Preparation of Some *cis*-1,*trans*-5-Germacratriene Derivatives

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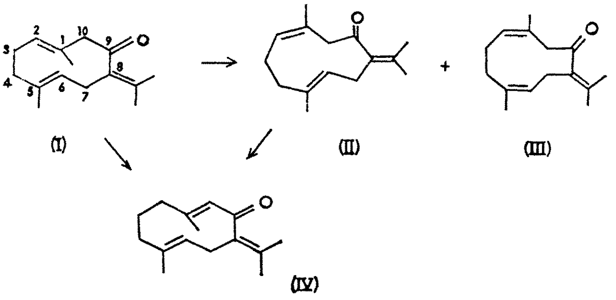
Summary By photoisomerisation, germacrone (I) was transformed into two photoisomers, *cis*-1,*trans*-5-germacrone (II) and *cis*-1,*cis*-5-germacrone (III): *cis*-1,*trans*-5-germacratriene (VI) was derived from (II).

IN a previous paper,[1] the abnormal Cope rearrangement of *cis,trans*-cyclodeca-1,5-diene type furan sesquiterpenes was reported. To obtain compounds with the same double-bond system, we prepared some *cis*-1,*trans*-5-germacratriene derivatives. Photoisomerisations of cyclodecadienes afforded the geometrical isomers[2] of one or both double bonds, although positional isomers[3] or intramolecular cycloaddition products[4] were also obtained in some cases. Germacrone (I) was therefore photoisomerised.

Upon irradiation in ether in the presence of acetophenone under an atmosphere of nitrogen at room temperature for 5 h, using a Pyrex apparatus with a 300 W high-pressure mercury-vapour lamp, germacrone (I) was transformed into two photoisomers, (II) and (III). The products were separated into *cis*-1,*trans*-5-germacrone (II, 27%) and *cis*-1,*cis*-5-germacrone (III, 48%) by alumina and then silver nitrate–alumina chromatography.

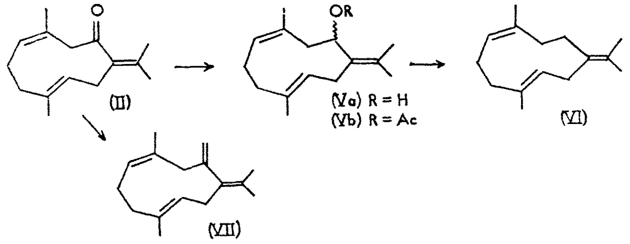
cis-1,*trans*-5-Germacrone (II) was a colourless oil, b.p. 100° (bath)/1 mm, $\nu_{\max}$ (CCl$_4$) 1699, 1661, 1299, 1152, 991, and 857 cm^{-1}, $\lambda_{\max}$ (EtOH) 245 nm (ϵ 2100) and 301 (230). Application of the intramolecular nuclear Overhauser effect[5] (N.O.E.) to (II) showed that a vinyl methyl (τ 8·12) and a vinyl proton (τ 4·72) are in a *cis*-relationship, by an increase of 17% in the intensity of the vinyl proton signal on double irradiation at the vinyl methyl signal. However, it could not be resolved whether the vinyl methyl is situated at C-1 or C-5 and whether the vinyl proton is at C-2 or C-6. Compound (II) was heated under reflux in 1N KOH–EtOH for 6·5 h giving isogermacrone[6] (IV) m.p. 50—52°, indicating therefore, that (II) should possess a *cis*-1,2-double bond and a *trans*-5,6-double bond.



cis-1,*cis*-5-Germacrone (III), a colourless oil, b.p. 100° (bath)/1 mm, $\nu_{\max}$ (CCl$_4$) 1684, 1668, 1614, 1297, and 832 cm^{-1}, $\lambda_{\max}$ (EtOH) 255 nm (ϵ 5000) and 311sh (ϵ 182) was shown to be a geometrical isomer of germacrone (I) by n.m.r. Measurement of the N.O.E. (in benzene) indicated that a vinyl methyl (τ 8·26) and a vinyl proton (τ 4·68) are in a *cis*-relationship (N.O.E. value, 19%), as are another vinyl methyl (τ 8·43) and vinyl proton (τ 4·85) (N.O.E. value, 17%). Therefore, compound (III) is *cis*-1,*cis*-5-germacrone.

When (II) was reduced with lithium aluminium hydride, it gave *cis*-1,*trans*-5-germacratrien-9-ol (Va), m.p. 124—125°

in good yield. On reduction with lithium in liquid ammonia, its acetate (Vb) was converted into *cis*-1,*trans*-5-germacratriene (VI), a colourless oil, b.p. 90° (bath)/4 mm, ν_{max} (CCl$_4$) 1659 and 852 cm^{-1}, τ 8·37 (Me, s), 8·35 (Me, s), 8·28 (Me, s), 8·02 (Me, s), and 4·88 (2H, m).



Wittig reaction of (II) with methyltriphenylphosphonium bromide gave *cis*-1,*trans*-5,9-methylenegermacratriene (VII), an oil, b.p. 95° (bath)/1 mm, ν_{max} (CCl$_4$) 1615, 900, and 832 cm^{-1}, τ 8·36 (2 Me), 8·25 (Me, s), 8·24 (Me, d, J 2·0 Hz), which was distinguished from 9-methylenegermacratriene[7] obtained from (I) by the same reaction.

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