THALLIUM

ANNUAL SURVEY COVERING THE YEAR 1971

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For the purposes of this survey the chemistry of organothallium compounds will be broken down into several broad areas. These include: structure and spectroscopic properties of thallium containing species, preparation and reactions of Tl(I) derivatives, preparation of Tl(III) derivatives, including alkyls and related compounds, reactions of these species, and finally the use of thallium compounds in organic reactions. The latter topic constitutes the area in which most work has been carried out in the past year.

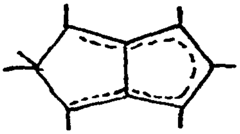
Whittle, et al. [1, 2] have observed the microwave spectrum of cyclopentadienylthallium and have discussed the interactions between The low lying vibrational states of this molecule, having C_5 symmetry, in terms of the first and second order coriolis interactions between the A_1 and E_1 states.

The ir spectra of a series of cis and trans chloro and bromo vinyl derivatives of Hg, Sn, Tl, and Sb were observed [3]. The integral intensities of the bis derivatives were 3-4 times those of the mono derivative. This increased intensity was ascribed to specific interactions between the metal and the double bond. Band assignments were postulated for a number of the species studied.

The mass spectrum of Me_3Tl was reported along with those of Me_3Ga, Vi_3Ga and Me_3In [4]. The general features of these mass spectra were those which one would anticipate, increasing abundance of the molecular ion as the source temperature or ionization energies were lowered and a relatively high abundance of Tl^+ ion relative to other ionic species. This work is discussed more extensively in the review on gallium and indium.

Thallium proton coupling constants have been measured in Me_2TlX derivatives with X = OEt, O(t-Bu), OPh, SMe, SO_2Me, Cp, and -C≡CPh [5]. J_{Tl-H} was in the range 368 to 379 Hz., except for the SO_2Me and -C≡CPh which have values of 426 and 303 Hz, respectively. It was suggested that these increases in coupling constants could be associated with more ionic character in the bonds in these derivatives. A temperature dependent line broadening was observed for the dimeric $Me_4Tl_2(OEt)_2$ which could not be readily explained. Several postulates were considered in an attempt to account for this phenomenon. The ^1H-Tl coupling constants in the Me_3Tl-NMe_3 system was also measured as a function of NMe_3/Me_3Tl ratio and it was concluded that J_{H-Tl} does not change signs on the complex formation in this system.

Fritz and Kuhler [6] have prepared a series of Tl(I) cyclopentadienide derivatives and have fully assigned their ^1H nmr spectra. These data and the failure to observe ^1H - $^{(203)205}Tl$ coupling was interpreted to mean that the bonding is predominantly ionic in these compounds. The ligand of (hydropentalenyl) thallium(I) has no dienyl grouping but appears to be a more symmetric and highly conjugated system, possibly as indicated in I.



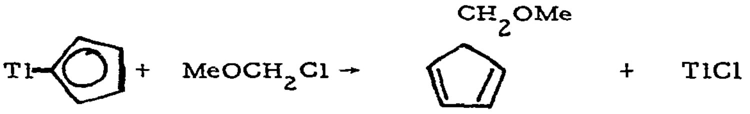
I

A number of reactions involving the production or use of the Tl(I) species have appeared in the literature. Cross and Wardle [7] have made extensive use of CpTl as a reagent for the preparation of cyclopentadienide derivatives of Pt and Pd in $(R_3P)(\pi\text{-Cp})PdX$ and $[C_6H_4(AsEt_2)_2]Pt(\sigma\text{-Cp})Cl$. The general preparative reactions are indicated in 1 and 2.

$$(Et_3P)_2Pt_2X_2R_2 + 2CpTl \rightarrow 2\ Et_3P(\pi\text{-Cp})PtR + 2\ TlX \qquad (1)$$

$$[C_6H_4(AsEt_2)_2]PtCl_2 + CpTl \rightarrow [C_6H_4(AsEt_2)]Pt(\sigma\text{-Cp})Cl + TlCl \qquad (2)$$

Corey, et al., [8] have shown that methoxymethylation of cyclopentadienide proceeds readily and in high yields. This reaction

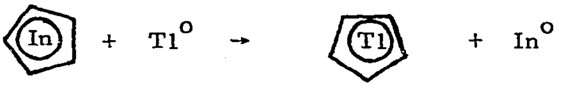


(3)

is of significant value since it provides a convenient route to the methoxymethylated product from readily available material via convenient reactons.

Lee [9] has reported the preparation of a number of Tl(I) derivatives of β-diketones, phenols, and carboxylic acids. These derivatives have been characterized by conductance measurements and by their ir, uv, and mass spectra. The uv studies in particular were interpreted at length and on the basis of these and other results it was suggested that Tl-O bonds have considerable more covalent character in these species than the analogous alkali metal-oxygen bonds. The mass spectral studies showed dimeric species were present even though the resulting ions were in low abundance. These results were discussed along with possible ionization paths.

Lalancette and Lachance [10] have shown that CpIn undergoes exchange with thallium metal as shown in 4. They also have shown that the cyclopentadienide ion will exchange with this species as shown in 5. In addition, they carried out a variety of pyrolysis experiments



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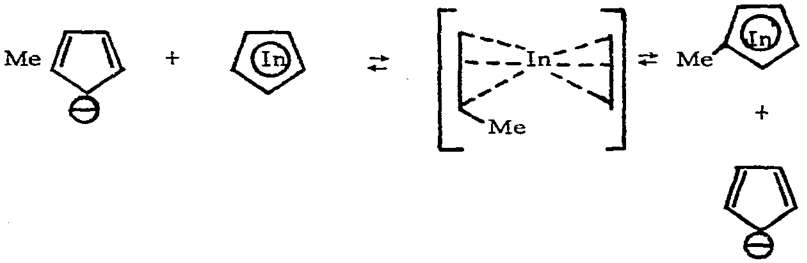
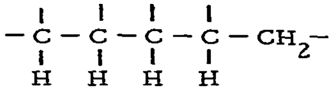


(5)

in which hydrocarbons were pyrolized in the presence of Tl. When the fragment  $-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}-CH_2-$ was present, cyclopentadienylthallium was formed in moderate yield.

Haupt and Neumann [11] have shown that $Tl[Mn(CO)_5]_3$ can be prepared via two different reactions which involve the disproportionation of Tl(I) as seen in 6 and 7. Neither TlCl or Tl reacted with $Mn_2(CO)_{10}$

$$3TlX + NaMn(CO)_5 \xrightarrow[25^o]{THF} Tl[Mn(CO)_5]_3 + Tl + NaX \qquad (6)$$

$$TlX + NaMn(CO)_5 + Mn_2(CO)_{10} \rightarrow Tl[Mn(CO)_5]_3 + NaX \qquad (7)$$

Turning our attention to reactions of Tl(III) we might first look at the electrochemical behavior of compounds in this oxidation state since oxidation and reduction steps will play a major roll in the behavior of these species. Issleib, et al. [12] have investigated the polarographic reduction of R_2TlX compounds (R = Me, Et, Pr, Bu, n-amyl; X = Cl, Br, OAc). They have proposed that the principle reactions is the one electron reduction leading to the unstable R_2Tl radical which then

$$R_2Tl^+ + e^- \rightarrow \{R_2Tl\} \qquad (8)$$

$$\{R_2Tl\} + 2e^- \rightarrow 2R^- + Tl^o \qquad (9)$$

$$3\{R_2Tl\} \rightarrow Tl^o + 2R_3Tl \qquad (10)$$

further reacts or undergoes disproportionation to yield Tl^o. The route followed in the second step depends upon the condition involved. These steps are likely of importance in many of the organic reactions even though they have not been explored in detail. Favier, et al. [13] have carried out thallium catalyzed oxidation of alkenes via electrochemical methods. The principle reactions were reported to be 11 and 12.

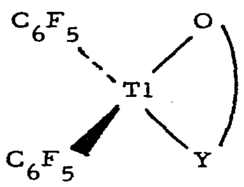
$$Tl(I) \xrightarrow{anode} Tl(III) \qquad (11)$$

$$Tl(III) + alkene \rightarrow products \qquad (12)$$

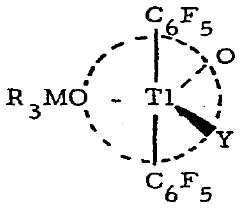
Relative high current efficiencies were obtained for this process under controlled potential conditions. This fact allows the use of this procedure for synthesis in cases where thallic oxidation is selective. The general oxidation and reduction steps represented in these two papers are the basis on which the majority of organic applications are based and also provide some knowledge of the behavior of compounds in which Tl(I) or (III) are possible.

A variety of new compounds or new methods for preparation of old compounds have been reported. The majority of these compounds are complex in nature and contain different types of substituents on the thallium atom. Mueller [14] has prepared Me_2TlN_3 from the reaction of Me_3Tl with ClN_3 and from the reaction of Me_2TlOH and HN_3. On the basis of vibrational and mass spectral data it was proposed that Me_2TlN_3 has an ionic structure with $[Me-Tl-Me]^+N_3^-$.

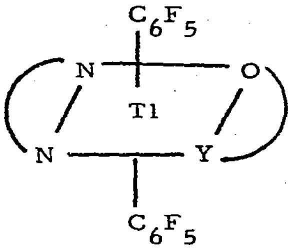
Deacon and Garg [15] have prepared a variety of complexes of $(C_6F_5)_2TlX$ (X = acac, $CF_3COCHCOMe$, $CF_3COCHCOCF_3$, $PhCOCHCOMe_3$, PhCOCHCOPh or quinolin-8-olate) by reaction of $(C_6F_5)_2TlBr$ with the appropriate sodium or thallous salt. Complexes were prepared from several of these derivatives by reaction with 1, 10-phenanthroline or 2, 2'-bipyridyl to give $(C_6F_5)_2TlX\cdot L$. Similarly several complexes were obtained with Ph_3AsO. Molecular weight, conductance, and spectroscopic measurements all indicate monomeric 4, 5 or 6 coordinate compounds except for the quinolin-8-olate species $(C_6F_5)_2Tl\cdot Ox$ which is considered to have an associated structure with bridging oxinate groups. Several of the proposed structures are indicated in II, III, IV, and V.



II

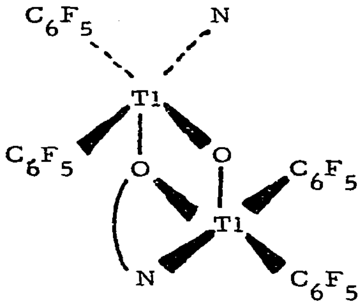


III



IV

M = P, As; Y = O, N



V

Bregadze, et. al. [16] have reported several reactions yielding simple organothallium compounds. They found that in $ClCH_2NO_2$, $ClCH(NO_2)_2$, $CH_2(NO_2)_2$, and $CF_3CH_2NO_2$ reacted with Et_3Tl via reaction 13 in which ethane was generated and new thallium derivatives

$$XCH_2NO_2 + Et_3Tl \rightarrow C_2H_6 + Et_2TlCHX(NO_2) \qquad (1\ )$$

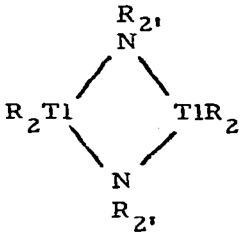
were obtained having electronegative substituents present.

When fluorine was present on the same carbon atom as the NO_2, then fluorine abstraction occurred yielding Et_2TlF as found for $F_2CH\ NO_2$. Fluorine abstraction also occurred for $(CF_3)_2CHNO_2$ while for $FC(NO_2)_2H$ the reaction yielded Et_2TlONO. Et_2TlOH was shown to react with $HC(NO_3)_3$ to yield $Et_2TlC(NO_3)_3$ while with $(CF_3)_2CHNO_2$ fluorine abstraction resulted in the formation of Et_2TlF.

The compound $Et_2TlCHCl(NO_2)_2$ rearranged when heated in THF to give Et_2TlONO also prepared by reaction of $AgNO_2$ on Et_2TlCl. The compounds were reported to have internal coordination between the Tl and N(O) or CCl groups. Both $Et_2TlCHCl(NO_2)$ and $Et_2TlCH(NO_2)CF_3$ were reported to explode at approximately 100° and it is suggested that all of these derivatives should be treated with caution when heating or handling because of the potential hazards involved.

Walther and Theide [17] have prepared dimethyl-, diethyl-, and di-n-propylthalliumamides from NMe_2, NEt_2 and NPr_2. Cryoscopic molecular weight measurements showed that these derivatives were dimeric and the amino bridged structure VI was proposed. The

$$R_2TlBr + LiNR'_2 \rightarrow LiBr + R_2TlNR'_2 \qquad (14)$$

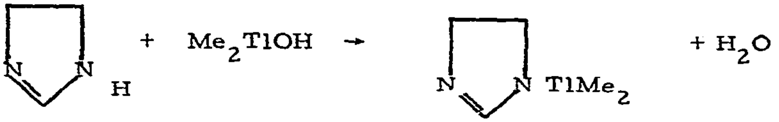


VI

compounds were further characterized by ir, nmr and mass spectra. The ^1H nmr spectra showed $J_{Tl-C-H} \simeq 340-380$ Hz and $J_{Tl-N-C-H} \simeq 80 - 100$ Hz.

Diethyl(diethylamino)thallium has also presumably been prepared by reaction of Et_2NH with $Et_2TlOCMe_3$ [18]. The reaction proceeds very slowly at room temperature but is accelerated at 80° to give 8-9% conversion in 15 hours under these conditions.

Lee [19] has prepared Tl(I) and $Me_2Tl(III)$ derivatives of imidazole, 1, 2, 4-triazole and benzimidazole by the reaction indicated in 15. These species were characterized by ir, nmr, and mass spectra.



(15)

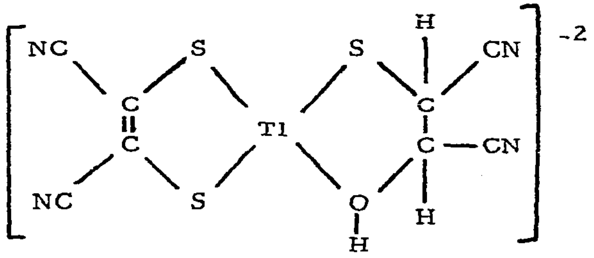
The results are consistent with a polymeric structure for these compounds in the solid state as indicated in VII.

VII

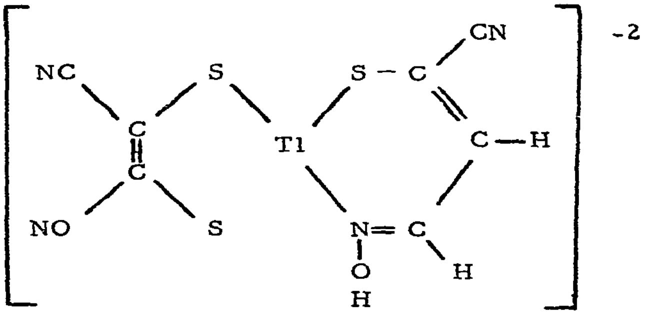
A series of new alkyl(cyano)thallium derivatives has been prepared and characterized by their uv and ir spectra [20]. A linear relationship between the ν (C ≡ N) and ν (Tl-CN) was observed and interpreted in terms of the Tl-C bond strength as a function of the Tl-ligand interaction.

The diarylthallium(III) selenocyanates (phenyl, o-, m-, and p-tolyl) have been prepared by the interaction of Ar_2TlCl with KSeCN [21]. The compounds have been characterized by ir spectra and a normal structure $Ar_2TlSeCN$ has been proposed.

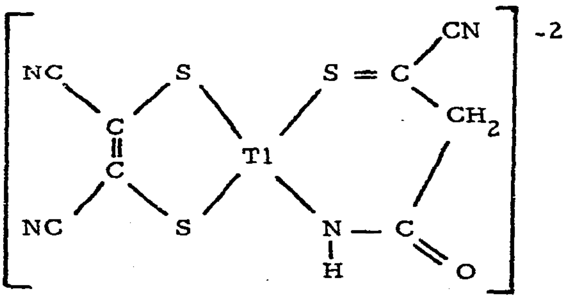
Hunter and Williams [22] have investigated the reaction of $TlCl_3$ with dicyanoethylene-1, 2-dithiolate and toluene-3, 4-dithiolate and have obtained the Tl(III) complexes. The dicyanoethylene-1.2-diothiolate complexes reacted with sodium or potassium halides to form $[C_8H_3N_4OS_3Tl]^{-2}$ ions. On the basis of conductance measurements, and spectroscopic evidence, three possible structures with thallium in the +1 oxidation state were proposed.



VIII



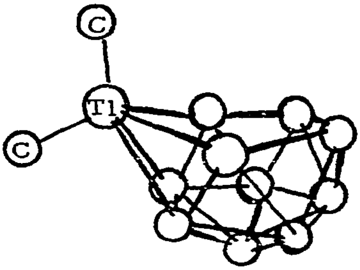
IX



X

Methyl vitamin B_{12} (MeB_{12}) has been shown to methylate Tl(III) but not Tl(I) [23]. This reaction occurs over a wide range of pH and is first order in Tl(III) and in MeB_{12}.

Trimethylthallium has been shown to react with decaborane (14) to give the simple salt $(Me_2Tl)^+ (B_{10}H_{13})^-$ and a complex $(Me_2Tl)^+$ $(B_{10}H_{12}TlMe_2)^-$ [24]. The latter compound contains two distinct types of methyl groups. One associated with the $TlMe_2{}^+$ ion and the other is thought to be bound to the boron framework as indicated in XI.



XI

The compounds both react with HCl to liberate $B_{10}H_{14}$ and Me_2TlCl. They were characterized by their nmr spectra. It has also been shown that Bu_2SnO reacts with a variety of organometallic compounds including $(C_6F_5)_2TlCl$ to yield the addition product $Bu_2ClSnOTl(C_6F_5)_2$ [25].

Numerous reactions of Tl(III) derivatives have appeared. The first of these to be reported here dealt with the oxidation of Et_3Tl in octane solution by dry O_2 between -50 and 50° [26]. The reaction is first order in Et_3Tl and O_2 and initially yields Et_2TlO_2Et. The compound formed is stable to approximately 50° where it decomposes to Et_2TlOH. It reacts with water to give Et_2TlO_2H and Et_2TlOH and with HCl to yield EtO_2H and Et_2TlCl.

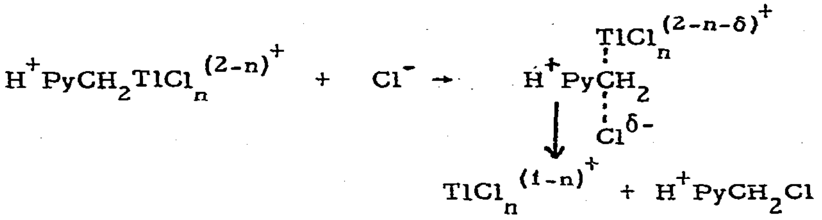
Another deals with the pyrolysis of $Et_2TlOCMe_3$ [27]. Heating $Et_2TlOCMe_3$ for 10 hours at 180° gave $TlOCMe_3$, C_2H_6, C_4H_{10} and a trace of butenes. Et_2TlNEt_2 decomposed to give 100% Tl^0, 40% Et_2NH and volatile hydrocarbons as well.

Another interesting reaction which has been reported is the insertion of $:CCl_2$ into the Tl-C bond of Et_3Tl yielding the unstable intermediate $Et_2TlCCl_2C_2H_5$ [28]. This compound undergoes Cl abstraction followed by rearrangement leading to the formation of Et_2TlCl and $ClHC = CHCH_3$. It was also shown that reaction of Et_3Tl with CCl_4 is accompanied by a carbonoid process since this reaction produces dichloronorcarane when run in the presence of a cyclohexene trapping reagent.

Johnson and Vamplew [29] have examined the mechanism of decomposition of pyridiniomethylthallium (III) species in some detail. They discussed this reaction first in terms of the complex equilibria as seen in 16. These equilibria which have not been evaluated make

$$\begin{tikzcd}
H^+PyCH_2Tl^{+2} \arrow[r, shift left, ""] & H^+PyCH_2TlCl^+ \arrow[l, shift left, "\pm Cl^-"] \arrow[d, shift left] \\
H^+PyCH_2TlCl_3^- \arrow[r, shift left] & H^+PyCH_2TlCl_2 \arrow[l, shift left, "\pm Cl^-"] \arrow[u, shift left, "\pm Cl"']
\end{tikzcd} \qquad (16)$$

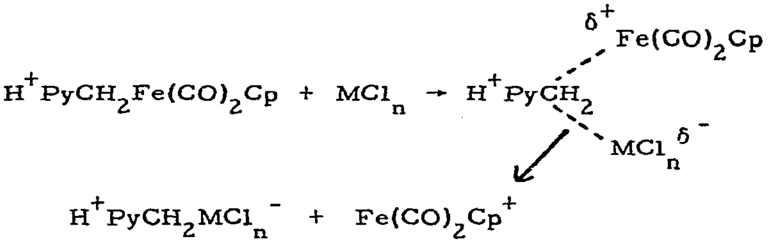
any unequivocal statements concerning the mechanism of the reaction out of the question. The authors did, however, postulate possible routes and provide supporting arguments for the path illustrated in 17.



$$H^+PyCH_2TlCl_n^{(2-n)+} + Cl^- \rightarrow H^+Py\overset{TlCl_n^{(2-n-\delta)+}}{\underset{Cl^{\delta-}}{CH_2}} \rightarrow TlCl_n^{(1-n)+} + H^+PyCH_2Cl \qquad (17)$$

As indicated, alternate paths may be available for this reaction. It was also pointed out that the mechanism of reaction may change depending on the species present in solution; thus, the Cl^- concentration which determines the concentrations of the species proposed may also cause significant change in the mechanism of reaction.

Dodd and Johnson [30] have investigated the $Hg(ClO_4)_2$ and $Tl(ClO_4)_3$ displacement reactions occurring with pyridiniomethyldicarbonyl-π-cyclopentadienyliron ions in aqueous solution. These reactions were believed to involve the S_E2 displacement reaction at saturated carbon as illustrated in 18. The initial products of reaction

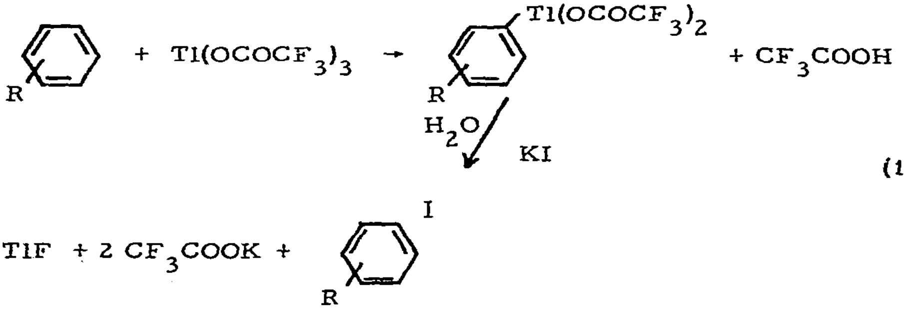


$$H^+PyCH_2Fe(CO)_2Cp + MCl_n \rightarrow H^+Py\overset{\delta^+ Fe(CO)_2Cp}{\underset{MCl_n^{\delta-}}{CH_2}} \rightarrow H^+PyCH_2MCl_n^- + Fe(CO)_2Cp^+ \qquad (18)$$

are the pyridiniomethyl derivatives which undergo further reaction. The influence of Cl^- ion on these reactions is discussed and, as noted in the previous paper, plays an important role by change in the relative concentration of the reacting species.

The same research group [31] has also investigated the reaction between Hg^{+2} and Tl^{+3} ions with pyridiniomethylpentacarbonyl-manganese ions. The same general pattern was observed involving the formation of an open transition state and the subsequent formation of products. They have [32] also dealt with the reactions of Hg^{+2} and Tl^{+3} with 2-, 3-, and 4-pyridiniomethylchromium(III) ions. In this latter paper the same general mechanism was considered operative. The results recorded in this study show that substitution at the 2-position is slower than that at the 3- position, by approximately the same factor regardless of the charge or the character of the electrophile. Any significant bond breaking prior to bond formation in the transition state may be ruled out and the direct influence of the charge on the pyridinium ion on the incoming charged electrophile is the same for each position of substitution. They also discussed the influence of ion pairing on the relative rates of a reaction of Hg^{+2} and Tl^{+3}.

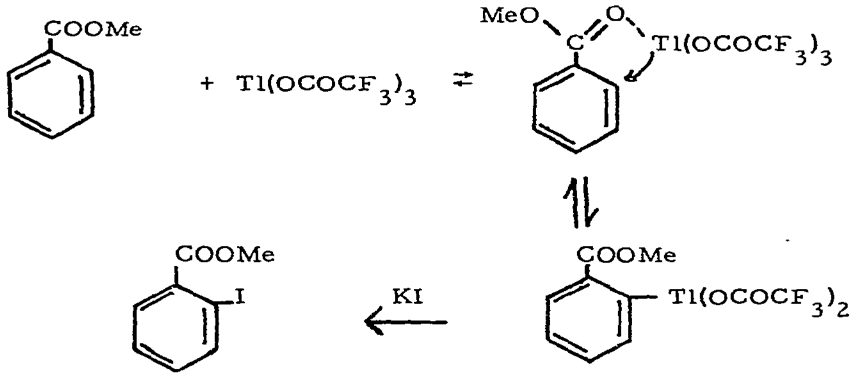
McKillop, et al. [33] have studied the thallation of aromatic compounds as a means for the preparation of aromatic iodides via the overall reaction indicated in 19. This reaction was examined under



(19)

a variety of conditions and was shown to give high yields of aromatic iodides. For extremely reactive aromatic species, some modifications in procedure were required to prevent side reactions while for compounds with deactivating groups present more vigorous conditions were required.

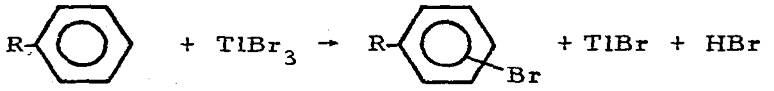
The iodination step always occurred at the thallium cite. The isomer ratios produced were determined by the initial thallation step. This was discussed in the following paper [34]. It was suggested that the reaction proceed via the path indicated in 20. This path suggests that



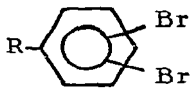
(20)

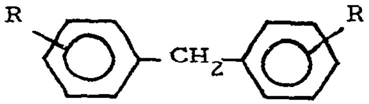
the chelate formation indicated in the intermediate plays an important role in the determination of the product distribution. When five or six membered rings can readily be formed as indicated above, ortho thallation predominates under mild conditions in which kinetic control dominates. When this type of intermediate cannot be formed para-substitution occurs. When the reaction is equilibrated the predominate product is the meta isomer. The various factors determining the isomer distribution are discussed in detail and it has been shown that a desired product may be obtained by careful control of the experimental conditions.

Uemura, et al. [35] have investigated the bromination of aromatic compounds with thallium catalysts. They have shown that bromination with $TlBr_3 \cdot 4H_2O$ proceeds as indicated in 21. In addition, varying


(21)

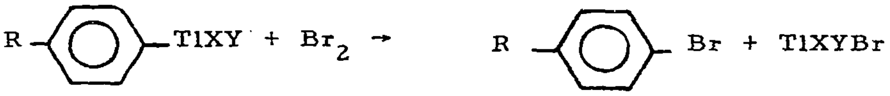
amounts of the dibromide XII and the coupled product XIII were produced during the course of the reaction. With less reactive aromatic


XII


XIII

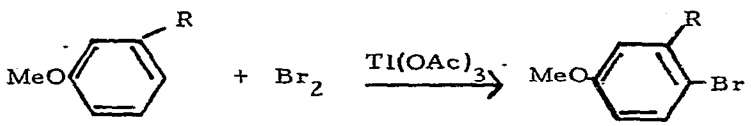
compounds such as nitrobenzene ethyl benzoate, and pyridine no reaction occurred. Bromination with Br_2 and either a Tl(III) or Tl(I) catalyst gave good yields of the monobromide when carried out in CCl_4. When enough water was added to the reaction mixture to dissolve all of the thallium salt, then benzene gave no reaction and toluene gave only benzyl bromide.

Bromination of arylthallium derivatives in CCl_4 proceeded as indicated in 22. If excess Br_2 was present additional reaction occurred giving a dibromide as well. The possible mechanisms of reaction were


(22)

considered and proposed paths for bromination in the presence of Tl(I) and Tl(III) were presented.

Erickson and Barkowsky [36] have shown that $Tl(OAc)_3$ induced bromination of meta-substituted anisoles leads primarily to the bromine para to the methoxy group as indicated in 23. This is in



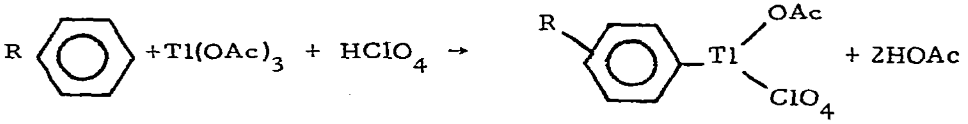
R = Me 96%
Et 93%
iPr 88%
tBu 40%

(23)

contrast to the phenols which have major steric effects upon bromination.

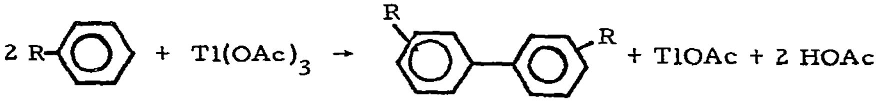
In preparation of ethylphenylthallic acetate perchlorate via the reaction of $Tl(OAc)_3$, ethyl benzene and $HClO_4$, Uemura, et al. [37] reported a violent explosion while removing the solvent (acetic acid) on a rotary vacuum evaporator. This again illustrates the instability of organometallic compounds particularly in the presence of strong oxidizing agents such as ClO_4^- or NO_3^-.

Arylthallic acetate perchlorate monohydrates, $ArTl(OAc)(ClO_4)\cdot H_2O$, were obtained as the major products via reaction 24 carried out in



(24)

acetic acid containing perchloric acid [38]. Minor products including various types of oxidation products and oxidative coupling products as indicated in 25, were obtained. The reactivity order of the aromatics

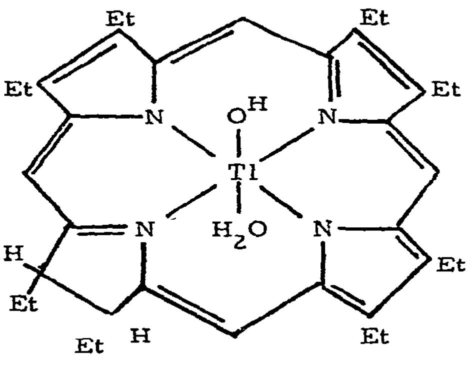


(25)

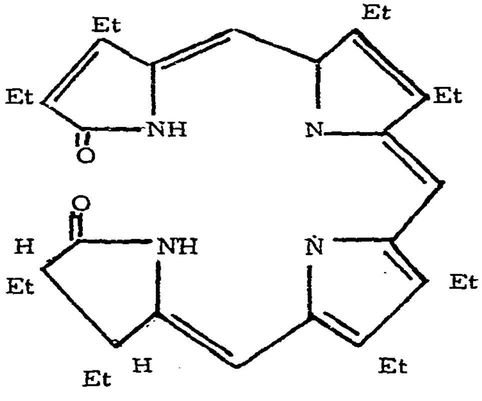
and the isomer distributions of the products were the same as those in the usual electrophilic aromatic substitution. Compounds observed to undergo these reactions included benzene, toluene, o-, m-, p-xylene and anisole. Aromatic compound with electron withdrawing substituents such as nitro or chloro group did not react at all.

Uemura [39] has reported that HOAc solutions of ArTlXY undergoes coupling when treated with $PdCl_2$ and NaOAc when refluxed. Yields were in the 50-70% range for compounds such as PhTlCl OAc $_2$, $PhTl(OAc)_2$, $p\text{-}MeC_6H_4Tl(OAc)ClO_4$. and $PhTl(OCOCF_3)_2$. With Ph_2TlCl a low yield of coupling product was obtained.

It has been shown that treatments of trans-octaethylchlorin with thallium trifluoroacetate yields predominately XIV [40]. If four equivalents of $Tl(OOCCF_3)_3$ are used then up to 25% of the open ring compound XV is obtained. In a subsequent paper the ^1H nmr of octaethylporphinatothallium (III) was examined [41]. The methylene protons in this compound were found to be magnetically non-equivalent



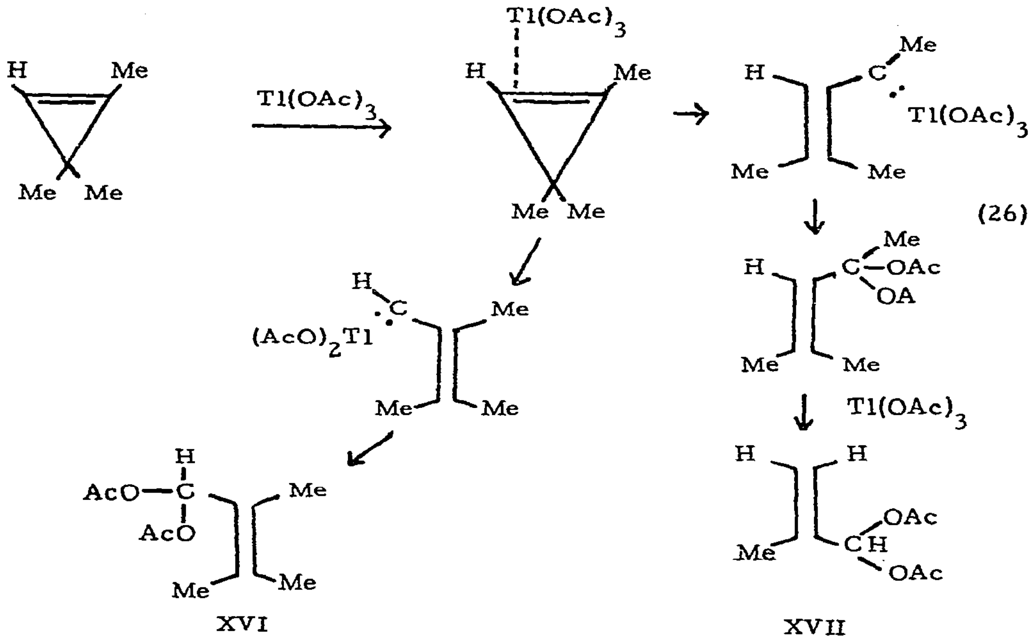
XIV



XV

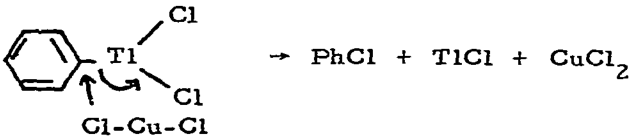
This was thought to be the result of a slow inversion of the methylene groups on the nmr time scale.

It was shown that $Tl(OAc)_3$ reacted in methylene chloride according to 26 [42]. With a 1/1 ratio 50% of XVI and 20% of XVII were obtained with a 1/2 ratio, the yields were 20% and 40% respectively.



(26)

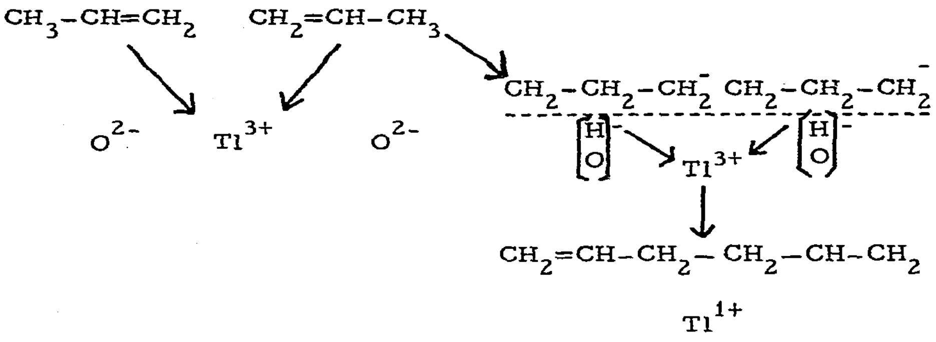
Ichikawa and Ikeda [43] have shown that phenylthallium(III) comp-pounds PhTlXY (X, Y, = Cl, OAc, CF_3CO_2; Y = Cl, OAc, ClO_4, CF_3CO_2) react with $CuCl_2$ and Cu_2Cl_2 as seen in 27 to yield chlorobenzene. Benzene and biphenyl were by-products. The reactions were



(27)

carried out in HOAc, MeCN and THF. A four centered mechanism was proposed for this reaction.

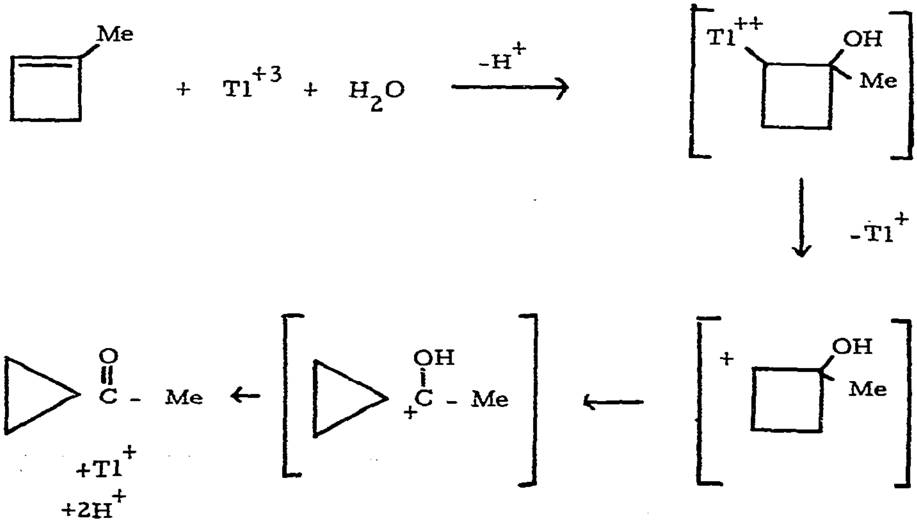
Trimm and Doerr [44] have investigated the catalytic oxidative dimerization of propylene and postulated the following reaction path:



(28)

The Tl^+ was reoxidized by O_2 in the gas stream passing over the thallium catalyst bed. Several factors affecting the process were discussed, including temperature and gas composition.

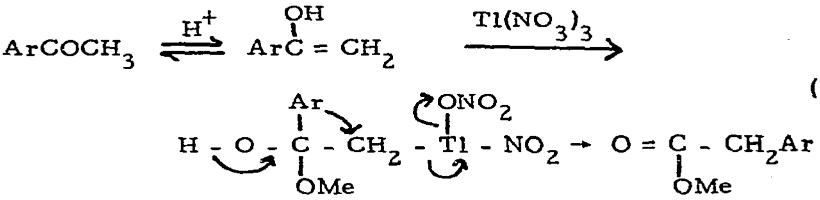
Byrd, et al. [45] have studied the oxidation of methyl cyclobutene in an aqueous Tl(III) system and have postulated the mechanism indicated in 29 for this conversion.



(29)

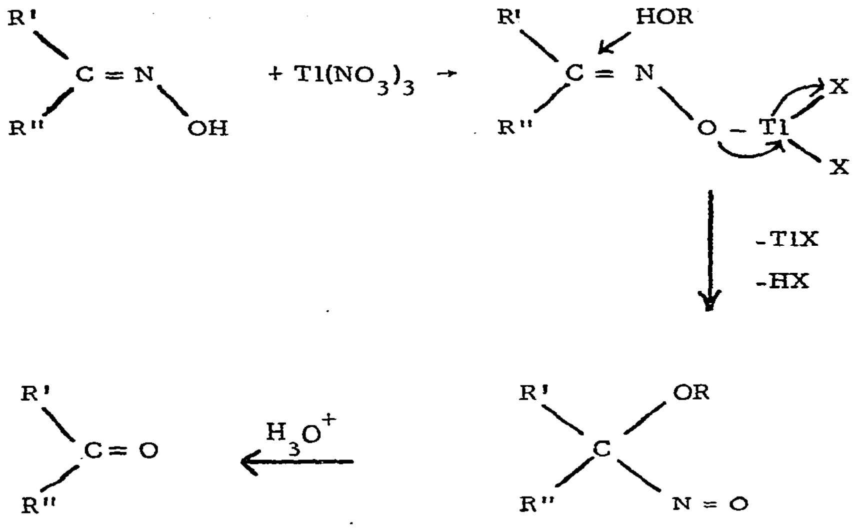
The kinetics of the oxidation of PhCHMeOH with $Tl(OAc)_3$ in H_2SO_4 has also been studied [46]. The results show that the overall order of the reaction is third order, first order in alcohol, Tl^{+3}, and H^+. The rate is slightly increased by addition of Na_2SO_4. The observed second order rate constant at 50° is 0.145 mole l^{-1} sec^{-1}.

McKillpp, Swann, and Taylor [47] have reported a convenient conversion of acetophenones into methylphenylacetates using $Tl(NO_3)_3$. The scheme proposed for this reaction is indicated in 30. The reaction was unsuccessful when applied to compounds containing amino substituents due to preferential complexation of the amino group with the thallium. The corresponding amides, however, reacted normally. Secondly, acetophenones in which the aromatic ring is highly deactivated by electron-withdrawing substituents undergo enolization, oxythallation, and aryl migration only very slowly, and under the circumstances only low yield were obtained.



(30)

In another study, McKillop et. al. [48] examined the direct conversion of oximes into aldehydes and ketones by reaction with $Tl(NO_3)_3$. They proposed a general reaction scheme as illustrated in 31. An alter-



(31)

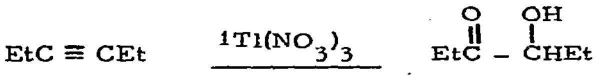
nate path involving a one electron transfer was also suggested and the observation of an epr signal for the intermediate in this case supported the second path. Thus it would appear that two paths are operative.

The procedure is generally applicable and has been used to prepare a wide variety of aldehydes and ketones. There are some complicating features generally resulting from other reactions between the thallium compound and a functional group present in the oxime.

McKillop, et.al.[49] have extended their investigations of reactions of $Tl(NO_3)_3$ to include its reactions with various acetylenes. They have shown that this reagent does not yield hydration products but gives rise to oxidation of the triple bond. The reaction is strikingly dependent on the structure of the acetylene used. Monoalkylacetylenes react as indicated in 32 giving rise to carboxylic acids containing one carbon less

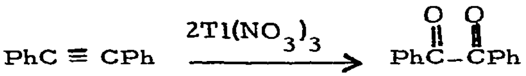
$$C_6H_{13}C \equiv CH \xrightarrow[\substack{H^+ \cdot H_2O \\ \text{glyme}}]{2Tl(NO_3)_3} C_6H_{13}COOH \qquad (32)$$

than the starting material. Under the same reaction conditions dialkylacetylenes give rise to acyloins as shown in 33. With diarylacetylenes



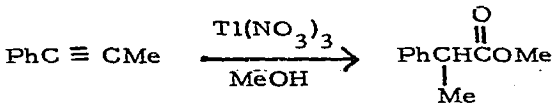
$$\mathrm{EtC{\equiv}CEt}\ \xrightarrow{1\mathrm{Tl(NO_3)_3}}\ \mathrm{Et}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}\mathrm{HEt} \qquad (33)$$

one equivalent of $\mathrm{Tl(NO_3)_3}$ gave a 50/50 mixture of benzil and starting material, but two equivalents led to a high yield of product via 34.



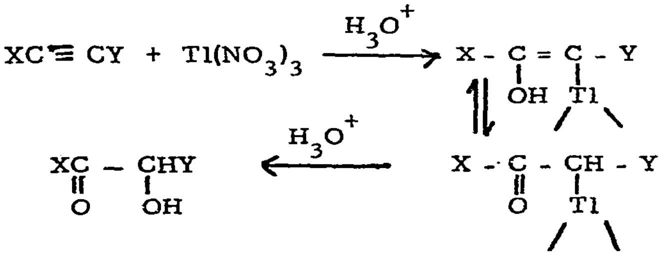
$$\mathrm{PhC{\equiv}CPh}\ \xrightarrow{2\mathrm{Tl(NO_3)_3}}\ \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} \qquad (34)$$

Alkylarylacetylenes under similar conditions gave rise to products of the types seen in 33 and 34, when the reaction was carried out under similar conditions. In methanol solution, however, the reaction proceeded via 35.



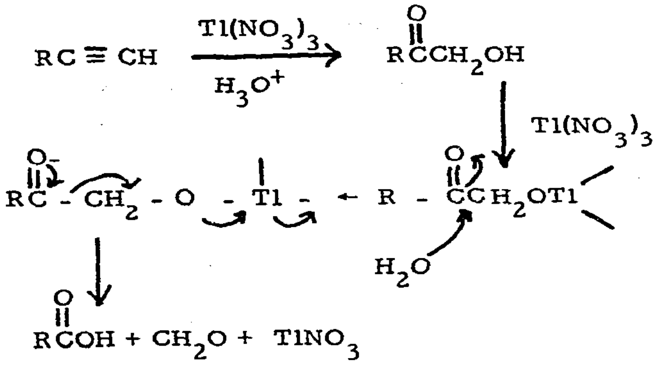
$$\mathrm{PhC{\equiv}CMe}\ \xrightarrow[\mathrm{MeOH}]{\mathrm{Tl(NO_3)_3}}\ \mathrm{Ph}\underset{\mathrm{Me}}{\underset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OMe} \qquad (35)$$

The specificity of the reactions was accounted for in term of reaction scheme 36. This initially gives the corresponding α-hydroxy ketone. This accounts for the products in 33. Secondary steps may occur, however, as proposed in 37 and 38.



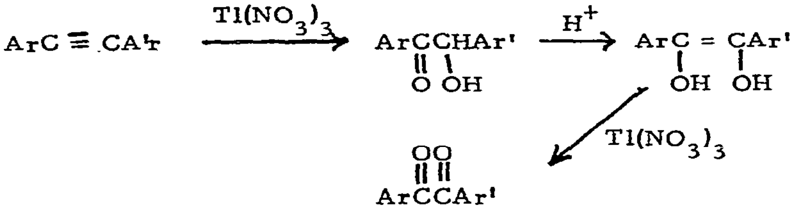
(36)

X = Y = H, alkyl, aryl



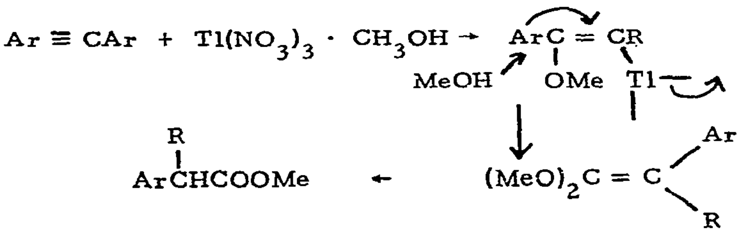
(37)

OR



(38)

In methanol solution, it was proposed that the reaction proceeded via 39.



(39)

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