

CHAPTER II

PRELIMINARY WORK

The discovery of thallium in 1861 did not, unlike the discovery of many elements, represent a milestone in the development of modern chemistry. Investigation of thallium and its compounds proceeded rather slowly and, during the first half of the present century, led to relatively unspectacular results. To the organic chemist, thallium was regarded as an obscure toxic metal, organothallium chemistry was dull and predictable, and the utility of organothallium compounds in organic chemistry was virtually non-existent. Only in the last decade, scientists have paid intensive attention to thallium chemistry for the purpose of synthesis. More than 50 specific and often unique synthetic transformations based on the use of thallium reagents have been discovered.

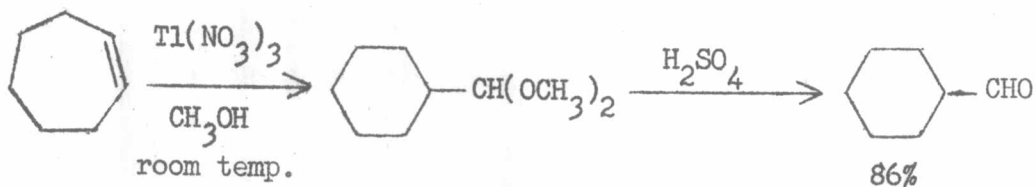
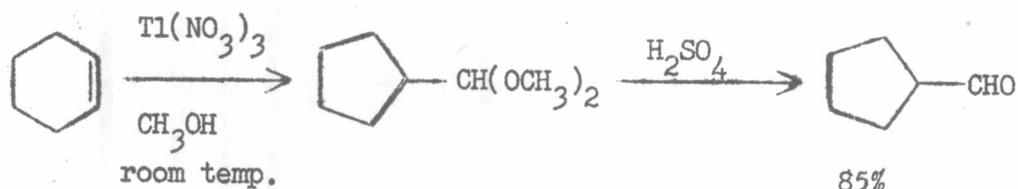
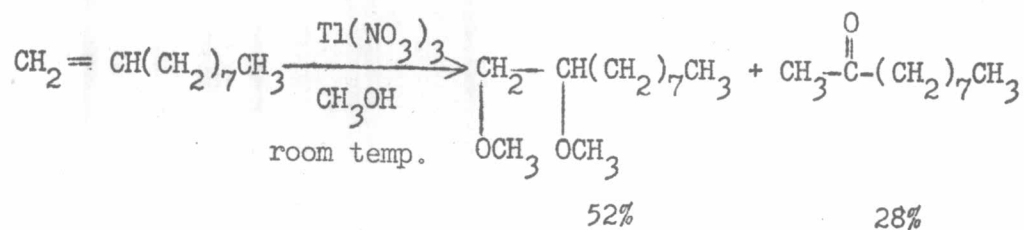
Grinstead⁽²⁴⁾ first reported the oxidation of ethylene and 2-hexene by thallium (III). Aqueous thallic ion oxidises alkenes to mixtures of glycols and carbonyl compounds. Unfortunately, the exact reaction conditions and the nature of the thallium species in solution are difficult to ascertain from the note. The low-molecular-weight alkenes containing up to four carbon atoms have been oxidised by thallium (III) in aqueous perchloric acid⁽²⁵⁾ and aqueous acetic acid⁽²⁶⁾. Both glycols and carbonyl products are observed, the kinetics and mechanism are discussed also. The yields of the products

are given below:-

Product Distribution for the Thallium (III) Oxidation
of Various Alkenes in Aqueous Acetic Acid.

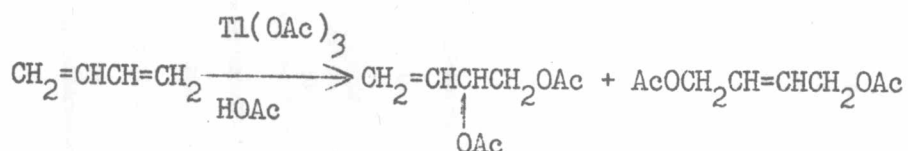
Alkene	Carbonyl product	Yield of carbonyl product(%)	Yield of glycol product(%)
Ethylene	Acetaldehyde	45	55
Propylene	Acetone	81	17
1-Butene	Methyl ethyl ketone	75	16
cis-2-Butene	Methyl ethyl ketone	85-90	<0.5
trans-2-Butene	Methyl ethyl ketone	85-90	<0.5
Isobutene	Isobutyraldehyde	37	52

McKillop and Taylor reported the oxidation of 1-decene⁽²⁷⁾, cyclohexene and cycloheptene⁽²⁸⁾ by thallium (III) nitrate in methanol.



Oxidation of several conjugated dienes by thallium (III) acetate in acetic acid has been reported in a communication⁽²⁹⁾.

1,3-Butadiene at 60°C is converted to a mixture of 1, 2-diacetate and 1, 4-diacetate in 66 and 34% yield, respectively.

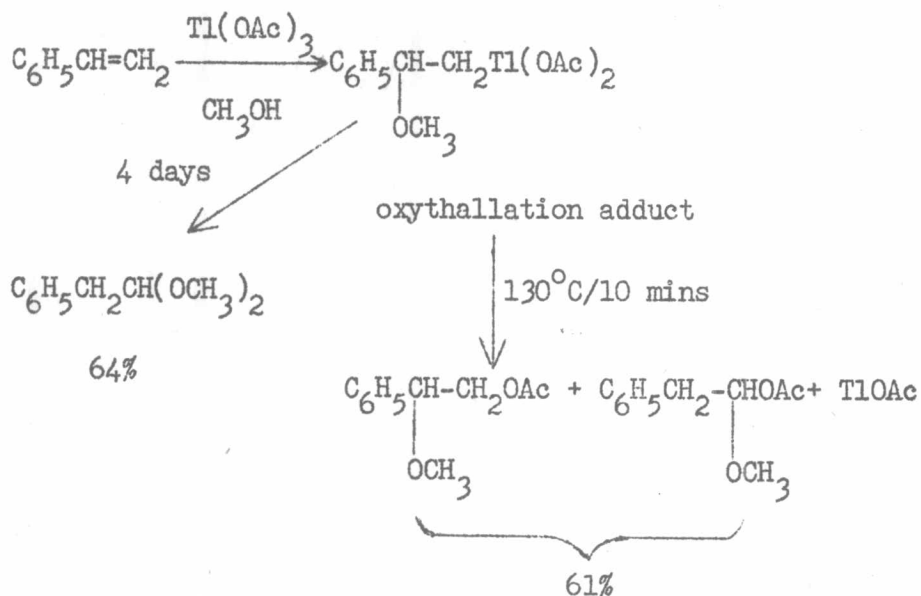


Oxidation of styrene and substituted styrenes by thallium (III) acetate have been reported by Criegee⁽¹⁷⁾, Kabbe⁽¹⁶⁾ and Ouellette.⁽³⁰⁾

Cocton and Paulet⁽³¹⁾ reported the oxidation of 3-methylcholest-2-ene by thallium (III) acetate. Ollis⁽³²⁾ has studied the oxidative rearrangement of chalcones by thallium (III) acetate in methanol and a convenient synthesis of isoflavones from chalcones has been described.

Mechanism of the oxidation of alkenes by thallium (III) involves electrophilic attack to produce an oxythallation adduct. The direction of addition is of the Markownikoff type and probably involves trans stereochemistry. Subsequent solvolysis of the oxythallation adduct proceeds via carbonium ion intermediates which react as predicted.

Both Criegee and Kabbe⁽¹⁶⁾ reported the isolation of the oxythallation adduct of styrene with thallium (III) acetate in methanol. The decomposition point, solubility in a variety of solvents, and elemental analysis are given. However, the structure is assigned on the basis of analogy to the mercury (II) adduct.



The general conclusions that can be drawn from the experimental data available for styrene are as follows:

- (1) The oxidation rate is increased by polar solvents;
- (2) more ionic thallium salts, such as thallium nitrate, react faster than the covalent thallium acetate; and
- (3) yields of rearranged products are higher in methanol than in acetic acid.

Winstein⁽¹⁸⁾ obtained adducts of thallium (III) acetate with both norbornene and norbornadiene in chloroform. Solubility characteristics and the infrared spectra of the carbonyl bands of both acetates bound to carbon and thallium are given.

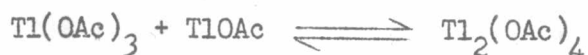


Only in these cases have acceptable structure proofs been undertaken. Anet⁽³³⁾ employed nuclear overhauser effects to pair all thallium

satellites in the nuclear magnetic resonance (NMR) spectrum. As a result, he assigned chemical shifts and coupling constants which demonstrate convincingly that the adducts are cis-diexo. Thus, the stereochemistry of oxythallation parallels that of oxymercuration⁽³⁴⁾ observed for norbornene. It should be noted that the oxymercuration of norbornene is an atypical reaction since the reaction yields trans products for most alkenes.

Henry^(25,35) has reported his detailed studies of the oxidation of simple alkenes by aqueous thallium (III). The reaction of ethylene is first order in thallium (III) and ethylene. Added salts accelerate the reaction, and this result is interpreted in terms of an inverse relationship between the rate constant and the activity of water. Halpern⁽³⁶⁾ has reported $\rho^* = -2.77$ for the hydroxymercuration of alkenes. He observed "a high degree of positive charge localization (approaching carbonium ion character) in the transition state". However, the carbonium ion is not free or open since cis-trans isomerization was not observed. Using Henry's data, Ouellette calculates $\rho^* = -4.7$. The ordering of ρ^* values for Hg^{2+} and Tl^{3+} in aqueous solutions for the oxidation of alkenes finds a parallel with the ρ^* values of -3.2 and -4.3 for the cleavage of arylcyclopropanes by mercury (II) acetate and thallium (III) acetate. Therefore, thallium (III) seems to be a more selective electrophile than mercury (II) under comparable reaction conditions regardless of the solvent or attached ligands.

The kinetics of the oxidation of a series of substituted styrenes by thallium (III) acetate in acetic acid has been reported in detail.⁽⁸⁾ Since solvolysis of the oxythallation adduct is rapid under the reaction conditions and lead to thallium (I) acetate, the effect of thallium (I) acetate in a reaction with thallium (III) acetate leads to kinetic complications



The formation of the double salt causes a rapid decrease in the rate of oxidation of the styrene. As the reaction proceeds, thallium (III) acetate is effectively removed by double salt formation. However, by using twice the concentration of thallium (III) acetate, the stoichiometry of the reaction is given by the equation:-



The function given by this equation

$$1/(\text{Ao}-2\text{X}) = kt + \text{Ao}^{-1}$$

yields straight-line plots, the term Ao is the initial concentration of thallium (III) acetate and X is the concentration of products or the decrease in the oxidative titer of the solution.

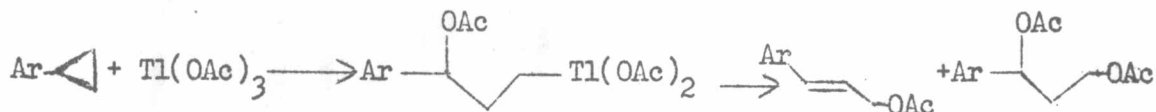
A Hammett-type plot with σ^+ gives $\rho^+ = -2.2$ for the series of six styrenes reported at 50.1°C. The activation parameter for p-methylstyrenes over the temperature range 19.7° - 75.1°C are $\Delta H^\ddagger = 33022$ joule/mole and $\Delta S^\ddagger = -171.38$ joule/mole °K. Both the negative ρ^+

and the large negative entropy of activation suggest an ordered transition state resembling a π complex in which considerable carbon-thallium bond making has occurred and a substantial amount of positive charge has developed at the benzylic carbon atom. However, the ρ^+ and ΔS^\ddagger for the oxidative cleavage of arylcyclopropanes by thallium (III) acetate are -18.39 and -122.06 joule/mole $^\circ\text{K}$, respectively.⁽¹¹⁾ Thus even more bond cleavage occurs in the case of the cyclopropanes and a larger amount of positive charge develops at the benzylic carbon atom, indicating that the transition state has more σ -complex character. The difference in the entropies of activation probably reflects release of the constrain of the atom in the cyclopropane ring.

The kinetics of the bromination of styrenes in acetic acid⁽³⁷⁾ contains a second-order rate component which correlates with σ^+ and $\rho^+ = -2.23$. The activation parameters are $\Delta H^\ddagger = 47234$ joule/mole and $\Delta S^\ddagger = -112.86$ joule/mole $^\circ\text{K}$. Since this reaction is postulated to involve a cyclic bromonium ion, the similarities of the kinetics of oxythallation and bromination make it reasonable to assign considerable π -complex character to the oxythallation transition state.

Six substituted arylcyclopropanes with substituents ranging from electron-donating p-CH₃O to the electron-with drawing m-Cl have been oxidatively cleaved by thallium (III) acetate in acetic acid.⁽¹⁴⁾ The products observed are substituted cinnamyl acetates and 1-aryl-1, 3-diacetoxy-propanes. Both NMR and GLPC (gas-liquid phase

chromatography) determined yields as a function of ring substituents.

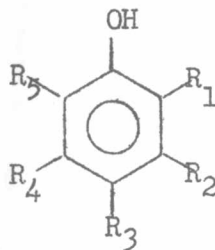


The products and kinetics of the oxidative cleavage of bicyclo [4, 1, 0] heptane, bicyclo [3, 1, 0] hexane and bicyclo [2, 1, 0] pentane by thallium (III) acetate and lead (IV) acetate have been studied in detail by Ouellette et al.⁽³⁸⁾ From these data, it can be seen that the selectivity of thallium (III) acetate exceeds that of lead (IV) acetate.

Substituted 4-tert-butylphenols and 4-substituted phenols are oxidised to 1,4-benzoquinones by thallium (III) trifluoroacetate (TTFA) in good yield.^(28, 39) Hydroquinones are oxidised to 1,4-benzoquinones by TTFA in a few minutes. The yields of various 1,4-benzoquinones obtained are listed below:-

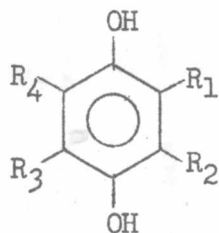
Oxidation of Phenols to 1,4-benzoquinones with

Thallium (III) Trifluoroacetate



R_1	R_2	R_3	R_4	R_5	Yield (%) Method A.
H	H	NH ₂	H	H	88
Br	H	NH ₂	H	Br	81
Br	H	Br	H	Br	77
Br	H	Br	H	tert-C ₄ H ₉	81
Br	CH ₃	Br	H	tert-C ₃ H ₇	94
Br	CH ₃	Br	H	tert-C ₄ H ₉	90
Br	H	Cl	H	Cl	57
Cl	H	Cl	H	Cl	82
Cl	H	Cl	H	CH ₃	80
I	H	I	H	I	62
tert-C ₄ H ₉	H	CH ₃ CO ₂	H	tert-C ₄ H ₉	97

Oxidation of Hydroquinones to 1,4-Benzoquinones with
Thallium (III) Trifluoroacetate



R ₁	R ₂	R ₃	R ₄	Yield (%)	
				Method A.	Method B.
H	H	H	H	68	69
CH ₃	H	H	H	77	83
tert-C ₄ H ₉	H	H	H	91	81
C ₆ H ₅	H	H	H	73	83
Br	H	tert-C ₄ H ₉	H	63	-
tert-C ₄ H ₉	H	tert-C ₄ H ₉	H	94	93
C ₂ H ₅ C(CH ₃) ₂	H	C ₂ H ₅ C(CH ₃) ₂	H	92	95
CH ₃	CH ₃	CH ₃	H	85	92
Br	Br	Br	CH ₃	94	-
Cl	Cl	Cl	Cl	73	74

Methods A and B as listed in the Table both involve the use of thallium (III) trifluoroacetate with the difference being only in the solvent used. Method A uses trifluoroacetic acid as the solvent and method B uses carbon tetrachloride as the solvent. The suggested mechanism is given below.

