THALLIUM

ANNUAL SURVEY COVERING THE YEAR 1972

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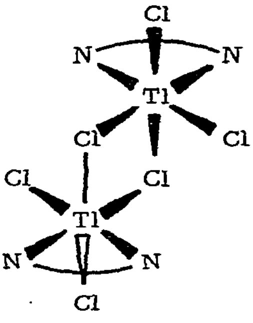
The pace of organothallium chemistry has slowed considerably from the past year and as a result there are no major new advances in this area. There have been a number of scattered reports which are included here. These range from papers on the crystal structure of halide complexes to compounds involving metal-metal bonded species. The order in which these studies will be taken up is: 1) structural and spectroscopic studies, 2) kinetic studies, 3) formation and reactions of alkyl-and arylthallium compounds, and 4) compounds containing thallium-metal bonds.

Structure and Spectroscopic Studies

The only crystal structures reported which are of interest here are those of tri-chloro(1, 10-phenanthroline)thallium(III)[1] and of the 2, 2', 2''-terpyridyl complex. In the phenanthroline derivative it was shown that the thallium exists in a distorted octahedral environment with weak chlorine bridging which gives rise to dimeric units as indicated in Figure I.

A similar result has been observed in the terpyridyl derivatives.[2] In the latter study the ir spectra of the Al, Ga, In, and Tl derivateves were



I

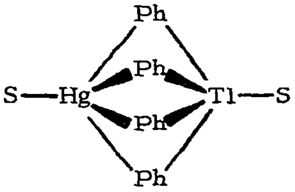
also examined and the use of ir spectra for structural assignment in species of this type was discussed.

The Raman spectra of both single crystals and solutions of Me_2TlClO_4 have been obtained and carbon-thallium bond polarizabilities derived.[3] These studies have been compared with those for the Me_2Sn^{++} species. In another study the ring vibration modes in R_2TlY (R = Ph, o-MePh, m-MePh and p-MePh; Y = CN, Cl, CNO, NCS, N_3, NO_2, NO_3, OAc, OPh) and in $(R_2Tl)_2S$ and $(R_2Tl)_2O$ have been reported and assignments for them have been made.[4] The data have been interpreted to mean that these absorptions are insensitive to the nature of the electronegative group attached to the thallium atom.

The only significant nmr study which appeared was that reported by Maher et. al. who investigated the $^1H-^{205}Tl$ coupling constants for a series of monoarylthallium dichlorides and substituted monoarylthallium dichlorides in DMSO solution.[5] This was done in order to compare these coupling constants with the corresponding $^1H-^1H$ coupling constants in aryl compounds. It was concluded from these studies that there is a close resemblance in the behavior of the $^{205}Tl-^{1}H$ and $^{1}H-^{1}H$ coupling constants. The possibility of developing an additive relationship was discussed.

Kinetic Studies

Several kinetic studies have appeared which are of interest. Hammond and Pollard have examined the exchange of Ph_2Hg with Ph_2Tl^+ as a model for the electrophilic substitution at the carbon atom.[6] The exchange proceeds in a second order fashion with activation parameters, $E_a = 21.3$ kcal/mole, $\Delta F^* = 27.6$ kcal/mole, $\Delta H^* = 20.6$ kcal/mole, and $\Delta S^* = -18.6$ kcal/mole. They proposed a transition state as indicated in Figure II. This model shows a four bridged transition state with solvent participation and is based on the apparent exchange of all groups simultaneously.



II

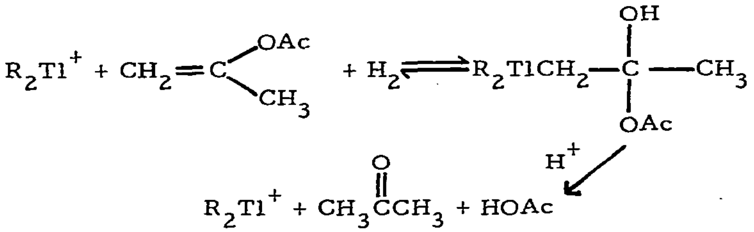
Briody and Moore have examined the kinetics and mechanism of the thalliation of benzene and toluene by thallium(III) acetate and this reaction when it is catalyzed by $HClO_4$ and H_2SO_4.[7] The mechanism of catalysis was discussed and explained on the basis of the equilibria indicated in 1 which yields more reactive species as it proceeds to the right. The observed

$$Tl(OAc)_3 \underset{}{\overset{+X}{\rightleftharpoons}} Tl(OAc)_2X \overset{+X}{\rightleftharpoons} Tl(OAc)X_2 \overset{+X}{\rightleftharpoons} TlX_3 \qquad (1)$$

isomer ratio and the relative reactivity of toluene to benzene indicate that the thalliation is a typical electrophilic aromatic substitution.

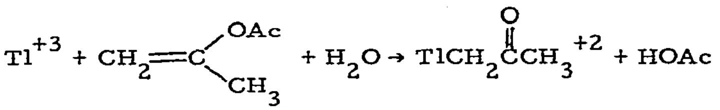
In an extensive study Kitching et al.[8] have also investigated the $M(OAc)_n$ catalyzed reactions of $RCH = CHCH_2HgOAc$ (R = Me, Ph). On the basis of their kinetic studies they have proposed several possible mechanisms for the reactions and suggested that σ bonded allylic groups may be involved. Clearly this report indicates these reactions are complex and definitive mechanisms have not been developed.

In another investigation the rate and mechanism of the organometallic ion catalyzed hydrolysis of isopropenyl acetate has been reported.[9] The mechanism proposed from these studies is indicated in 2. They also reported on kinetic measurements for the reaction shown in 3 and 4.



(2)

$R = CH_3COCH_2$, CH_3, Ph etc.



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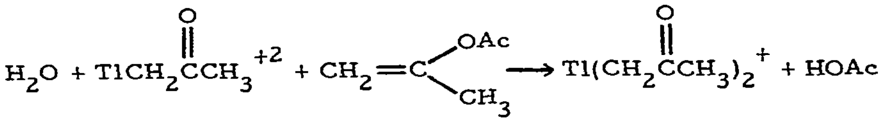


(4)

Uemura et. al.[10] have reported that Pd-Tl exchange occurs as indicated in 5 (73 - 93%) when carried out in methanol with sodium acetate present.

$$PhCH(OR')CH_2Tl(OCOR'')_2 + PdCl_2 \xrightarrow[MeOH]{NaOAc} \qquad (5)$$

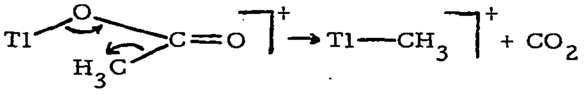
$$PhCOMe + Pd + Tl^{+3}$$

$R' = Me,\ Et,\ i\text{-}Pr,\ i\text{-}Bu$

$R'' = Me,\ i\text{-}Pr$

Use of deuteromethanol, MeOD, did not lead to incorporation of deuterium into the product.

A mass spectral study of the decarboxylation of $Tl(OOCR)_3$ derivatives has been reported.[11] It was suggested that decarboxylation occurred by a rearrangement of the type indicated in 6. Examination of $Tl(OOCCF_3)_3$



(6)

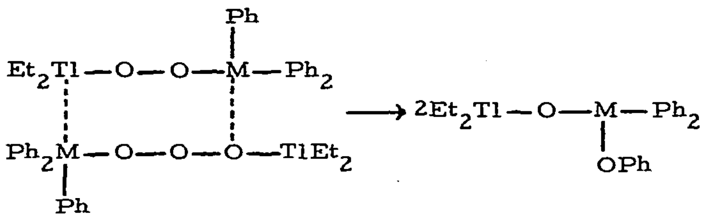
under the same conditions did not lead to formation of $Tl(CF_3)_3$ species but to other rearrangement and decomposition products.

Razuvaev et al.[12] have investigated the synthesis and decomposition of mixed organometallic peroxides as indicated in 7. They observed the formation of the germanium derivative, but the silicon derivative could not be

$$Et_3Tl + Ph_3MOOH \longrightarrow Et_2TlOOMPh_3 + C_2H_6 \qquad (7)$$

$M = Si,\ Ge$

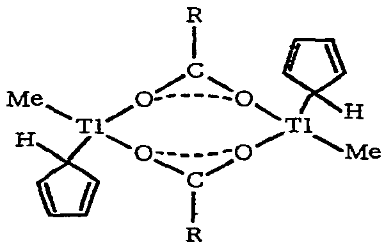
isolated. The germanium derivative underwent rearrangement by a second order reaction with an Arrhenius activation energy of 20.4 kcal/mole. The mechanism proposed for this rearrangement is indicated in 8.


(8)

The kinetics of the decomposition of Et_2TlOH in aqueous medium with and without added Et_2TlOAc, KO_2Ac or AcOH involved the formation of Et_2TlO_2Ac which dissociated into Et_2Tl^+ and AcO_2^-. A mechanism for the formation of Et_2TlOAc was discussed.[13]

Formation and Reactions of Alkyl-and Arylthallium Compounds

Abe and Okawara have prepared a variety of $Me(C_5H_5)TlX$ derivatives ($X = OAc, OCOC_2H_5, OCOi\text{-}Pr$) and have characterized these compounds by ir and nmr spectroscopy.[14] They concluded from these studies that the structure involved a σ bonded system as indicated in III. They also noted that the cyclopentadienyl ring undergoes rapid interchange resulting in all protons on the ring being equally coupled to the thallium atom.


III

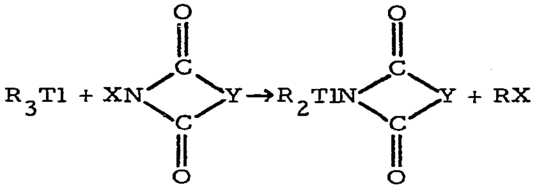
The direct synthysis of trialkyl- and mixed alkyl arylthallium derivatives by reaction of R_2TlX with a Grignard reagent has been reported.[15] The reactions were carried out in diethyl ether at low (-60°) temperatures.

$(C_6F_5)_2TlOH$ was prepared from reactions of $(C_6F_5)_2TlBr$ with KOH or AgOH in EtOH as well as by hydrolytic decomposition of $[(C_6F_5)_2Tl]_2CO_3$ aqueous EtOH.[16] The hydroxide has a hydroxy-bridged dimeric structure in nondonor solvents but these bridge bonds are easily broken in donor solvents although the rate is extremely slow at room temperature. The ir spectrum of $(C_6F_5)_2TlOH$ in Nujol was given.

The thallium(I) compounds $Tl(C_5Cl_5)$ and $Tl(C_5Cl_5)\cdot 2C_6H_5CH_3$ have been prepared and studied along with other derivatives of the pentachlorocyclopentadiene moiety.[17] The compounds were obtained by direct reaction of C_5Cl_6 with thallium amalgam or by reaction of TlOEt with C_5Cl_5H in pentane at -78°. If the reactions were carried out in toluene then two moles of toluene form a complex with the thallium derivative. The compounds are unstable at room temperature, but are stable at -80°. They ignite spontaneously in the air. The compounds were studied in detail by uv, ir, and nqr spectroscopy.

Several complexes of the form PhTlL have been prepared from $PhTlCl_2$ with the tri- or tetradentate ligands.[18] The ligands used were 2-pentanone-4-(2-benzothiazolinyl) and 2-(o-hydroxyphenyl)benzothiazoline which contain SON donor atoms, 2, 2'-methylidynenitrilodiphenol contianing the ONO donor atoms and N, N'-ethylenebissalicylaldimine which contains ONNO donor atoms. The compounds were characterized by their ir spectra and some speculation on the structures were presented.

Triorganothallium compounds have been shown to react in benzene with N-bromodicarbonylimides and the dicarbonylimides as seen in **9** yielding

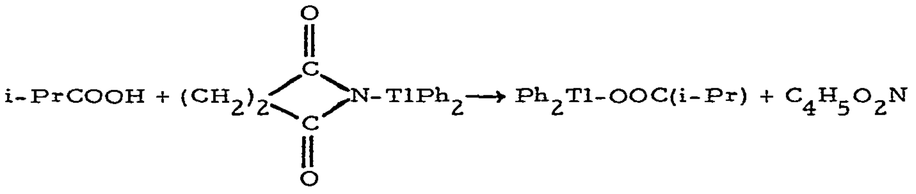


(9)

R = Me, Et, Ph; X = Br, H; Y = $-(CH_2)_n^-$, $O\text{-}C_6H_4$

the corresponding diorganothalliumdicarbonylimides.[19] The products were characterized by a number of physical and chemical studies including ir, nmr, mass spectral analysis. Tl-^{1}H coupling constants were reported of approximately 430 Hz for the methyl derivatives.

It was shown in some instances that carbonylimide could be regenerated by treatment with acid as indicated in **10**.



(10)

Hooz and Smith investigated the possible use of thallium enolates of β- keto sulfoxides and β-diketones for C alkylation and found that although the desired products may be obtained, the reactions are often complex yielding a mixture of products.[20] Therefore, the approach does not offer an advantage over other methods.

Et_3Tl was treated with i-PrOH in benzene under an inert atmosphere to give C_2H_6 and $Et_2TlOCHMe_2$ which with Bz_2O_2 in benzene gave O_2 and

$EtTlOCH_2Ph$ as well as i-PrOBz in solution.[21] Et_3Tl and Ph_3SiOH in benzene gave $Et_2TlOSiPh_3$ which with Bz_2O_2 gave, after 1.8 days at 40 - 50°, Et_2TlOAc and i-PrOAc. $Et_2TlOOCMe_3$ and Ac_2O gave Et_2TlOAc and Me_3COOAc. $EtOOTlEt_2$ and AcO gave Et_2TlOAc, AcH and AcOH.

Abe and Okawara have formed alkyl- and aryl-(chloromethyl)thallium chlorides and have reported on some of their physical and chemical properties.[22] The preparation was carried out as indicated in **11**. The resulting

$$ArTlCl_2 + CH_2N_2 \longrightarrow Ar(ClCH_2)TlCl \qquad (11)$$

Ar = Ph, p-MePh

product was converted to the carboxylate by treatment with thallium(I) carboxylate and could be converted to the dicarboxylate as indicated in **12**.

$$Ar(ClCH_2)TlOCOR' + Hg(OCOR')_2 \longrightarrow (ClCH_2)Tl(OCOR')_2 + ArHgOCOR' \qquad (12)$$

R' = Me, i-Pr

The dicarboxylate was alkylated with R_4Sn. This product underwent disproportionation as indicated in **13** with the unsymmetrical compound favored.

$$2R(ClCH_2)TlOCOR' \rightarrow R_2TlOCOR' + (ClCH_2)_2TlOCOR' \qquad (13)$$

R = Me, Ph, p-MePh; R' = Me, i-Pr

The compounds were characterized by ir, nmr, and their physical properties.

Abe et. al.[23] have observed the intermediate production of aryl(N, N-dimethyldithiocarbamoylmethyl)thallium acetate in **14**. The reaction could

$$\mathrm{Ar(ClCH_2)TlOAc + NaS_2CNMe_2 \longrightarrow Ar(Me_2NCS_2CH_2)TlOAc}$$

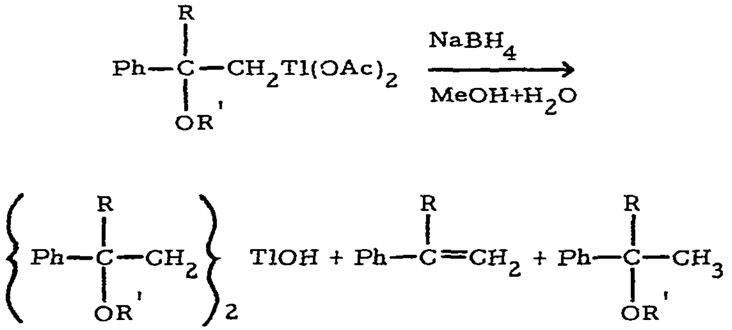
$$\xrightarrow{\mathrm{NaS_2CNMe_2}} \mathrm{Ar(Me_2NCS_2CH_2)TlS_2CNR_2} \qquad (14)$$

Ar = Ph, *p*-MePh; R = Me, Ph

be driven to the dithiocarbamate by addition of more NaS_2CNR_2.

They investigated the nmr spectra of the compounds obtained and suggested on the basis of the solvent dependence of the chemical shifts that rotation was restricted about the C-N bond. They also noted large long range coupling constants (${}^6J_{Tl-H}$ = 5 - 10 Hz) and suggested that the coupling occurred through the π system in these derivatives.

Alkaline $NaBH_4$ reduction of alkoxythalliated compounds of olefins gives a mixture of the parent olefin, alkyl ethers and dialkylthallium compounds; hydrogen for replacement of thallium arises from the solvent and not from BH_4^-.[24]

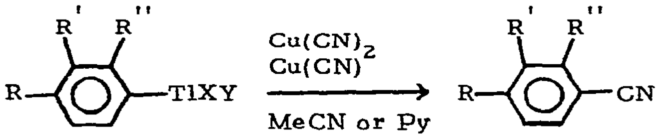


$$\mathrm{Ph{-}\overset{R}{\underset{OR'}{C}}{-}CH_2Tl(OAc)_2} \xrightarrow[\mathrm{MeOH+H_2O}]{\mathrm{NaBH_4}}$$

$$\left(\mathrm{Ph{-}\overset{R}{\underset{OR'}{C}}{-}CH_2}\right)_2\mathrm{TlOH} + \mathrm{Ph{-}\overset{R}{C}{=}CH_2} + \mathrm{Ph{-}\overset{R}{\underset{OR'}{C}}{-}CH_3} \qquad (15)$$

R = H, Me; R' = Me, Et, Pr, i-Pr

Uemura et al. have studied the reaction of arylthallium(III) salts with $Cu(CN)_2$ and CuCN and have shown that this reaction yields the corresponding nitrile as indicated in 16.[25] This reaction goes in fair yield (10-90%) in 5 - 10 hours in the refluxing solvent. Best results were obtained in pyridine.



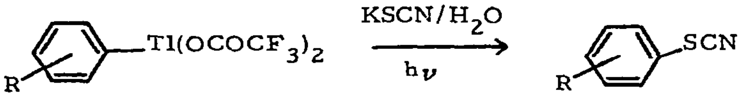
(16)

X = OAc; Y = $ClO_4 \cdot H_2O$; R = H, Me, MeO; R'R'' = H, Me

The mechanism was discussed.

Aryl thiocyanate derivatives can be prepared in reasonable yield by the reaction given in 17 in which the thallium derivative is photolized.[26] Yields range from 30-50%.

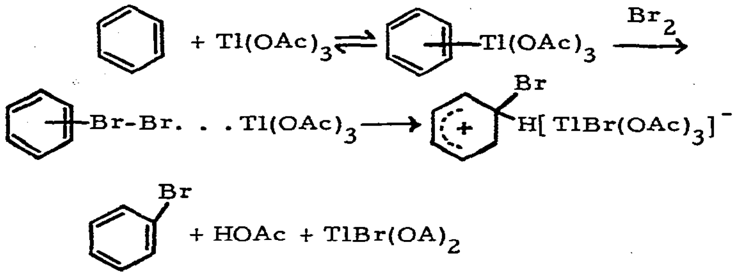
McKillop et al. have shown that a mixture of $Tl(OAc)_3$ and Br_2 is a mild and efficient reagent for electrophilic aromatic bromination.[27] The reaction is applicable to the preparation of a wide range of isomerically



(17)

R = 4-Me, 4-Et, 4-OMe, 4-Cl, 2,4-di-Me, 2,5-di-Me, 3,4-di-Me

pure monobromo aromatic compounds but is successful only when the substrate is activated toward electrophilic substitution. Several possible mechanisms of reaction were considered and that shown in scheme 18 appears to best account for the observed reaction.



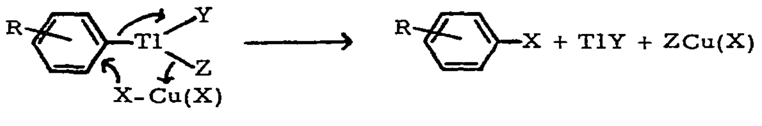
(18)

In contrast to aromatic bromination with $TlBr_3 \cdot 4H_2O$ the reaction of lower aromatic hydrocarbons (C_6-C_8) with $TlCl_3 \cdot 4H_2O$ in boiling carbon tetrachloride proceeds as indicated in 19 yielding the corresponding benzoic

$$RC_6H_5 \longrightarrow RC_6H_4Cl + RC_6H_4CO_2H \qquad (19)$$

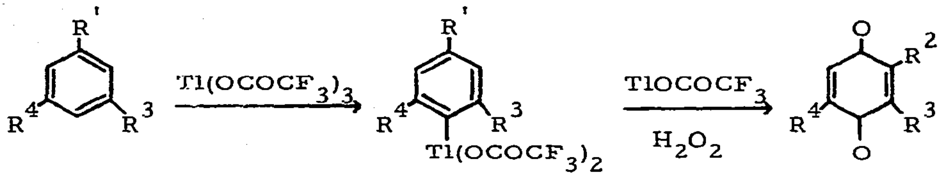
acid and the o and p chlorinated hydrocarbons.[28] The carboxylation was favored at lower temperatures. Several possible mechanisms were discussed.

Uemura et.al. have also investigated the halogenation of aromatic thallium derivatives, ArTlYZ, with $CuCl_2 \cdot 2H_2O$, $CuCl_2$ and Cu_2Cl_2.[29] They studied these reactions under a variety of conditions and in several organic solvents. They concluded reaction was very solvent dependent with the best choice for production of the aromatic halide dioxane. A concerted ionic mechanism as indicated in 20 was proposed.



(20)

Another use of thalliation has been reported by Chip and Grossert[30] in which they formed 1, 4-benzoquinones via the reaction indicated in 21. The reaction appears to be general and provides 40-70% yields for a variety of

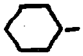


(21)

simple aromatic species. The mechanism of reaction was discussed and is complex with either elimination or migration occurring on the ring depending upon the substituents on the starting aromatic compound.

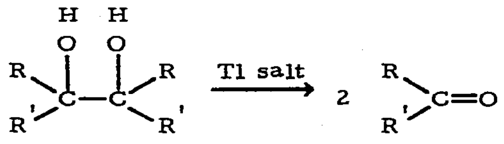
Kienzle has reported the oxidation of isonitriles with $Tl(NO_3)_3$ to yield carbamates in a simple normally high yield process as indicated in 22.[31]

$$R\text{—}NC + Tl(NO_3)_3 \xrightarrow[H_2O]{MeOH} RNHCOOMe + TlNO_3 + 2HNO_3 \qquad (22)$$

R = $EtOCOCH_2$ - (84%), -(90), t-Bu (35), Ph (93),
Me-(85),  (97)

The thallic oxidation of the tetrasubstituted and gem-disubstituted olefins, $RMeC = CH_2$ on the other hand is not selective with respect to the olefinic[32] carbon atom which is attacked by $Tl(NO_3)_3$. $RMeC = CMe_2$ (R = Me, Et) gave mixtures of the branched ketones, RMe_2CCOMe and $RCOCMe_3$ while mixtures of the branched aldehydes, RMeCHCHO and the ketones, RCOEt, are obtained from $RMeC = CH_2$ (R = Et, t-Bu). Probably, a delocalized-charge π thallic complex is formed.

McKillop and Raphael[33] have investigated the oxidative cleavage of glycols by thallium salts and have shown the reaction proceeds smoothly when at least two aryl groups are present on the glycol yielding the ketone as seen in 23. The reaction was not effective for saturated derivatives.

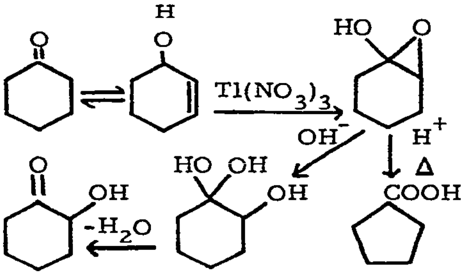


(23)

R = Me, Ph; R' = Ph, 2-MePh, 4-MePh, 4-ClPh

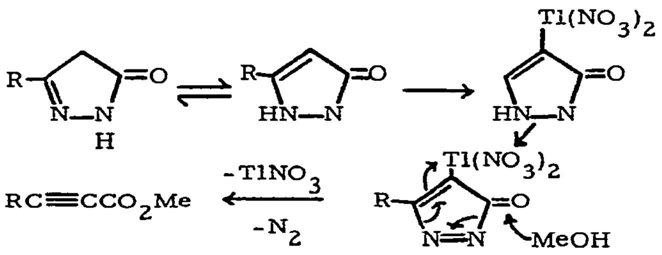
Tl salt = $Tl(NO_3)_3 \cdot 3H_2O$ or TlOEt

McKillop et al.[34] have reinvestigated the reaction of $Tl(NO_3)_3$ on cyclohexanone and have shown that it yields initially the epoxy enol which may yield either the adipoins or the carboxylic acid depending upon reaction conditions.



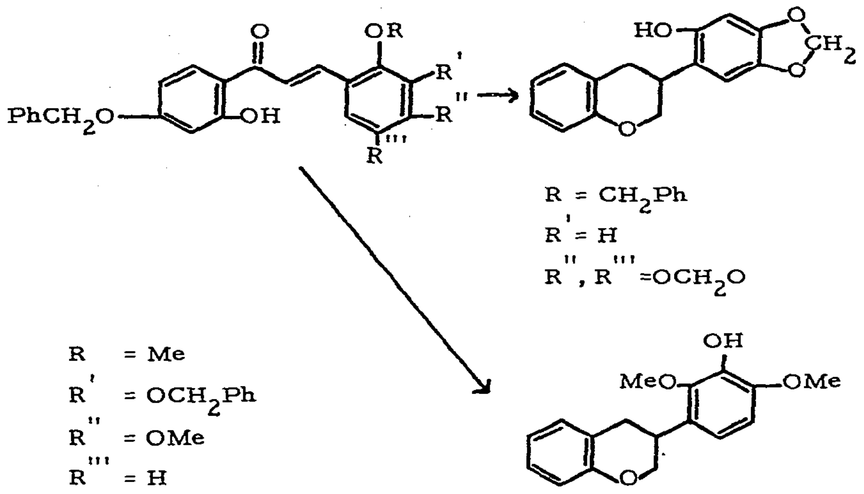
(24)

A one step synthesis of 2-alkynoic esters from readily available 5-pyrazolones by reaction with two equivalents of $Tl(NO_3)_3$ has been reported.[35] `The reaction appears to proceed as reported in 25 in 70-90% yield.



(25)

Rearrangement of 2'-hydroxychalcones with methanolic $Tl(NO_3)_3$ followed by treatment with acid gives iso-flavones.[36]

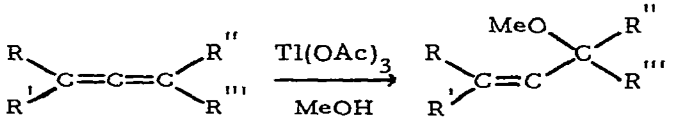


$R = CH_2Ph$
$R' = H$
$R'', R''' = OCH_2O$

(26)

$R = Me$
$R' = OCH_2Ph$
$R'' = OMe$
$R''' = H$

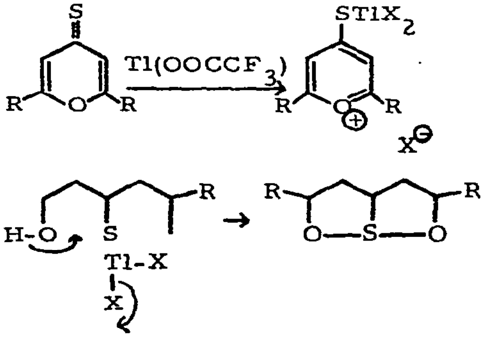
Treatment of allenes with thallium(III) acetate in methanol gave stable methoxy-thalliation products.[37]



(27)

$R = R' = R'' = R''' = Me$ $R = R''' = H,\ R' = R'' = Me$
$R = R'' = Me,\ R' = R''' = H$ $R = R' = R''' = H,\ R'' = Et$

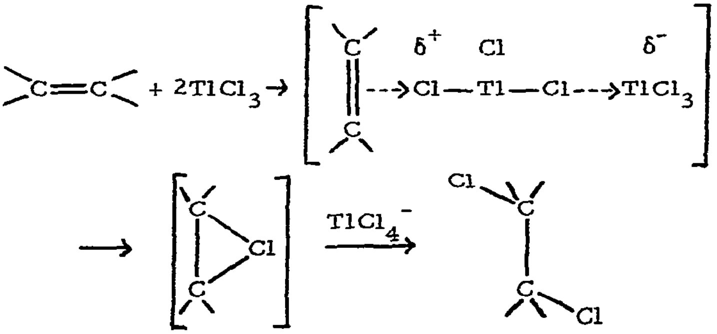
4-H-pyran-4-thiones react with $Tl(OOCCF_3)_3$ to yield pyrylium derivatives which rearranges to give a 1,6-dioxa-6a-thiapentalene derivative on treatment with water as indicated in 28.[38]



(28)

Uemura et al.[39] have examined the chlorination of olefins with $TlCl_3 \cdot 4H_2O$ in CCl_4 and have shown that 20-40% of vic-dichlorinated products are formed along with some monochlorinated material. It was suggested that the reaction may go through formation of a transition state involving the $TlCl_3$ as indicated in 29.

Thallium(I) derivatives of carbazole, phenothiazine and (to a lesser estent) dibenz(b, f)azepine may be alkylated by reactions with n-alkyl iodides and bromides under extremely mild conditions.[40] The lack of reactivity of other more stericly crowded derivatives lead to a postulated mechanism involving a four center transition state as indicated in 30. Secondary halides were unreactive under these conditions.



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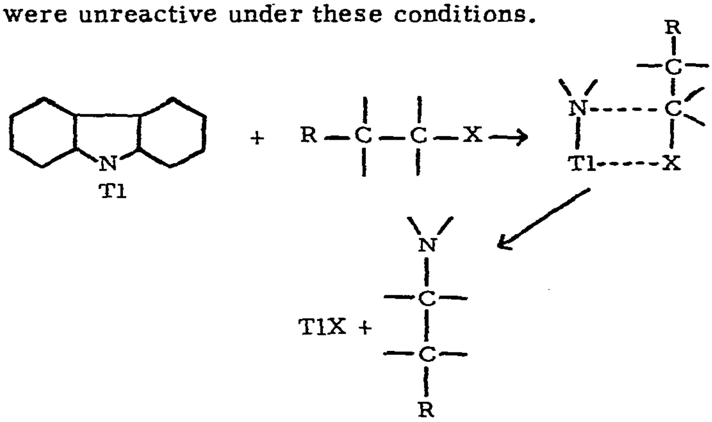


(30)

Sakai et al. have shown that thallous alkoxides react with CS_2 to yield orthocarbonates in good yield.[41] The reaction also yields spiroorthocarbonates when dithallous glycolates are used.

$$\begin{tikzcd}
1/2(TlOR)_4 + CS_2 \arrow[r] & (RO)_2C = S + TlS \arrow[dl, "1/2(TlOR)_4"] \\
(RO)_4C + TlS &
\end{tikzcd} \qquad (31)$$

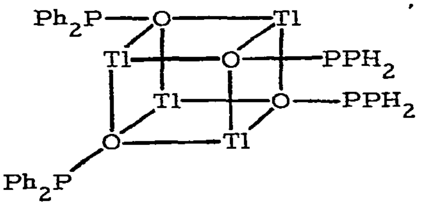
$R = Me,\ Et,\ i\text{-}Pr$

Diphenylphosphine oxide has been shown to react as indicated in **32** with TlOH.[42] It reacts with Me_2TlNMe_2 as seen in 33. The products have

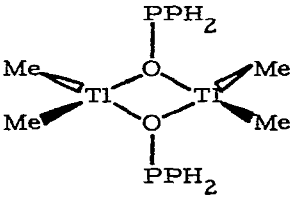
$$Ph_2P(O)H + TlOEt \longrightarrow Ph_2POTl \qquad (32)$$

$$\begin{tikzcd}
Ph_2P(O)H + Me_2TlNMe_2 \arrow[dr, "-HNMe_2"] & \\
& Ph_2P{-}O{-}TlMe_2 \\
Ph_2P(O)H + Me_3Tl \arrow[ur, "-CH_4"'] &
\end{tikzcd} \qquad (33)$$

been characterized by ir, nmr, and mass spectral data and it has been proposed that they have the structures indicated in IV and V based on these data.



IV



V

Compounds Containing Thallium-Metal Bonds

Walther and Rockstroh[43] have prepared Tl-Mo and Tl-W bonded compounds by the reaction indicated in **34**. The compounds were characterized

$$\underset{\text{(or W)}}{Me_3Tl + HMo\text{-}\pi\text{-}Cp(CO)_3} \xrightarrow[-78^{o}]{CH_2Cl_2} \begin{array}{c} Me_2TlMo\text{-}\pi\text{-}Cp(CO)_3 \\ + CH_4 \end{array} \qquad (34)$$

by the physical and spectroscopic properties and were shown to be *monomeric* in benzene. The Tl-C^1H_3 coupling constants were shown to be 273 Hz for the Mo derivatives and 265 for that of W.

In other studies it has been shown that disproportionation of Tl(I) occurs on treatment with $NaMn(CO)_5$ to yield the product containing Tl-Mn bonds nearly quantitatively.[44]

$$3Tl^+ + 3Mn(CO)_5^- \longrightarrow 3TlMn(CO)_5 \longrightarrow 2Tl + Tl[Mn(CO)_5]_3 \qquad (35)$$

On the other hand a stable Tl(I)-metal compound, $TlCo(CO)_4$ has been obtained.[45] It was prepared by the direct reaction indicated in **36**. The

$$2Tl + Co_2(CO)_8 \xrightarrow{\text{toluene}} 2Tl[Co(CO)_4] \qquad (36)$$

resulting $Tl[Co(CO)_4]$ has been shown to be an excellent source of the anion $[Co(CO)_4]^-$ for use in reactions both in polar and nonpolar media undergoing the normal reactions associated with this anion. The compound is reasonable stable permitting brief exposure to air without extensive decomposition when in a crystaline form.

In other studies Weibel and Oliver[46] have prepared and isolated $LiTlMe_4$ by reaction of Li metal with Me_3Tl. They characterized this species by analysis and by its nmr spectrum which showed $^{3}J_{Tl-^{1}H}$=224.1 Hz. The compound appeared to be light sensitive.

It was also shown that reaction of Me_3Tl with $LiSnMe_3$ lead to several products containing Tl-Sn bonds. This was indicated by across metal coupling $^{4}J_{TlSnCH}$ = 32, 29 and 44 Hz. These compounds are presumably species of the type $[TlMe_n(SnMe_3)_{4-n}]^-$ which result from the exchange of methyl and $SnMe_3$ groups. These Tl-Sn bonded species are relatively unstable showing approximately 25% decomposition when stored three days in sealed ampules kept in the dark at room temperature. The variations in Tl-H coupling constants were discussed.

The final paper to be discussed dealing with thallium chemistry reports that addition of TlOAc to an aqueous alkaline solution of (3)-1, 2-$C_2B_9H_{12}^-$ or its C-alkyl derivatives yields the new complex $Tl_2R'R''C_2B_9H_{12}$ ($R' = R''$ = H, pale yellow, R' = H, R'' = Me, yellow, $R' = R''$ = Me, bright yellow).[47] One of the thallium ions can readily be replaced by a cation while the other cannot which suggests that it is present in an icosahedral ion $[TlR'R''C_2B_9Hg]^-$.

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