# Lead Tetra-acetate Oxidation of the Longifolols. Formation of Cyclopropane Derivatives

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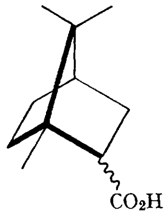
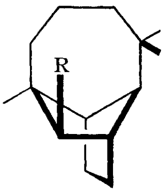
THE oxidation of alcohols with lead tetra-acetate is considered as proceeding *via* radicals, although carbonium ions have been postulated to explain the formation of side-products resulting from a fragmentation.[1] In the case of primary alcohols, such a fragmentation is very similar to the oxidative decarboxylation of acids, which involves ionic intermediates (there may exist the possibility of a two-step mechanism: homolytic cleavage followed by oxidation to the cation). For example, the rearranged products camphene and tricyclene are obtained from the epimeric acids (1a) and (1b);[2] these reactions require ionic intermediates. We now describe the lead tetra-acetate oxidation of alcohols in the longifolene series, where similar ions are certainly involved when judged by the "abnormal" products isolated.

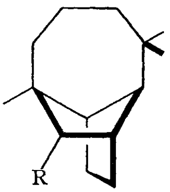
Longifolol (2) and isolongifolol (3), when treated with lead tetra-acetate in boiling benzene, gave the corresponding acetates and the expected cyclic ethers (4) and (5) (20—30%), respectively [(5) has recently been obtained in the same way[3]]. These "normal" products are accompanied in both cases by norlongicyclene (6) (5—6%) and, in the case of (2), by the dimeric hydrocarbon (7) (2—3%), and by $\psi$-longifolaldehyde (8) (8—10%) (structures proved by various correlations which will be described in the full paper). There are precedents



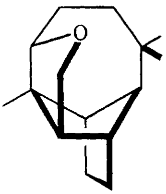
(1a) α-$CO_2H$
(1b) β-$CO_2H$



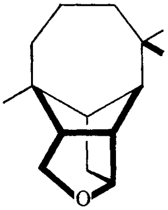
(2; R=$CH_2OH$)
(17; R=CHO)
(16; R=$CH_2O^+$)



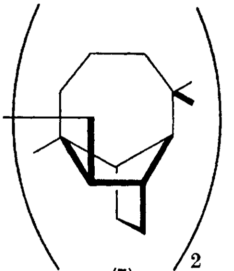
(3; R=$CH_2OH$)
(12; R=$CO_3Bu^t$)



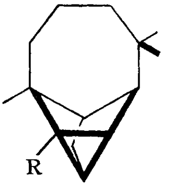
(4)



(5)



(7)



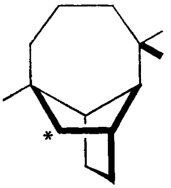
(6; R=H)
(8; R=CHO)
(9; R=Ph)
(10; R=$CO_2H$)

in the literature for the formation of (7);[4] therefore, we shall discuss particularly the formation of (6) and (8).

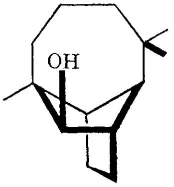
Norlongicyclene (6) is also formed by the action of lead tetra-acetate on ψ-longifolaldehyde (8), which could therefore have been an intermediate. However, this reaction is slower than the first one by several orders of magnitude and gives the phenylated hydrocarbon (9), which could not be isolated from the alcohols. Norlongicyclene is obtained from both epimers (2) and (3), while only longifolol (2) gave the aldehyde (8). Furthermore, norlongicyclene is not the product of decarboxylation of ψ-longifolic acid (10), which is not attacked by the reagent under the reaction conditions.

Norlongicyclene (6) cannot result from a cyclisation of the longicamphenylyl radical (11). When this radical was prepared by thermal decomposition of t-butyl perisolongifolate (12) it gave no trace of (6), but only (13). However, the cation (14), generated from longicamphenylol (15) by *p*-toluenesulphonic acid in benzene, gave in particular norlongicyclene (6). We therefore conclude that norlongicyclene is the product of a *fragmentation of the cation* (16) (or of the corresponding radical) to the carbonium ion (14) [directly or through the radical (11)].

ψ-Longifolaldehyde (8) is *not* obtained by lead tetra-acetate oxidation of isolongifolol (3). It is



(11; $* = \cdot$)
(14; $* = +$)



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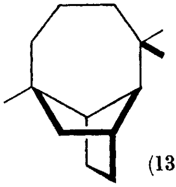

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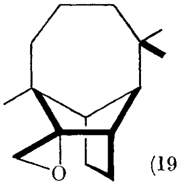

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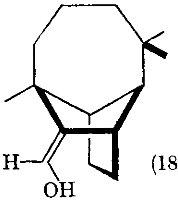
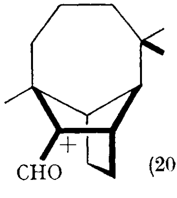
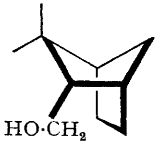


(18)



(20)

however formed by a similar oxidation of longifolaldehyde (17) which points to the probable intermediacy of the enol (18). Another precursor of this enol, the epoxide (19), gave indeed the same results as longifolaldehyde.



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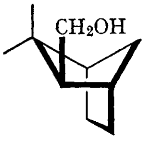

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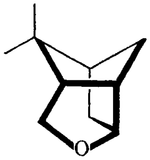

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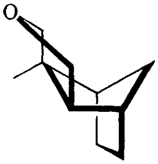

(24)

This suggests a mechanism such as that indicated, whereby the enol (18) is oxidized to the hybrid cation (20), *via* the radical, and cyclizes in the same way as the simpler ion (14).

These results can probably be observed in other, less complex, systems; they seem however to be singularly linked with the strained and compact nature of the longifolene skeleton.[5] For instance, the epimeric *endo*- and *exo*-camphanols (21) and (22) gave, with lead tetra-acetate, the corresponding acetates and the cyclic ethers (23) and (24), but no detectable trace of cyclopropane derivatives.

We thank Professor M. Lj. Mihailović for having informed us that he has also observed in other cases the formation of minor side-products with cyclopropane rings.

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