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NOVEL FRAGMENTATION OF LONGIBORNANE SYSTEM: SYNTHONS FOR α-LONGIPINENE SYNTHESIS

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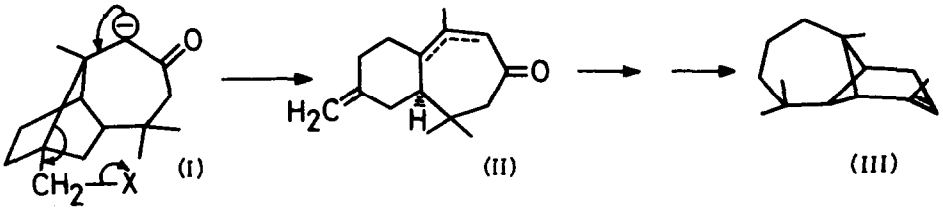
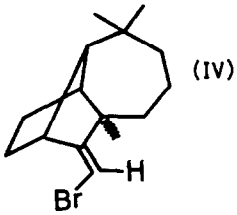
The synthesis of sesquiterpene hydrocarbon α-longipinene (III)[1] constitutes an attractive and formidable synthetic objective. We contemplated a bridge scission-cyclisation pathway to (III) employing a tricyclic precursor the longibornane derivative (I).



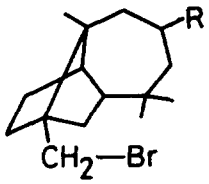
(I) (II) (III)

In this communication we describe an extremely facile bridge scission involving C_1-C_7 bond[2] of bicyclo [2.2.1] heptane moiety present in (I) and formation of a suitably functionalised bicyclic himachalene derivative capable of elaboration[3] to (III).

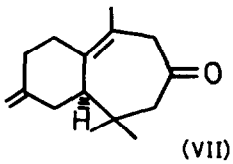


(IV)

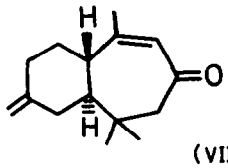
(V) R = —OH
(VI) R = =O



Rearrangement of ω-bromolongifolene (IV)[4] with trifluroacetic acid in CH_2Cl_2 gave a complex mixture[5] of trifluroacetates, which on hydrolysis and chromatography furnished a crystalline bromo-alcohol (V)[6] m.p. 63-5° in 50% yield derived via a precendented[7] Wagner-Meerwein rearrangement and intramolecular 1,5-hydride shift. Jones oxidation of (V) furnished a crystalline ketone m.p. 72° formulated[8] as (VI). Brief expouser of (VI) to DMSO-NaH reagent



(VII)



(VIII)

resulted in the formation of two ketones (VII) and (VIII)[9] in a ratio of 5:1 and in 80% yield. The gross structure of the two ketones was confirmed through transformation of (VII) to himachalane[10] (IX) prepared from natural himachalenes via Wolff-Kishner reduction and catalytic hydrogenation. The α,β-unsaturated ketone (VIII) is a product of equilibration as revealed by deuterium labelling experiment and is therefore tentatively assigned the thermodynamically more stable trans ring junction.[11] The chemical transformation of ketones (VII) and (VIII) to various naturally occurring himachelenes and α-longipinene (III) is under progress.

REFERENCES

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2. This bond scission is the reversal of the bond formation in the biogenesis of longibornane types from himachalene precursor, see, J.B. Hendrickson, Tetrahedron 7, 83 (1959).
3. For a recent striking example of bridged cyclobutane formation, see, G. Stork and P.A. Grieco, Tetrahedron Letters, 1807 (1971).
4. G. Mehta, J. Org. Chem. 36, 3455 (1971).
5. Several interesting products derived from deep seated structural rearrangement of (IV) have been encountered in this reaction and will be reported elsewhere.
6. Compound V: $C_{15}H_{24}OBr$, IR: νOH 3300, NMR: δ,0.95, 1.03 (s, $\underline{CH_3}$-$\overset{|}{C}$-); 3.45 (q, J=12 Hz, -$\underline{CH_2}$-Br) and 4.05 (m, -$\overset{|}{\underset{H}{C}}$-OH).
7. G. Mehta, Chem. and Ind. 1264 (1970); J.R. Prahlad, U.R. Nayak and S. Dev, Tetrahedron 26, 665 (1970).
8. Compound VI: $C_{15}H_{25}OBr$, IR: ν C=O, 1700 cm^{-1}, NMR: δ, 0.91, 0.97 and 1.07 (s, $\underline{CH_3}$-$\overset{|}{C}$-); δ3.5 (q, J=12 Hz, -$\underline{CH_2}$-Br). The structure of VI was further confirmed by its transformation to known longi rnane.
9. Compound VII: $C_{15}H_{24}O$, IR: ν C=O 1705 and νC=CH_2 3100, 1600, 890 cm^{-1}, NMR: δ0.93, 1.03 (s, $\underline{CH_3}$-$\overset{|}{C}$-); δ1.81 (s, $\underline{CH_3}$-C=$\overset{|}{C}$-) and 4.75 (d, CH_2=$\overset{|}{C}$-) and compound VIII: $C_{15}H_{24}O$, UV: λ_{max}^{EtOH} 244 nm, IR: ν C=O, 1660, νC=CH_2 890, 1630, 3040 cm^{-1}, NMR: δ, 1.06 and 1.14 (s, $\underline{CH_3}$-C-), 2.01 (d, $\underline{CH_3}$-C=C-H), 6.1 (broad s, CH_3-C=C-$\underline{H}$); 4.65 (s, broad, $\underline{CH_2}$=C-).
10. T.C. Joseph and S. Dev, Tetrahedron, 24, 3809 (1968).
11. T.C. Joseph and S. Dev, Tetrahedron, 24, 3841 (1968) and reference cited therein.