

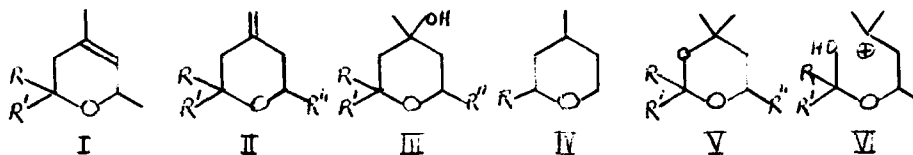
THE REACTION OF 3-ALKENE-1-OLS WITH ALDEHYDES:
A SYNTHESIS OF (+)-CIS-2-(2'-METHYL-1'-PROPENYL)-4-METHYLTETRAHYDROPYRAN

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The acid-catalysed interaction of 2-methyl-1-pentene-4-ol with a carbonyl compound ($RR'CO$) was believed¹ to yield the pyran (I) by way of the pyranol (III; $R'' = Me$) although in the case of acetaldehyde, (II; $R = H, R' = R'' = CH_3$) was also thought to be present. The isomeric pyrans were however not separated and no supporting physical evidence was given. In the reaction of benzaldehyde the pyran (I; $R = H, R' = Ph$) was described whereas others² formulated the product as the alternative endocyclic olefin. In the present work the reaction of 2-methyl-1-pentene-4-ol with benzaldehyde has been shown to yield two major stereoisomeric pyranols and two others in small amount. Dehydration with potassium bisulphate gave essentially two products, the main one being the exocyclic olefin (II; $R = H, R' = Ph, R'' = Me$) presumably in the chair conformation by loss of an equatorial hydroxyl group and the other, the endocyclic olefin, in the twist conformation by loss of an axial hydroxyl group from the respective pyranol. It has not been possible as yet to assign the double bond to one position in the endocyclic olefin.



The pyran (II; $R = H, R' = Ph, R'' = CH_3$) had $\nu_{(max)}$ (film) at 700, 760, 895, 1070, 1455, 1500, 3032, 3068 cm^{-1} , parent ion m/e 188 and τ ($CDCl_3$) 2.6-2.9 (5H,m) 5.2-5.3 (2H,o), 5.65-5.70, 5.80, 5.85 (1H,d), 6.25-6.75, (1H,c), 7.40-8.25 (4H,c) and 8.65-8.80 (3H,d).

The preceding observations have been utilised in a synthesis of (+)-cis and (+)-trans "dihydroroseoxides" and of (+)-cis-"roseoxide". Most syntheses of the latter have involved acyclic intermediates³ or the introduction of the 2-isobutenyl group into a pyran ring⁴ and no route for developing a 4-methyl group has previously

been described.

3-Methylbutanal and 2-methyl-1-butene-4-ol interacted under acidic conditions to give the pyran (II; $R = R'' = H$, $R' = C_4H_9$) in greater proportion via the intermediate pyranols (III; $R = R'' = H$, $R' = C_4H_9$). Heterogeneous or homogeneous hydrogenation according to the conditions in Table 1, yielded a mixture of the cis and trans forms of (IV; $R = C_4H_9$), spectroscopically and chromatographically identical with the products of hydrogenation of cis and trans-2-(2'-methyl-1'-propenyl)-4-methyltetrahydropyran.

Table 1.

Catalyst	% composition of product	
	cis	trans
Pd/C	83	17
Pt	53	47
$SnCl_2/H_2PtCl_6$ (ref.5)	90	10
$RhCl(PPh_3)_3$ (ref.6)	39	61

Similarly the reaction of 3-methyl-2-butene-1-al and 2-methyl-1-butene-4-ol followed by dehydration of the pyranols (III; $R = R'' = H$, $R' = C_4H_9$) yielded the pyran (II; $R = R'' = H$, $R' = C_4H_9$) as the major product. Homogeneous hydrogenation with $SnCl_2/H_2PtCl_6$ yielded (IV; $R = C_4H_9$), (+)-cis-2-(2'-methyl-1'-propenyl)-4-methyltetrahydropyran which was spectroscopically and chromatographically identical with the cis natural product, together with less than 9% of the trans isomer. A small proportion of (IV; $R = C_4H_9$) was also formed.

The reactions in this series are believed to proceed through cyclisation following loss of water from an oxonium ion (via the protonated hemiacetal from the aldehyde and the alcohol) rather than through the carbonium ion (VI) since in this case the presence of the dioxan (V; $R'' = Me$) might be expected. None was however found.

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