Synthesis of Cadinane Type Sesquiterpenes[1]

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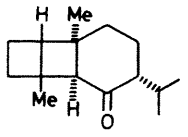
Summary A new and convenient synthesis of cadinane type sesquiterpenes is reported from the tricyclo-[4.4.0.0^{2,5}]decane photoadduct (**1**).

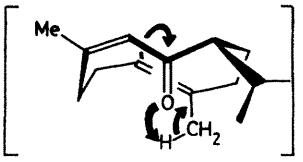
IN recent years sesquiterpenes as a class of compounds have generated a great deal of interest owing to their many isomeric forms and their broad based activity as pheromones,[2a] anti-tumour agents,[2b] and antibiotics.[2c] Cadinanes, which are derived biogenetically from germacranes,[3] have been isolated from various plant sources and have been studied as possible insect stimulants.[4] We now report a synthesis of the cadinane dienol (**3**) and the related cadinanes (**6**) and (**7**) whose enantiomers have been derived from naturally occurring isocalamendiol (**8**).[5,6]

Thermolysis of the tricyclo[4.4.0.0^{2,5}]decane (**1**)[1] in a sealed tube (xylene; 250 °C; 0·5 h) afforded the cadinane dienol (**3**)† in 40% isolated yield; i.r. (neat) 3500 cm^{-1} and 1639 cm^{-1}; n.m.r. ($CDCl_3$) δ 5·86 (s, 1H), 4·87 (s, 1H), 4·61 (s, 1H), 1·70 (s, 3H), and 0·94 (d, 6H, J 7·8 Hz). In order to establish the exact structure of the dienol (**3**) it was related to the known cadinane derivatives (**6**) and (**7**). Treatment of (**3**) with 1 equiv. of $Hg(OAc)_2$ followed by basic $NaBH_4$[7]

† All new compounds have given satisfactory analytical and spectral data.



(1)



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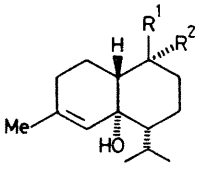
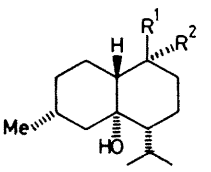
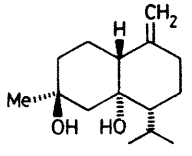


(3) $R^1R^2=CH_2$
(4) $R^1=OH, R^2=Me$



(5) $R^1=OH, R^2=Me$
(6) $R^1R^2=CH_2$



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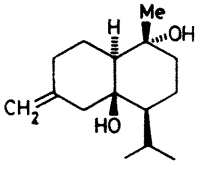

(8)

gave an enediol (**4**) which was found to be unstable to chromatography. Catalytic reduction (Pt; EtOAc) of (**4**) afforded the diol (**5**): m.p. 67—68 °C; i.r. (KBr) 3366 cm^{-1}; n.m.r. ($CDCl_3$) δ 1·23 (s, 3H), 1·14 (d, 3H, J 6·6 Hz), 0·94 (d, 3H, J 7 Hz), and 0·88 (d, 3H, J 7 Hz). This diol (**5**) was dehydrated to the known unsaturated alcohol (**6**) using $POCl_3$–pyridine.[5]

Treatment of the dienol (**3**) with excess of $Hg(OAc)_2$ followed by reduction[7] yielded the known enediol (**7**) together with two triols of unknown stereochemistry.

We postulate that thermolysis of the photoadduct (**1**) proceeds through an unisolated *Z,E*-germacrene intermediate (**2**)[1] and then *via* an ene type reaction to yield the dienol (**3**). This reaction pathway has precedent among the known thermal reactions which were performed on similar germacrenes: acoragemacrane and preisocalamendiol.[5,8] Based on the above chemistry and inspection of Dreiding models of (**2**), it is felt that (**3**) is the correct structure for the dienol rather than that recently reported for a similar system.[9]

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