

Novel Carbanion-induced Type of Ene reaction

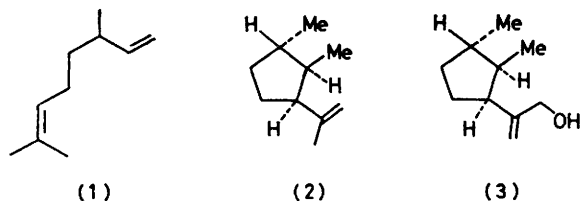
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Summary With BuⁿLi-tetramethylethylenediamine, 3,7-dimethylocta-1,6-diene is cyclised to the allylic carbanion of 1,2-dimethyl-3-isopropenyl cyclopentane.

FOLLOWING a survey of reactions of 3,7-dimethylocta-1,6-diene (**1**) *via* carbonium ion,¹ and radical² intermediates, we have examined the reaction of (**1**) with BuⁿLi which has led us to recognise an apparently novel polar equivalent of the ene reaction.

With BuⁿLi and tetramethylethylenediamine (TMEDA) (each 1 equiv.) in hexane, (**1**) gave a red-brown solution. After 12 h at 20 °C addition of D₂O gave a product, *m/e* 138 and 139, 50% ²H, with a ¹³C n.m.r. spectrum showing the presence of (**1**), but with new signals due to an isomeric alkene which was shown to be (**2**): (**1**) 17.7, 20.2, 25.0, 25.8, 36.9, 37.5, 110.0, 112.5, 124.8, and 131.1; (**2**) 15.7, 21.4, 23.4, 28.0, 33.1, 41.2, 43.1, 49.4, and 109.9 p.p.m. from Me₄Si in CDCl₃.



The nature of the isomeric alkene was established by oxygenation³ of the solution from the action of BuⁿLi-TMEDA on (**1**), and reduction (NaBH₄) of the derived hydroperoxide. This gave an alcohol, *m/e* 154 (C₁₀H₁₈O), δ 0.7 (3H, d, *J* 6 Hz), 0.98 (3H, d, *J* 5 Hz), 3.1 (1H, s), 4.0 (2H, s), and 4.84 and 5.14 (each 1H, s), which could be

hydrogenated to a dihydro-alcohol, *m/e* 156. Jones' oxidation gave an aldehyde, *m/e* 152, δ 0.62 (3H, d, *J* 6 Hz), 1.0 (3H, d, *J* 5 Hz), 5.95, 6.09 (each 1H), and 9.53 (1H, s); λ_{max} 221 nm, ε 9200, *i.e.* clearly conjugated, suggesting (**3**) as the structure of the parent alcohol.

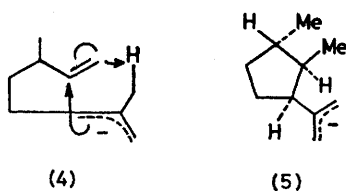
TABLE

R	% Yield of (6)	<i>m/e</i>	δ
CO ₂ Me	15	196	5.0, 4.9, 3.7, 3.9, 1.05 ^a , 0.7 ^a
CH(OH)CH:CH ₂	35	194	4.9, 4.85, 1.03 ^a , 0.7 ^a
CH ₂ C:CH	35	176	4.8, 4.7, 2.38, 1.0 ^a , 0.7 ^a
1-Hydroxycyclopentyl	22	222	4.9, 1.0 ^a , 0.7 ^a
CH(OH)Pr ¹	42	210	4.8, 0.7 ^a
COPr ¹ ^b	—	208	4.8, 1.06 ^a
CH ₂ COMe	—	194	4.75, 1.0 ^a , 0.7 ^a

^a Doublet. ^b From oxidation of [**6**; R = CH(OH)Pr¹]. ^c From hydration (HgSO₄) of (**6**; R = CH₂C:CH).

Birch reduction of the alcohol gave an alkene; *m/e* 138 (C₁₀H₁₈), δ 0.91 (3H, d, *J* 6 Hz), 1.0 (3H, d, *J* 5 Hz), 1.71 (3H, s), and 4.67 and 4.78 (each 1H, s). This was shown to be identical (g.l.c., n.m.r.) with the major product of ene cyclisation of (**1**), which we have shown^{1a} to have the stereochemistry as in (**2**). Further, the alkene (**2**) from ene cyclisation of (**1**), with BuⁿLi-TMEDA in hexane followed by O₂ and NaBH₄ gave an alcohol identical (g.l.c., n.m.r.) with (**3**).

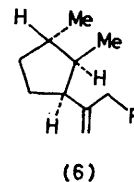
The alcohol (**3**) is most logically considered to arise *via* oxygenation of an allylic anion (**5**) which we suggest derives from (**1**) *via* the allylic anion (**4**).



Hydrogen transfer as in (4), *i.e.* a low temperature polar equivalent of the ene cyclisation, offers an attractive possible route to (4), and there is precedent⁴ for reaction of a carbanion with a simple alkene. However, the known⁵ interconversion of carbanions may offer an alternative, *i.e.* by transfer of Li rather than H followed by inter- or intramolecular hydrogen exchange.

The diene (1) is obtained by pyrolysis of pinane followed by fractionation, and, in order to substantiate our conclusion above, it was necessary to exclude the possibility that (3) might arise from (2) formed during pinane pyrolysis and present in our sample. However, the following evidence indicates clearly that this is not the case. The yield, 30%, of distilled alcohol (3), b.p. 54–60 °C at 0.1

mmHg, could be reproduced by recycling the unchanged recovered (1) in a second reaction with BuⁿLi and oxygen. A sample of (1) prepared by dehydration (toluene-*p*-sulfonic acid, benzene, azeotrope) of a pure sample of 3,7-dimethyloct-1-en-7-ol gave the same yield of (3) on treatment with BuⁿLi-O₂. Further, reaction of the carbanion from (1) with a range of electrophilic addends (CO₂, CHO-CH₂CHMe₂, CHOCH:CH₂, BrCH₂C:CH, cyclopentanone, or CHOCHMe₂) gave yields of products (6), *cf.* Table, similar to those obtained under similar conditions from limonene.³



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