Synthesis of a Substituted *cis*-Decalin as a Potential Insect Antifeedant

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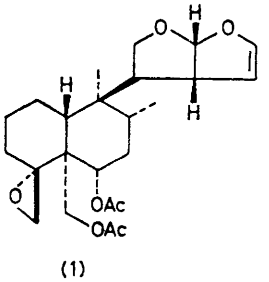
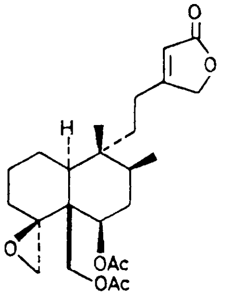
Summary A *cis*-decalin containing epoxydiacetate functions has been synthesised as a potential insect antifeedant.

IN order to probe the insect antifeedant activity of a number of clerodane diterpenes such as clerodin (**1**)[1] and ajugarin I (**2**),[2] we have begun a programme of synthesis of a number of model compounds. Here we report the stereospecific synthesis of a *cis* fused derivative (**7**) by a route which allows sufficient flexibility to prepare other analogues.

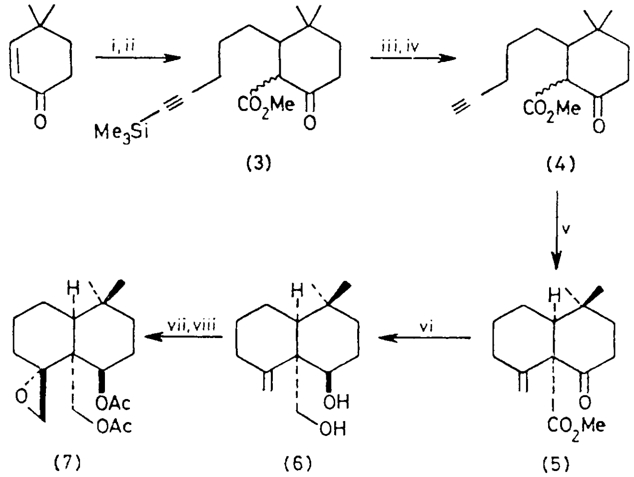


(1)



(2)

Copper(I) catalysed addition of trimethylsilyl protected pentynylmagnesium iodide to 4,4-dimethylcyclohex-2-enone and subsequent trapping of the intermediate regiospecific enolate with methyl chloroformate gave (**3**) in 60% yield. Deprotection[3] of (**3**) proceeded smoothly to give (**4**) in 89% yield. Cyclisation of (**4**) to (**5**) could be accomplished by a variety of methods. Firstly, under typical conditions used by Conia,[4] *i.e.* at 300 or at 170 °C in the presence of zinc stearate,[5] good conversion was achieved. As these high temperatures were not suitable for more highly substituted derivatives of (**4**) we sought milder conditions. Thus (**4**), in toluene at reflux with a trace of ZnI$_2$ or in methylene chloride at room temperature with SnCl$_4$ as catalyst, gave quantitative formation of (**5**) over a similar period of time. Reduction of (**5**) with lithium aluminium hydride gave the corresponding diol (**6**) (89%), m.p. 132—133 °C, as the only observable product. Although it was not possible to



SCHEME. i, Me$_3$Si-C≡C-[CH$_2$]$_3$MgI, Cu^I, Et$_2$O, − 23 °C; ii, Cl-CO$_2$Me; iii, AgNO$_3$; iv, KCN; v, heat and ZnI$_2$–toluene or SnCl$_4$–CH$_2$Cl$_2$ at room temperature; vi, LiAlH$_4$; vii, MCPBA or VO(acac)$_2$–Bu^{t}OOH; viii, Ac$_2$O–pyridine then 4-*NN*-dimethylaminopyridine.

assign the ring junction and reduction stereochemistry from spectral data they can be derived from a knowledge of the relative configurations of the final epoxydiacetate (**7**).

The synthesis was completed by epoxidation of (**6**) by either *m*-chloroperbenzoic acid (MCPBA) or VO(acac)$_2$–Bu^t-OOH[6] to give the epoxydiol which was converted directly into the diacetate (**7**) using Ac$_2$O–pyridine–4-*NN*-dimethylaminopyridine in 79% overall yield (Scheme). Compound (**7**) was also obtained on epoxidation of the diacetate of (**6**) with MCPBA in 89% yield.

The structure of (**7**), m.p. 64 °C, follows from its spectral and *X*-ray crystallographic properties.† For example, ^{1}H n.m.r. spectroscopy shows characteristic absorptions at δ 1·04 (s, 3H), 1·05 (s, 3H), 1·24—1·8 (m, 11H), 1·97 (s, 3H), 2·02 (s, 3H), 2·33 (d, 1H, *J* 4 Hz), 3·05 (d, 1H, *J* 4 Hz), 3·82 (ABq, 1H, *J* 12 Hz), 4·18 (ABq, 1H, *J* 12 Hz), and 4·76 (t, 1H, *J* 6 Hz). Compound (**7**) did not show any appreciable antifeedant activity against *Spodoptera Littoralis* and *Heliothis Virescens* when sprayed on *Gosypium Hirsatum* δ-pine (cotton leaves). However, when tested against *Locusta Migratoria* on GF/A discs +5% sucrose and 1000 p.p.m. of (**7**) a 72% inhibition of feeding was observed.‡ The stereospecific preparation of the *trans*-isomer of (**7**) and other analogues by another route will be reported later. Satisfactory microanalyses were obtained for all new compounds.

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