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THALLIUM (III) TRIACETATE OXIDATION OF OLEFINS. NEIGHBORING GROUP PARTICIPATION IN THE NORBORNENYL SYSTEM

R. M. Moriarty (1) and Harsh Gopal (2)
The Department of Chemistry
The Catholic University of America, Washington, D. C. 20017

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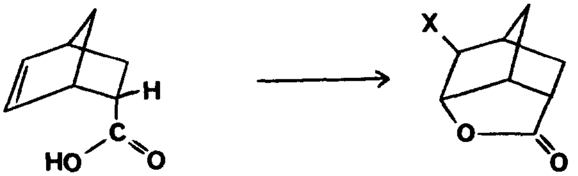
We have examined systematically electrophilic addition to the double bond of 2-endo substituted norbornenyl derivatives. Our work on the lead tetraacetate oxidation (3,4,5), and acid-catalysed hydration (6), together with the work of others (7,8), on mercuric acetate oxidation (9), and halogen addition (10) conform to a reaction scheme involving initial electrophilic addition to the olefinic double bond followed by intramolecular nucleophilic attack by the 2-endo group. Acid catalysed hydration, halogenation and oxymercuration yield stable products, i.e. in the case of 2-endo norbornene carboxylic acid one obtains, respectively, the lactone, halolactone, or acetoxymercurinium lactone.

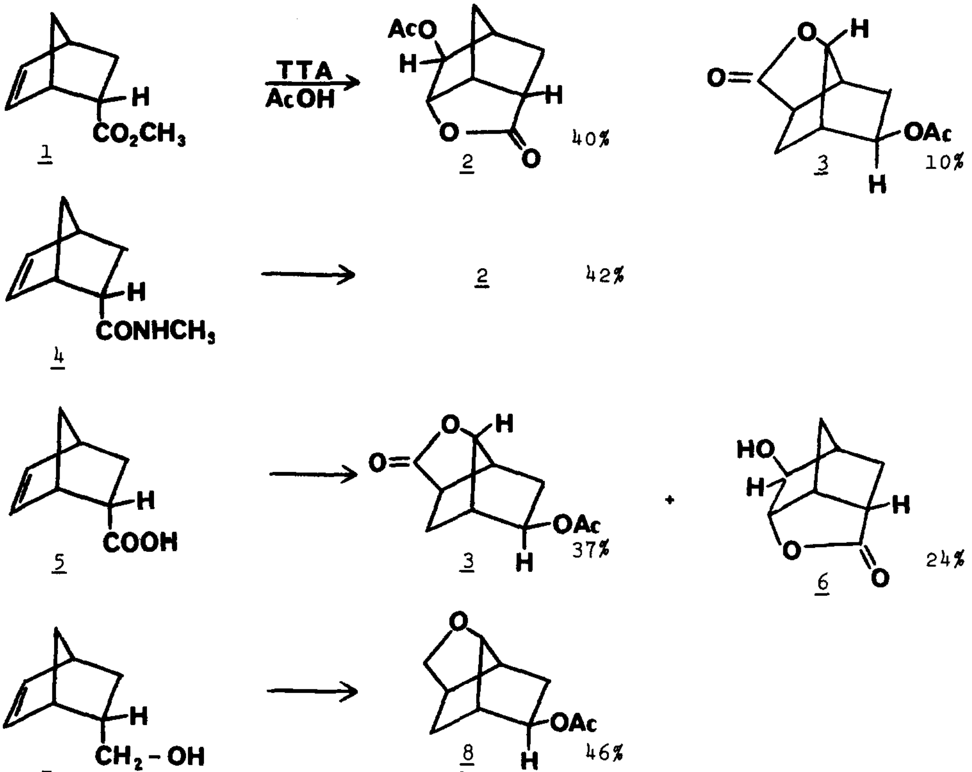


x = hydrogen, halogen
or HgOAc

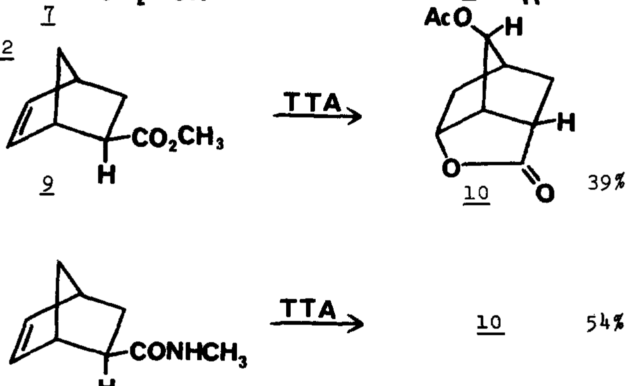
In the case of lead tetraacetate probably an intermediate in which $x=Pb(OAc)_3$ is formed initially but this undergoes rapid C-Pb cleavage to yield ultimately an acetoxylactone x = OAc. Furthermore, other endo groups may function in the role of intramolecular nucleophile such as CO_2CH_3, $CONHCH_3$, and CH_2OH.[3,4]

We now report analogous results in the case of the addition of thallium triacetate (TTA) to substituted norbornene derivatives.

Scheme 1



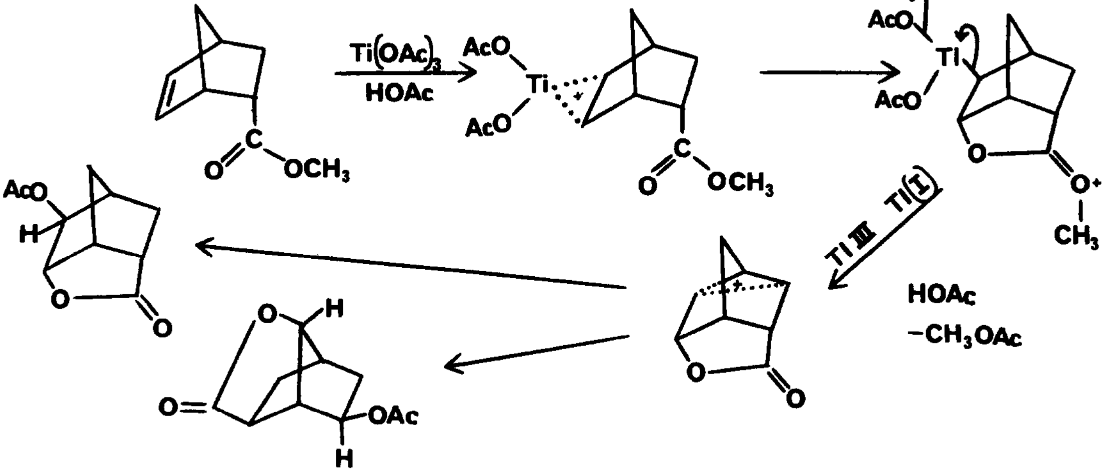
Scheme 2



In the endo series (Scheme 1) intramolecular lactone formation occurs. With the free carboxylic acid Wagner-Meerwein rearrangement predominates. The hydroxymethyl group also participates but again Wagner-Meerwein rearrangement occurs.

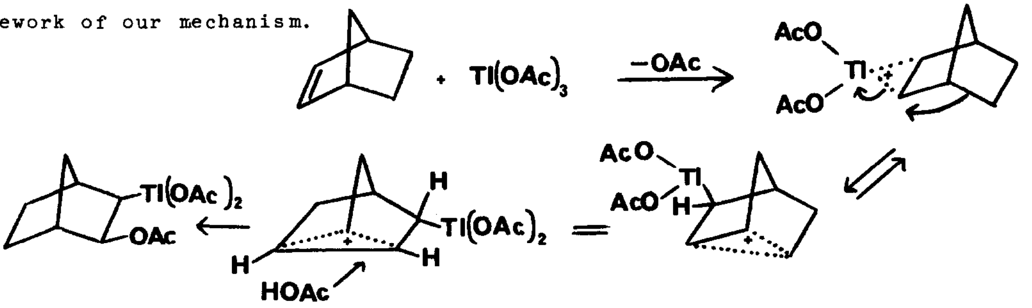
In the exo series (Scheme 2) rearrangement and participation, or perhaps more properly, intramolecular capture of the rearranged carbonium ion occurs.

Compounds 2, 3, and 6 are known (5,11). Acetoxyether 8 is new and it was converted by chromic acid oxidation to the known acetoxylactone (2). Compound 10 has been obtained previously (5), and an x-ray diffraction study on this acetoxylactone is presented in the accompanying communication. The formation of acetoxylactones and acetoxyethers in these reaction parallels results obtained with lead tetraacetate (3,4,5). Similarly, the pathway we propose for the reaction in the case of the ester is the following:



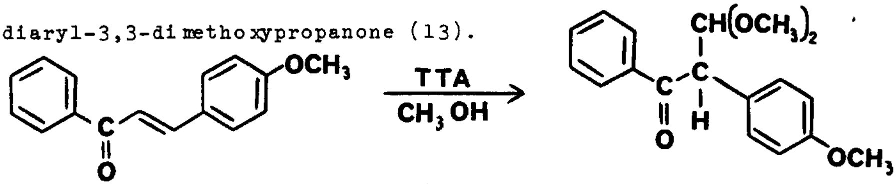
This description may be extended to the N-methylamide case with the consequence that an iminolactone intermediate must form and subsequently hydrolyse to the lactone.

Attempts were made, to no avail, to isolate the proposed organothallium intermediate in the present examples. This was accomplished successfully by Pande and Winstein (12) in the oxythallation of norbornene in which a cis-exo-exo-2,3-disubstituted product is obtained. This result also fits within the framework of our mechanism.



The apparent absence of products derived from the alternative mode of addition of acetic acid to the intermediary ion, to give the <u>syn</u> 2, 7, disubstituted product, may be a result of kinetic control in the product forming step.

Finally, a reaction which should be mentioned in connection with the subject of this paper is the oxidation of 4-methoxychalcone with TTA to yield the 1,2-diaryl-3,3-dimethoxypropanone (13).



This result may be understood in terms of electrophilic addition and participation by the anisyl group.

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