# THALLIUM IN ORGANIC SYNTHESIS. XX. OXIDATIVE REARRANGEMENT OF OLEFINS WITH THALLIUM(III) NITRATE: A SIMPLE ONE-STEP SYNTHESIS OF ALDEHYDES AND KETONES [1]

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Oxidation of olefins with metal salts can lead to a variety of products depending on the nature of the metal cation, the anion, the solvent, and the structure of the olefin. Oxymercuration with mercury(II) acetate has been extensively investigated;[3] analogous reactions with lead[3,4] and thallium[3,5] salts have been studied much less comprehensively, and in contrast to oxymercuration there are only a few synthetically useful procedures based on oxythallation or oxyplumbation.

We now report a simple synthesis of aldehydes and ketones from olefins by treatment with thallium(III) nitrate (TTN)[6] in methanol.[7] The reactions are characterised by manipulative simplicity, high yields and the high state of purity of the products. Thus, a solution of TTN in methanol is added to a stirred solution of an equimolar amount of the olefin in methanol at room temperature. Thallium(I) nitrate precipitates almost immediately, and the reaction is generally complete within a few minutes. The inorganic salt is removed by filtration, and the dimethyl ketal or acetal hydrolysed by shaking the filtrate with 2N sulphuric acid for five minutes. Extraction with ether, removal of the solvent and distillation or crystallisation gives the pure aldehyde or ketone. Representative conversions are listed in Table 1.

The redox potential of thallium lies between those of mercury and lead, and comparative studies of oxymetallation of olefins with the acetates of the three metals have established the intermediate position of the thallium salt.[8,9] Thus, treatment of olefins with lead(IV) acetate gives complex mixtures of

TABLE 1

Reaction of Olefins with TTN in Methanol

| Cmp. No. | Olefin | Product[a] | Yield, % |
|---|---|---|---|
| 1 | p-Methoxystyrene | p-Methoxyphenylacetaldehyde | 75 |
| 2 | α-Methylstyrene | Phenylacetone | 81 |
| 3 | 1,1-Di-p-anisylethylene | 4,4'-Dimethoxydeoxybenzoin | 95 |
| 4 | 1-p-Anisyl-1-p-bromophenylethylene | 4-Bromo-4'-methoxydeoxybenzoin | 98 |
| 5 | α-Methylstilbene | 1,1-Diphenylacetone | 66 |
| 6 | Cyclohexene | Cyclopentanecarboxaldehyde | 85[b] |
| 7 | Cycloheptene | Cyclohexanecarboxaldehyde | 86[b] |
| 8 | 1-Decene | 1,2-Dimethoxydecane (52%) + 2-Decanone (28%) | 80 |

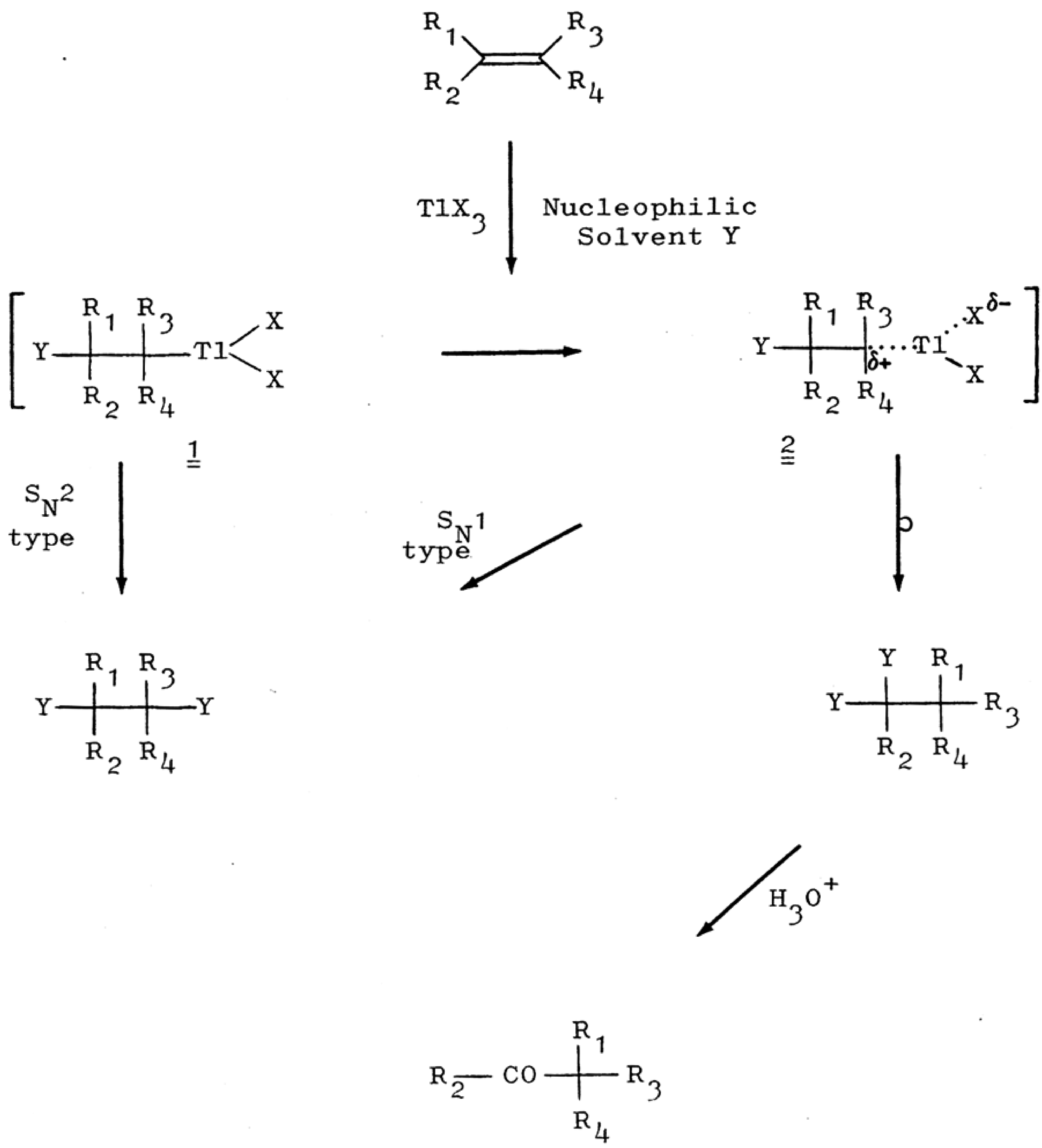
[a]Identity of products was established by comparison with authentic material and/or by spectral data. [b]Isolated as the 2,4-dinitrophenylhydrazone.

products,[4] while stable oxymercuration adducts are formed with mercury(II) acetate.[3] Oxythallation adducts have been isolated only occasionally,[8,10,11] and usually mixtures of products derived by subsequent decomposition are obtained.[5,8,9,12-15]

Alkylthallium(III) compounds (e.g. 1) are notoriously unstable,[16] and C-Tl bond heterolysis proceeds via a transition state approaching carbonium ion character (e.g. 2, Scheme 1).[17] Subsequent reaction may then lead either to glycol or to carbonyl derivatives. Formation of the latter necessitates a Wagner-Meerwein type rearrangement, probably via the carbonium ion species 2. Glycols, however, can arise either from 1 or 2. Assuming that the rate of $S_N2$ type displacement from 1 by the solvent does not vary markedly with the nature of X, the rate of progression from 1 to 2 should be a function of the ease of heterolysis of the Tl-X bond; that is, carbonium ion intermediates should be formed most rapidly from highly ionic compounds, $RTlX^+ X^-$.

No data are available which indicate the degree of ionic character in alkylthallium(III) compounds.[18] Comparison of the oxidation of cyclohexene by thallium(III) trifluoroacetate[19] in trifluoroacetic acid with that by

Scheme 1



thallium(III) acetate in acetic acid[9] confirmed[20] the rate enhancement possible in oxythallation when a highly ionic reagent is employed. Although approximately the same mixture of products was obtained, oxidation with thallium(III) trifluoroacetate was complete in 10 min at room temperature whereas the reaction with thallium(III) acetate required 13 hr at elevated temperatures.

With TTN, which is probably completely ionic,[21] reaction occurs within seconds at room temperature in methanol solution and very little, if any, glycol derivatives are formed[22] from substrates having substituents with good migratory aptitudes (cmp 1-5). Substituent migration also occurs in the reaction of six- and seven-membered cyclic olefins (cmp 6,7) with TTN; the ring bond ($C_2$-$C_3$) in the oxythallation adduct is probably conformationally trans to the departing thallium, and ring contraction to cycloalkanecarboxaldehyde derivatives is the almost exclusive reaction course. In fact, this TTN-induced ring contraction constitutes the method of choice for the preparation of cyclohexanecarboxaldehyde and cyclopentanecarboxaldehyde. With aliphatic straight chain olefins (cmp 8), glycol formation is the major reaction course, although a considerable amount of ketone is also formed.

Comparison of thallium(III) and mercury(II) reveals that: (i) Tl(III) ⟶ Tl(I) is the more powerful oxidising system;[21] (ii) under comparable reaction conditions $Tl^{3+}$ is a more selective electrophile than $Hg^{2+}$;[15] and (iii) carbon-metal bond heterolysis takes place more rapidly with thallium due to the greater electron affinity of thallium relative to mercury.[17] Consequently, by an appropriate choice of thallium reagent and reaction conditions it should prove possible to extend substantially the synthetic utility of oxythallation reactions.[23]

References

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6. The salt is easily prepared by dissolving 50 g of thallium(III) oxide in 150 ml of warm conc. nitric acid and cooling the pale yellow solution to 0°. The colourless crystals of thallium(III) nitrate trihydrate are filtered, washed with a little dilute nitric acid, and dried *in vacuo* over phosphorus pentoxide. The salt is stable indefinitely if stored in tightly sealed bottles.
7. TTN is readily soluble in methanol, dilute mineral acids, and mixed

solvent systems such as aqueous glyme. Use of the latter or dilute nitric acid as solvents leads directly to carbonyl compounds, but under these conditions yields are generally lower than in methanol due to concomitant decomposition of the reagent.

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18. Conductance measurements in methanol on the more stable $ArTlX_2$ compounds have shown that when X = Cl or $CH_3COO$ these compounds are only partially ionised, while $ArTl(OOCCF_3)_2$ type compounds are 1/1 electrolytes (A. G. Lee, J. Organometal. Chem., 22, 537 (1970)).
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22. Formation of appreciable quantities of glycol ethers under these conditions has been noted only with styrene and p-bromostyrene, which gave mixtures consisting of the arylacetaldehydes (30 - 40%) and the 1-aryl-1,2-dimethoxyethanes (50 - 60%). When the oxidation was carried out in dilute nitric acid, however, no glycol derivatives were isolated, and the arylacetaldehydes in 80-85% yield.