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Reaction of (20S)-3 β -Acetoxymorpho-15-ene Acid with Lead Tetraacetate; Structure of Pregnane Derivatives and a Dimer*

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The reaction of lead tetraacetate with carboxylic acids is known to effect oxidative decarboxylation. As a part of our studies on steroid chemistry, we carried out the reaction of 3 β -acetoxymorpho-15-ene acid (1) with lead tetraacetate, and the results are reported herein.

1 was treated with lead tetraacetate and the products were examined by thin-layer

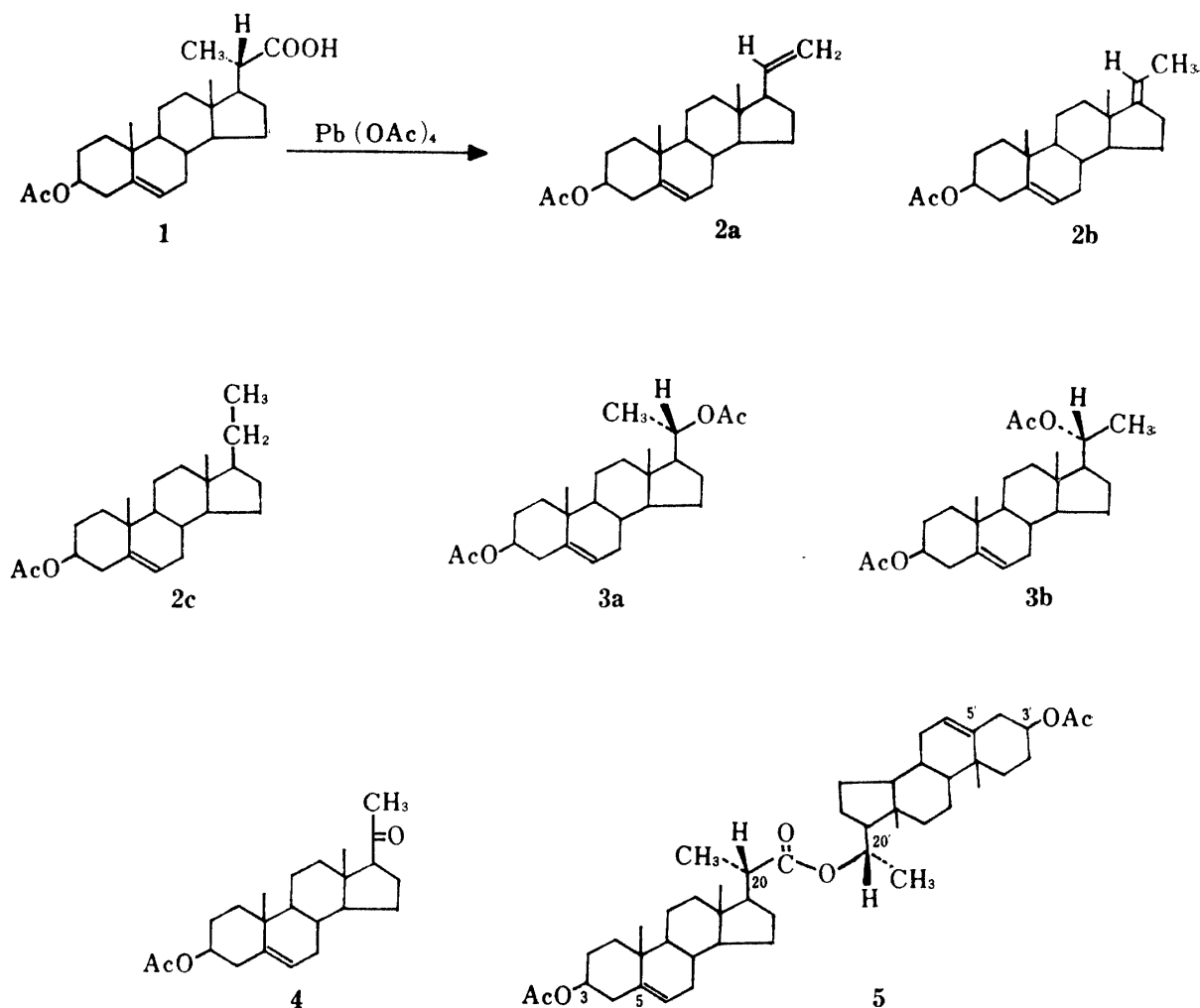


Chart 1. Reaction Products of 1 with Lead Tetraacetate

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chromatography. Four spots were obtained, and the corresponding substances, 2a, b, c, 3a, b, 4 and 5, were separated by silica gel column chromatography. Their structures were determined as shown in Chart 1.

Reduction of 5 with LiAlH_4 in tetrahydrofuran was then attempted and its reaction products were identified as $3\beta,20\alpha$ -dihydroxypregn-5-ene (9a) and $3\beta,22$ -dihydroxybisanorchol-5-ene (11) by GC-MS, mixed mp determination and PMR spectroscopy (Chart 2).

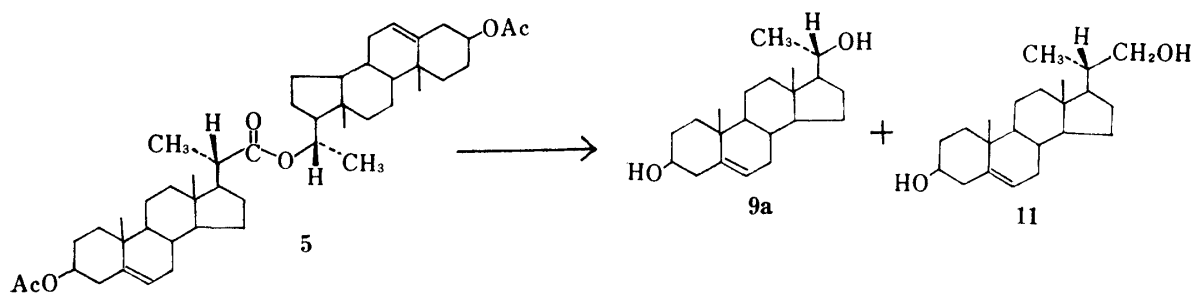


Chart 2.

In view of these results and PMR and MS analyses, the structure of 5 was considered to be $3'\beta$ -acetoxypregn-5'-en-20' α -yl 3 β -acetoxybisanorchol-5-enate with the ester linkage at positions 22 and 20'.

Further, the reactions were examined under various conditions and the reaction mechanisms are discussed.