

## **<sup>13</sup>C Nuclear Magnetic Resonance Study of the Formation of a Cyclopentyl Cation from Thujan-3-ol**

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*Summary* In solution in  $\text{SbF}_5\text{-HSO}_3\text{F-SO}_2$  at  $-50^\circ$ , 4 $\alpha$ -H-thujan-3 $\beta$ -ol forms a cation with the *p*-menthane structure; in the absence of  $\text{SbF}_5$ , this ion decomposes slowly to yield a 2,3-dimethyl-1-propylcyclopentyl cation.

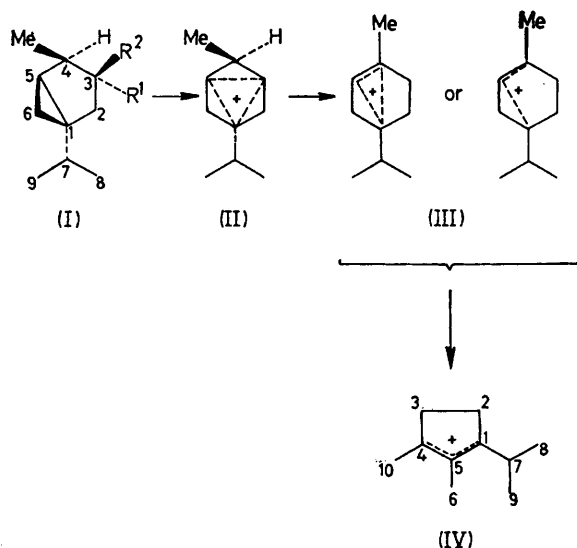
KINETIC and product studies of the acetolysis of the toluene-*p*-sulphonates of 4 $\alpha$ -H-thujan-3 $\alpha$ -ol (isothujol; I;  $\text{R}^1 = \text{OH}$ ,  $\text{R}^2 = \text{H}$ ) and 4 $\alpha$ -H-thujan-3 $\beta$ -ol (neoisothujol; I;  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{OH}$ ) have led Norin<sup>1</sup> to suggest that the results may

TABLE

		<sup>13</sup> C Chemical shifts <sup>a</sup>									
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
4 $\alpha$ -H-thujan-3 $\alpha$ -ol <sup>4</sup>	..	30.1	37.0	77.0	42.7	26.7	11.0	33.1	19.7	19.7	15.9
4 $\alpha$ -H-thujan-3 $\beta$ -ol <sup>4</sup>	..	33.1	38.6	74.4	40.4	28.8	13.3	32.8	19.9	19.9	12.1
(III)	..	260.7	45.2	22.5	158.3	219.8	12.2	68.4	(16.4	25.7.)	33.7
(IV)	..	247.0	43.9	39.2	238.9	150.6	7.3	34.7	17.8	17.8	21.6

<sup>a</sup> $\delta$  values downfield from Me<sub>4</sub>Si.

be interpreted in terms of a trishomocyclopropenyl cation (II) similar to that proposed by Winstein<sup>2</sup> from a study of the bicyclo[3,1,0]hexan-3-yl toluene-*p*-sulphonates. Similar results were obtained from the 4 $\beta$ -H-thujan-3-yl esters. In concentrated sulphuric acid, however, all four thujanyl esters gave the same cation, which on the basis of <sup>1</sup>H n.m.r. studies has been assigned the structure (IV).<sup>3</sup>



Numbering of (IV) follows that of (I)

We have investigated the mechanism of formation of (IV) by a <sup>13</sup>C n.m.r. study of the ions formed from the 4 $\alpha$ -H-thujan-3-ols at low temperatures. At -50° in SO<sub>2</sub>-SbF<sub>5</sub>-

HSO<sub>3</sub>F, both alcohols gave an ion whose spectrum is consistent with either of the ions (III), the charge being spread over C-1, C-4, and C-5. This ion remained stable, in the absence of SO<sub>2</sub>, at room temperature. In SO<sub>2</sub>-HSO<sub>3</sub>F, however, 4 $\alpha$ -H-thujan-3 $\beta$ -ol gives the spectrum of a mixture of (III) and (IV). (They are not interconverting at a detectable rate). On removal of SO<sub>2</sub>, followed by warming the solution to room temperature, the spectrum shows only the presence of (IV). Results are given in the Table.

The assignments of the spectra of the thujan-3-ols have been given elsewhere.<sup>4</sup> Ion spectra are assigned by comparison, with the peaks carrying a charge shifted downfield. In each case, where the carbon atoms carrying the charge show similar multiplicities in the off-resonance spectra, the peak with the largest downfield shift is assigned to the carbon atom best able to stabilise the charge.

We suggest that our data are consistent with the formation of (IV) from (I) via the route shown. Although we have not detected (II) spectroscopically, formation of racemic 4 $\alpha$ -H-thujan-3 $\beta$ -yl acetate by acetolysis of its optically active toluene-*p*-sulphonate ester requires the intervention of (II), since reaction of  $\alpha$ -thujene in acid, believed to be via (III)<sup>5</sup> does not yield derivatives of 4 $\alpha$ -H-thujan-3 $\beta$ -ol. Conversion of (II) into (III) would be expected to proceed readily via a 1,2-hydride shift, since the unsubstituted version of (III) is formed in preference to the unsubstituted version of (II) in hydration of bicyclo[3,1,0]hex-2-ene,<sup>6</sup> and the methyl group will in any case facilitate this shift. The ion (III) can be stabilised by SbF<sub>5</sub>, but in the absence of this stabilisation will open the C-1-C-6 bond to yield (IV), a reaction well known in the thujanyl system.<sup>7</sup>

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<sup>1</sup> T. Norin, *Tetrahedron Letters*, 1964, 37.

<sup>2</sup> S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, 1959, **81**, 6523.

<sup>3</sup> S. Forsén and T. Norin, *Tetrahedron Letters*, 1966, 4183.

<sup>4</sup> R. J. Abraham, C. M. Holden, P. Loftus, and D. Whittaker, *Org. Magnetic Resonance*, 1974, in the press.

<sup>5</sup> M. A. Cooper, C. M. Holden, P. Loftus, and D. Whittaker, *J.C.S. Perkin II*, 1973, 665.

<sup>6</sup> P. K. Freeman, M. F. Grostic and F. A. Raymond, *J. Org. Chem.*, 1965, **30**, 771.

<sup>7</sup> D. Whittaker and D. V. Banthorpe, *Chem. Reviews*, 1972, **72**, 305.