

REARRANGEMENTS IN BICYCLO[3.1.0]HEXYL SYSTEMS

THE STABLE CARBONIUM ION IN SULPHURIC ACID SOLUTIONS OF THUJYL p-TOLUENESULPHONATES

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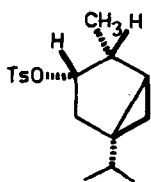
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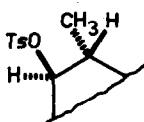
(Received 16 June 1966)

In view of the recent work by Winstein et al.<sup>1</sup> on the trishomocyclopropenyl carbonium ion and by Roberts and co-workers<sup>2</sup> on the cyclobutonium ion, the chemistry of carbonium ions derived from bicyclo[3.1.0]hexyl systems has attracted special interest. During the course of a current investigation<sup>3</sup> concerning the nature of intermediate carbonium ions derived from substituted bicyclo[3.1.0]hexyl derivatives of thujane type we have studied the cationic species generated by dissolving thujyl p-toluenesulphonates in concentrated sulphuric acid.

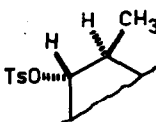
The solutions of all four epimeric thujyl p-toluenesulphonates (I-IV) in concentrated sulphuric acid (96 %) became slightly yellow. Surprisingly, the spectral data of the four solutions were identical. The UV spectrum of such a



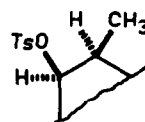
I (-)-Thujyl



II (-)-Neothujyl



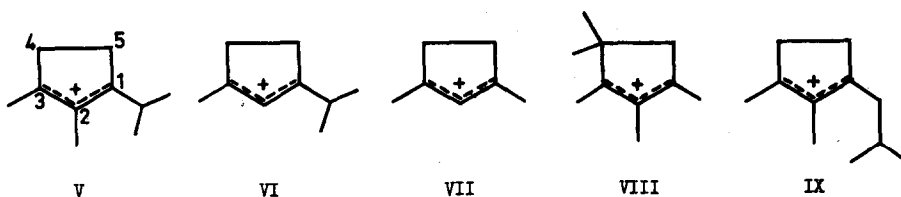
III (+)-Isothujyl



IV (+)-Neoisothujyl

solution exhibits a maximum at 292 m $\mu$  with strong absorption ( $\log \epsilon = 4.20$ ). The NMR spectrum of the solution is shown in Fig. 1. If the solution was kept at room temperature for 24 h under nitrogen atmosphere its NMR spectrum did not change. Similarly, no spectral changes were observed after heating the sample at 100° for 1 hour.

The spectral data of these sulphuric acid solutions show that the thujyl p-toluenesulphonates were transformed quantitatively into a single cationic species. The structural assignment of this cation (V) is based on a comparison of its spectral data with those of various aliphatic alkenyl cations recently studied by Deno *et al.*<sup>4</sup>.



The UV spectrum of cation (V) agrees very well with those of a tri-substituted cyclopentenyl cation<sup>5,6</sup> (Table I). The NMR spectrum of the cation is also in very good agreement with the assigned structure. The doublet at 1.38 ppm ( $J$  6.5 cps) must be due to the methyl protons of the isopropyl group. Cf. the corresponding signal of cation (VI)<sup>7</sup> which has its resonance position at 1.43 ppm with a coupling constant of 6.6 cps (Table I). The methine proton of the isopropyl group of cation (V) resonates at about 3.4 ppm and is thus partly overlapped by the slightly broadened band assigned to the C(4)- and C(5)-methylene groups. The integrated area of this signal group corresponds to five protons. In a decoupling experiment an irradiation at this frequency caused a collapse of the isopropyl doublet into a singlet. The frequency difference between irradiation and observed frequencies for optimum decoupling was 130 cps.

The slightly broader band at 2.91 ppm and the sharp band at 2.19 ppm, both with integrated areas corresponding to three protons, are assigned to the C(3)- and C(2)-methyl groups, respectively.

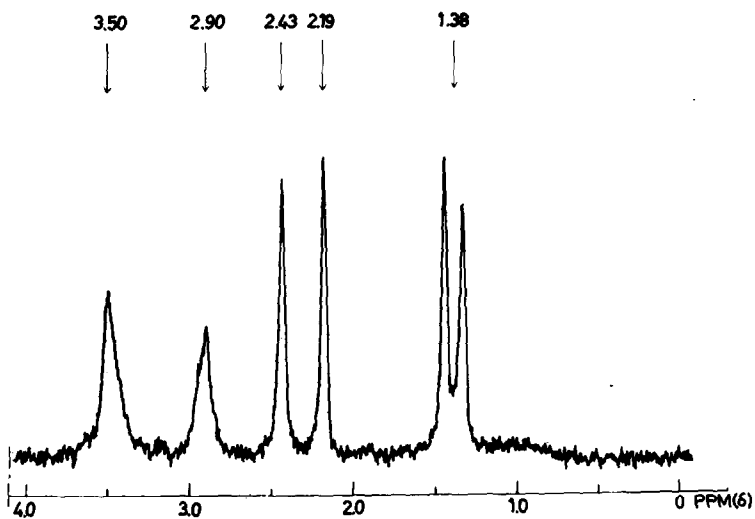


Fig. 1. NMR spectrum of thujyl p-toluenesulphonate in concentrated sulphuric acid. Shifts are in ppm from tetramethylsilane.

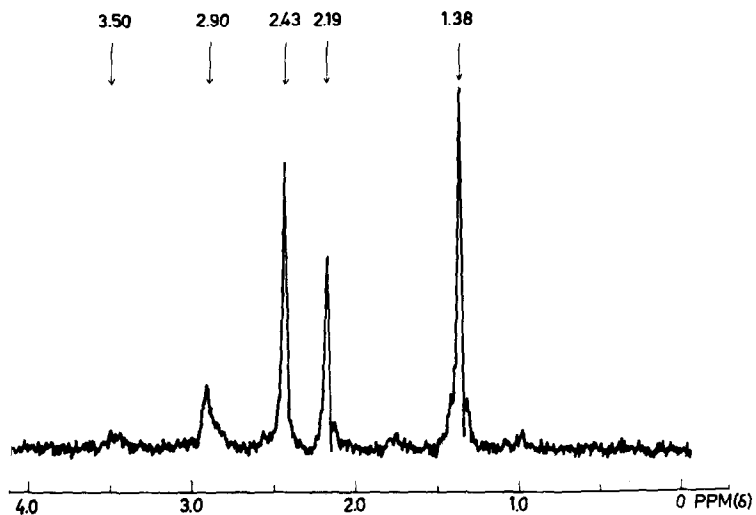
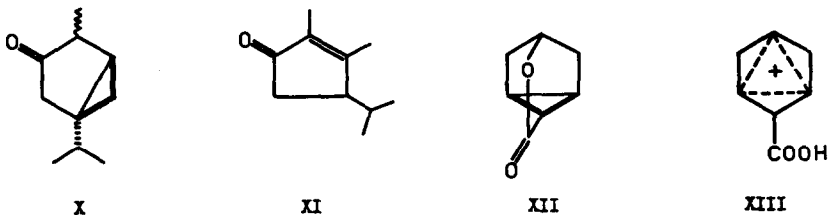


Fig. 2. NMR spectrum of thujyl p-toluenesulphonate in concentrated deuteriosulphuric acid. The spectrum is recorded after 15 minutes at 100°.

The sharp signal at 2.43 ppm is due to the methyl group of p-toluene-sulphonic acid. The signals due to the aromatic protons of the acid are not shown in Fig. 1. They appear as an AB-quartet centered at 7.60 ppm.

The structural assignment of cation (V) is supported by data from spectra taken in concentrated (96 %) deuteriosulphuric acid. At 100° the intensity of the band at 3.50 ppm due to the C(4)- and C(5)-methylene protons and the isopropyl methine proton rapidly decreased due to hydrogen-deuterium exchange. Parallel to this the isopropyl doublet became a singlet. A much slower exchange rate was observed on the methyl carbons at C(2)- and C(3)-positions. Fig. 2 shows the spectrum after about 15 minutes at 100°. These observations agree with those reported by Deno *et al.*<sup>8</sup> for similar cations (e.g. VI and VII).

If the NMR spectrum of a deuteriosulphuric acid solution of a thujyl p-toluenesulphonate is recorded at room temperature immediately after the preparation of the solution, the signal due to the methylprotons of the isopropyl group is not a doublet but a three line signal. The intensity ratio of the bands was about 1:2:1. This three line pattern did not change even after several hours at room temperature. The obvious explanation for this pattern is that, during some step in the transformation of a thujyl p-toluenesulphonate to cation (V) the methine hydrogen of the isopropyl group is partly (50 %) replaced by deuterium.



The mechanism for the formation of cation (V) is probably rather complex. It is interesting to note that this reaction from a mechanistic point of view might be analogous to that of the acid treatment of thujone (X) to give isothujone (XI)<sup>9</sup>. The extensive rearrangements which take place with the thujane derivatives contrasts to the behaviour of lactone (XII) studied by Sauers<sup>10</sup>. The structure of this compound was assigned on the bases of its NMR spectrum taken in a solution of concentrated sulphuric acid. The structure of the cationic species of the solution was proposed to be of the trishomocyclopropenyl type (XIII).

Table I. Spectral data of some cyclopentenyl cations in solutions of concentrated sulphuric acid

Compound	UV data		NMR data *							Ref.
	max m $\mu$	log $\epsilon$	H on C(2)	H on C(4) and C(5)	CH <sub>3</sub> on C(3) and C(1) when present	CH <sub>3</sub> on C(2)	CH <sub>3</sub> of iso- propyl	CH <sub>3</sub> on C(4) and C(5)		
V	292	4.20		3.50	2.90	2.19	1.38 (J 6.5) cps		This work	
VI	280	4.03	7.68	3.54	2.90		1.43 (J 6.6) cps			
VII	275	4.04	7.64	3.55	2.98				7	
VIII	299	(4.6)**		3.30	2.87 2.78	2.15		1.39		
IX	-	-		3.50	2.90	2.15	1.04 (J 6.5) cps ***		6	

\* ) Band positions in ppm downfield from tetramethylsilane. \*\* ) The sample not homogeneous.

\*\*\* ) CH<sub>3</sub> of isobutyl group.

Experimental:

The NMR spectra were recorded on a Varian A-60 instrument. The positions of the NMR bands were calibrated by reference to the methyl signal of p-toluenesulphonic acid (internal reference). The chemical shifts are expressed as the difference in ppm relative to tetramethylsilane (TMS) using a value of 2.43 ppm for the internal reference. This value is based on the measured difference of 2.43 ppm between the resonance positions of the methyl protons of p-toluenesulphonic acid and the TMS signal in a chloroform solution.

The alkenyl cation was generated by adding the crystalline thujyl p-toluenesulphonate to cold (about 0°) concentrated (96 %) sulphuric acid (e.g. 50 mg sample in 0.5 ml H<sub>2</sub>SO<sub>4</sub>). A homogeneous solution was obtained when the temperature was raised to room temperature (about 25°) with continuous shaking.

## REFERENCES

1. S. Winstein, P. Bruck, P. Radlick and R. Baker, J. Am. Chem. Soc. 86 (1964) 1867 and previous references cited therein.
2. M.S. Silver, M.C. Caserio, H.E. Rice and J.D. Roberts, J. Am. Chem. Soc. 83 (1961) 3671.
3. T. Norin, Tetrahedron Letters 1964, 37.
4. N.C. Deno, D.B. Boyd, J.D. Hodge, C.U. Pittman and J.O. Turner, J. Am. Chem. Soc. 86 (1964) 1745 and previous papers in the same series.
5. N.C. Deno, J. Bollinger, N. Friedman, K. Hafer, J.D. Hodge and J.J. Houser, J. Am. Chem. Soc. 85 (1963) 2998.
6. N.C. Deno and J.J. Houser, J. Am. Chem. Soc. 86 (1964) 1741.
7. N.C. Deno, H.G. Richey, N. Friedman, J.D. Hodge, J.J. Houser and C.U. Pittman, J. Am. Chem. Soc. 85 (1963) 2991.
8. N.C. Deno, N. Friedman, J.D. Hodge and J.J. Houser, J. Am. Chem. Soc. 85 (1963) 2295.
9. For references see J.L. Simonsen, *The Terpenes*, Vol. II, second edition, Cambridge 1949, p. 39.
10. R.R. Sauers, Tetrahedron Letters 1962, 1015.