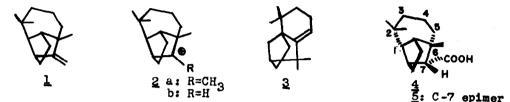
Tetrahedron Letters No. 18, pp 1533 - 1534, 1977. Pergamon Press. Printed in Great Britain.

## UNIQUE OXIDATIVE DECARBOXYLATION BY LEAD TETRAACETATE TO CYCLOPROPANE: FORMATION OF NORLONGICYCLENE FROM LONGIFOLIC ACIDS<sup>1</sup>,<sup>2</sup>

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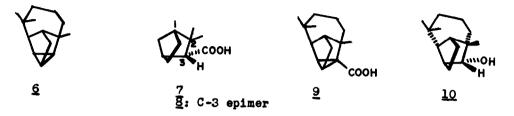
(Received in UK 8 March 1977; accepted for publication 21 March 1977)

Of the two closely related carbocations of the general structure 2 (a: R=CH<sub>3</sub>; b: R=H) derivable from longifolene <u>1</u>, the tertiary species <u>2a</u> is



easily formed on exposure of  $\underline{1}$  to acid reagents<sup>3</sup> while generation of the secondary entity  $\underline{2b}$  is obviously much more difficult since it involves chemical scission of a carbon atom and hence a suitable longifolene derivative/reaction capable of producing the desired species becomes a hard imperative. As a consequence, while the longifolyl cation ( $C_{15}$ )  $\underline{2a}$  has been studied<sup>3</sup> extensively as the harbinger for one of the most fascinating and convoluted skeletal rearrangements (cf. isolongifolene 3) known in sesquiterpene chemistry, the norlongifolyl cation ( $C_{14}$ )  $\underline{2b}$  has remained almost obscure so far although a comparison of their fates is undoubtedly of considerable theoretical interest. We now describe a rational approach to this problem and a preparatively-significant novel observation made in the process.

Practical considerations (vide infra, note 7) prompted us to generate the norlongifolyl cation 2b under essentially nonacidic conditions exploiting the oxidative decarboxylation approach of Kochi<sup>4</sup>. Longifolic acid<sup>5</sup> 4 and its epimer isolongifolic acid<sup>5</sup> 5 (derived from 1), provided ideal substrates for this study. When the  $C_{15}$ -secondary acid 4 or 5 was refluxed with Pb(OAc)<sub>4</sub>-Cu(OAc)<sub>2</sub>-C<sub>5</sub>H<sub>5</sub>N in C<sub>6</sub>H<sub>6</sub> (4 hr), oxidative decarboxylation proceeded smoothly, evidently through the intermediacy of the cationic species<sup>6</sup> 2b. In both cases, chromatography of the neutral product furnished a single C<sub>14</sub>H<sub>22</sub> hydrocarbon (ca 70%): M<sup>+</sup> 190;  $\Im$  3000 and 845 cm<sup>-1</sup>; singlets at 34, 39, 44, 54 (3H x 2) and 59 (3H) Hz, characterized as norlongicyclene 6 by direct comparison with an authentic sample<sup>7</sup>. Cyclopropanation<sup>8</sup> in such a high yield and purity in the  $Pb^{IV}/Cu^{II}$  oxidative decarboxylation of acids is unprecedented. In a comparative study of the monoterpene analog of <u>2b</u> viz. the norcamphyl cation



(generated in a similar fashion by applying the Kochi reaction conditions to camphenilanic acid 7 and isocamphenilanic acid 8) no trace of norcyclene could be detected (GLC) and the product consisted of only a mixture of acetates (55%). It may be relevant to mention here that pseudo-longifolic acid 9 was highly resistant to  $Pb^{IV}/Cu^{II}$  under the above conditions and could be recovered unscathed.

## REFERENCES AND NOTES

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- 6 It has also been experimentally found that the norlongifolyl radical (<u>via t-butyl perisolongifolate</u>) does not give norlongicyclene but forms norlongifolane: J. Lhomme and G. Ourisson, <u>Tetrahedron 24</u>, 3177 (1968).
- 7 Acid-catalyzed (p-TsOH) dehydration<sup>6</sup> of longicamphenilol <u>10</u> generates norlongicyclene in a negligibly poor yield (<u>ca</u> 5%).
- 8 Formation of minor side products with cyclopropane ring (e.g.  $6 \le 5\%$ ) has been observed in the Pb(OAc)<sub>4</sub> reaction on the longifolols<sup>6</sup>.
- 9 G. Mehta, U. R. Nayak and Sukh Dev, Tetrahedron 24, 4105 (1968).