THALLIUM; ANNUAL SURVEY COVERING THE YEAR 1979*

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The number of papers dealing with organothallium compounds during the year 1979 dropped considerably from the level of the past several years. 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

The crystal structure of $(p\text{-}C_6F_4H)_2TlBr$ has been determined (1). The Tl-Br interaction (3.214, 3.172 A) between the dimeric $[R_2TlBr]_2$ units shown in Fig. 1 gives rise to a polymeric chain structure (Fig. 2). Each thallium is five-coordinate with a distorted trigonal bipyramidal configuration of ligands. The C-Tl-C angles (144.2, 149.9°) are somewhat larger than those of $(C_6F_5)_2TlOH$ which is also a five-coordinate polymer in the solid state. Cyclopropylthallium diisobutyrate, **1**, was prepared by reaction 1 (2).

$$(C_3H_5)_2TlOOC^iPr + Hg(OOC^iPr)_2 \longrightarrow \underset{\mathbf{1}}{C_3H_5Tl(OOC^iPr)_2} + C_3H_5HgOOC^iPr \qquad (1)$$

An X-ray crystal structural analysis of **1** provided the first details of the coordination around thallium in monoorganothallium dicarboxylates. Each thallium atom is seven-coordinate (Fig. 3) in linear polymeric chains (Fig. 4) with one carboxylate group exhibiting both bridging and chelating functions. The other carboxylate group makes an unsymmetrical chelate (O_3 and O_4 in Fig. 3). These results were compared with the IR spectral characteristics of both **1** and $MeTl(OOCR)_2$ (R= Me, ^iPr) [see also J. Organometal. Chem., 10 (1967) 211].

Reaction of R_2TlBr with metal polyfluorobenzenesulfinates in boiling pyridine gave the corresponding R_3Tl compounds, which were isolated as the

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*Thallium; Annual Survey covering the year 1978 see J. Organometal. Chem., Vol. 183 (1979) p. 265-280.

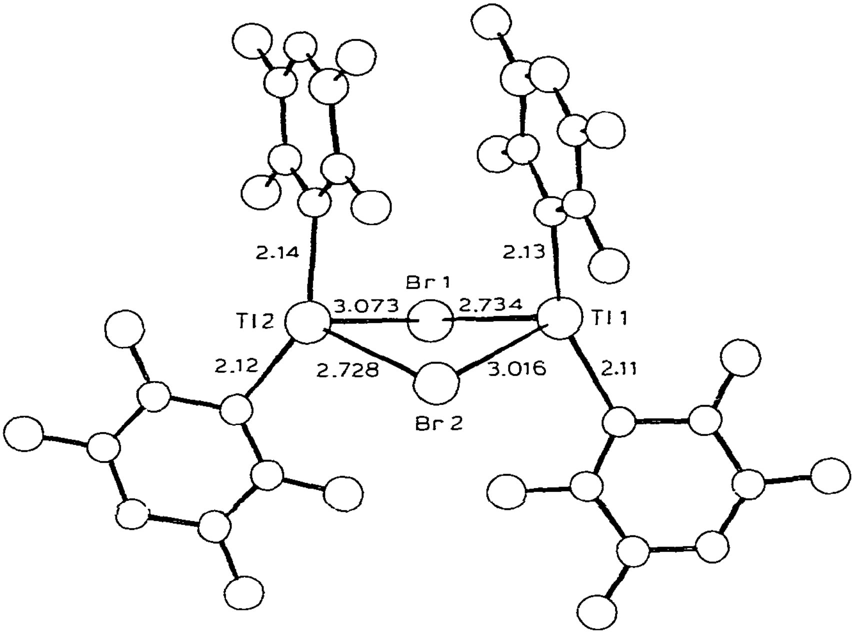


Fig. 1. The two crystallographically independent $(C_6F_4H)_2TlBr$ units. [Reproduced from Inorg. Chim. Acta, 35 (1979) L335].

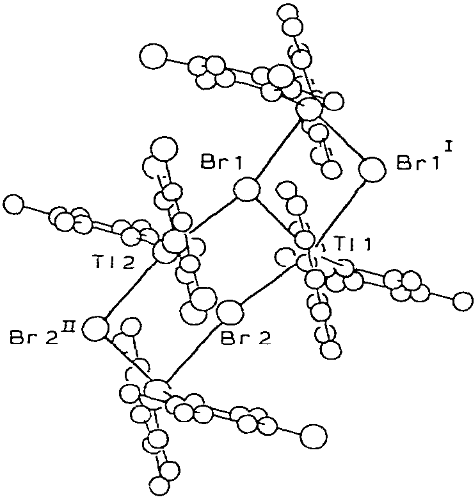


Fig. 2. Part of the polymeric chain of $(C_6F_4H)_2TlBr$. [Reproduced from Inorg. Chim. Acta, 35 (1979) L335].

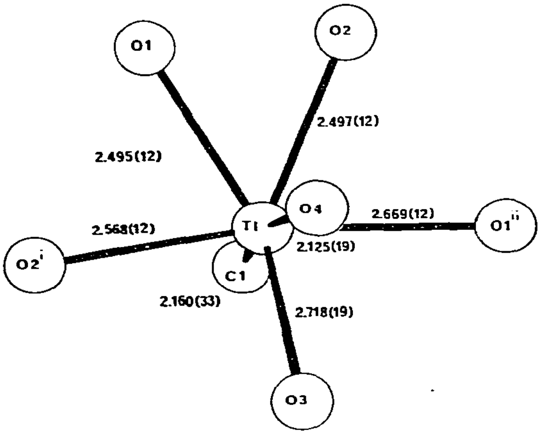


Fig. 3. Coordination geometry around Tl in 1. [Reproduced from *J. Organometal. Chem., 165 (1979) 21*].

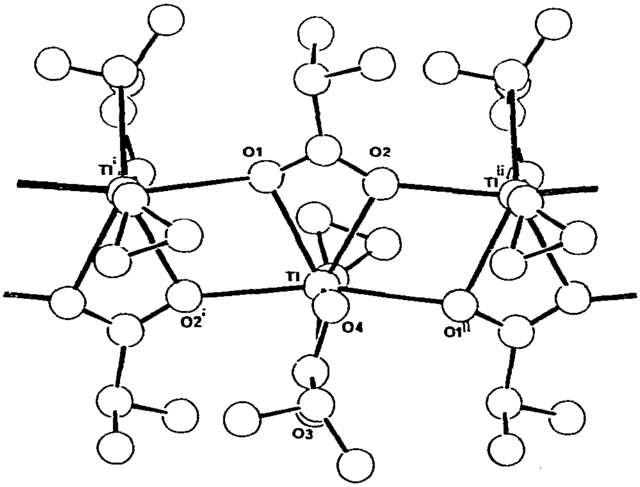


Fig. 4. Part of the polymeric chain in 1. [Reproduced from J. Organometal. Chem., 165 (1979) 21].

dioxane adducts (eq. 2) (3,4). The reaction was considered to proceed by

$$R_2TlBr + M(OOSR)_n \longrightarrow R_3Tl + SO_2 \qquad (2)$$

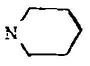
$$R = C_6F_5,\ \underline{p}\text{-}C_6F_4H,\ \underline{o}\text{-}C_6F_4H;\ M = Ba\ (n = 2),\ Tl\ (n = 1)$$

formation and desulfination of $R_2Tl(OOSR)$ intermediates.

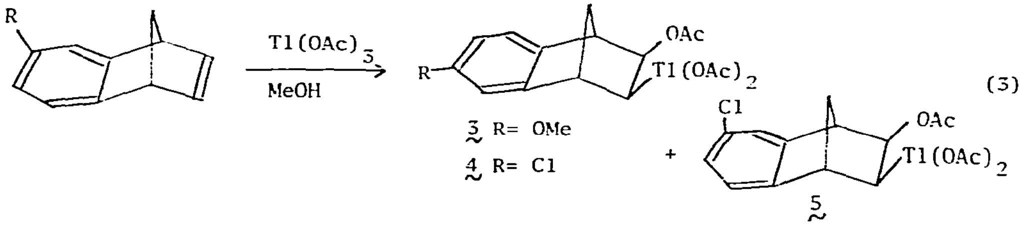
^{1}H and ^{13}C NMR spectra of some dimers of dimethylthallium compounds $[Me_2TlX]_2$ (X= NMe_2, NEt_2, NHMe, NHPh, OEt, SEt, pyrazolido, PPh_2) were examined (5). Studies of exchange reactions among different ligand groups provided evidence for a dimer-monomer equilibrium. Complexes of the radical ion of tetracyanoquinodimethane (Y^-), $R_2Tl^+Y^-$ (R= Ph, o-tolyl, p-C_6H_4Cl) were prepared from $R_2TlOOC(CH_2)_4Me$ and LiY (6).

Preparation and ^{1}H NMR spectra of monoarylthallium compounds containing the Tl-S bonds, 2, were reported (7). Attempts to isolate $ArTl(SR)_2$ (R= Ph, Et, COMe) from reactions of $ArTlX_2$ (X= Cl, $OOCCF_3$) with NaSR failed owing to formation of the Ar_2TlX and RSSR compounds. Other arylthallium dithiocarbamates, $ArTl(SSCNRR')_2$ and $Ar_2TlSSCNRR'$ (Ar= Ph, p-tolyl; R= H, R'= Ph, $PhCH_2$; R= R'= Me, Et, $PhCH_2$; RR'N= morpholino) were prepared from, e.g., Ph_2TlCl and NaSSCNRR' in benzene (8).

$ArTl(SSCY)_2$

2 Ar= Ph, p-tolyl; Y= NMe_2, NEt_2,  , OMe

Acetoxythallation of norbornene, norbornadiene and benzonorbornadiene occurred in reactions with $Tl(OAc)_3$ even in methanol solution (9). The addition was cis and exo. The reaction with 9-methoxybenzonorbornadiene gave 3 almost exclusively, while the 9-chloro analog gave a mixture of 4 and 5 (4/5= 20/80). Lactonization occurred in the reaction with 6 - 8.

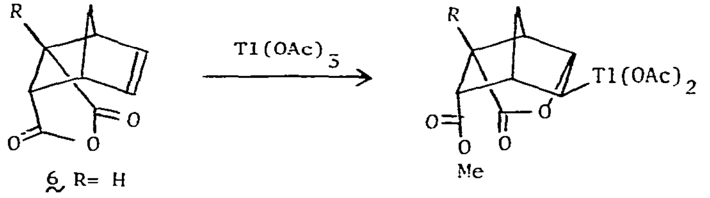


3 R= OMe

4 R= Cl

5

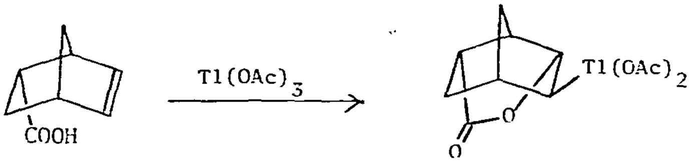
(3)



6 R= H

7 R= Me

(4)



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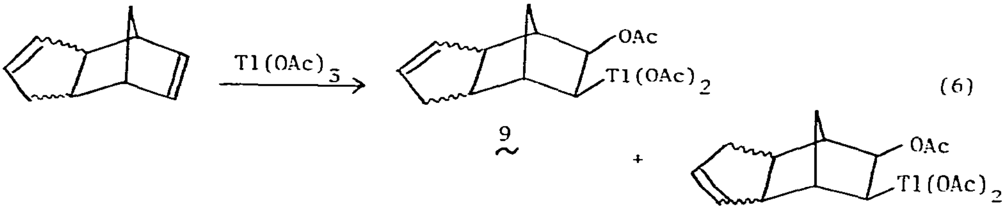
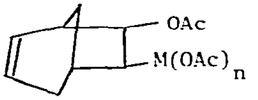
(5)

^{13}C NMR spectra were recorded to determine the structure of the organothallium adducts. The $NaBH_4$ reduction of these products was described. The same authors also described that acetoxythallation of endo- and exo-dicyclopentadiene affords a regioisomeric mixture of cis-exo adducts (eq. 6) (10).



(6)

The isomer ratios were determined by ^{13}C NMR. The regioselectivity in these reactions, as well as in the analogous oxymercuration, is higher in the case of the endo olefin where **9** and its mercury analog are the major products. Acetoxythallation and mercuration of bicyclo[3,2,1]octa-2,6-diene in CH_2Cl_2 gave a single isomer, **10**. These results were explained in terms of the through-space homoconjugation.



10 M= Tl (n= 2), Hg (n= 1)

Thallium trifluoromethanesulfonate, prepared from thallium oxide and trifluoromethanesulfonic acid, was found to be a good, new thallation agent for relatively unreactive polyfluoroarenes (eq. 7) (11). The products were

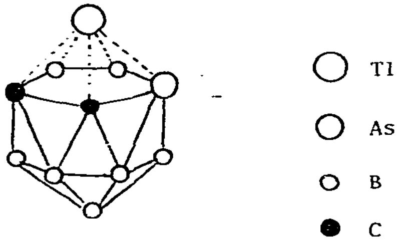
$$Tl(O_3SCF_3)_3 + RH \xrightarrow{CF_3COOH} RTl(O_3SCF_3)_2 + CF_3SO_3H \qquad (7)$$

R= p-C_6F_4(OMe), p-C_6F_4(Me), m-C_6F_4H, p-C_6F_4H, o-C_6F_4H, C_6F_5, 3,5-$C_6F_3H_2$, 3,6-$C_6F_3H_2$

characterized either spectroscopically (^{19}F and ^{1}H NMR), by conversion to the corresponding iodoarenes (with NaI), or conversion to the corresponding R_2TlOAc compounds (heating in the presence of NaOAc).

2. Thallium-metal Bonded Compounds

The boron-thallated carboranes, $(B_{10}H_9C_2RR')Tl(OOCCF_3)_2$, **11** (R= H, Me, Ph, R'= H; R= R'= Me), and the m-carborane analog (R= R'= Me) were prepared from $Tl(OOCCF_3)_3$ and the corresponding carboranes (12). Treating **11** (R= R'= H) with 1-phenyl-2-lithio-o-carborane gave $(B_{10}H_{11}C_2)(B_{10}H_{10}C_2Ph)TlOOCCF_3$.



12

The reaction of arsacarborane, $B_8C_2AsH_{11}$, with TlOH in diethyl ether gave a beige solid, $B_8C_2TlAsH_{10}$, whose structure was proposed as shown in 12 (13). Ion pairs formed between Tl^+ and $Co(CO)_4^-$ were found to exhibit a strongly solvent-dependent, cobalt-to-thallium CT band in the visible region, with the energy of this transition correlating with the Z number of the solvent (14). This band disappeared on addition of dibenzo-18-crown-6. The ion pair

$$Tl^+ + Co(CO)_4^- \overset{K}{\rightleftharpoons} Tl^+Co(CO)_4^- \qquad (8)$$

association constant, K, varies from 1.2 x 10^5 in toluene to less than 10 in DMF, DMSO and water. The IR spectra and the interatomic separation in the ion pair calculated from electrostatic theory suggest a contact ion pair of C_{3v} symmetry with a direct Tl-Co interaction.

3. Reactions and Kinetics

Reaction of $(C_6F_5)_3Tl$(dioxane) with 1,3-diorganotriazene (HL) in refluxing benzene gave TlL_3 compounds for the first time (eq. 9) (15).

$$(C_6F_5)_3Tl + 3HL \longrightarrow TlL_3 + 3C_6F_5H \qquad (9)$$

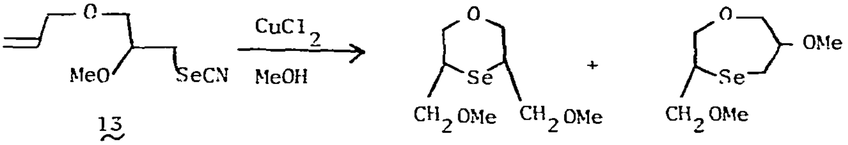
L= PhNNNPh, PhNNN-pyridyl-2

The IR and UV spectra and molecular-weight (monomeric) suggested the TlL_3 compounds to contain a six-coordinate thallium atom with bidentate (possibly 1,3-chelate) triazenido ligands. Reaction of $(C_6F_5)_3Tl$(dioxane) with HL in hot (not refluxing) benzene resulted in formation of a five-coordinate complex, $C_6F_5TlL_2$ (L= PhNNNPh). The reaction of Ph_2TlCl with $TeCl_4$ was reported to proceed as in eq. 10 (16). The yield of Ph_2TeCl_2 was 94 %.

$$2Ph_2TlCl + TeCl_4 \longrightarrow 2PhTlCl_2 + Ph_2TeCl_2 \qquad (10)$$

Kinetic studies on the reaction of methylcobalamin (MeCo) with various methyl derivatives of heavier metals including Me_2TlOAc were reported (17). The reaction was first-order with respect to the concentration of both MeCo and the thallium compound, with the rate being slower than that between MeCo and inorganic Tl^{III} compounds. However, the products of these reactions were not described.

Treatment of oxythallated adducts of diallyl ether or 1,5-hexadiene with KSeCN afforded vicinal alkoxyselenocyanates, 13 and 14 (18). Compounds 13 and 14 were thought to be intermediates in $CuCl_2$-mediated intramolecular oxyselenation of diolefins with KSeCN, since the products in this reaction were the same as those obtained in reaction 11 and 12.



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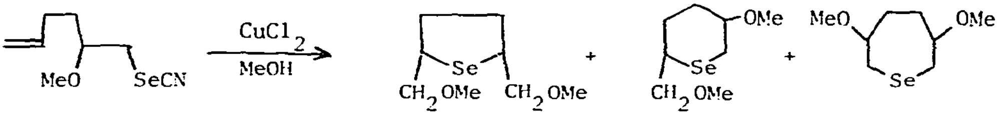
(11)



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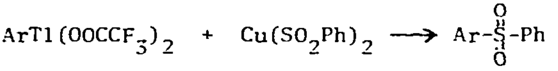
(12)

A convenient method of preparing unsymmetrical diaryl sulfones was described (eq. 13) (19). This utilizes the reaction of arylthallium compounds with $Cu(SO_2Ph)_2$ in aqueous dioxane.

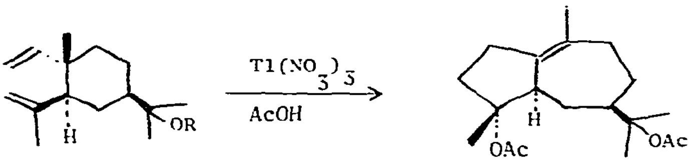


$$ArTl(OOCCF_3)_2 + Cu(SO_2Ph)_2 \longrightarrow Ar-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Ph \qquad (13)$$

$$Ar = 2,4\text{-}C_6H_3Me_2,\ 2,4,6\text{-}C_6H_2Me_3,\ \underline{p}\text{-}C_6H_4Cl$$

4. Organic Synthesis with Thallium(III) Compounds

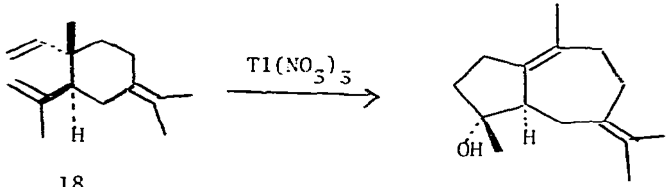
Cyclization of diolefin compounds with thallium(III) compounds was reported recently [Chem. Comm., (1976) 997]. It was now found that treatment of (-)-elemol acetate, 15, with $Tl(NO_3)_3$ in acetic acid gives 16 in good yield (20). 16 could be converted to 17, which was prepared also from 18 and $Tl(NO_3)_3$. Oxymercuration-hydrodemercuration of 19 gave 20. The common intermediate in these oxymetallation reactions was postulated as shown in eq. 16 (M= TlX_2 or HgX).



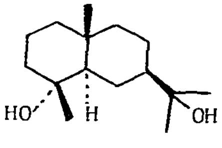
15 R= MeCO
19 R= H

16

(14)



18 17 (15)



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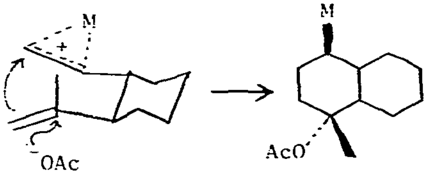
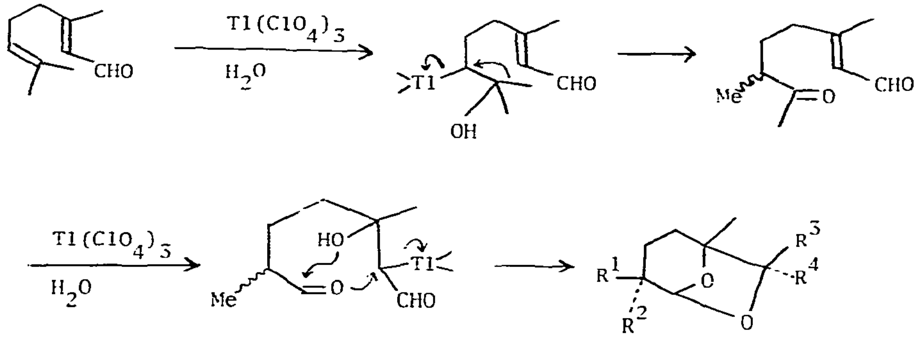


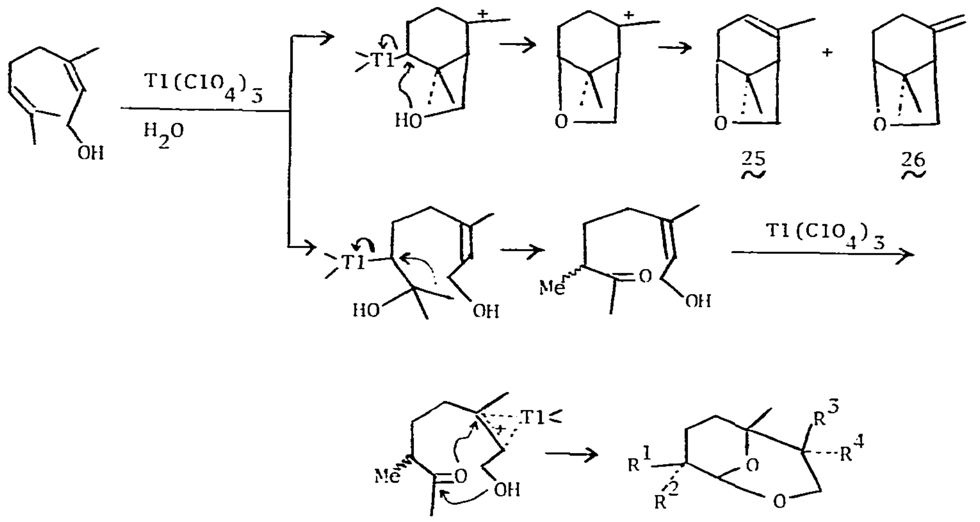
(16)

Treatment of citral with aqueous Tl(ClO$_4$)$_3$ gave a mixture of four stereoisomeric aldehydes, 21 – 24 (21). These authors also described the cyclization



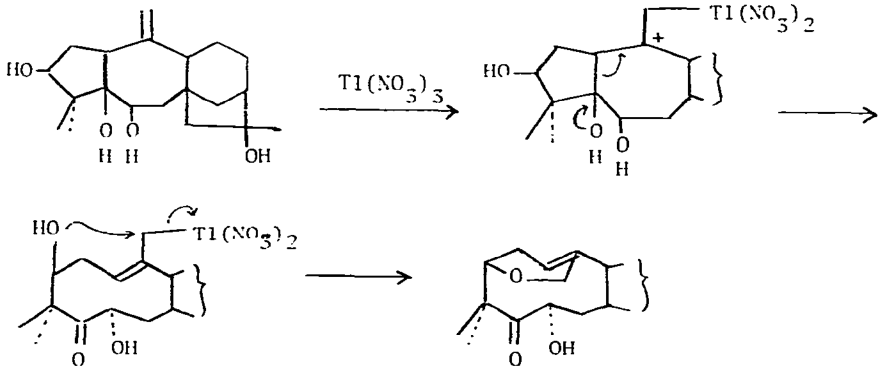
21 $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = CHO$
22 $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = CHO$
23 $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = CHO$
24 $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = CHO$

of nerol with Tl(ClO$_4$)$_3$ to give 25 – 30 (22).



27 $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = OH$
28 $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = OH$
29 $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = OH$
30 $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = OH$

Oxidation of grayanotoxin-II with $Tl(NO_3)_3$ gave 31, whose structure was elucidated by an X-ray study of its reduction product (23).



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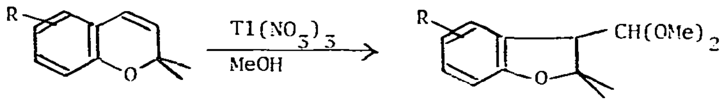
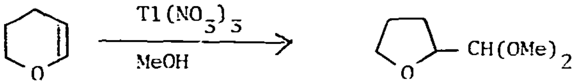
The $Tl(NO_3)_3$-mediated ring contraction of 2,2-dimethyl-2H-chromenes in methanol was described (eq. 17) (24). Similarly, 3,4-dihydro-2H-pyran gave



(17)

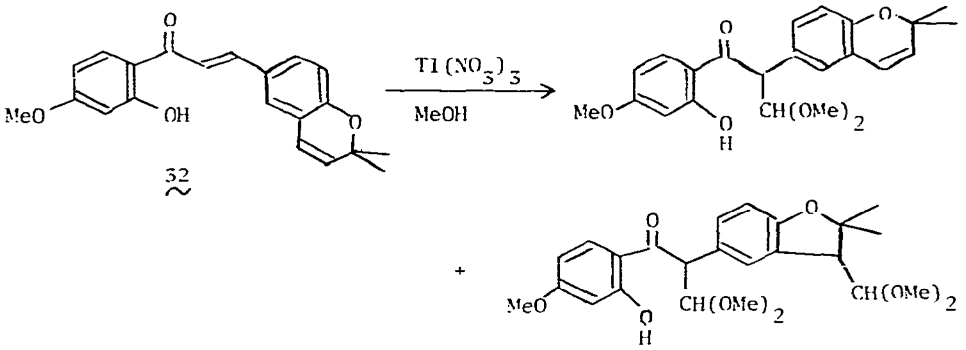
R= 6-CHO, 6,7-(MeO)$_2$, 5,6,7-(MeO)$_3$

the tetrahydrofuran derivative (eq. 18). A similar ring-contraction occurred



(18)

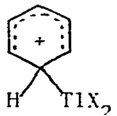
during the oxidation of a chalcone derivative, 32, in an attempt to synthesize corylins.



32

(19)

Kwok et al. measured the partial rate factors for the thallation of toluene by $Tl(OOCCF_3)_3$ in CF_3COOH (25). On the basis of the value, log p_f^{Me}/ log m_f^{Me}= 3.6, in this case being in the range of those for many conventional electrophilic substitution reactions, these authors concluded that the thallation proceeds via a conventional mechanism through the Wheland intermediate (33). Thallation and iodination of aromatic compounds were applied



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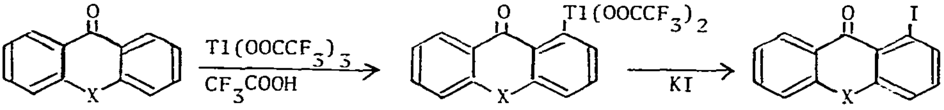
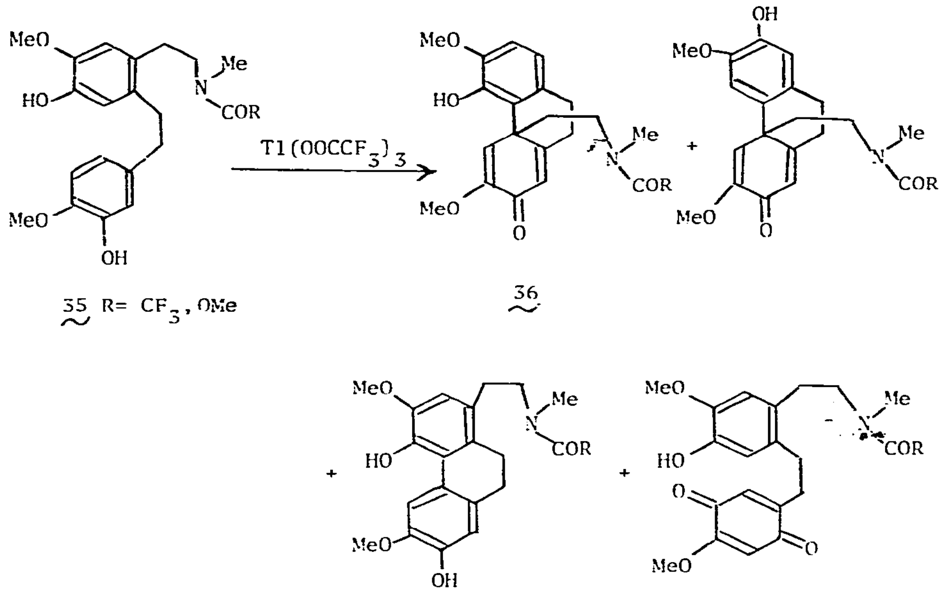
to some diaryl ketones, 34 (eq. 20) (26). Benzophenone, fluorenone, xanthone and N-methylacridone failed to undergo the thallation reaction.



(20)

34 X= CMe_2, $-CH_2CH_2-$, S

Application of oxidative coupling of phenols with $Tl(OOCCF_3)_3$ for morphine alkaloid synthesis [J. Am. Chem. Soc., 97 (1975) 1239] was extended to the oxidation of 35 to afford a mixture of four compounds (eq. 21) (27).



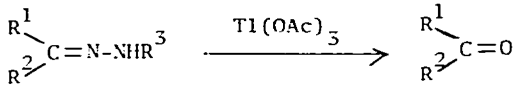
35 R= CF_3, OMe

36

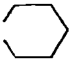
(21)

The para-ortho coupling product, 36, a precursor of hasubanans and 9,17-secomorphinans, could not be obtained by oxidation of 35 with $VOCl_3$.

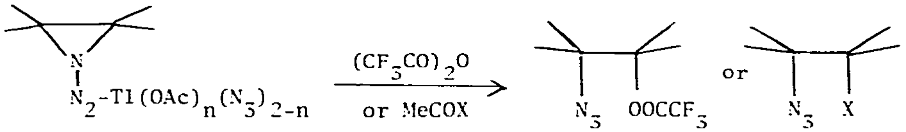
Treatment of hydrazones with $Tl(OAc)_3$ was found to be an efficient method of regenerating carbonyl compounds (eq. 22) (28). In each case the remaining products were hydrazones and $TlO_3SC_6H_4Me$. Comparison of the reactivity pattern was made of the reaction with $Hg(OAc)_2$, $Tl(OAc)_3$ and $Pb(OAc)_4$.



$$R^1R^2C{=}N\text{-}NHR^3 \xrightarrow{Tl(OAc)_3} R^1R^2C{=}O \qquad (22)$$

R^1, R^2= Ph, H; p-C_6H_4Cl, H; p-tolyl, H; Ph, Me; Ph, Ph; camphor, 
R^3= $SO_2C_6H_4Me$-p

Reaction of 1-hexene, 3-(4-methoxyphenyl)propene and cyclohexene with $Tl(OAc)_3$/ Me_3SiN_3 gave the 3-membered ring compounds, 37, which on treatment with $(CF_3CO)_2O$ and MeCOX (X= Cl, Br) gave 38 and 39 (29). Thermolysis of 37 gave the trans-1,2-diazido compounds and the parent olefins.



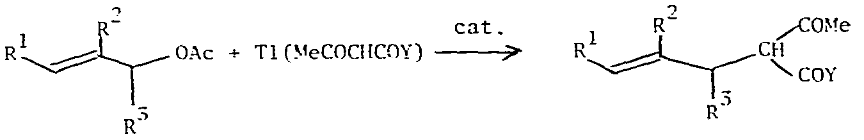
37 38 39

(23)

The mode of interaction of $TlCl_3$ with some organometallics such as RLi, RMgX, R_3Al and R_4Sn was investigated by IR spectra and analyses (e.g. iodometry) of the complex mixtures, and compared with that of $TiCl_4$ in the Ziegler-Natta catalyst systems (30). The results indicated an identity of the behavior of $TlCl_3$ and $TiCl_4$ in the formation of complexes with the organometallics.

5. Organothallium(I) Compounds

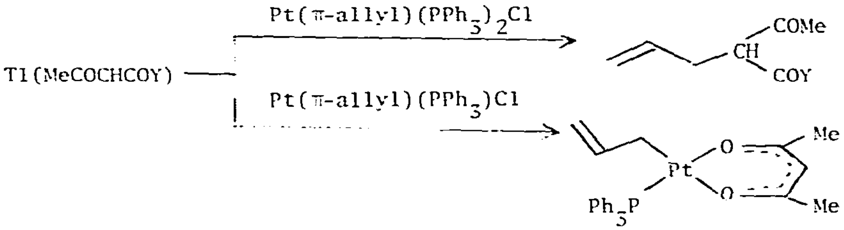
Cyclopentadienylthallium was used for high yield synthesis of an interesting class of organophosphine ligands, Cp_nPF_{3-n} (Cp= C_5H_5, C_5H_4Me; n= 1, 2) from PF_2Br, PF_2Cl, or $PFCl_2$ (31). The thallium(I) salts, Tl-(MeCOCHCOY) (Y= Me, OMe) were used to alkylate allylic acetates in the presence of phosphine-platinum catalysts (eq. 24) (32). The stoichiometric reaction



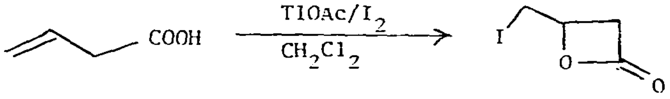
(24)

R^1, R^2, R^3= H, Me; cat.= $Pt(PPh_3)_3$, $Pt(\pi\text{-allyl})(PPh_3)_2Cl$

of Tl(MeCOCHCOY) with π-allylplatinum(II) complexes resulted in either ligand coupling or σ-allylplatinum(II) formation, depending on the amount of the phosphine ligand used.



A method of iodolactonization by the use of thallium(I) salts of unsaturated carboxylic acids and I_2 [J. Chem. Soc. Perkin I, (1974) 1864] was improved (33). The improved method involves treatment of the parent unsaturated acids with TlOAc, not with TlOEt as described previously, and I_2 in a non-polar solvent (e.g. eq. 25).



(25)

References

1. G. B. Deacon, R. J. Phillips, K. Henrick and M. MacPartlin, Inorg. Chim. Acta, 35 (1979) L335.
2. F. Brady, K. Henrick and R. W. Matthews, J. Organometal. Chem., 165 (1979) 21.

3. R. J. Phillips and G. B. Deacon, Aust. J. Chem., 32 (1979) 2381.
4. G. B. Deacon and R. J. Phillips, J. Organometal. Chem., 171 (1979) C1.
5. S. Bauer, A. Zschunke and B. Walther, Z. Anorg. Allg. Chem., 450 (1979) 70.
6. O. P. Syutkina, E. M. Panov and K. A. Kocheshkov, Zh. Obshch. Khim., 49 (1979) 651; Chem. Abstr., 91 (1979) 20575.
7. U. Baudis and M. Wieber, Z. Anorg. Allg. Chem., 448 (1979) 79.
8. T. N. Srivastava, O. P. Agarwal and R. S. Kapoor, J. Ind. Chem. Soc., 56 (1979) 204; Chem. Abstr., 91 (1979) 140893.
9. S. Uemura, H. Miyoshi, M. Okano, I. Morishima and T. Inubushi, J. Organometal. Chem., 165 (1979) 9.
10. S. Uemura, H. Miyoshi, M. Okano, I. Morishima and T. Inubushi, J. Organometal. Chem., 171 (1979) 131.
11. G. B. Deacon and D. Tunaley, Aust. J. Chem., 32 (1979) 737.
12. V. I. Bregadze, A. Ya. Ustyatinskii and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1876; Chem. Abstr., 92 (1980) 22543.
13. H. M. Colquhoun, T. J. Greenhouse and M. G. H. Wallbridge, J. Chem. Res. (S), (1979) 248.
14. C. Schramm and J. I. Zink, J. Am. Chem. Soc., 101 (1979) 4554.
15. D. St. C. Black, V. C. Davies, G. B. Deacon and R. J. Schultze, Inorg. Chim. Acta, 37 (1979) L528.
16. T. N. Srivastava, R. C. Srivastava and K. Kapoor, J. Inorg. Nucl. Chem., 41 (1979) 413.
17. J. S. Thayer, Inorg. Chem., 18 (1979) 1171.
18. A. Toshimitsu, S. Uemura and M. Okano, J. Chem. Soc. Perkin I, (1979) 1206.
19. R. A. Hancock and S. T. Orszulik, Tetrahedron Lett., (1979) 3789.
20. W. Renold, G. Ohloff and T. Norin, Helv. Chim. Acta, 62 (1979) 985.
21. Y. Yamada, H. Sanjoh and K. Iguchi, Tetrahedron Lett., (1979) 423.
22. Y. Yamada, H. Sanjoh and K. Iguchi, Tetrahedron Lett., (1979) 1323.
23. T. Kaiya, N. Shirai, J. Sakakibara and Y. Iitaka, Tetrahedron Lett., (1979) 4297.
24. S. Antus, A. Gottsegen, M. Nogradi and A. Gergely, Chem. Ber., 112 (1979) 3879.
25. P. Y. Kwok, L. M. Stock and T. L. Wright, J. Org. Chem., 44 (1979) 2309.
26. R. A. Hollins and V. M. Salim, Tetrahedron Lett., (1979) 591.
27. M. A. Schwartz and R. A. Wallace, Tetrahedron Lett., (1979) 3257.
28. R. N. Butler and A. M. O'Donohue, Tetrahedron Lett., (1979) 4583.
29. G. Emmer and E. Zbiral, Lieb. Ann. Chem., (1979) 796.
30. Iv. Glavchev and Vl. Kabaivanov, Inorg. Chim. Acta, 35 (1979) L359.
31. R. T. Paine, R. W. Light and D. E. Maier, Inorg. Chem., 18 (1979) 368.
32. H. Kurosawa, J. Chem. Soc. Dalton, (1979) 939.
33. R. C. Cambie, K. S. Ng, P. S. Rutledge and P. D. Woodgate, Aust. J. Chem., 32 (1979) 2793.