Novel Carbanion-induced Type of Ene reaction

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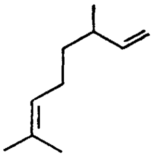
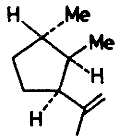
Summary With Bu^{n}Li–tetramethylethylenediamine, 3,7-dimethylocta-1,6-diene is cyclised to the allylic carbanion of 1,2-dimethyl-3-isopropenyl cyclopentane.

Following a survey of reactions of 3,7-dimethylocta-1,6-diene (**1**) *via* carbonium ion,[1] and radical[2] intermediates, we have examined the reaction of (**1**) with Bu^{n}Li which has led us to recognise an apparently novel polar equivalent of the ene reaction.

With Bu^{n}Li and tetramethylethylenediamine (TMEDA) (each 1 equiv.) in hexane, (**1**) gave a red-brown solution. After 12 h at 20 °C addition of D_2O gave a product, *m/e* 138 and 139, 50% ^{2}H, with a ^{13}C 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 Me_4Si in $CDCl_3$.



(**1**)



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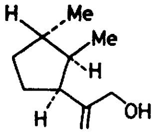


(**3**)

The nature of the isomeric alkene was established by oxygenation[3] of the solution from the action of Bu^{n}Li–TMEDA on (**1**), and reduction ($NaBH_4$) of the derived hydroperoxide. This gave an alcohol, *m/e* 154 ($C_{10}H_{18}O$), 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.

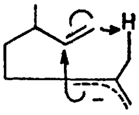
Table

R	% Yield of (**6**)	*m/e*	δ
CO_2Me	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_2C:CH	35	176	4·8, 4·7, 2·38, 1·0,[a], 0·7[a]
1-Hydroxycyclo-pentyl	22	222	4·9, 1·0[a], 0·7[a]
CH(OH)Pr^i	42	210	4·8, 0·7[a]
COPr^i [b]	—	208	4·8, 1·06[a]
CH_2COMe	—	194	4·75, 1·0[a], 0·7[a]

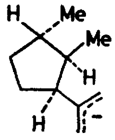
[a] Doublet. [b] From oxidation of [**6**; R = CH(OH)Pr^i]. [c] From hydration ($HgSO_4$) of (**6**; R = CH_2C:CH).

Birch reduction of the alcohol gave an alkene; *m/e* 138 ($C_{10}H_{18}$), 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 Bu^{n}Li–TMEDA in hexane followed by O_2 and $NaBH_4$ 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**).



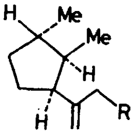
(4)



(5)

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 precedent[4] for reaction of a carbanion with a simple alkene. However, the known[5] 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 Bu^{n}Li and oxygen. A sample of (**1**) prepared by dehydration (toluene-*p*-sulphonic acid, benzene, azeotrope) of a pure sample of 3,7-dimethyloct-1-en-7-ol gave the same yield of (**3**) on treatment with Bu^{n}Li–O_2. Further, reaction of the carbanion from (**1**) with a range of electrophilic addends (CO_2, $CHOCH_2CHMe_2$, $CHOCH{:}CH_2$, $BrCH_2C{\vdots}CH$, cyclopentanone, or $CHOCHMe_2$) gave yields of products (**6**), *cf.* Table, similar to those obtained under similar conditions from limonene.[3]



(6)

We thank Bush, Boake, Allen for gifts of materials.

(*Received*, 8*th August* 1977; *Com.* 833.)

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