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A Short, Stereoselective Synthesis of the Eudesmane Sesquiterpene Selina-3,7(11)-diene

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The intramolecular Diels–Alder reaction of the C_{15} tetraene (**6**) prepared by attachment of a long-chain alkyl group with a terminal double bond to 2,5-dihydro-3-methyl thiophene *S,S*-dioxide, followed by extrusion of SO_2, has been employed in an efficient total synthesis of selina-3,7(11)-diene.

Recently, the use of 2,5-dihydro-3-methyl thiophene *S,S*-dioxide (**1**) as an anionic isoprene building block in a regioselective deprotonation/alkylation process has been established.[1] Attachment of a long-chain alkyl group with a terminal double bond to the sulphone (**1**) by this process, followed by stereospecific SO_2 extrusion and intramolecular Diels–Alder reaction of the intermediate triene, provides an extremely efficient route to *trans*-fused decalin derivatives.[2] We now report the stereoselective total synthesis of a eudesmane sesquiterpene, selina-3,7(11)-diene (**2**), in essentially three steps by this strategy.[3]

Deprotonation of (**1**) with lithium hexamethyldisilazide (LiHMDS) in the presence of compound (**4**) [prepared *in situ* by the reaction of the readily available 2-isopropylidene-1,3-dibromopropene (**3**)[4] and methallylmagnesium chloride] afforded compound (**5**), readily separated from unchanged (**1**) by h.p.l.c. The overall yield of (**5**) from (**3**) was 17%. Thermolysis of compound (**5**), by passing its dilute solution in n-hexane through a hot tube under nitrogen at 180 °C gave compound (**6**) (>97%) (the *Z*-isomer was not detected). Compound (**6**) was heated at 190 °C in a sealed tube for 110 h to give the cycloadduct (**2**) as the only product (75%). The

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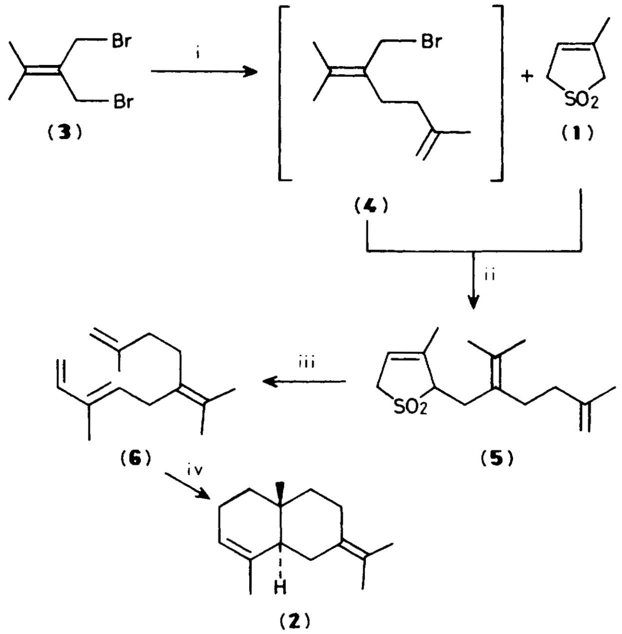

Scheme 1. *Reagents and conditions*: i, CH_2=CMeCH$_2$MgCl (1.1 equiv.), Et_2O, −10 °C, then CuI (0.1 equiv.), −10 to 0 °C, 15 h; ii, THF-P(O)(NMe$_2$)$_3$, LiHMDS, −78 °C; iii, 0.07 M in hexane, 20 ml h^{-1} through a hot tube at 180 °C; iv, toluene, sealed tube, 190 °C, 110 h.

stereochemistry of compound (**2**) was confirmed by comparing its spectral data with those reported.[3a,b] The stereospecificity in this intramolecular Diels-Alder reaction is remarkable.[5]

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