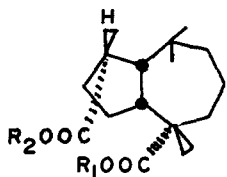
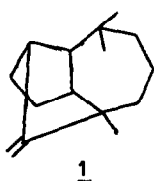


UNIQUE ESTER PARTICIPATION IN THE LEAD TETRAACETATE
OXIDATIVE DECARBOXYLATION OF THE SECONDARY HALF ESTER
OF α -LONGIFORIC ACID - A CIS 1,4-DICARBOXYLIC ACID
FROM LONGIFOLENE¹

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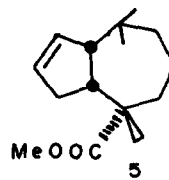
IN A SYSTEMATIC approach to an azulene from longifolene 1, the Pb(IV)/Cu(II) oxidative bisdecarboxylation strategy on α -longiforic acid 2 (derived from 1) proved quite unsatisfactory as a result of more effective lactone formation² in a competing reaction. For by-passing this undesired lactone-formation we envisaged a step-wise Pb(OAc)₄ reaction on the secondary/tertiary half ester 3 / 4. In this communication we describe an exotic



2: R₁=R₂=H

3: R₁=H, R₂=Me

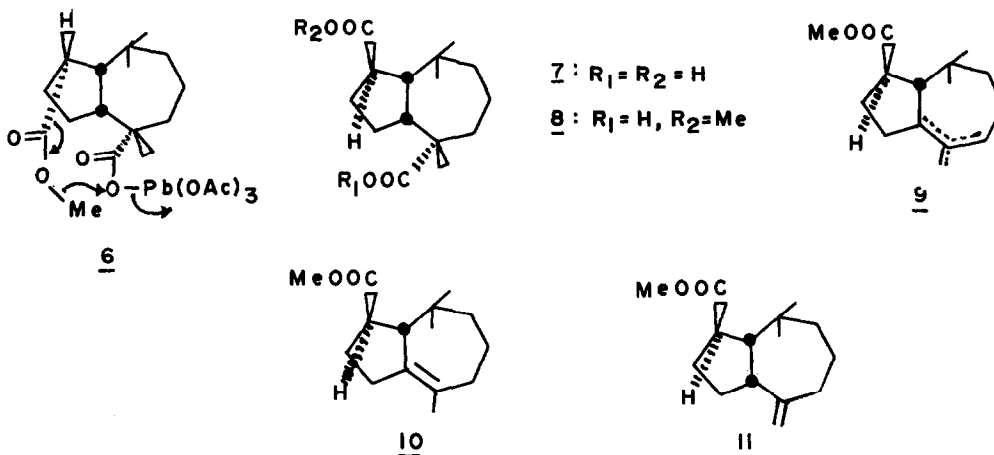
4: R₁=Me, R₂=H



ester participation which takes place in the Kochi reaction on the secondary half-ester 3.

The secondary half-ester 3 (m.p.165°; 20%) was accessible with some difficulty by the partial esterification (6% hydrogen chloride in MeOH) of α -longiforic acid³ 2 while the tertiary half-ester 4 (m.p.135°; 35%) was generated relatively more easily by partial hydrolysis³ of the dimethyl ester of 2. Pb(OAc)₄-Cu(OAc)₂ reaction (benzene/4 hr) on the tertiary half-ester 4 generated the expected olefinic ester 5 [PMR(CCl₄): three tertiary Me singlets at 0.83, 0.87, 1.37 ppm; COOMe singlet at 3.53 ppm; broad (W_H = 5 Hz) unsymmetrical "singlet" at 5.70 ppm (2H, olefinic)]. Formation of the same olefinic ester 5 (GLC, IR, PMR) from the secondary half ester 3 also, however, was quite unusual. Mechanistic rationalization of this rather bewildering observation was quite simply achieved by invoking a carbomethoxyl participation with the Pb(IV) ester function which is so favourably close to it in space (cf.6). In order to provide experimental proof for this hypothesis, the secondary half ester 3 ⁴ (m.p.75°; 30%) from β -longiforic acid⁵ 7 (carboxyl groups trans) was

also subjected to the Kochi reaction⁶ under the same conditions. No ester



participation⁷ was theoretically possible in this case nor was it observed. A mixture of two of the three possible, normal olefinic esters (cf. 9) was obtained: chromatographic resolution over 15% $AgNO_3$ -silica gel furnished the pure compounds 10 and 11. Compound 10 - IR: 1600-1650 cm^{-1} region transparent. PMR(CCl_4): two tertiary Me singlets at 0.75, 0.80 ppm; one vinylic Me singlet at 1.72 ppm; COOMe singlet at 3.60 ppm. Compound 11 - IR (smear): 1620 and 895 cm^{-1} (*exo* methylene). PMR(CCl_4): two tertiary Me singlets at 0.78, 0.87 ppm; COOMe singlet at 3.60 ppm; olefinic singlets at 4.58 and 4.62 ppm (together 2H).

REFERENCES AND NOTES

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- 3 P. Naffa and G. Ourisson, Bull. Soc. Chim., 1115 (1954).
- 4 Prepared by the partial esterification method as before. Besides the downfield tertiary methyl signal at ca 1.40 ppm, common to all the half esters 3, 4 and 8, the secondary half ester 3 from the β -series was characterized by a 3H x 2 singlet at 0.95 ppm (3: 1.02 and 1.12 ppm; 4: 0.90 and 0.95 ppm).
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- 7 That anhydride formation was not in any way involved in the anomalous LTA reaction on the half ester 3 was ascertained when α -longiforic anhydride was recovered unscathed under the same reaction conditions.

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