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THE MOLECULAR STRUCTURE OF 7-SYN-6-ENDO-DIHYDROXYBICYCLO [2.2.1]HEPTANE 2-ENDO-CARBOXYLIC ACID-α-LACTONE

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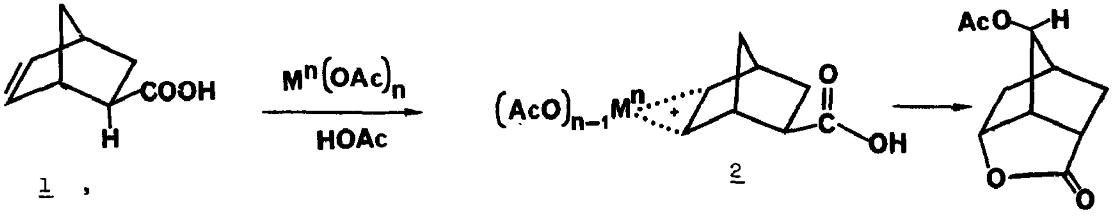
In the preceding communication[1] we reported the formation of a rearranged acetoxylactone (3) in the thallium triacetate oxidation of 2-exo-norbornene-carboxylic acid (1). Acetoxylactone (3) was also formed in the lead tetra-acetate oxidation of 1 and both reactions presumably involve a Wagner-Meerwein type rearrangement of a bridged organo-metallic such as 2.



1 , 2

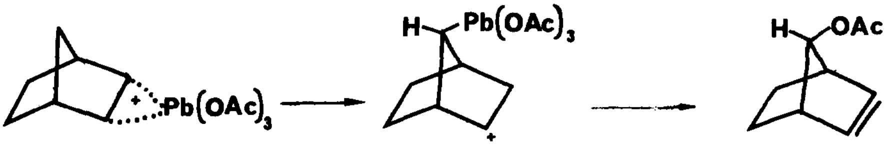
M = Tl^{III}, Pb^{IV} 3

While the structure of 3 was proven by chemical degradation, the stereo-chemical relationship of the acetoxyl with respect to the lactone moiety was not established. The mechanism by which 2 converts to 3 is unknown and as a step towards understanding this process it is essential to determine the stereochemistry of the C_3 acetoxyl group. For this purpose an X-ray crystal structure analysis was performed on 3. The material crystallizes in space group P^2_1/c with cell parameters a = 13.810 A, b = 6.206 A, c = 12.555 A, and β = 120.4°. The structure was solved by the symbolic addition procedure[2] and refined to an R factor of 0.051.

The stereoconfiguration of the molecule can be seen in Fig. 1 and the bond lengths and angles are shown in Fig. 2. The C_3-C_4-C_5 angle of 96.2° is characteristically small as has been found for other bicyclo[2.2.1]heptyl derivatives such as 5-norbornene-2, 3-<u>endo</u>-dicarboxylic anhydride 93°[3], the cyclopentadiene dimer 92.7°[4], anti-8-tricyclo[3.2.1.0^{2,4}]octyl p-bromobenzene 96.7°[5], norbornane 93.2°, and norbornadiene 92.0°[6], anti-7-norbornenyl p-bromobenzoate 96°[7], longifolene hydrochloride 94°[8], and 3-(N-benzyl-N-methylaminomethyl) -2-norbornanol 93.5°[9].

The C_2-C_3-C_7 angle of 97.8° is also small but it is expected to be in this range because it is in the bridging position of a bicyclo[3.2.1]octyl system, including C_1-O_3, C_2-C_3-C_7, C_4-C_5-C_6, and C_2.

The mechanism proposed for the formation of 7-acetoxynorbornene involved a C_7 organolead intermediate.[10]



This proposal was criticized by Erman[11] on the basis that ring-contraction to a bicyclo[3.2.0]heptyl system should occur.

Alternatively one could have the following process:

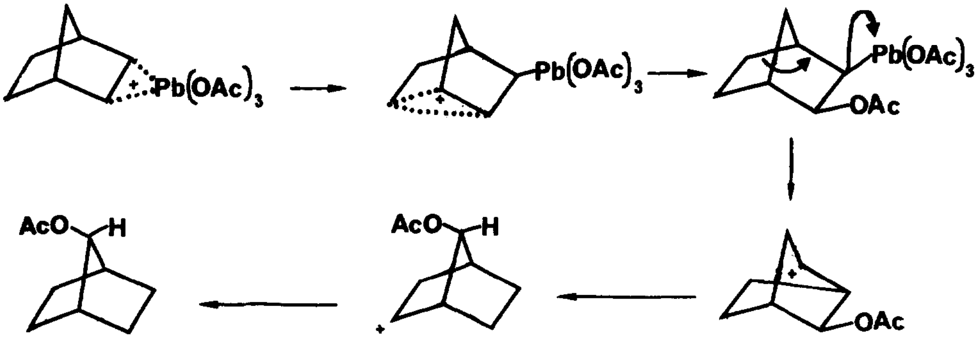
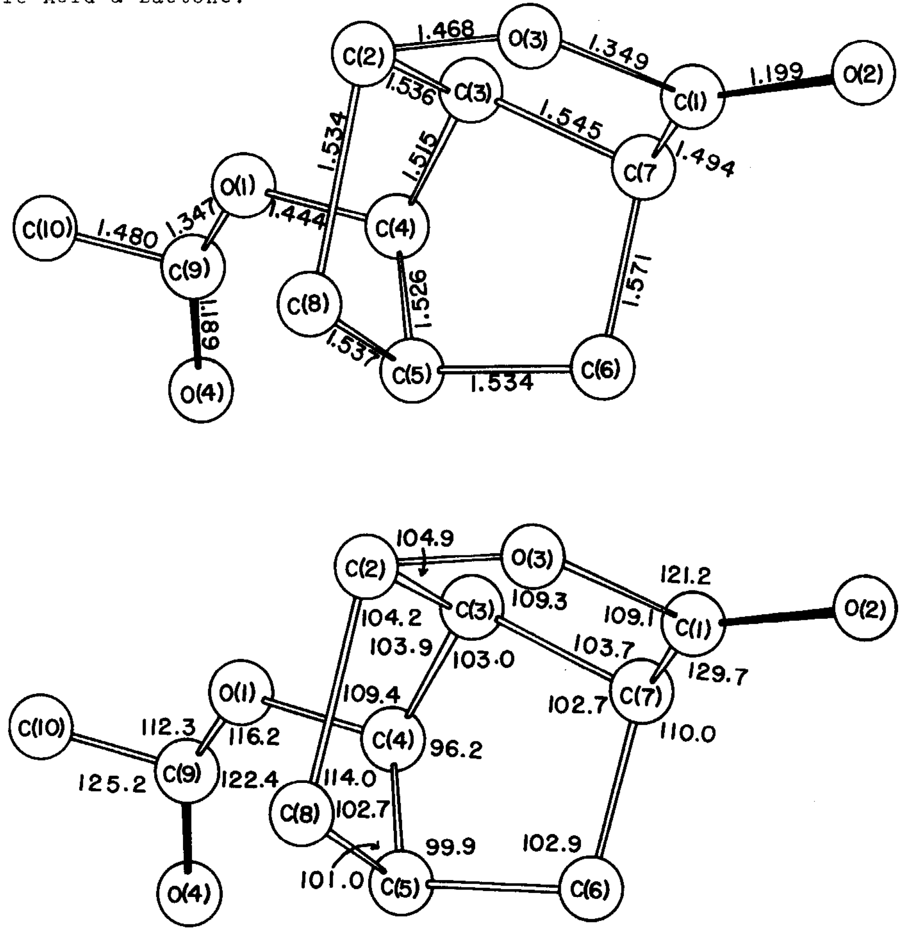


Fig. 2 Bond lengths and bond angles for 7-syn-6-endo-dihydroxybicyclo [2.2.1] Heptane 2-endo-carboxylic Acid-α-Lactone.



O(3)-C(2)-C(8) 111.3
C(2)-C(3)-C(7) 97.8
C(6)-C(5)-C(8) 109.7

This latter pathway is preferable in the reaction 1→3 based upon the stereochemistry of 3 as determined in this study.

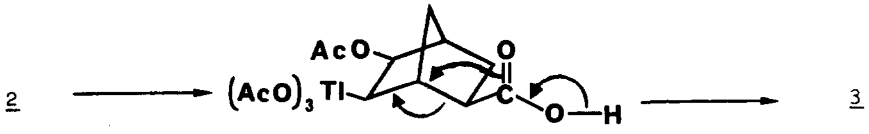


Fig. 1 Stereoconfiguration of 7-syn-6-endodihydroxybicyclo (2.2.1) Heptane 2-endo Carboxylic Acid-α-Lactone.

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