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# THE OXIDATIVE RING CLEAVAGE OF 1,3,3-TRIMETHYLCYCLOPROPENE BY TRANSITION METAL ACETATES

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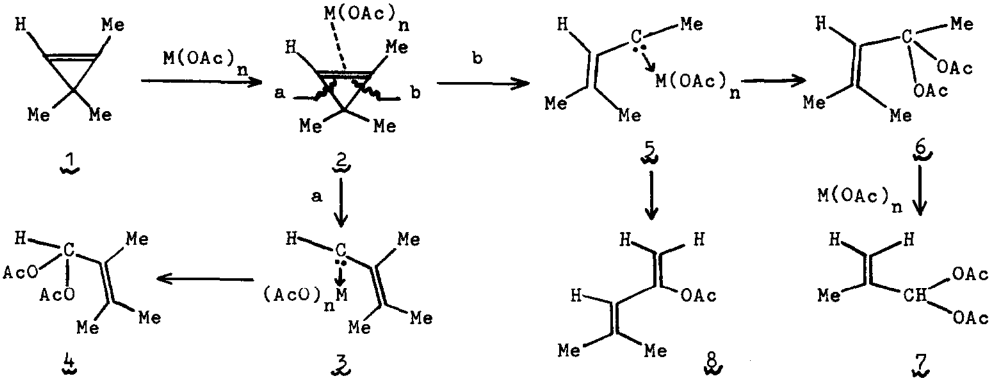
The $\sigma$-bond of highly strained polycyclic molecules, for example, bicyclobutane derivatives[1,2,3] or a propellane[1d] is easily cleft by the catalytic action of transition metal species to afford carbene-metal complexes as reaction intermediates in a formal retrocarbene-addition manner. We report the title reaction which proceeds similarly *via* carbene-metal complexes.[4]

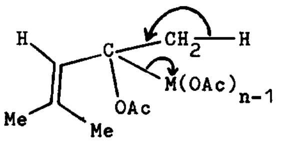
The reaction of 1,3,3-trimethylcyclopropene (**1**) with $Hg(OAc)_2$ (1:1 or 1:2 molar ratio) in methylene chloride was performed at room temperature for 18 hr in $N_2$ atmosphere. The reaction mixture was immediately filtered from the precipitated metal salts and the filtrate was distilled to give a single product, 1,1-diacetoxy-2,3-dimethyl-2-butene (**4**), mp 53-54.5°, in a 65% yield (based on the starting amount of **1**). The compound **4** was identified by comparison with the authentic sample obtained by the acetylation of 2,3-dimethylcrotonaldehyde according to a method similar to the reported one.[5] Treatment of **1** with $Tl(OAc)_3$ (1:1) in methylene chloride at room temperature for 16 hr afforded **4** (50%) and 3,3-diacetoxy-2-methylpropene (**7**, 20%). When the

Scheme 1

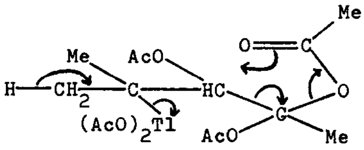


molar ratio was taken to be 1:2, the reaction products were **4** (20%) and **7** (40%). These products were isolated by GLC separation. The compound **7** was identified by comparison with the authentic sample.[5] The ring cleavage of **1** was effected also by $Pb(OAc)_4$ in methylene chloride at room temperature to give **4** (40%), **7** (a trace amount) and 2-acetoxy-4-methyl-1,3-pentadiene (**8**, 5%) after 17 hr reaction. The product distribution was not affected by the molar ratio of the components (1:1 or 1:2).

Formation of **4** is ascribed to the ring cleavage of **1** *via* the path *a* in the scheme 1. The key intermediate would probably be a formal carbene-$M(OAc)_n$ complex **3** (M= Hg, Tl or Pb), which furnishes **4** upon liberating $:M(OAc)_{n-2}$. The complex **2** can be converted to another carbene-metal complex **5** *via* the path *b* and then to **9**, which affords **8** as indicated.[6] Furthermore, the complex **5** is possibly transformed to an intermediate, 4,4-diacetoxy-2-methyl-2-pentene (**6**), whose second acetoxymetallation to **10** and the following cleavage as indicated may account for **7**. The fate of acetoxymethylcarbene is not clear yet. The absence of such cleavage in **4** is ascribed to the tetrasubstitution of its olefinic bond and to the resulting congestion.



**9**



**10**

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