadon et al. (28). The reaction involved the formation of the thallium-organic intermediate as the rate-determining step, followed by the migration of aryl groups. Henry investigated deuterium isotope effects for reaction 11 employing C_2D_4, cis and trans-1,2-dideuterioethylene (29). The $k(C_2H_4)/k(C_2D_4)$ ratio observed for eq. 11 was less than unity (0.8), consistent with the fact that hydrogen is a better electron withdrawer than deuterium. The Tl(III) oxidation may be very sensitive to electronic effects. Furthermore, the ratio of the tendencies for H to transfer as opposed to D in eq. 12 was found to be 1.92. These findings, together with similar results with Pd(II)-deuterioethylene systems, led the author to confirm the earlier conclusion that hydroxymetalation is the rate determining step in both Tl(III) and Pd(II) oxidation of ethylene, followed by the rapid demetalation process.

$$C_2H_4 \xrightarrow[H_2O]{Tl(ClO_4)_3} CH_3CHO + HOCH_2CH_2OH + Tl^+ \qquad (11)$$

$$\begin{tikzcd} & & CHD_2CHO \\ C_2H_2D_2 + Tl(III) \arrow[r, "H_2O"] & TlCHD\text{-}\overset{H}{\underset{D}{C}}OH \arrow[ur, "D\ shift"] \arrow[dr, "H\ shift"] & \\ & & CH_2DCDO \end{tikzcd} \qquad (12)$$

Halpern et al. reported kinetic measurements of the reaction of $Tl(ClO_4)_3$ with organocobalt compounds (eq. 13), and some kinetic parameters obtained were compared with those for the better defined reaction of Hg^{2+} with $RCo(DH)_2(H_2O)$ (30).

$$RCo(DH)_2(H_2O) + Tl^{3+} + H_2O \longrightarrow RTl^{2+} + Co(DH)_2(H_2O)_2^{\ +} \qquad (13)$$

DH= dimethylglyoximate; R= Me, Ph

There was no indication of the formation of R_2Tl^+ by further reactions of RTl^{2+} with $RCo(DH)_2(H_2O)$.

Reaction of organothallium(III) compounds

Investigation of the reactivity of arylthallium(III) derivatives was extende by several groups. Taylor et al. found that treating $ArTl(OOCCF_3)_2$ with HCl and

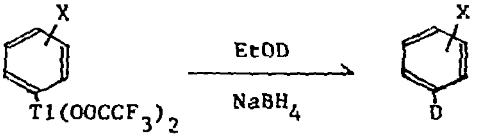
NOCl yielded the arylnitroso compounds with the orientation control potential inherent in the initial thallation process (31) as shown in eq.14 .

$$\mathrm{ArTl(OOCCF_3)_2} + \mathrm{2HCl} \longrightarrow \mathrm{ArTlCl_2} + \mathrm{2CF_3COOH} \qquad (14)$$

$$\mathrm{ArTlCl_2} \xrightarrow{\mathrm{NOCl}} \mathrm{ArNO} + \mathrm{TlCl_3}$$

Ar= Ph, p-$MeOC_6H_4$, p-ClC_6H_4, p-MeC_6H_4, p-EtC_6H_4 and some polymethylated phenyl

Electrophilic displacement of Tl(III) with a 4-centered transition state was suggested. Herbert reported a convenient method for the specific introduction of a single deuterium atom into aromatic compounds (32). Thus, reduction of $ArTl(OOCCF_3)_2$ with $NaBH_4$ in EtOD gave the corresponding o- or p-deuterio compounds (eq. 15).



(15)

X= p-^{n}Pr, p-OMe, o-COOMe, o-COOH, o-CH_2COOH

The reaction of $ArTl(OAc)ClO_4$ with $Cu(SCN)_2$ in the presence of KSCN afforded aryl thiocyanates as shown in eq.16 (33). It was shown that the yields are very solvent dependent and that the use of CuSCN is less effective for the thiocyanatio

$$\mathrm{ArTl(OAc)ClO_4} + \mathrm{Cu(SCN)_2} \xrightarrow{\mathrm{KSCN}} \mathrm{ArSCN} + \mathrm{TlClO_4} + \mathrm{Cu(OAc)SCN} \qquad (16)$$

Ar= Ph, p-MeC_6H_4, 3,4-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$, p-$MeOC_6H_4$

Some RC_6H_4SCN (R= H, Cl, F, Me, OMe, Me_3C) were prepared by photolysis of $RC_6H_4Tl(OOCCF_3)_2$ in DMSO in the presence of excess KSCN (34).

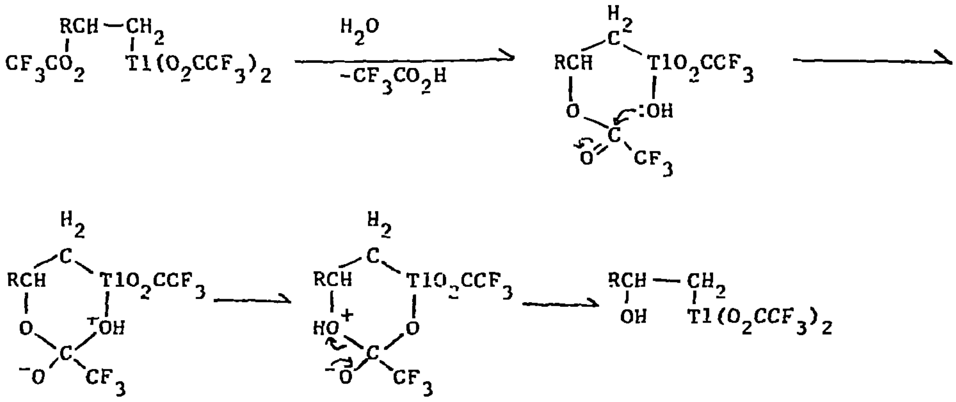
The reaction of $LiMR_4$ (M= B, Al, Ga, Tl; R= H, Me) with Me_6Sn_2 has been studied (35). The formation of $Li[(Me_3Sn)_nTlMe_{4-n}]$ (n= 1,2) derivatives in the reaction of $LiTlMe_4$ was suggested on the basis of the observation of Sn and Tl satellites in the methyl proton signals in NMR spectra. A possible reaction sequence reported is:

$$\mathrm{LiTlMe_4 + Me_6Sn_2 \longrightarrow Me_4Sn + Li[Me_3SnTlMe_3]} \quad (17)$$

$$\mathrm{Li[Me_3SnTlMe_3] + Me_6Sn_2 \longrightarrow Me_4Sn + Li[(Me_3Sn)_2TlMe_2]} \quad (18)$$

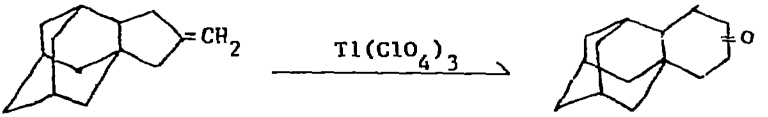
$$\mathrm{2Li[Me_3SnTlMe_3] \rightleftharpoons LiTlMe_4 + Li[(Me_3Sn)_2TlMe_2]} \quad (19)$$

A study of the oxidation of 1-octene by $\mathrm{Tl(OOCCF_3)_3}$ in a number of solvents showed that the initial organothallium adduct is stable under the reaction conditions employed (36). When treated with water, it rapidly decomposed to give mainly octan-2-one, 1,2-epoxy octane and octane-1,2-diol. It was suggested that the neighboring Tl substituent aids hydrolysis as shown in eq. 20, which may exp the product distribution.



(20)

The scope, limitations and synthetic utility of $\mathrm{Tl(NO_3)_3}$ oxidation of olefi have been studied (37). The reactions investigated include rapid rearrangement of olefins to carbonyl compounds <u>via</u> ring-contraction of cyclic olefins (see also ref. 26 and eq. 9) and aryl migration. Applications of ring enlargement by $\mathrm{Tl(ClO_4)_3}$ of methylenecycloalkanes (eq. 10) to adamantane systems were reported Although the four- and five-membered systems gave moderate yields of ring-expands ketones, the method was found to suffer from incompleteness of oxidation and sensitivity of the ketone products toward further oxidation. Typical examples are shown in eq. 21-23. The high ratio of VIII/IX obtained in eq. 23 led the authors to suggest the intermediacy of X rather than its endo epimer XI.



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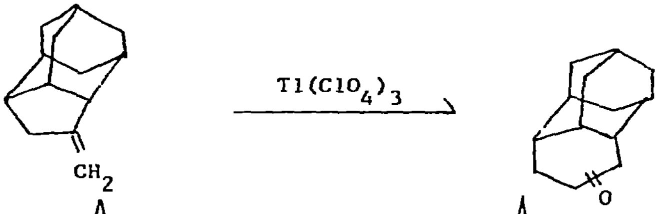

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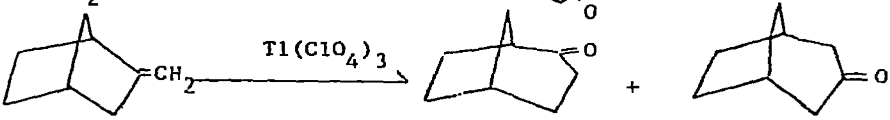
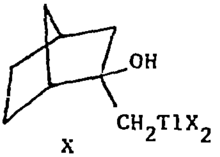
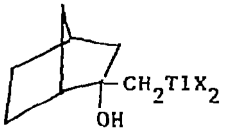


(23)

VIII (50%) IX (0.6%)

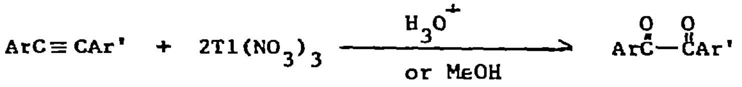


X

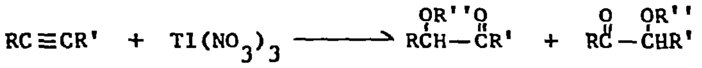


XI

A full account of oxidations of several acetylenes with $Tl(NO_3)_3$ has appeared (39). It was found that the nature of the products depends on the solvent employed and the structure of the acetylenes as shown in eq. 24-27. The specificity in oxidation was explained in terms of the mechanisms of the various reactions.



$$ArC\equiv CAr' + 2Tl(NO_3)_3 \xrightarrow[\text{or MeOH}]{H_3O^+} Ar\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}Ar' \qquad (24)$$

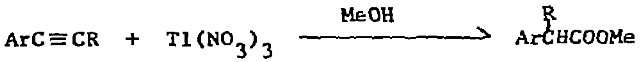


$$RC\equiv CR' + Tl(NO_3)_3 \longrightarrow R\overset{OR''}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}R' + R\overset{O}{\overset{\|}{C}}-\overset{OR''}{\overset{|}{C}}HR' \qquad (25)$$

R"= H (in aqueous solution)

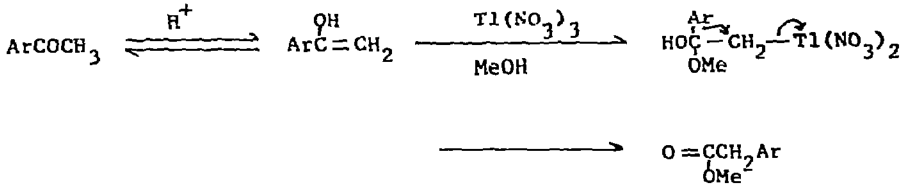
R"= Me (in MeOH)

$$RC\equiv CH + 2Tl(NO_3)_3 \xrightarrow{H_3O^+} RCOOH \qquad (26)$$



$$ArC\equiv CR + Tl(NO_3)_3 \xrightarrow{MeOH} Ar\overset{R}{C}HCOOMe \qquad (27)$$

McKillop et al. continued to study a one-step synthesis of methyl arylacetat by using $Tl(NO_3)_3$ in methanol (40). The reaction involves aryl migration (eq. 28 and the scope and limitations of the synthesis have been defined.



(28)

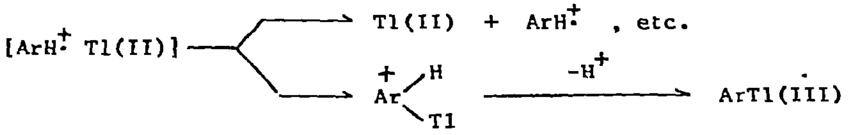
These workers also extended their previous report on the oxidation of chalcones, deoxybenzoins and benzoins with $Tl(NO_3)_3$ (41). They have shown that Tl(III) oxidation of chalcones to benzils, with loss of one carbon atom, takes place by means of a discrete series of three independent oxidations involving the intermediacy of deoxybenzoins and then benzoins as shown in eq. 29. A mechanism involving organothallium intermediates was postulated.

$$ArCH{=}CHCOAr' \xrightarrow{Tl(NO_3)_3} ArCH_2COAr' \xrightarrow{Tl(NO_3)_3}$$

$$ArCH(OH)COAr' \xrightarrow{Tl(NO_3)_3} ArCOCOAr' \qquad (29)$$

A cleavage of the cyclopropane ring in methyl ent-trachyloban-19-oate with $Tl(OAc)_3$ was reported to give four major products including the ent-atisane derivatives (42). An intramolecular oxidative phenol coupling with $Tl(OOCCF_3)_3$ was reported by Schwartz et al. (43). Elson and Kochi observed ESR evidence for a novel one-electron oxidation of polyalkylated aromatic compounds by $Tl(OOCCF_3)_3$ (44). Thus, paramagnetic species, the arene cation radicals, were readily detected in solution under thallation conditions involving the initial formation of charge-transfer complexes (eq. 30). Aromatic substitution can then proceed by collapse of the cage species or the arene cation radical can be observed after diffusive separation (eq.31).

$$\mathrm{Tl(III)} + \mathrm{ArH} \rightleftharpoons [\mathrm{ArH\ Tl(III)}] \rightleftharpoons [\mathrm{ArH^{\dot{+}}\ Tl(II)}] \qquad (30)$$



(31)

Reaction of $PhN{=}CCl_2$ with Me_2TlR (R= NMe_2, OEt, SPh, $P(O)Ph_2$, 1-pyrrolidinyl) in 1:1 and 1:2 molar ratio gave $PhN{=}CClR$ and $PhN{=}CR_2$, respectively (45).

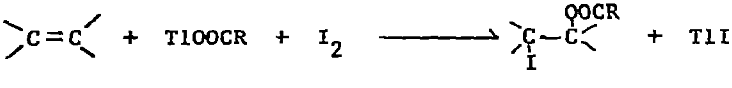
Reactions of Tl(I) compounds

A rapid synthesis of cobalticium salts XII-XIV was reported by using thallium(I) cyclopentadienide derivatives (eq. 32) (46).

$$C_5H_5Tl + MeC_5H_4Tl + CoCl_2 \xrightarrow{\mathrm{DMSO}}$$

$$\underset{\mathrm{XII}}{(C_5H_5)_2Co^+} + \underset{\mathrm{XIII}}{(C_5H_5)(MeC_5H_4)Co^+} + \underset{\mathrm{XIV}}{(MeC_5H_4)Co^+} \qquad (32)$$

The reaction of Tl(I) salts of 1,3-cyclohexanedione and 1,3-cyclopentanedione with a series of alkyl halides and α-haloesters gave, unlike the alkylation of acyclic diketone salts of Tl(I), the O-alkylation products predominantly rather than C-alkylation (47). Cambie et al. found that the use of a Tl(I) carboxylates and iodine provides an effective means for the high yield conversion of alkenes into the corresponding α-iodocarboxylates (eq. 33) (48).



(33)

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