A Convenient Synthesis of the Tricyclo[3,2,1,$0^{2,7}$]octane System: a Simplified Synthesis of the Diterpenoid Trachylobane

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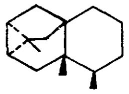
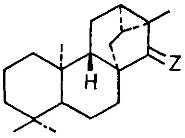
Summary A convenient and efficient method for the construction of the tricyclo[3,2,1,$0^{2,7}$]octane system, involving a homoallylic cyclization, is reported; the application of this method results in a considerably simplified and more efficient synthesis of trachylobane.

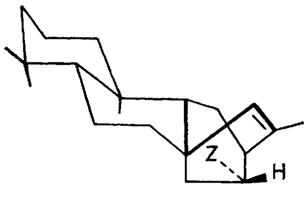
The tricyclo[3,2,1,$0^{2,7}$]octane system is a novel structural feature of a group of sesquiterpenoids related to the naturally occurring hydrocarbon ishwarane (I)[1] and of a larger group of diterpenoids of which the naturally occurring parent hydrocarbon is trachylobane (II).[2] We have recently described in detail total syntheses of (I)[3] and (II).[4] However, subsequent to the publication of these syntheses,[3,4] we have discovered a more convenient and efficient method for the construction of the tricyclo-octane system. We now report briefly on this new method.



(I)



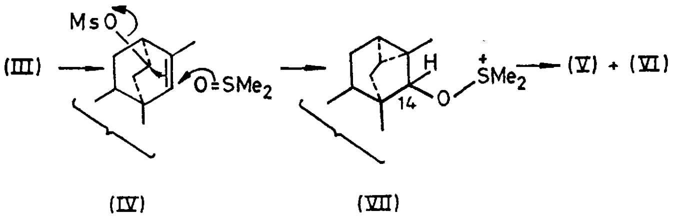
(II) Z = H,H
(V) Z = O
(VI) Z = H,OH



(III) Z = OH
(IV) Z = OMs

The totally synthetic enol (III) has already been described as an intermediate in our recently published synthesis of trachylobane (II).[4] The mesylate (IV) of (III) was converted into a mixture of a ketone (60%) and an alcohol (30%) by heating for 90 min at 60° in Me$_2$SO containing one equivalent of methyl sulphinyl carbanion.[5] The ketone was identical with the cyclopropyl ketone (V), the immediate precursor of trachylobane (II) in our previous synthesis of this diterpenoid.[4]

The crystalline alcohol (m.p. 119°) possessed properties in accord with structure (VI) [i.r. (Nujol) 3240 cm^{-1}; δ (CDCl$_3$) 3·25 s, 1H, *H*–C–OH), devoid of signals for vinylic proton and vinylic Me] and, also in accord with structure (VI), it was oxidized in 70% yield with Jones reagent to the ketone (V). The ketone (V) was also obtained in 70% yield from (III) by direct oxidation of the crude cyclization product. By contrast, the conversion of (III) into (V) by the sequence previously employed in our synthesis of trachylobane[4] was accomplished in 14% yield and required six steps. The conversion of (III) into (V) by the method described herein therefore constitutes a second, more convenient and efficient synthesis of trachylobane by a method which should be generally applicable to the construction of the tricyclo-octane system.



SCHEME

The mechanism whereby (III) is converted into (V)and (VI) can be envisaged as proceeding through the intermediate (VII) which arises by the homoallylic mechanism shown in the Scheme. Elimination of the proton at C-14 of (VII) would give the ketone (V) (*cf.* ref. 6) whereas hydrolysis of (VII) would give the alcohol (VI) (See Scheme).

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