Total Synthesis of Racemic α- and β-Longipinenes

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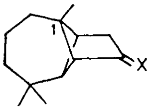
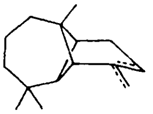
Summary α- and β-Longipinenes (IIa and IIb) have been synthesised in racemic forms from the ketone (Ib).

IN a previous paper[1] we reported on the intramolecular photocyclisation product (Ia) of 1,5,5-trimethyl-8-methylenecyclodeca-6,10-diene. This paper deals with the total synthesis of α-[2] and β-longipinenes (IIa and IIb) utilizing (Ia) as the key intermediate.

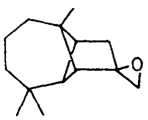
Since attempts to construct longipinenes by adding a one-carbon unit to (Ia) were unsuccessful, the norketone[1] (Ib) was subjected to a ring expansion reaction. The reaction of (Ib) with dimethylsulphonium methylide[3] under standard conditions afforded a single oxiran (III),† which was subsequently converted into the azido-alcohol (IVa) (85%), ν_{max} 3420 and 2100 cm^{-1}, by heating with sodium azide in dimethylformamide.[4] Compound (IVa) was smoothly hydrogenated over Adams catalyst in acetic acid



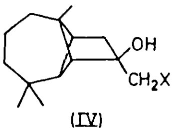
(I)
a; X = CH_2
b; X = O



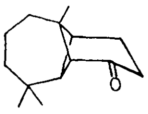
(II)
a; *endo*-double bond
b; *exo*-double bond



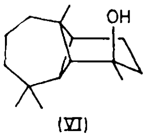
(III)



(IV)
a; X = N_3
b; X = NH_2



(V)



(VI)

giving the amino-alcohol (IVb), and the latter, without isolation, was treated with sodium nitrite in aqueous acetic acid. The ketonic product (90%) consisted of 80% of the ketone (V), ν_{max} 1710 cm^{-1}, and other minor ketones. The reaction of (V), separated by preparative g.l.c., and methyllithium gave *trans*-longipinanol (VI),† m.p. 94·5—96·5° (80%). On treatment with phosphorus oxychloride in pyridine the carbinol was dehydrated to an olefin mixture (84%),‡ from which on preparative g.l.c. α- (IIa) and β-longipinenes (IIb), ν_{max} 3060, 1640, and 870 cm^{-1}, were isolated. The former was identified by comparison of the i.r. and n.m.r. spectra with those of natural α-longipinene.

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† The stereochemistry was assigned by consideration of the stereoselective outcome of the reaction and the presumable steric retardation due to the methyl group at C(1) against nucleophilic attack.

‡ The α- and β-isomers were formed in the ratio of 4 : 3 as indicated by g.l.c.

[1] M. Miyashita and A. Yoshikoshi, *Chem. Comm.*, 1971, 1091.
[2] L. Westfelt, *Acta Chem. Scand.*, 1967, **21**, 159.
[3] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.
[4] D. N. Kirk and M. A. Wilson, *Chem. Comm.*, 1970, 64.