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MONOTERPENE SYNTHESIS VIA ALKENYLIDENECYCLOPROPANES: METAL REDUCTIONS AND PERACID OXIDATIONS

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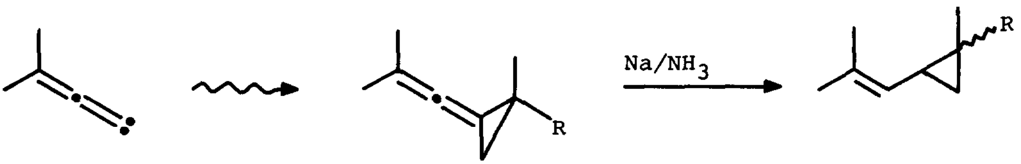
In the preceding Letter we showed that both acid and base-catalysed rearrangements of the C_{10}-alkenylidenecyclopropanes (1) and (3), prepared by the addition of 3,3-dimethylallene carbene to the corresponding alkene substrates, provided a novel approach to the synthesis of acyclic monoterpenes. A feature of the acid catalysed reactions is that they led to regular ('head-to-tail') monoterpene structures containing diverse functionality. In this companion Letter, we report the results of dissolving metal reductions and of peracid oxidations of the alkenylidenecyclopropanes (1) and (3). The studies further demonstrate the scope provided by these molecules in the synthesis of novel, functionalised and regular monoterpenes.

Treatment of the alkenylidenecyclopropane (1b) with excess sodium in liquid ammonia resulted in regiospecific reduction of the ylidenecyclopropane double bond, and led (~70%) to a 1:1 mixture of cis- and trans-



(1)

(2)

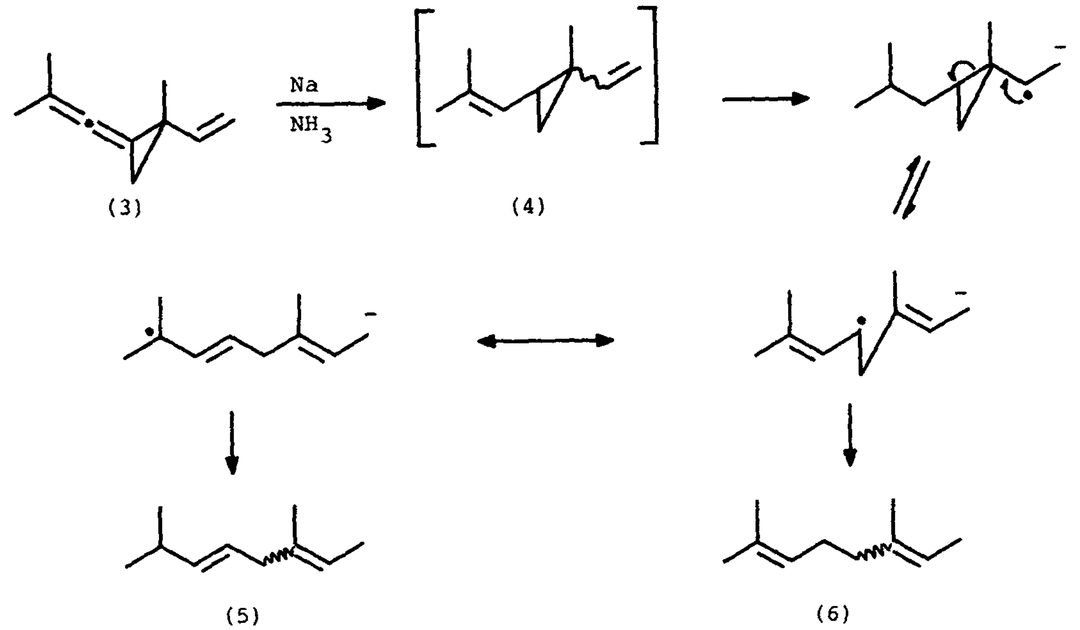
a R = $\cdot C \equiv CH$;
b R = $\cdot CH_2CH_3$.

isomers of the vinylcyclopropane (2*b*). This type of reduction is not without precedent,[1] and in a similar manner the acetylenic derivative (1*a*) gave rise to (2*a*).

By contrast, reduction of the alkenylidenecyclopropane (3), which contains a vinylcyclopropane moiety, led largely to dihydromycene (6) (50%), τ $\sim$8.45 (: CH*Me*), 8.41 (2x : CMe), 8.34 (: CMe), 7.86-8.12 (4H), 4.7-5.1m (2H) which was accompanied by small amounts ($\ngtr$ 5%) of the positional isomer (5). We envisage the formation of (5) and (6) from (3) as proceeding *via* 1,4-addition to the intermediate(4)(Scheme)[2];some support for this came from independent studies of the reduction of synthetic (4), which also led to a mixture of (5) and (6).

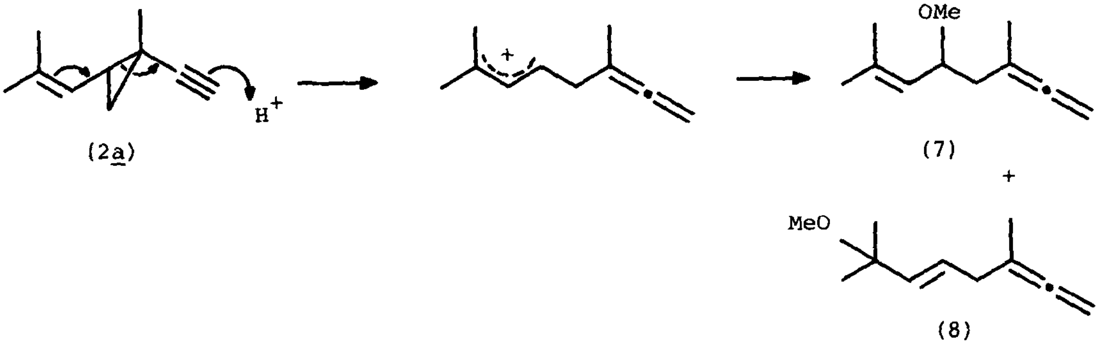
Treatment of the acetylenic cyclopropane (2*a*) with MeOH-HCl gave largely the allene (7) ($\sim$30%) ν_{max} 1955, 1675cm^{-1}, τ 8.2-8.4 (3x:CMe), 7.6-8.0 (3H), 6.82 (OMe), 6.05dt (*J* 10 and $\sim$7, C*H*OMe), 5.3-5.6 (: CH_2) 5.0d (*J* 8, : C*H*), accompanied by (8) ($\sim$10%), whereas the rearrangement of (2*b*) in MeOH-HCl led to the methyl ether (9).

Reactions between the alkenylidenecyclopropanes and *m*-chloroperbenzoic acid gave rise to mixtures of *cis*- and *trans*-isomers of the corresponding keto-esters (e.g. 10*a*) resulting from initial attack of the peracid at the terminal olefin portions of the allene moieties in (1/3).[3] Saponification of either the *cis*- or the *trans*-esters then led to mixtures of *cis*- and *trans*-isomers of the hydroxy-ketones (e.g. 10*b*). Brief treatment of these cyclopropyl ketones in methanol, with hydrochloric acid,[4] then effected their smooth rearrangement to highly oxygenated head-to-tail monoterpene carbon skeletons, e.g. (10*b*), gave a mixture of (11) (48%), ν_{max} 3460, 1710cm^{-1}, τ 8.77 (Me), 8.64 (2xMe), 7.9-8.3m (2H), 7.2-7.5 (2H), 6.9 (OMe), 4.91dd (*J*2 and 16; C*H*H), 4.84dd (*J* 2 and 10; CH*H*), 4.22dd (*J* 16 and 10; C*H*:CH_2), and its positional isomer (12) (18%).

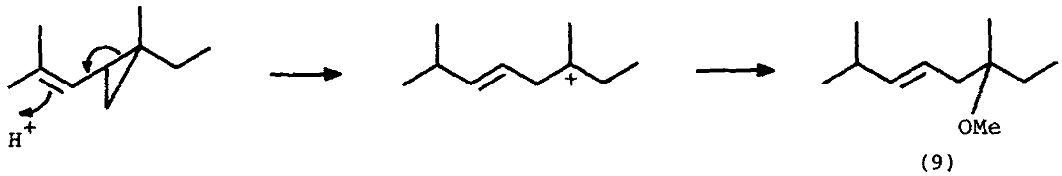


(3) (4) (5) (6)

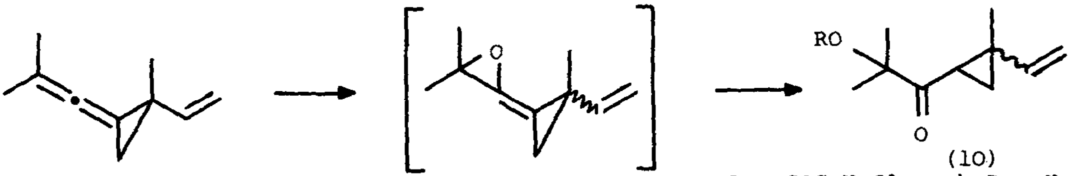
Scheme



(2a) (7) (8)

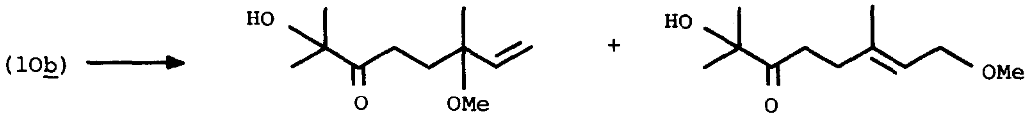


(9)



(10)

a R = COC_6H_4Cl-m; b R = H.



(11) (12)

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3. cf. J.K. Crandall, D.R. Paulson and C.A. Bunnell, Tetrahedron Letters, 5063 (1968); M. Poutsma and P.A. Ibarbia, J. Amer. Chem. Soc., 93, 440 (1971).
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