Oxidation of 1-Methylcyclobutene by Metal Ions

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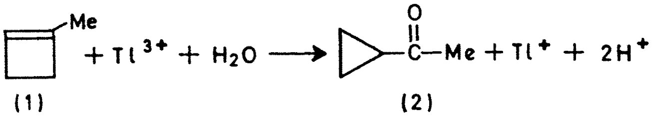
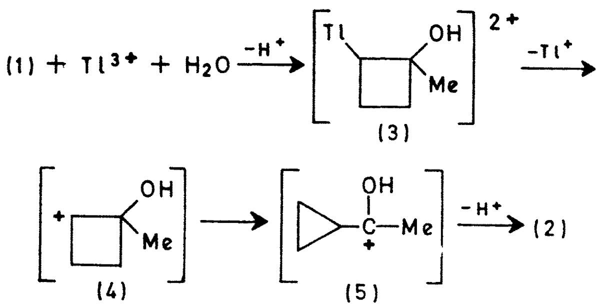
Summary Metal ions such as thallium(III), mercury(II), and palladium(II) oxidize 1-methylcyclobutene in aqueous solution to cyclopropyl methyl ketone; these reactions, as well as the silver(I)- and palladium(II)-catalysed rearrangements of cubane and related compounds, are interpreted in terms of carbonium-ion mechanisms.

1-METHYLCYCLOBUTENE (**1**) was found to undergo rapid and quantitative oxidation by thallium(III) (10^{-4} to 0·2 M) in aqueous $HClO_4$ (0·1 to 5 M) to yield cyclopropyl methyl ketone (**2**) according to Scheme 1. The reaction is complete within 10 min. at room temperature. The stoicheiometry was established by spectral titrations at 212 nm which confirm that (**1**) and thallium(III) react in equimolar proportions, and by quantitative determination of (**2**) (*ca.* 90% yield) by ^1H n.m.r. No other organic products could be detected by either n.m.r. or g.l.c.



SCHEME 1

These observations are readily accommodated by the generally accepted mechanism of oxidation of other olefins by thallium(III) involving an oxythallium adduct such as (**3**) which loses Tl^+ to form a carbonium ion.[1] The application of this mechanism to the present reaction is depicted in Scheme 2. The rearrangement of (**4**) to (**5**) parallels the rearrangement of methylcyclobutyl to cyclopropylmethylcarbinyl carbonium ions observed, for example, in the nitrous acid deamination of 2-methylcyclobutylamine.[2]



SCHEME 2

Ready oxidation of (**1**) to (**2**) can also be effected by palladium(II) chloride in 1M-HCl and by mercury(II) perchlorate in 1M-$HClO_4$, with accompanying formation of metallic palladium or mercury, respectively. In more dilute $HClO_4$ ($< 0{\cdot}5$ M), Hg^{2+} and (**1**) react in equimolar proportions (confirmed by spectral titration) to form the relatively stable oxymercurial (**6**), identified by ^1H n.m.r. Decomposition of (**6**) to (**2**) and metallic mercury is promoted by increasing the acid concentration.

These observations prompt us to suggest the mechanism depicted in Scheme 3 for the recently discovered silver(I)- and palladium(II)-catalysed rearrangements of cubane (**7**) to cuneane (**11**).[3] Oxidative addition, analogous to that

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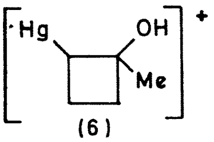
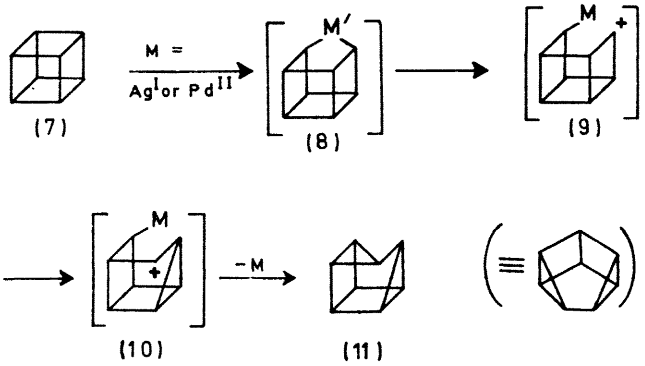
previously demonstrated for cubane with rhodium(I),[4] leads to adducts (**8**), formally of silver(III) or palladium(IV) (M′). The strongly oxidizing character of these metal ions, like that of thallium(III), is expected to promote heterolysis to the cyclobutyl carbonium ion (**9**). The latter, in turn, should rearrange in a manner analogous to that of (**4**) to the more stable cyclopropylcarbinyl ion (**10**). Subsequent reductive elimination of the metal ion would yield the product (**11**). This mechanism can be extended to the analogous silver(I)-catalysed rearrangements of the homocubyl and 1,1′-bishomocubyl systems.[5,6]



(6)

On the other hand, the rhodium(I)-catalysed rearrangement of cubane to *syn*-tricyclo-octadiene can be interpreted instead in terms of homolysis of the organorhodium adduct corresponding to (**8**).[4] This is consistent with the lesser oxidizing tendency of rhodium(III).



SCHEME 3

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