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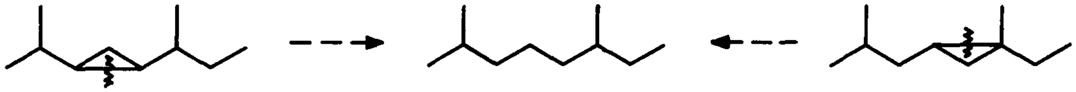
MONOTERPENE SYNTHESIS VIA ALKENYLIDENECYCLOPROPANES: ACID- AND BASE-CATALYSED REARRANGEMENTS

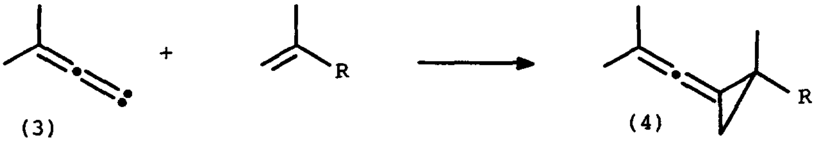
Leslie Crombie, Peter J. Maddocks and Gerald Pattenden
Department of Chemistry, The University,
Nottingham NG7 2RD, England.

Considerable effort has been expended towards developing methods for the synthesis of monoterpenes by head-to-tail linking of isopentane units.[1] We were attracted by the possibility of accomplishing this objective via the elaboration of C_{10}-cyclopropane intermediates (e.g. 1 and 2), obtained from the combination of a C_5-carbene and an appropriate C_5-alkene substrate. In this Letter, we report the results of acid- and base-catalysed rearrangements of the C_{10}-alkenylidenecyclopropanes (4a-c) prepared by addition of the allene carbene (3)[2] to 2-methylbut-1-en-3-yne,[3] isoprene,[4] and 2-methylbut-1-ene[5] respectively.

Treatment of the acetylenic alkenylidenecyclopropane (4a) with boron trifluoride etherate in methanol led directly to the head-to-tail terpenoid allene-acetylene structure (5) (~50%), b.p. 78-79.5°/6mm., ν_{max} 1960 cm^{-1}.,



(1) (2)



(3) (4)

a R = $\cdot C \equiv CH$; b R = $\cdot CH = CH_2$;

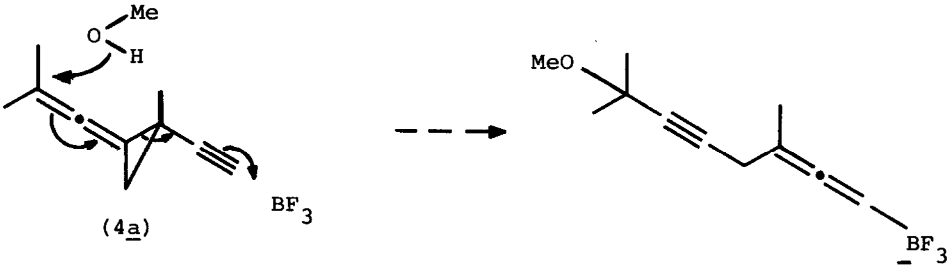
c R = CH_2CH_3.

τ8.57 (Me_2C), 8.25t (*J* 3, : $C\underline{Me}$), 7.1t (*J* 3, : $CC\underline{H}_2$), 6.66 (OMe), 5.36 sextet (*J* 3, : $C\underline{H}_2$); δ 17.8q, 24.2t, 28.5q, 51.3q, 70.6, 75.1t, 81.3, 83.7, 94.9, 225.7 p.p.m. Under similar reaction conditions, the allene adduct (4*b*) from isoprene led to the acetylenic terpene (6) (∿40%), whereas the allene cyclopropane (4*c*), having no non-allenic unsaturation, gave the 1,3-diene (7), ν_{max} 1660 $cm.^{-1}$, τ 9.23t (*J* 7, $CH_2\underline{Me}$), 8.77 (Me), 8.42q (*J* 7, $C\underline{H}_2Me$), 8.2 (: $C\underline{Me}_2$), 6.9 (OMe), 5.02m (: $C\underline{H}H$), 4.8m (: $CH\underline{H}$), 4.3m (: $C\underline{H}$), with an irregular terpene carbon skeleton.

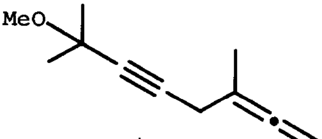
Both the formation of (5) from (4*a*) and of (6) from (4*b*), are best rationalised in terms of initial co-ordination of boron trifluoride at the non-allenic unsaturation in (4*a*) and (4*b*) as shown. Where this site of attack is precluded, as in the allene cyclopropane (4*c*), we envisage the initial co-ordination taking place at the central carbon centre of the allene moiety (see Scheme).[6]

The corresponding rearrangement of (4*c*) in methanol containing hydrochloric acid resulted in protonation at the terminal geminal methyl substituted carbon centre of the allene moiety,[7] leading to the acetylene (8) ν_{max} 2250 $cm.^{-1}$, τ 9.15t (*J* 9, $CH_2\underline{Me}$), 8.88d (*J* 9, $CH\underline{Me}_2$), 8.84 (Me), 8.3-8.6 (3H), 7.82m (⋮ $C.C\underline{H}_2$), 6.84 (OMe), whereas the acetylenic allene cyclopropane (4*a*) under similar conditions led solely to (5) (60%) by way of initial protonation at the acetylenic centre in (4*a*). By contrast, treatment of (4*b*) with MeOH-HCl resulted in simultaneous protonation at both the allene and alkene centres of unsaturation giving rise to a 4:1 mixture of (9) and (10). The initial sites of protonation in the allene cyclopropanes were established conclusively by deuteriation studies using MeOD-DCl.

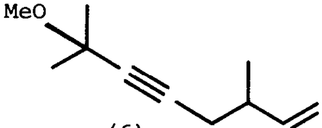
Treatment of the allene cyclopropanes (4) with potassium *t*-butoxide in dimethylsulphoxide effected their smooth isomerisation to mixtures of *Z*- and *E*- isomers of the corresponding vinylcyclopropylmethylenes.[8] Thus (4*b*) led to (11), and the isomerisation of (4*c*) gave (13). Subsequent treatment of (11) and (13) with MeOH-HCl then produced the irregular terpenoid structures (12) and (7) respectively as major products.



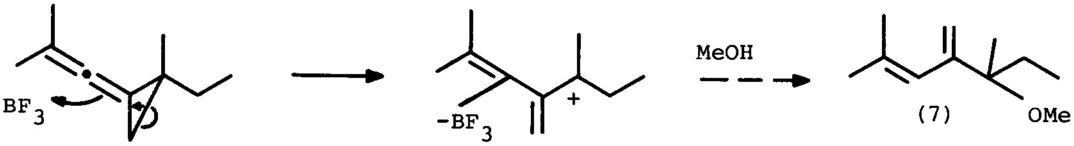
(4a)



(5)

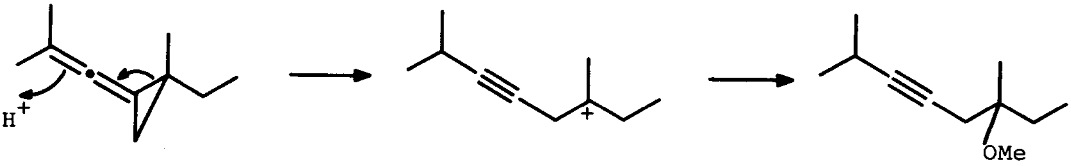


(6)

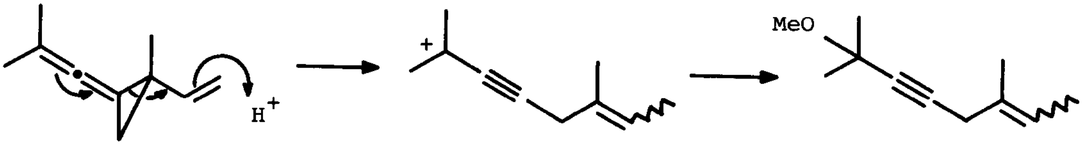


(4c) (7)

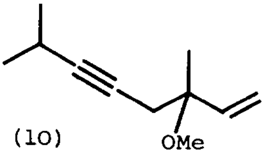
Scheme



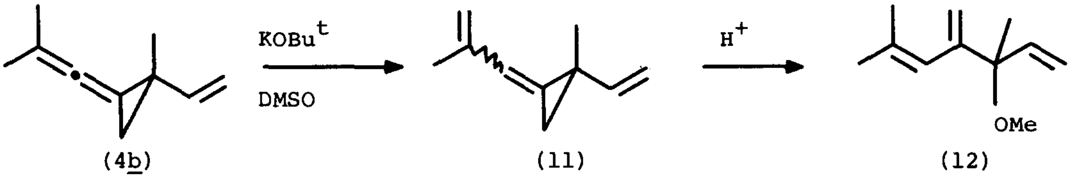
(4c) (8)

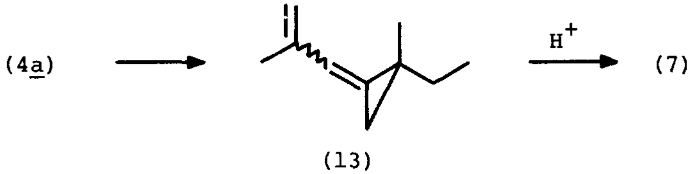


(4b) (9)



(10)





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