

THALLIUM; ANNUAL SURVEY COVERING THE YEAR 1976

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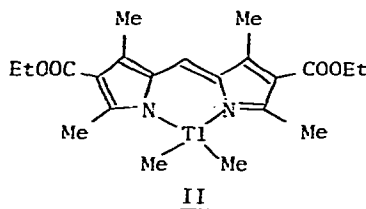
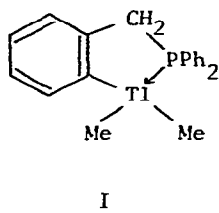
This survey will deal with 1) reviews, 2) synthesis, structure and spectroscopy of organothallium(III) compounds, 3) reactions and kinetics, 4) organic synthesis with thallium(III) and thallium(I) compounds and 5) organothallium(I) compounds.

1. Reviews

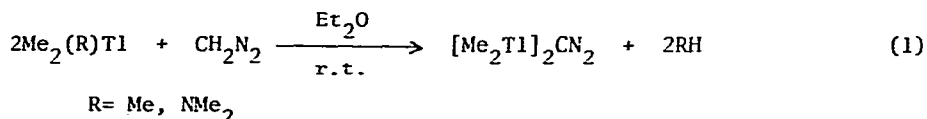
The use of $Tl(NO_3)_3$ in organic synthesis has been surveyed (1).

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

A novel triorganothallium compound containing a tertiary phosphine coordinated to thallium, I, was prepared from Me_2TlBr and (*o*-lithiobenzyl)di-phenylphosphine (2). Heating $(Me_3SiCH_2)_3MH$ with Et_3Tl at 20-50° gave



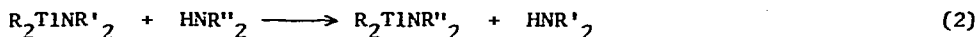
$[(Me_3SiCH_2)_3M]_3Tl$ (M= Sn, Ge) (3). Bis(dimethylthallium)diazomethane was prepared by reaction 1 (4). Its vibrational spectra suggested that the com-



pound has a high degree of ionic character. The compound failed to react both with $P(NMe_2)_3$ in a Staudinger reaction to give phosphazine, and $MeO_2CC \equiv CCO_2Me$ to give a cycloaddition product. Synthesis, properties and long range Tl-¹³C coupling in the ¹³C NMR spectrum of an unusual organothallium complex of 4,4'-diethoxycarbonyl-3,3',5,5'-tetramethyldipyrrromethene, II, were reported (5). Various dialkylthallium alkylamides have been prepared from R_2TlBr and $LiNR'_2$ (R= Me, Et, ⁿPr; R'₂= Me₂, Et₂, MeEt, (CH₂)₄, (CH₂)₅, H(Me), H(Et)) (6).

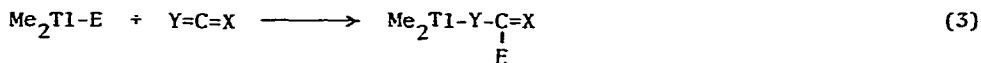
Thallium, Annual Survey covering the year 1975, see J. Organometal. Chem., 19 (1976) 131-148.

These amides reacted with other amines in benzene, n-hexane or THF according to eq. 2. Insertion of heterocumulenes into the Tl-N or Tl-O bonds yielded new



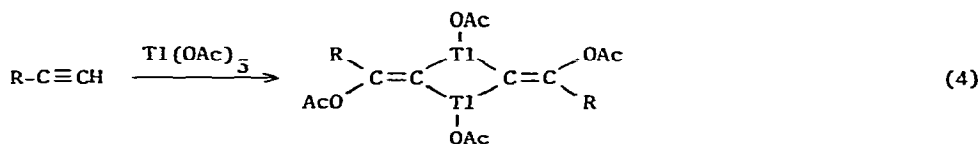
$HNR''_2 =$ aniline, imidazole, pyrazole

organothallium compounds as shown in eq. 3 (7). Prepared in this manner were:



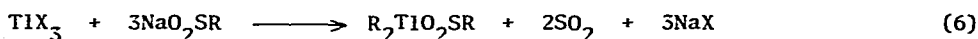
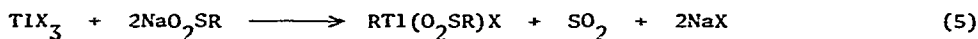
$Me_2TlYC(=NPh)NMe_2$ (Y= O, S), $Me_2TlYC(=NPh)OEt$ (Y= O, S), $Me_2TlYC(O)NMe_2$ (Y= O, S), $Me_2TlSC(X)NMe_2$ (X= O, S). Mass, infrared and 1H NMR spectral data have been interpreted in terms of the structure of these products.

The reaction of terminal acetylenes with $Tl(OAc)_3$ in chloroform gave new organothallium compounds, III, which were characterized by infrared, 1H NMR and mass spectra and cryoscopic molecular weight measurements (8). III reacted



III (R= Ph, C_6H_{13})

with $NaBH_4$ to give $R(AcO)C=CH_2$, $RCOMe$ and $RCH(OH)Me$. Heating III in refluxing acetic acid also gave ketones. An improved synthesis of various $[Me_2Tl]_2X$ (X= malonate, succinate, fumarate, maleate, CO_3 , S_2O_3) by metathesis with Me_2TlBr and the corresponding $Tl(I)$ salts was reported (9). $[R_2Tl]_2XO_3$ (X= C, S; R= Ph, o, m, p-tolyl) were obtained from R_2TlCl and Na_2XO_3 (10). Desulfination reactions between sodium mesitylenesulfinate and TlX_3 in aqueous acetic acid or water gave monomesitylthallium compounds at room temperature, and dimesitylthallium compounds at $100^\circ C$ (eq. 5 and 6) (11). Similar reac-

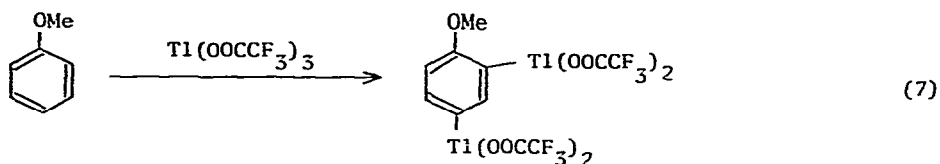


X= OAc, Cl; R= 2,4,6- $Me_3C_6H_2$

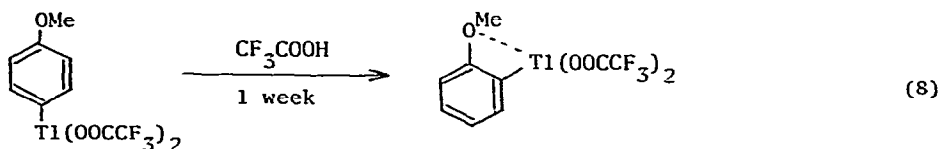
tions with 2,4,6-triisopropylbenzenesulfinate, benzene- or p-toluenesulfinate analogs failed to give organothallium products.

The reaction of $Tl(OOCCF_3)_3$ with anisole (mole ratio 3 : 1) in CF_3COOH for 65 hr yielded a dithallated product as shown in eq. 7 (12). A similar

reaction using equimolar amounts of $\text{Tl}(\text{OOCF}_3)_3$, after 1 week at room temperature,



followed by treatment with I^- , gave iodoanisoles ($\text{o/m/p} = 79/0/21$), in contrast to previous results with a shorter reaction period ($\text{o/m/p} = 7/0/95$). This led the authors to suggest the following isomerization.



Stable monoalkylthallium dichlorides, $\text{PhCH}(\text{OR})\text{CH}_2\text{TlCl}_2$ ($\text{R} = \text{Me, Et, } ^n\text{Pr, } ^i\text{Pr}$) have been prepared from $\text{PhCH}(\text{OR})\text{CH}_2\text{Tl}(\text{OAc})_2$ and KCl in methanol or acetonitrile (13). These dichlorides were found to be less susceptible to $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}\text{i}$ reactions than the acetate analogs. The reaction of Ph_2TlX with HgX'_2 gave PhTlXX' ($\text{X, X}' = \text{Cl, Br, I, CN, NCS, NO}_2$) (14). The infrared spectra of these compounds were discussed.

The crystal structure of $[\text{Me}_2\text{Tl}(\text{B}_{10}\text{H}_{12})][\text{Ph}_3\text{MeP}]$ has been determined (Fig. 1) (15). In the crystalline state, the anion contains an $\eta^4\text{-B}_{10}\text{H}_{12}^{2-}$ ligand and there is no indication of preferential η^2 -bonding from B(5)-B(6) as implied by the ^{11}B NMR spectrum in solution (see J. Chem. Soc. Dalton, (1975) 299). The structure of $\text{Me}_2\text{TlS}_2\text{COMe}$ was investigated by vibrational spectroscopy and X-ray crystallography (16). Thallium is seven-coordinate in the solid state (Fig. 2), with a C-Tl-C angle of 170.9° .

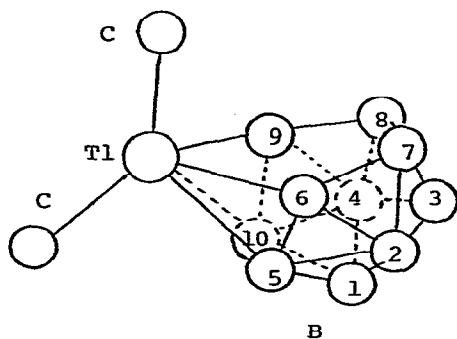


Fig. 1

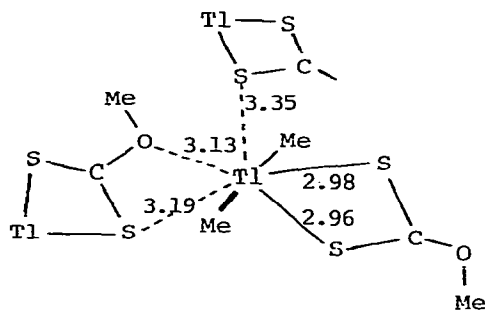
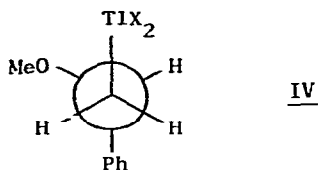


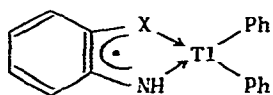
Fig. 2

^1H NMR conformational analysis of the oxythallated adducts of styrene, $\text{PhCH}(\text{OMe})\text{CH}_2\text{TlX}_2$ ($\text{X} = \text{OAc}, \text{Me}_2\text{NCSS}$) indicated the predominant rotamer of the compounds as shown in IV and allowed a full assignment of all the resonances (17). These results were applied to the oxythallated adduct from *trans*- β -*d*-styrene to provide the first evidence for *trans* oxythallation of acyclic olefins. The

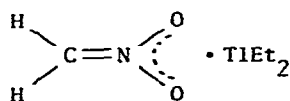


decrease of $^2J(\text{M}-\text{CH}_3)$ ($\text{M} = \text{Sn}, \text{Tl}, \text{Pb}$) in some dimethylmetal compounds measured in strong acids was attributed to the increase of the mean singlet-triplet excitation energy in the Fermi contact term (18). The lowering of the metal-carbon bond strengths in strong acids also was revealed from metal-carbon stretching frequencies. ^{205}Tl NMR spectra were obtained for various tri-, di- and monoorganothallium compounds as well as for inorganic thallium salts (19). The paramagnetic ^{205}Tl chemical shifts have been discussed in terms of substituent, solvent and concentration effects. The ^{205}Tl chemical shifts and $J(^{205}\text{Tl}-^{13}\text{C})$ also were found to be most sensitive to changes in the environment of the thallium atom in the ^{205}Tl , ^{13}C and ^1H NMR study of Me_2TlX ($\text{X} = \text{NO}_3, \text{I}, \text{OPh}$) in various solvents and concentrations (20). In another ^{205}Tl NMR study of a series of substituted arylthallium ditrifluoroacetates, Hinton and Briggs found that ^{205}Tl chemical shifts are remarkably sensitive to the substituents, with a correlation existing between the chemical shifts and the Hammett σ parameters (21). A correlation between the chemical shifts and the $J(^{205}\text{Tl}-^1\text{H})$ also was observed.

As an extension of the study on ESR spectra of paramagnetic diphenylthallium cation-semiquinone systems (see *J. Organometal. Chem.*, 101 (1975) 145), paramagnetic complexes derived from Ph_2TlOH and *o*-aminophenols or *o*-phenylenediamines, e.g. V, have been subjected to ESR measurements (22). The results



V ($\text{X} = \text{O}, \text{NH}$)



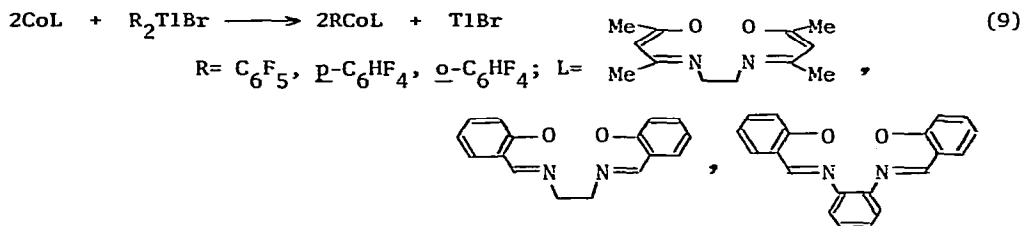
VI

have been discussed in terms of ion pair interaction between Ph_2Tl^+ and *NH*-analog semiquinone radicals. A vibrational spectral study of $\text{M}(\text{CH}_2\text{NO}_2)$ ($\text{M} = \text{Li}, \text{K}, \text{Et}_2\text{In}, \text{Et}_2\text{Tl}$) in the *CH* stretching region suggested the compounds to contain the *aci*-form of CH_2NO_2 , e.g. in VI (23). The nature of the metal-

oxygen bond in the thallium compound was not clarified.

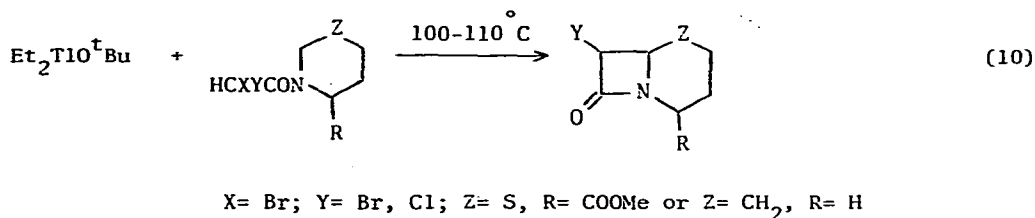
3. Reactions and Kinetics

Bis(polyfluorophenyl)thallium bromides reacted with Co(II) Schiff base complexes to afford organocobalt(III) complexes as shown in eq. 9 (24). Possible



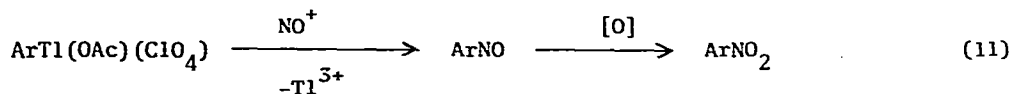
mechanisms in eq. 9 have been discussed. $(\text{C}_6\text{F}_5)_2\text{TlBr}$ also was used to oxidize $[\text{ClAu}]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ to give $[\text{Cl}(\text{C}_6\text{F}_5)_2\text{Au}]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (25).

$\text{Et}_2\text{TlO}^t\text{Bu}$ has been used to synthesize fused α -halo- β -lactams, though in only moderate to low yield, as shown in eq. 10 (26). The separation of ca. 85 % of



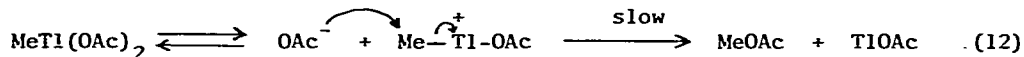
the calculated amount of Et_2TlBr and the low recovery of the starting dihaloamides (10-25 %) led the authors to suggest that the carbene generation is efficient in the above reaction.

Several arylthallium compounds, $\text{ArTl}(\text{OAc})(\text{ClO}_4)$ ($\text{Ar} = \text{Ph}, \text{p-tolyl}, \text{p-anisyl}, \text{o- and m-xyllyl}, \text{o- and p-chlorophenyl}$) reacted with NaNO_2 , KNO_2 or AgNO_2 in CF_3COOH to afford nitroarenes (27). The thallation products of other aromatic compounds such as *t*-butylbenzene, mesitylene, biphenyl and bromobenzene also gave the corresponding nitroarenes by similar reactions. In all reactions the initial step was assumed to be electrophilic substitution by NO^+ to give nitrosoarenes which were further oxidized under reaction conditions (eq. 11).



Kinetics of the reaction of $(\text{p-anisyl})_2\text{TlCl}$ with mercury metal in various solvents at 60°C has been investigated (28). In pyridine or ethylenediamine, the Hg/Tl exchange occurs mainly via the homogeneous reaction. These results

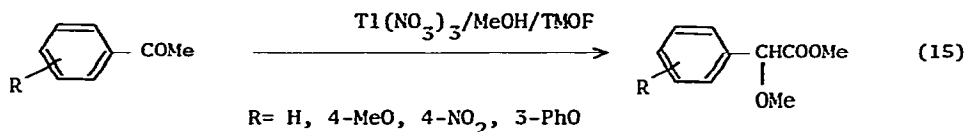
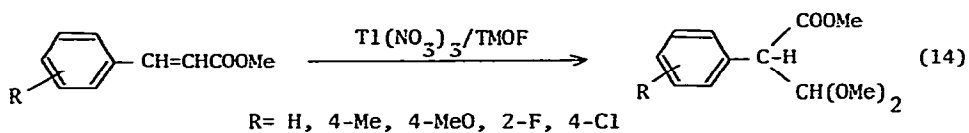
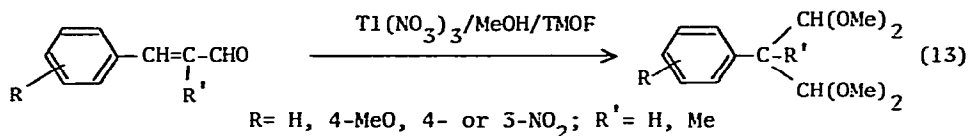
were compared with an analogous Hg/Hg exchange of organomercurials with mercury metal through a predominant heterogeneous reaction, and were explained in terms of the far lower adsorption of organothallium compounds on mercury. The kinetics of the decomposition of $\text{MeTl}(\text{OAc})_2$ into MeOAc and TlOAc was studied in various solvents using NMR spectroscopy (29). The decomposition followed a first order rate law in the order of decreasing rate, $\text{D}_2\text{O} > \text{CD}_3\text{OD} > \text{MeNO}_2 > \text{dioxane}$. In THF and CDCl_3 autocatalysis due to the formation of TlOAc was observed. Based on kinetic analysis and conductivity measurements, an $\text{S}_{\text{N}}2$ mechanism as shown in eq. 12 was proposed.



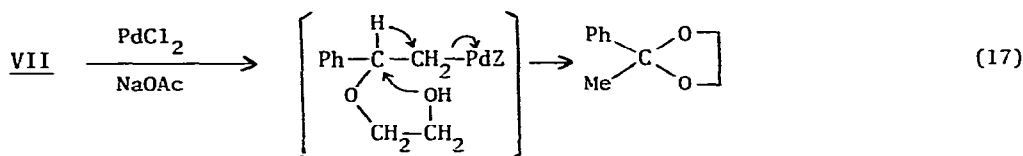
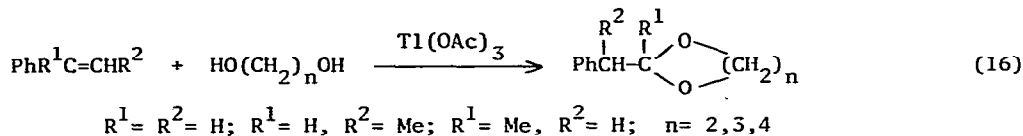
Reactions of some pyridiniummethylmolybdenum and tungsten complexes with $\text{Tl}(\text{ClO}_4)_3$ in aqueous solution gave no organothallium products, unlike the analogous reaction with $\text{Hg}(\text{ClO}_4)_2$ to give organomercurials, but the corresponding pyridiniumacetic acids were formed as a result of two electron transfer from Tl to the transition metal reactant (30).

4. Organic Synthesis with Thallium(III) and Thallium(I) Compounds

Taylor *et al.* observed that $\text{Tl}(\text{NO}_3)_3$ adsorbed on an acidic montmorillonite clay, K-10 is a remarkably effective reagent for oxidative rearrangement of alkyl aryl ketones and olefins (31). The superiority of $\text{Tl}(\text{NO}_3)_3/\text{K-10}$ over the usual $\text{Tl}(\text{NO}_3)_3/\text{MeOH}$ system is found in the rapid, highly selective, high yield and room-temperature oxidation with the former reagent. The same research group also described novel oxidative rearrangements of unsaturated organic substrates with $\text{Tl}(\text{NO}_3)_3$ in trimethyl orthoformate (TMOF) which do not proceed in the solvents commonly used for the reaction of $\text{Tl}(\text{NO}_3)_3$ (32). Typical examples are shown in eq. 13-15.

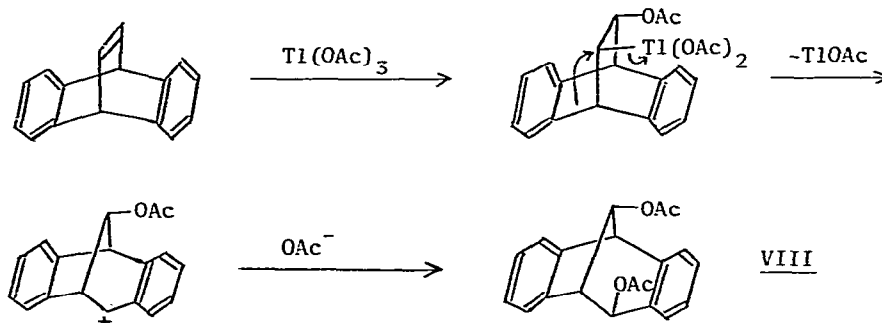


Oxidation of olefins and cyclopropanes with $Tl(NO_3)_3$ in pentane gave mainly dinitrate esters such as $RCH(ONO_2)CHR'(ONO_2)$ or $PhCH(ONO_2)CH_2CH_2ONO_2$, where rearrangement products occur to a lesser extent, but there is a loss of stereospecificity as compared to the similar reaction in methanol (35). The oxidation of styrene and 1-octene with $Tl(OAc)_3$ in several diols was studied (54). Thus, oxythallation of styrene in $HOCH_2CH_2OH$ afforded $PhCH(OCH_2CH_2OH)CH_2Tl(OAc)_2$, VII, which in turn produced $PhCH_2CH(OCH_2CH_2O)$ on heating at $80^\circ C$. In similar ways, styrene and methylstyrenes reacted with diols in the presence of $Tl(OAc)_3$ according to eq. 16. VII also reacted with $PdCl_2/NaOAc$ as shown in eq. 17.



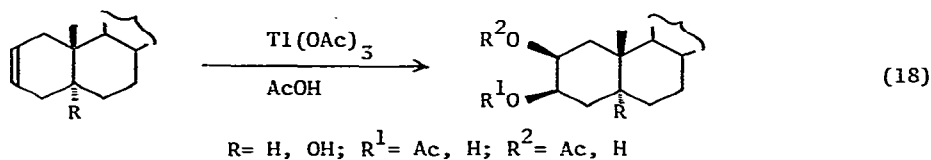
Dibenzobicyclo[2.2.2]octatriene reacted with $Tl(OAc)_3$ in acetic acid to give VIII according to Scheme 1 (35). Similarly, a polycyclic olefin, IX, reacted with

Scheme 1

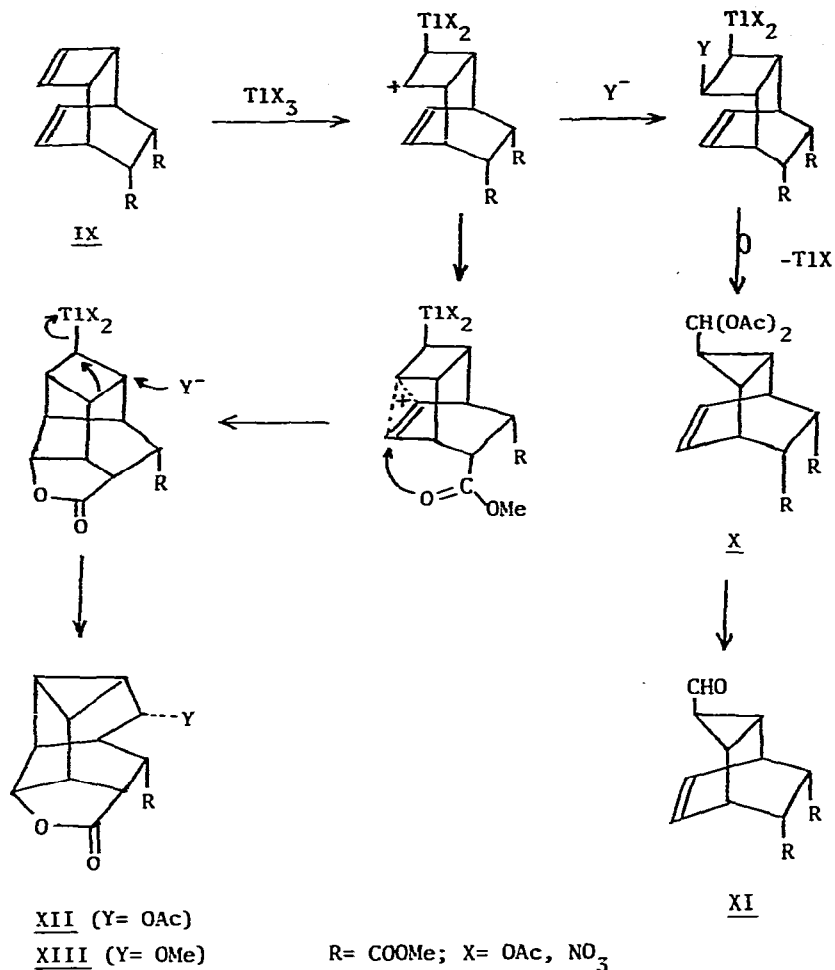


TlX_3 ($X = OAc, NO_3$) to give X-XIII through organothallium intermediates as shown in Scheme 2 (36).

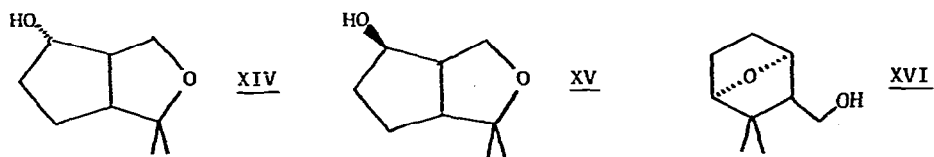
Glotter and Schwartz reported that treatment of steroidal olefins with $Tl(OAc)_3$ constitutes a convenient procedure for cis-hydroxylation of disubstituted olefins from the hindered side of the molecule as shown in eq. 18 (37).



Scheme 2

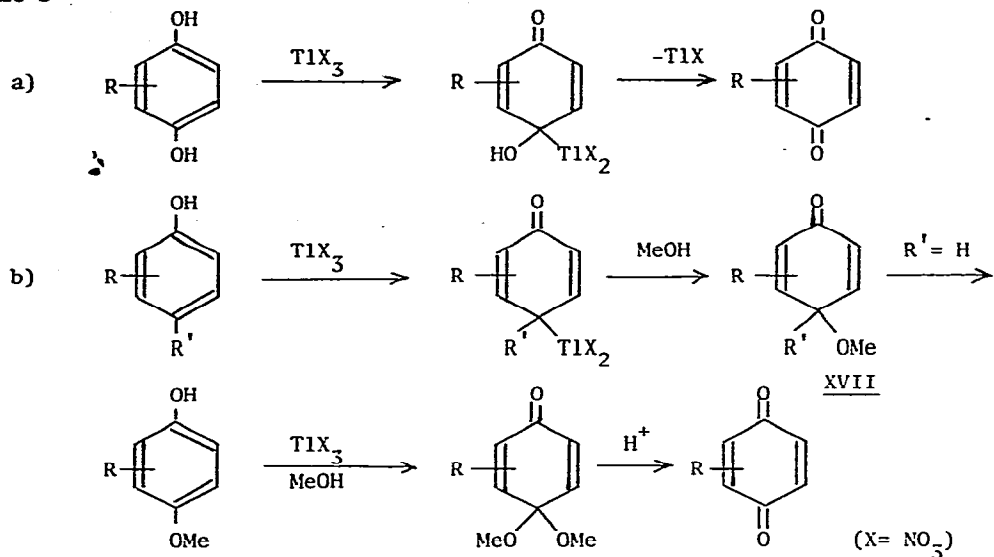


A new type of olefinic cyclization was observed in the reaction of geraniol with $\text{Ti}(\text{ClO}_4)_3$ to give XIV-XVI (38).

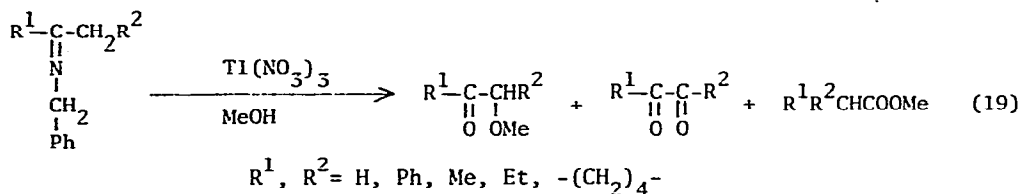


Hydroquinones or 2,6-disubstituted phenols reacted with 1 or 2 equivalents of $\text{Ti}(\text{NO}_3)_3$ in methanol to give the corresponding *p*-benzoquinones (39). A new mechanism involving an ipso thallation step for these transformations has been proposed as in Scheme 3. Intermediates XVII in this scheme indeed have been isolated from the reaction between a variety of 4-substituted phenols and $\text{Ti}(\text{NO}_3)_3$, and the scope and limitations of this reaction were defined.

Scheme 3



The study of the action of Tl(OAc)₃ on several steroidal ketones revealed three distinct oxidation modes, namely an acetoxylation, a dehydrogenation and a rearrangement of the carbon skeleton (40). Oxidation of tautomeric imines with Tl(NO₃)₃ in methanol gave, after hydrolytic work-up, α-methoxyketones and α-diketones as in eq. 19 (41). Only small amounts of methyl esters of



carboxylic acids were obtained, in contrast to the oxidation of the corresponding ketones. A possible mechanism was discussed in terms of a preferential coordination of the imino nitrogen atom with thallium. As an extension of oxidative rearrangement of chalcones with Tl(NO₃)₃ (Chem. Ber., 108 (1975) 3883), Antus *et al.* synthesized the isoflavone jamaicin and the pterocarpan leiocarpin starting from the corresponding chalcones (42).

Tl(NO₃)₃ effected conversion of α-(3,4-dimethoxyphenyl)-β-nitroethylthioethane into α-(3,4-dimethoxyphenyl)-β-nitroethoxyalkanes in alcohols (43). Importance of the coordination of sulfur with thallium in these reactions has been suggested.

Thallium(I) salts of 1-hydroxy-2(1H)-pyridones were used to prepare 1-alkoxy-2(1H)-pyridones, on reaction with alkyl halides (44). As extensions of the use of TlX/I₂ system in organic synthesis (see A.S. 1974, ref. 53, 54),

reactions of TiN_3/I_2 (45) or $TiOAc/I_2$ (46) with cyclic olefins have been investigated, and the mode of formation of the products was discussed. The same research group also described selective ortho-iodination of phenols by means of $TiOAc/I_2$ (47).

5. Organothallium(I) Compounds

A new method of preparing C_5H_5Tl by cocondensation of thallium metal with cyclopentadiene at $77^\circ K$ was reported (48). C_5H_5Tl was among several cyclopentadienyl derivatives of Group Ia, IIa and IIIb studied by ^{13}C NMR spectroscopy (49). The results indicated that neither the ^{13}C chemical shifts nor the C-H coupling constants may be used as a criterion for assigning a σ - or π -bonded structure.

An improved synthesis of $(C_5H_5)_2MCl$ ($M = Ti, V, Sc$) has been developed by the reaction of C_5H_5Tl with the appropriate metal halides (50). C_5H_5Tl was also used to prepare $Rh(C_5H_5)(C_4Ph_4)$ from $[RhCl(C_4Ph_4)]_2$ (51). Thallium(I) hexacarbonylvanadate(-1) reacted with iodosilane to give $SiH_3V(CO)_6$, the first Si-V bonded compound (52).

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