Synthesis of (±)-Dictyopterene A and (±)-Dictyopterene C′

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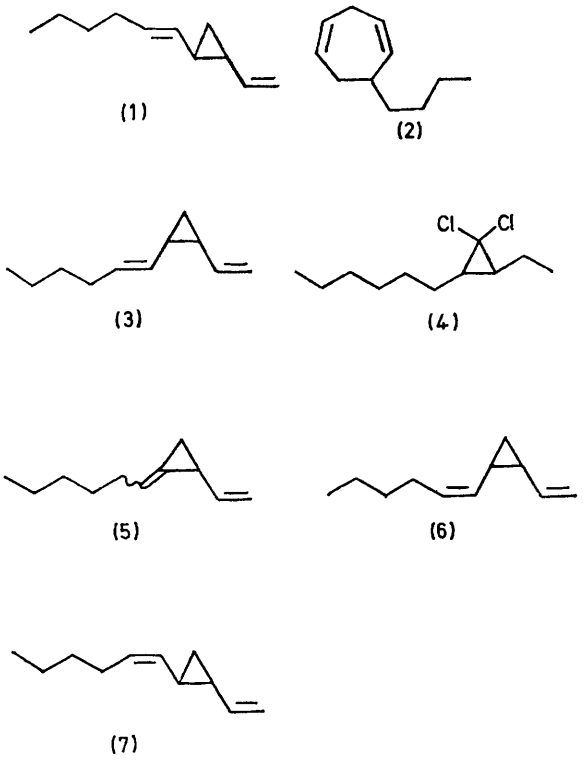
Summary Treatment of 1,1-dichloro-2-ethyl-3-hexylcyclopropane (**4**) with KOBu^t in dimethyl sulphoxide gives 1-hexylidene-2-vinylcyclopropane (**5**) which is converted into (±)-dictyopterene A (**1**) and its geometrical isomers after prolonged treatment with the base; thermolysis of these stereoisomers gives (±)-dictyopterene C′ (**2**) in 60% yield.

THE dictyopterenes[1–3] are a class of C_{11} hydrocarbons isolated from the essential oil of algae of the genus *Dictyopteris*. Dictyopterene A [compound (**1**)] and dictyopterene B[2] [(—)-(*RR*)-*trans*-1-(*trans,cis*-hexa-1,3-dienyl)-2-vinylcyclopropane] are the major constituents and dictyopterene C′ [compound (**2**)], dictyopterene D′ [(+)-6-*cis*-but-1-enylcyclohepta-1,4-diene], *trans,cis,cis*-undeca-1,3,5,8-tetraene, *trans,trans,cis*-undeca-1,3,5,8-tetraene, *trans,cis*-undeca 1,3,5-triene, and *trans,trans*-undeca-1,3,5-triene are minor constituents. Dictyopterene C [compound (**3**)] has not been found in the essential oil, although it is thought that compound (**2**) arises from a Cope rearrangement of dictyopterene C *in vivo*. In addition, it has been reported recently that dictyopterene D′ is the sex attractant produced by the female gametes of the brown alga *Ectocarpus siliculosus*.[4]

We report here a convenient synthesis of (±)-dictyopterene A (**1**) and (±)-dictyopterene C′ (**2**). Addition of the cyclopropane† (**4**) (1 mol. equiv.) to a solution of KOBu^t (2·5 mol. equiv.) in Me_2SO[5] at 25° gives *syn*- and *anti*-1-hexylidene-2-vinylcyclopropane (**5**) in 80—90% yield. Prolonged treatment (15 h) of (**5**) with KOBu^t in Me_2SO gives compound (**1**) and its geometrical isomers (**3**), (**6**), and (**7**). To simplify the isolation of (**1**), the crude mixture was pyrolysed in CCl_4 at 80° for 12 h to convert the thermally labile *cis*-isomers (**3**) and (**6**) into (**2**). The pyrolysate was shown by g.l.c. (Apiezon J) to contain 11% (4% yield) of compound (**1**). Alternatively, pyrolysis of the crude mixture at 175° for 2·5 h yielded only compound (**2**) in *ca.* 60% yield; the overall yield from dec-3-ene is 30%. Attempts to isolate the thermally labile[6] dictyopterene C (**3**) by column chromatography using 25% $AgNO_3$ on silica gel were unsuccessful.

Finally, the yield of divinylcyclopropanes reported here compares favourably with other current dictyopterene syntheses.[6,7] These rely on a Wittig reaction between the appropriate phosphonium ylide and *cis*- or *trans*-2-vinylcyclopropanecarbaldehyde, which are available in 16% yield by reduction of ethyl 2-vinylcyclopropanecarboxylate.[8] One group[6] reported on overall yield of 13%, although their yield of dictyopterene A was 5·2%.



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