THALLIUM; ANNUAL SURVEY COVERING THE YEAR 1981*

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This survey will deal with 1) synthesis, structure and spectroscopy of organothallium(III) compounds, 2) thallium-metal bonded compounds, 3) reactions and kinetics, 4) organic synthesis with thallium(III) compounds and 5) organothallium(I) compounds.

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

Diaryl- and monoarylthallium halides capable of forming intramolecular coordination bonds (1 and 2) were prepared from the corresponding organolithium compounds and $TlCl_3$ (1). The compounds were all monomeric in chloroform or benzene. The occurrence of intramolecular coordination of nitrogen to thallium was unambiguously confirmed by the low temperature ^{13}C NMR spectra of the α-aminoethyl substituted compounds. Structures suggested are 3 and 4.

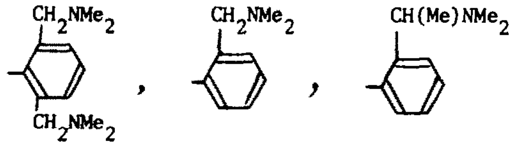
R_2TlCl

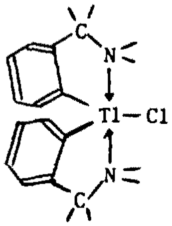
1

$RTlCl_2$

2

R =





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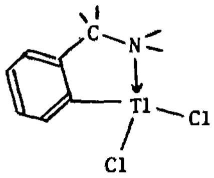

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*Thallium; Annual Survey covering the year 1980 see J. Organometal. Chem., 227 (1982) 301-316.

1 and **2** reacted with $Pd(OOCR')_2$ (R'= Me, Et, ^iPr) to afford RPdOOCR'. Inversely, the reaction of R_2Pd with $Tl(OOCR')_3$ gave RPdOOCR' and $RTl(OOCR')_2$.

Recent crystal structural studies of bis(polyfluorophenyl)thallium derivatives [e.g. J. Organometal. Chem., 193 (1980) 13; Inorg. Chim. Acta, 35 (1979) L335] led to a complete revision of earlier structural proposals for such a class of compounds. Henrick and co-workers now have determined the crystal structure of $(C_6F_5)_2TlOOCC_6F_5 \cdot OPPh_3$ which was previously proposed to be a four-coordinate monomer (2). As shown in Fig. 1, the molecular structure of the compound consists of two monomeric units linked by carboxylate bridges. No further association is evident. Each thallium atom has irregular six coordination with the C-Tl-C angle being 151.6(5)°. Relevance of this structure to those of $(C_6F_5)_2TlOOCC_6F_5$ as well as Me_2TlOAc was discussed.

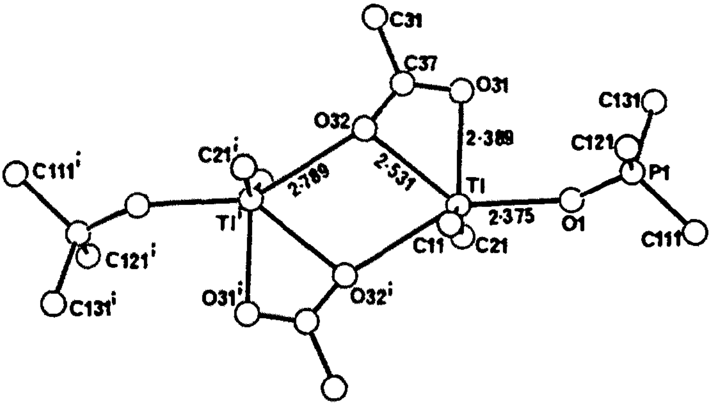
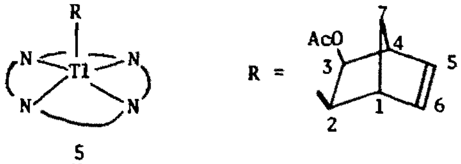


Fig. 1. The structure of $[(C_6F_5)_2TlOOCC_6F_5 \cdot OPPh_3]_2$. The first C atoms only of the phenyl rings are shown. [Reproduced from J. Organometal. Chem., 204 (1981) 287].

The five-coordinate complex **5** was formed from the oxythallated adduct of norbornadiene and tetraphenylporphyrin (3). The crystal structure of **5** determined is shown in Fig. 2. The structure is similar to that found for



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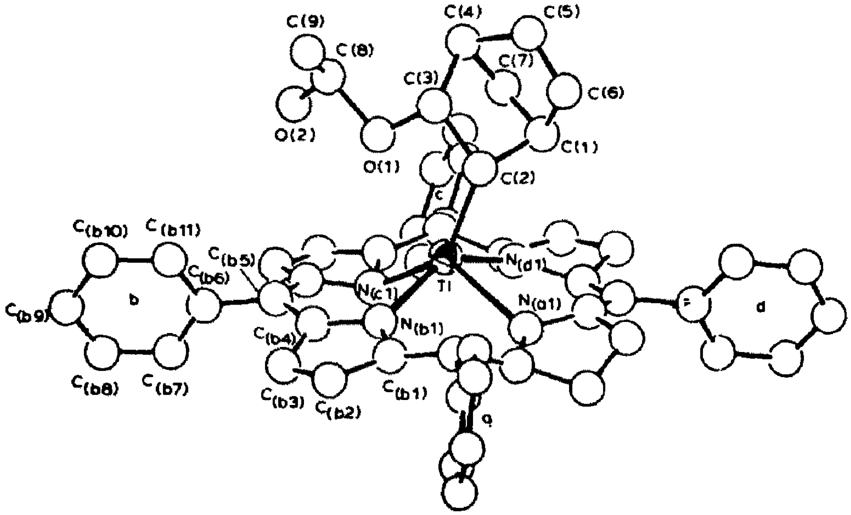
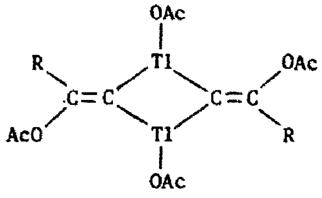


Fig. 2. The structure of 5. [Reproduced from J. Organometal. Chem., 210 (1981) 281].

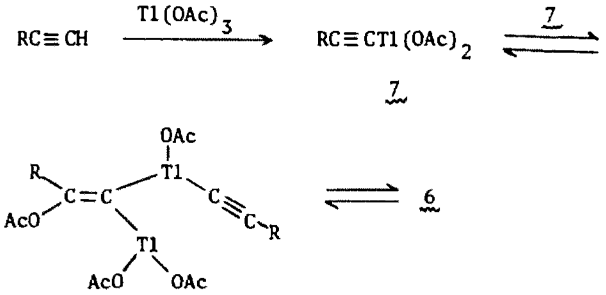
MeTl(tetraphenylporphyrin), and is characterized by a large displacement of the thallium atom from the N_4 plane (0.9 Å). The structure also reveals the cis-exo stereochemistry of the acetoxythallation process of norbornadiene. Shielding effects of the ^{13}C chemical shifts in the R group have been discussed in terms of the established structure and the porphyrin ring current.

Oxythallation intermediates 6 in the hydration of terminal acetylenes by $Tl(OAc)_3$ were isolated in reactions carried out in chloroform or acetic acid (4). A possible route to 6 is shown in Scheme 1, and NMR evidence suggested 6 to be in equilibrium with 7. Reduction of 6 with $NaBH_4$ in D_2O/THF gave $RC(OAc)=CD_2$. Heating 6 in acetic acid or methanol gave the corresponding ketones (RCOMe) and Tl(III) salt.



6 R= Ph, Me, ^{n}Bu, ^{n}Hex

Scheme 1



Solvent dependency of ^{205}Tl, ^{13}C and ^{1}H chemical shifts and coupling constants of Me_2TlBF_4 was examined by using nine different solvents (5). The ^{205}Tl shifts span ca. 230 ppm. Relationships were sought between the NMR parameters and each of the following solvent parameters: Dimroth-Reichardt acidity, Gutman donor number, Kosower Z value, pK_a and Drago base parameters (C_B and E_B). The last parameters correlated fairly well with $^2J_{TlH}$, $\delta(^{13}C)$ and δ(Tl) values. The same authors also determined ^{205}Tl chemical shifts of Me_2TlX (X= NO_3, BF_4, OAc) in several solvents as a function of temperature and concentrations of solutes and added anions (6). The temperature-dependent chemical shift range was larger than those resulting from changes in the solute or anion concentrations. The authors suggested that the temperature-dependent ^{205}Tl shifts largely originate from vibrational effects within the Me_2Tl^+ cations and/or from vibrational effects involving the interaction of the cations with solvent molecules.

2. Thallium-Metal Bonded Compounds

Boron-thallated carboranes, o- and m-$R^1CB_{10}H_9[Tl(OOCCF_3)_2\text{-}9]CR^2$ (R^1, R^2= H, Me) **8** reacted with KSCN, when heated or photolyzed, to give $R^1CB_{10}H_9(SCN\text{-}9)CR^2$ (7). Alkylation of **8** with R^3M/NaX (R^3= Me, Et, Bu; M= Li, MgX) gave mixed organothallium compounds, $HCB_{10}H_9[TlR^3X\text{-}9]CH$ (X= Cl, Br, I). Also, **8** disproportionated into $[9\text{-}R^1CB_{10}H_9CR^2]_2TlX$ (X= OAc, Cl) when treated with aqueous NaOAc or $LiAlH_4$/NaCl in THF (8).

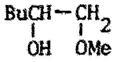
3. Reactions and Kinetics

Reductive decomposition of monophenyl- and diphenylthallium compounds with Hg, Sn and Se in pyridine or MeOH was described (9). For example, $PhTl(OAc)_2$ and Hg at 50° gave TlOAc (80 %) and PhHgOAc (78 %). Thallation of aromatic compounds with $Tl(OOCCF_3)_3$ has been a well-investigated process. Kooyman and co-workers found that $PhTl(OOCCF_3)_2$ reacts with anisole at 70-80° to afford $R(Ph)TlOOCCF_3$ (R= 2-, 3- or 4-$MeOC_6H_4$) (10). The corresponding reaction with chlorobenzene required trifluoroacetic acid, and gave only mono(chlorophenyl)thallium derivatives. Analogous transarylation was also observed between the diarylthallium compounds and the aromatic hydrocarbons.

Details of oxythallation of 1-hexene were studied under various conditions (11). The alkylthallium compound **9** formed *in situ* in MeOH reacted with KBr in the presence of 2,6-dimethyl-18-crown-6 to result in clean bromodethallation to give **10**. Decomposition of **9** (R= CF_3) in MeOH was fast, giving **11** and **12** possibly via an S_Ni attack of the coordinated alkoxy or hydroxy ligand. The reaction of $Tl(OOCCF_3)_3$ with 1-hexene in CH_2Cl_2 containing MeOH (2 equiv.) gave a mixture of **11**-**14** where **11**, **12** and **14** were supposed to form through an intermediate **15**.

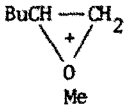
$\underset{\mathrm{OMe}}{\mathrm{BuCH}}-\underset{\mathrm{X}}{\mathrm{CH_2}}$

9 X= $Tl(OOCR)_2$ (R= Me, CF_3)
10 X= Br
11 X= OMe
12 X= OH
13 X= $OOCCF_3$



$\underset{\mathrm{OH}}{\mathrm{BuCH}}-\underset{\mathrm{OMe}}{\mathrm{CH_2}}$

14



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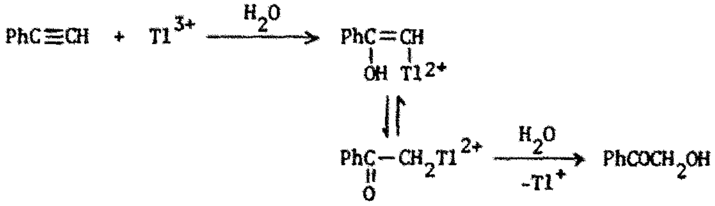
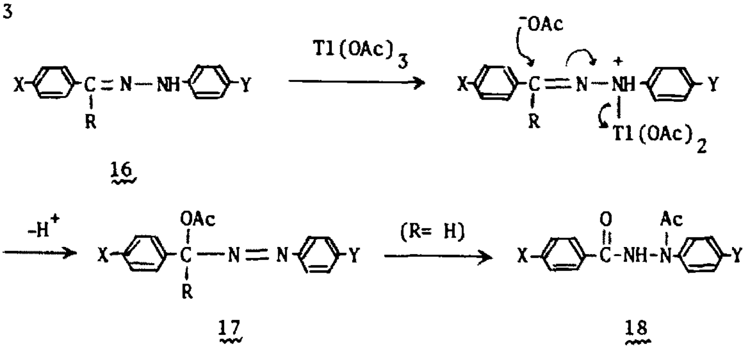
The kinetics of oxidation of phenylacetylene by $Tl(ClO_4)_3$ in aqueous solution to give 2-hydroxyacetophenone was studied by UV spectroscopy (12). The reaction proceeded via rapid formation of $PhC(OH)=CHTl^{2+}$ and much slower oxidative decomposition of this intermediate. (Scheme 2). The rate of the second process was uniquely slow when compared to the corresponding rate of the oxythallated adduct of styrene [Can. J. Chem., 52 (1974) 2667].

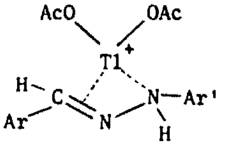
Scheme 2



Kinetics of the reaction between phenylhydrazones **16** and $Tl(OAc)_3$ in acetic acid was examined (13) [see also Tetrahedron Lett., (1979) 4583]. The main products were **17** and **18** (Scheme 3). The substituent effect (X, Y) on the reaction rate observed is consistent with a transition state shown in **19**.

Scheme 3





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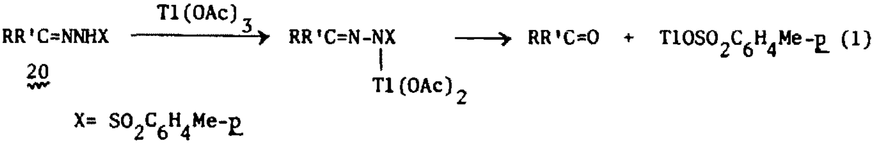
The same authors also described the first oxidation of substituted toluene-p-sulfonylhydrazones 20 with $Tl(OAc)_3$ to regenerate carbonyl compounds (eq. 1) (14). The reaction was assumed to proceed through an N-metallo intermediate,



$$\underset{\mathbf{20}}{RR'C{=}NNHX} \xrightarrow{Tl(OAc)_3} \underset{Tl(OAc)_2}{RR'C{=}N{-}NX} \longrightarrow RR'C{=}O + TlOSO_2C_6H_4Me\text{-}p \quad (1)$$

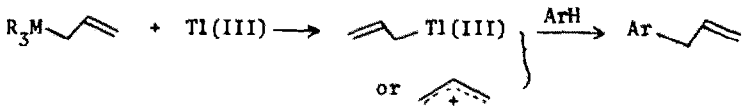
$X = SO_2C_6H_4Me\text{-}p$

followed by an external redox step which involves a solvolysis, giving rise to an unstable acetal species $RR'C(OAc)_2$. The different course observed in the reaction of 20 with $Pb(OAc)_4$, $Tl(OAc)_3$ and $Hg(OAc)_2$ has been discussed.

Thallium(III) ion is known to abstract methyl anion from methylcobalamin. Thayer reported effects of halide ions on the rate of such transmethylation involving Tl(III) ion and other non-transition metal (Hg(II), Pb(IV)) as well as transition metal (Au(I), Pd(II), Pt(II)) ions (15). As expected from the S_E2 reactivity, the rate constant decreased in the order, $Tl(OAc)_4^- > TlCl_4^- > TlBr_4^-$. No stable methylthallium(III) species could be detected during the transmethylation reaction.

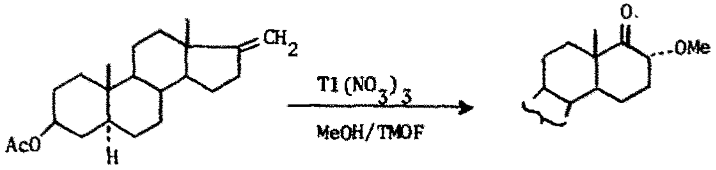
4. Organic Synthesis with Thallium(III) Compounds

Direct electrophilic allylation of aromatic compounds by using allyl halides or alcohols is usually very difficult. A mixture of allylmetallic compounds, $R_3MCH_2CH{=}CH_2$ (M= Si, Ge, Sn) and $Tl(OOCCF_3)_3$ reacted with various substituted (methyl, methoxy, chloro) benzenes and furan to give moderate to high yields of allylated products as shown in eq. 2 (16). Oxidation of



(2)

exocyclic olefins with Tl(III) salts is known to give ring-enlarged ketones [J. Am. Chem. Soc., 95 (1973) 2591]. This reaction was applied to some exocyclic steroids such as 21 to give α-oxy ketones (eq. 3; TMOF= trimethylorthoformate) (17).



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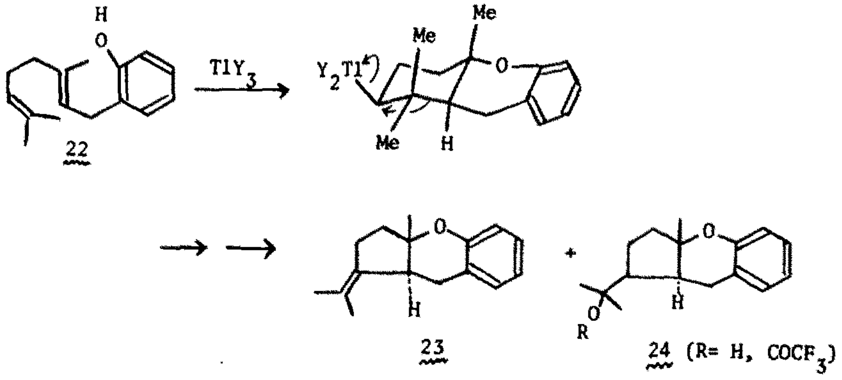
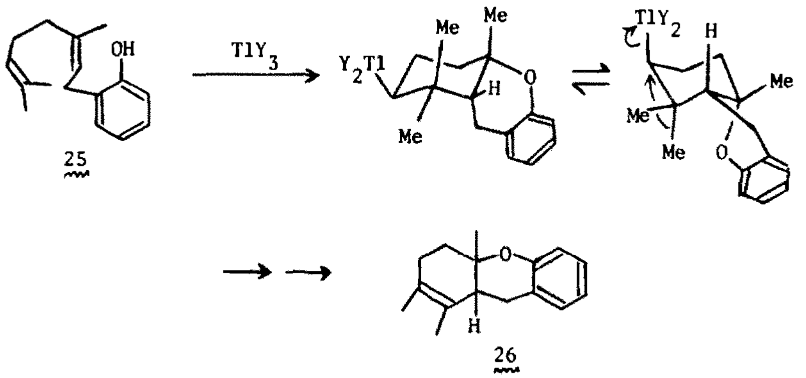
(3)

Yamada and co-workers described $Tl(OOCCF_3)_3$-induced cyclization of several o-prenylphenols with the reaction course depending on the geometry of the carbon-carbon double-bonds (18). Thus, o-geranylphenol 22 gave 23 and 24, while o-nerylphenol 25 gave 26. Key to the different reaction course would be the different oxidative rearrangement of the organothallium intermediates shown in Schemes 4 and 5 (Y= $OOCCF_3$).

Scheme 4

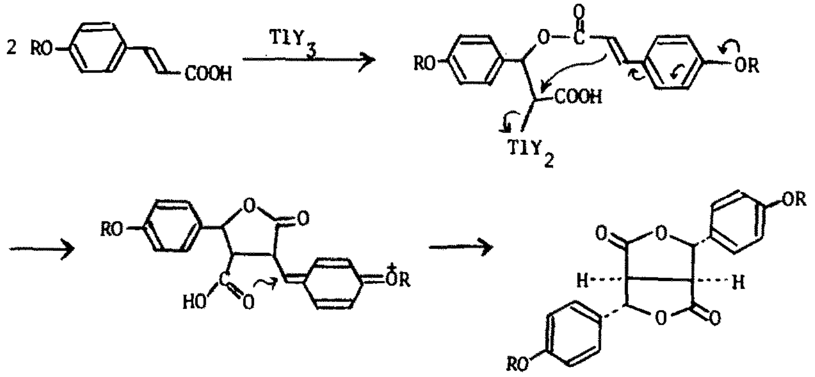


Scheme 5

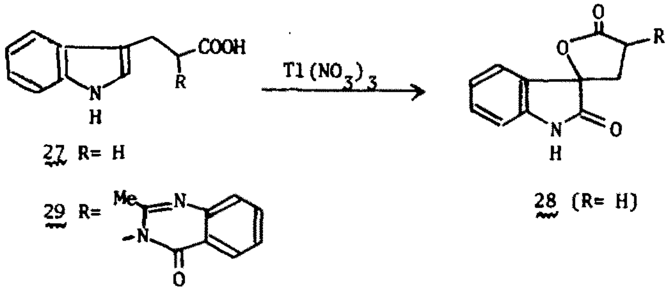


4-Alkoxycinnamic acid dimerized on treatment with $Tl(OOCCF_3)_3/BF_3{\cdot}OEt_2$ to give the cis-fused product (19). As shown in Scheme 6, the reaction was suggested to proceed through an oxythallation-dethallation sequence, rather than the radical cation intermediate formed by oxidation of the acid as originally proposed [Tetrahedron Lett., (1978) 3623].

Scheme 6

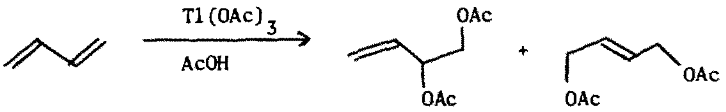


Oxidative lactonization of 27 with $Tl(NO_3)_3$ in 5 % aqueous MeCN at -10° gave spiro-lactone 28 in 54 % yield (20). Analogous lactonization of 29 was successfully applied to one of the steps to tryptoquivaline G, a potent tremorgenic toxin.



(4)

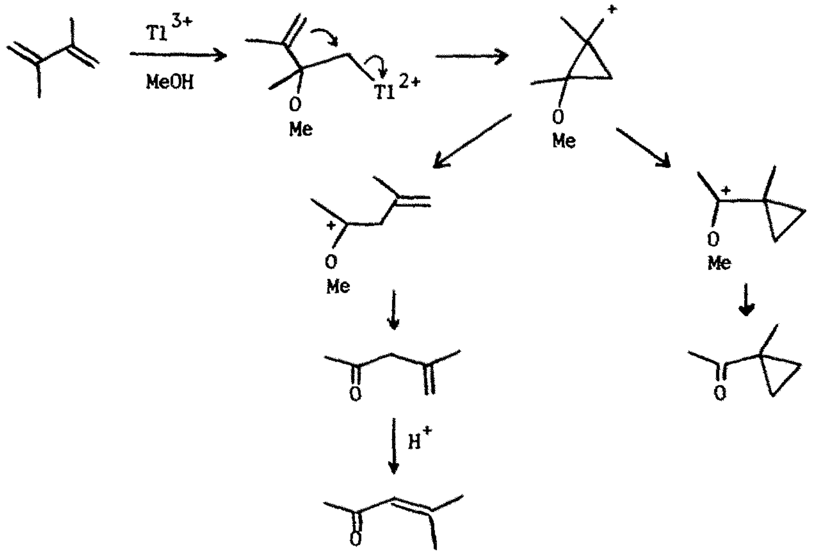
The reaction of several conjugated dienes with $Tl(OAc)_3$ in acetic acid gave both 1,2 and 1,4 diacetoxylated products in 10-90 % yields (e.g. eq. 5) (21). The dienes examined include butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, cyclopentadiene and 1,3-cyclohexadiene. A reaction path involving usual oxythallation and acetoxydethallation has been presented. On the other hand, Murakami and Nishida found that oxidation



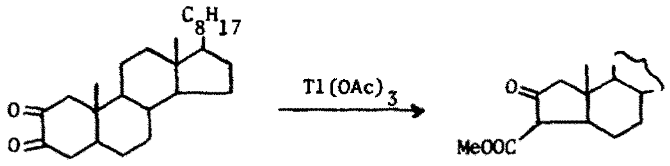
(5)

of the same 1,3-dienes with $Tl(NO_3)_3$ results in the migration of the vinylic groups as typically illustrated in Scheme 7 (22).

Scheme 7

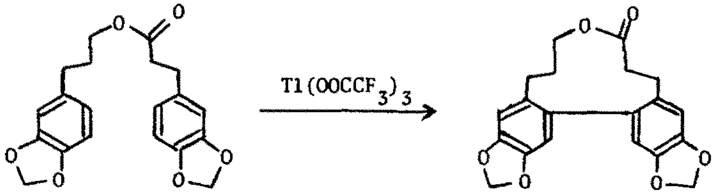


Oxidative skeletal rearrangement of carbonyl compounds with Tl(III) ions was applied to some steroidal α-diketones (e.g. eq. 6) (23).



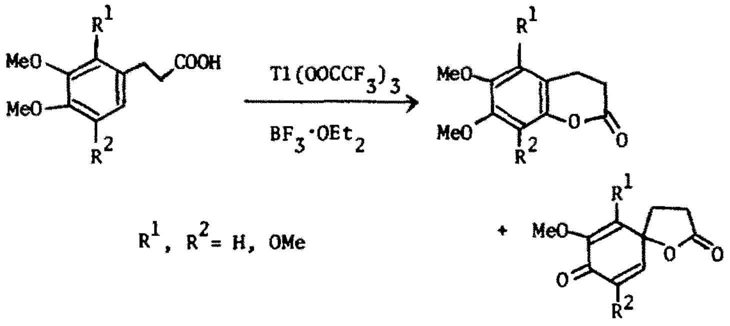
(6)

A novel bimetallic compound, $PdTl(OOCR)_5$ has recently been synthesized [Inorg. Chim. Acta, 39 (1980) 253]. A Russian group now utilized a combination of $Tl(OOCCF_3)_3$ and catalytic amount of $Pd(OAc)_2$ in a simple oxidation of various aromatic compounds to biaryls (24). The reaction proceeded well for those aromatic compounds which bear both electron-donating (Me, OMe) and medium electron-withdrawing (F, Cl) substituents. Aryl coupling reaction mediated by $Tl(OOCCF_3)_3$ was applied to the synthesis of the 11-membered lactone (eq. 7) (25).

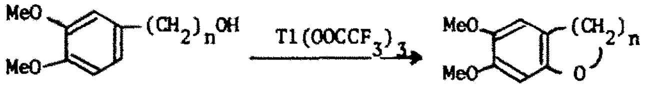


(7)

Reaction of $Tl(OOCCF_3)_3$ with highly activated aromatic compounds leads to a one-electron oxidation, instead of thallation, generating a radical cation [J. Am. Chem. Soc., 95 (1973) 5062]. Taylor and co-workers have examined intramolecular capture of aromatic radical cations thus formed by suitably positioned side-chain carboxylic acids or alcohols (26). Typical examples are shown in eq. 8 and 9. A formally similar reaction occurred between aromatic amides and $Tl(OOCCF_3)_3$ to result in mononuclear oxidation (eq. 10) (27).

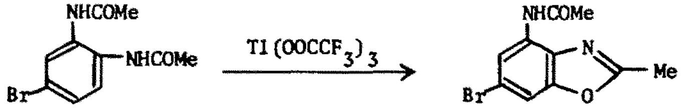


(8)



(9)

n= 3,4,5

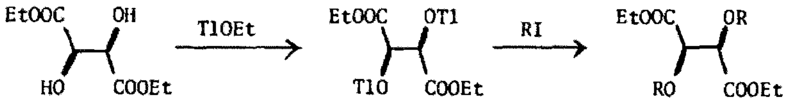


(10)

Thallation of aromatic compounds and subsequent iodination with KI were applied to iodination of polystyrene (28). The thallated polystyrene was also converted to polystyrenes containing phenylboronic acid residues and phenols on treatment with BH_3 and by subsequent hydrolysis/oxidation.

5. Organothallium(I) Compounds

Thallium(I) ethoxide was conveniently used for converting various diols, triols and hydroxy-carboxylic acid derivatives into the corresponding ethers through thallium(I) alkoxide intermediates followed by alkylation with alkyl halides (*e.g.* eq. 11) (29). The scope and limitations of this etherification method were described. The mechanism of the modified Hunsdiecker reaction to give alkyl bromides (eq. 12) was examined by employing long-chain fatty acids (30). Thus, treatment of thallium(I) octadecanoate with Br_2 in CCl_4 gave thallium(III) octadecanoate dibromide, which on treatment with 0.5 equiv. of Br_2 in refluxing CCl_4 gave 1-bromoheptadecane in 83 % yield, confirming the sequence eq. 13-15.



(11)

$$2\ RCOOTl + 3\ Br_2 \longrightarrow 2\ RBr + 2\ CO_2 + Tl_2Br_4 \qquad (12)$$

$$2\ RCOOTl + 2\ Br_2 \longrightarrow 2\ RCOOTlBr_2 \qquad (13)$$

$$2\ RCOOTlBr_2 + Br_2 \longrightarrow 2\ RCOOBr + Tl_2Br_4 \qquad (14)$$

$$2\ RCOOBr \longrightarrow 2\ RBr + 2\ CO_2 \qquad (15)$$

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