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SIMPLE SYNTHESES OF THE ATLANTONES, OCIMENONES, TAGETONES AND FILIFOLONE FROM ISOPRENE

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The formation of terpenes by step-wise addition of isoprene units has long been an objective of organic synthesis.[1] We describe here such synthesis of a range of terpenes by acylation of olefins and by Diels-Alder reactions, both catalysed by Lewis acids.

Addition of isoprene (0.13 mol.) in methylene chloride to senecioyl chloride (0.1 mol.) in methylene chloride containing stannic chloride (0.09 mol.) at -78° gave the crude chloroketone (8),[†] which was treated with lithium fluoride and lithium carbonate in dimethylformamide at 120° to give ocimenone[2] in 90% isolated yield, as a mixture of *cis* and *trans*-isomers[3] (1:9) (5) and (6)*. *cis*- and *trans*-Atlantone[5] (1:9) (1) and (2), identical, but for optical rotation, with samples isolated from the essential oil of *Cedrus atlantica* were obtained from ocimenone (0.004 mol.) by addition of isoprene (0.016 mol.) in methylene chloride containing aluminium chloride (0.003 mol.) at 20°, in an isolated yield of 85%.

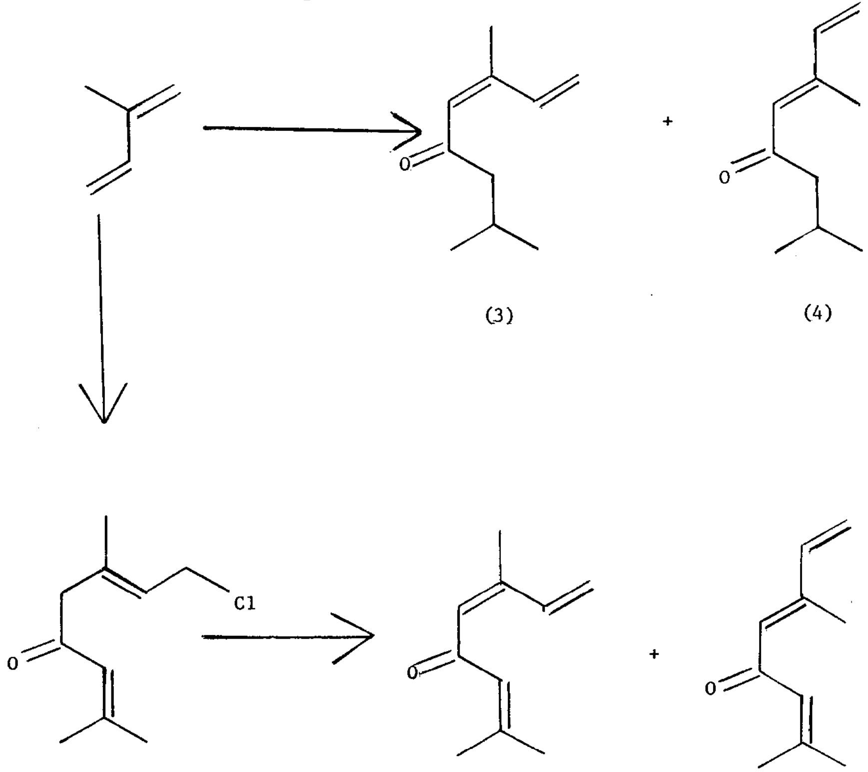
Treatment of ocimenone (0.004 mol.) in methylene chloride with aluminium chloride (0.003 mol.) at 40° resulted in the formation of filifolone[6] (7) (80% conversion after 3h.), probably through the intermediate (11) suggested in the rearrangement of chrysanthenone[7] to filifolone.

The *cis* and *trans*-atlantones (1:9 (1) and (2) were also synthesised by direct acylation and subsequent dehydrochlorination of limonene (9)(available by dimerisation of isoprene):

senecioyl chloride (0.05 mol.) in methylene chloride containing stannic chloride (0.045 mol.) cooled to -78° was added to limonene (0.05 mol.) in a mixture of methylene chloride and Freon 12 at -120°. The crude chloro-ketones were then treated with lithium fluoride and lithium carbonate in dimethylformamide at 120° to afford a mixture of isomers of which *cis* and *trans*-atlantone (1) and (2) were *ca.* 60% (glc) of the reaction mixture. The other major product (20%, glc) was the nonconjugated isomer (10).

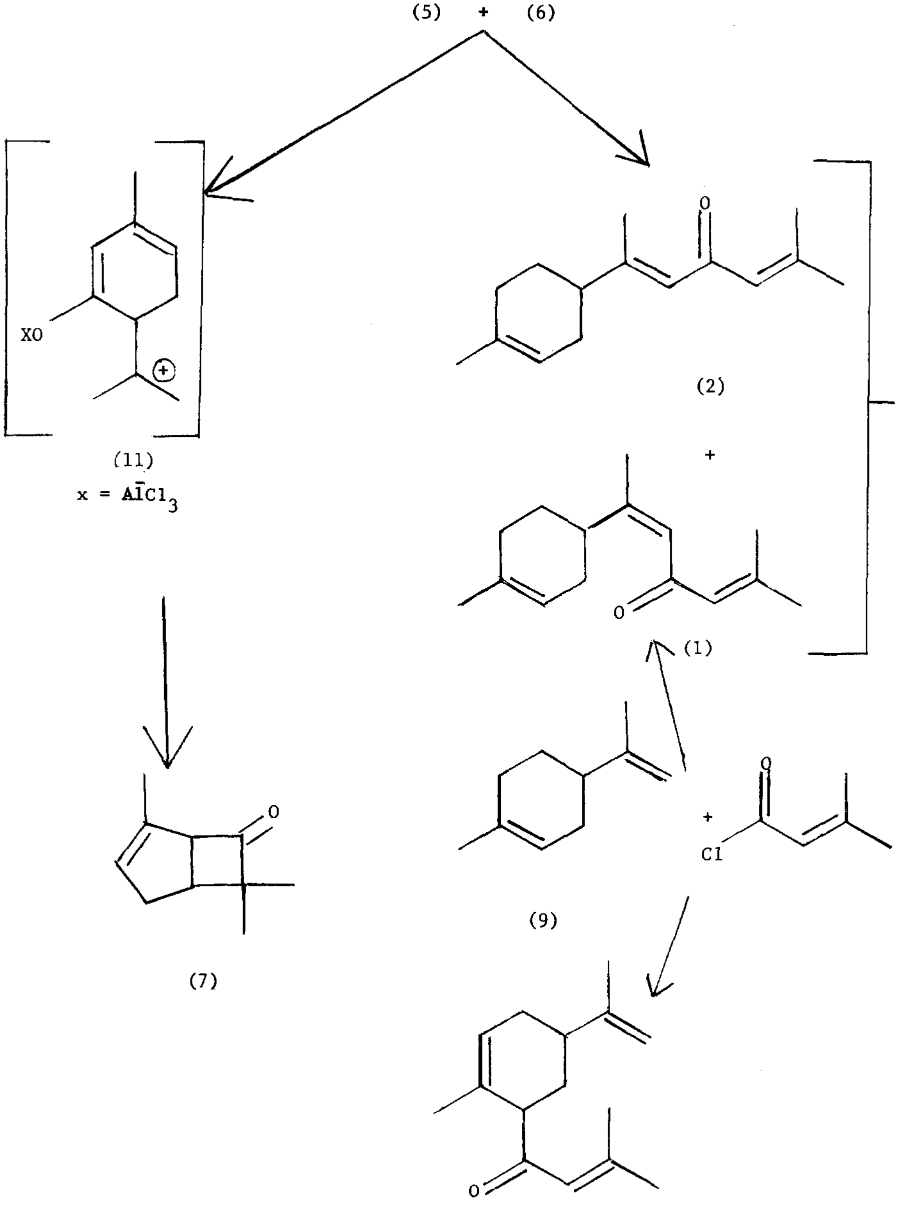
† Although the chloro-ketones could be isolated and identified (m.s., n.m.r., i.r.), in a typical run the dehydrochlorination was carried out using the crude material.

* A similar sequence but using isovaleryl chloride as the acid chloride, furnished a mixture of *cis*- and *trans*-tagetone[4] (40:60) (3) and (4).



(3) (4)

(8) (5) (6)



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