The Rearrangement of 9-Hydroxymethyloctalin

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IN the course of studies on the triterpenoid senegenin it was shown[1] that this substance (part-structure I) was an artifact produced from its precursor, presenegenin (part-structure II), by the action of the alcoholic hydrochloric acid used to cleave the glycosidic linkages in the original saponin. Senegenin was accompanied by the reverse-Prins product, polygalic acid[2] (senegnic acid[3]), (part-structure III).

The solvolysis of the simpler parent system (IV; R = H) had been studied earlier,[4] and the benzenesulphonate ester shown to give, in hot

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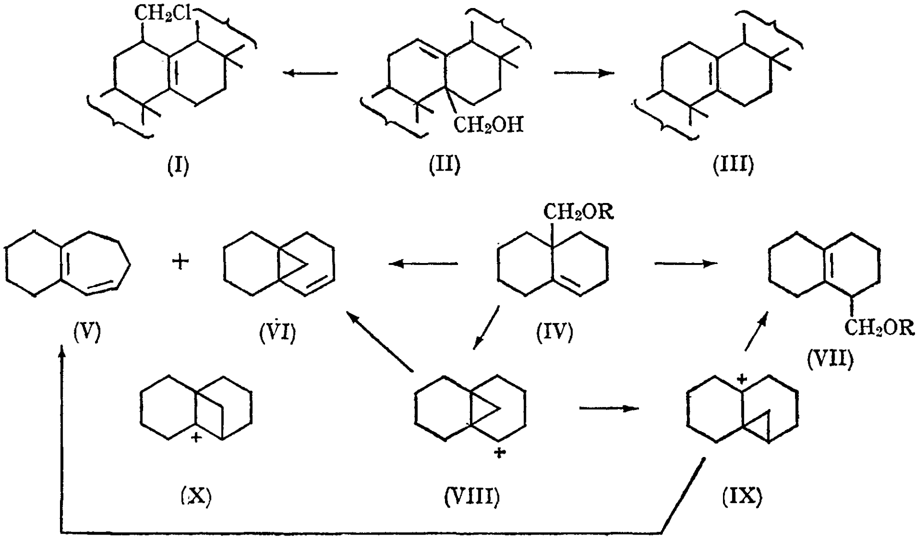
[1] J. J. Dugan and P. de Mayo, *Canad. J. Chem.*, 1965, **43**, 2033.

[2] J. J. Dugan, P. de Mayo, and A. N. Starratt, *Tetrahedron Letters*, 1964, 2657.

[3] S. W. Pelletier, N. Adityachaundhury, M. Tomasz, J. J. Reynolds, and R. Mechoulam, *Tetrahedron Letters*, 1964, 3065.

[4] J. W. Rowe, A. Melera, D. Arigoni, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, 1957, **40**, 1.

pyridine, a hydrocarbon mixture including (V) and (VI). Treatment of (IV) with alcoholic hydrochloric acid, under conditions suitable for the conversion of (II) into (I), did not give any halogen- or oxygen-containing products. On the other hand the benzenesulphonate ester,[4] when solvolysed in acetic acid (90°; 3 hours), was converted into (VII; R = Ac) in high yield.



The substance (VII; R = Ac) is unsaturated but shows no signals for vinyl protons in the n.m.r. spectrum. The alcoholic methylene group is found near τ 6·0, and the splitting indicates the presence of at least one proton at the point of attachment of this methylene group to the nucleus. The corresponding alcohol (VII; R = H) gave the aldehyde (aldehydic proton, doublet τ 0·5, J = 3 c./sec.) which with alkali gave a conjugated aldehyde (λ_{max} 247 mμ).

The rearrangement is that of one allylcarbinyl cation to another, and may be conceived as proceeding through the secondary cyclopropylcarbinyl cation (VIII) and the similar, but tertiary, cation (IX), or the bicyclobutonium ion when including contributions from (X).[5] The formation of (V) and (VI) under the conditions used is unexceptional, but (V) is very probably not formed by a neopentyl rearrangement as originally suggested[4,6] but by collapse of (IX). It is interesting that the cation formed first does not, apparently, collapse to the original structure: in the case of presenegenin no chloride corresponding to (II) can be detected during the formation of (I), nor does any (IV; R = Ac) accompany (VII; R = Ac).

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[5] W. G. Dauben and L. E. Friedrich, *Tetrahedron Letters*, 1964, 2675; and references there cited.

[6] The solvolysis of the decalyl derivative, however, proceeds in this manner *cf.* W. G. Dauben and J. B. Rogan, *J. Amer. Chem. Soc.*, 1957, **79**, 5002.