

The Pyrolysis of Nopinol

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Summary The pyrolysis of nopinol gives the hydroxy-olefin (6) and the aldehyde (5) *via* abnormal C-5-C-6, C-1-C-7 cleavage of the pinane cyclobutane ring, the mode of formation of the aldehyde being established by deuterium labelling experiments.

ON pyrolysis pinane derivatives (1) give¹ primary products (2) and (3) resulting from the cleavage of the C-1-C-6 bond or the C-1-C-6 and C-5-C-7 bonds of the pinane cyclobutane ring. We now report the pyrolysis of nopinol (4) which, in addition to products of the normal C-1-C-6,

C-5-C-7 cleavage, gives primary and secondary products *via* C-5-C-6, C-1-C-7 cleavage.

Pyrolysis of nopinol (4) on passage through a stainless-steel tube at 580° (contact time *ca* 0.1 s) gave a crude product shown (g.l.c.) to consist of nine major components. These were identified by i.r., u.v., n.m.r., and mass spectra as aldehyde (5) (6%), the isomeric hydroxy-dienes (6) (10%) and (7) (24%), the epimeric alcohols (8) (6%) and (9) (7%), and the four inseparable cyclopentanols (10) (20%).

The structure of the hydroxy-olefin (6) followed from a consideration of its i.r. spectrum, ν_{\max} 3370, 1679, 992, and 847 cm^{-1} , and its n.m.r. spectrum (Table) which showed the

4-H as a sextuplet, coupled both to the 3-H and the 5-methylene function, and the 2,2-dimethyl signals as doublets

The structure of the extensively rearranged aldehyde (5) was deduced as follows. The 6,6-dimethyl signals were

N.m.r. data^a for aldehyde (5) and hydroxy-olefin (6)

Functional group	Position of signals(s) p.p.m.	Nature of signal	Apparent coupling constants (Hz)
(5) 4-Me	0.95	doublet	$J(\text{CH}_3, 4\text{-H})$ 6.5 ^b
6,6-Me ₂	1.58, 1.67	doublets	$J(\text{CH}_3, 5\text{-H})$ 1.3 ^b
4-H	2.35 ^b		
2,2-H ₂	2.40 ^b		
5-H	4.85	multiplet	$J(5\text{-H}, 4\text{-H})$ 9.5 ^b $J(5\text{-H}; 6,6\text{-Me}_2)$ 1.3 ^b
(6) -CHO	9.75	triplet	$J(\text{CHO}; 2,2\text{-H}_2)$ 1.6 ^b
2,2-Me ₂	1.66, 1.71	doublets	$J(\text{CH}_3, 3\text{-H})$ 1.3
4-H	4.35	sextet	$J(4\text{-H}, 3\text{-H})$ 9 ^b $J(4\text{-H}, 5\text{-H}_a) = J(4\text{-H}, 5\text{-H}_b)$ = 6.5
3-H; 8-H ₂	4.78—5.32	multiplet	
7-H	5.87	multiplet	($W_{h/2}$ 41)

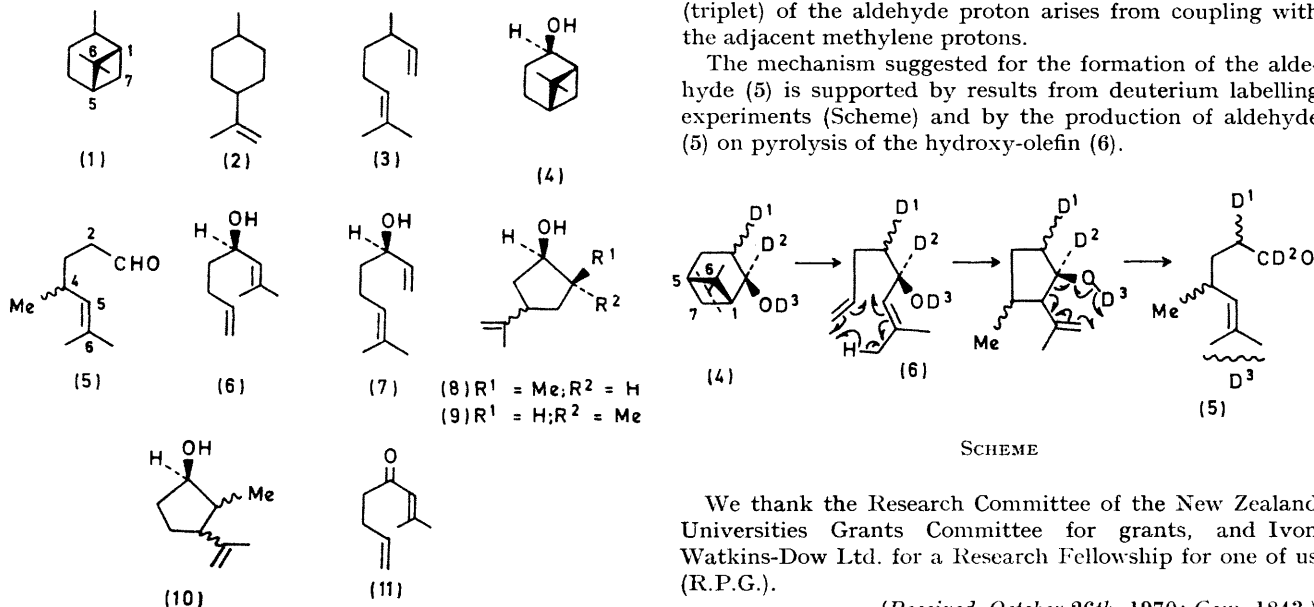
^a Determined at 60 MHz for 10% solutions (w/v) in CDCl₃ with CHCl₃ and Me₄Si as internal standards.

^b Established by double irradiation experiments.

with coupling to the 3-H. Oxidation of the hydroxy-olefin (6) with activated manganese dioxide gave the conjugated ketone (11), λ_{max} 237 nm (ϵ 5000).

doublets coupled to the 5-H. This 5-H is additionally coupled with the 4-H, which is itself coupled with the 4-methyl. These data point to the location of the 4-methyl adjacent to the C:Me₂ function. The multiplicity (triplet) of the aldehyde proton arises from coupling with the adjacent methylene protons.

The mechanism suggested for the formation of the aldehyde (5) is supported by results from deuterium labelling experiments (Scheme) and by the production of aldehyde (5) on pyrolysis of the hydroxy-olefin (6).



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¹ L. Steinbuch and J. Walt, *J. Org. Chem.*, 1965, **30**, 646; L. A. Goldblatt and S. Palkin, *J. Amer. Chem. Soc.*, 1941, **63**, 3517 and references cited therein.