Rearrangements of the Thujan-3-yl Cation [1]

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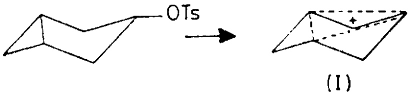
Heterolysis of the C–O bond of the thujan-3-ols or their derivatives can give rise to either an undelocalised cation or a trishomocyclopropyl cation, depending on the alignment of the leaving group. In either case, a 1,2-hydride shift converts the ion into the bishomocyclopropyl cation. The reaction also yields iridane derivatives, formed by a different mechanism from that yielding the 2,3-dimethyl-1-(1-methylethyl)cyclopentyl cation in SO_2–HSO_3F at −50°.

INVESTIGATION of the acetolyses of the *cis*- and *trans*-bicyclo[3.1.0]hexan-3-yl toluene-*p*-sulphonates led Winstein [2] to suggest that reaction of the *cis*-isomer proceeded through the trishomocyclopropyl cation (I). This conclusion was based on kinetic and product evidence, and on the pattern of scrambling of a deuterium label on C-3.



(I)

Subsequent work [3] showed that substitution of (I) by a methyl group at C-1 or -5 increased its reactivity at that carbon atom but that phenyl substitution [4] of the substrate at C-1 or -5 gave product mixtures which were not consistent with reaction *via* a phenyl substituted version of (I).

The work of Norin [5] on the toluene-*p*-sulphonates of the thujols (II) suggested that the *cis*-isomers may react *via* trishomocyclopropyl intermediates. Thus, acetolysis of the toluene-*p*-sulphonates of 4α*H*- (IIb) and 4β*H*-thujan-3α-ol (IId) proceeds more rapidly than that of 4α*H*- (IIa) and 4β*H*-thujan-3β-ol (IIc). The optically active toluene-*p*-sulphonates of (IIb and d) yield on acetolysis the racemic acetates of these alcohols, while acetolysis of the toluene-*p*-sulphonates of (IIa and c) yields mixtures of products which were not identified. In contrast to Winstein's work products of reaction at C-1 were not observed.

In concentrated sulphuric acid, all four alcohols gave

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[1] Preliminary communication, C. M. Holden and D. Whittaker, *J.C.S. Chem. Comm.*, 1974, 353.

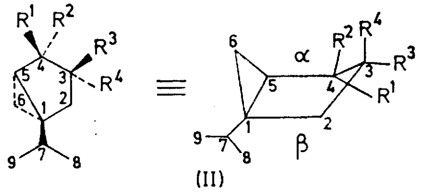
[2] S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, 1959, **81**, 6523.

[3] S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron*, 1966, Suppl. 8, Part II, 6211.

[4] E. J. Covey and H. Uda, *J. Amer. Chem. Soc.*, 1963, **85**, 1788.

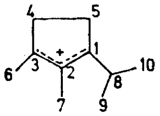
[5] T. Norin, *Tetrahedron Letters*, 1964, 37.

the same cation,[6] which on the basis of ^{1}H n.m.r. spectroscopy was assigned structure (III). The mechanism of its formation from (II) was not determined. We have therefore sought to determine the mechanism of reactions of the thujan-3-yl cation.



(II)

a; $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = OH$
b; $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = OH$
c; $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = OH$
d; $R^1 = R^3 = H$, $R^2 = Me$, $R^4 = OH$



(III)

EXPERIMENTAL

Materials.—α-Thujene was distilled from the phellandrene fraction of Eucalyptus Dives oil at 86° and 86 mmHg using a spinning band column. Sabinyl acetate was similarly distilled from Oil of Savin at 151—152° at 76 mmHg. We are grateful to Dr. D. V. Banthorpe of University College of London for a gift of Oil of Savin.

4βH-*Thujan*-3β-*ol* (*Isothujol*).—This was obtained from α-thujene by hydroboration.[7]

4βH-*Thujan*-3α-*ol* (*Neoisothujol*).—Sabinyl acetate (10 g) was dissolved in benzene (200 ml) and tristriphenylphosphinerhodium(I) chloride (0.4 g) added. Hydrogenation overnight at room temperature and atmospheric pressure yielded the acetates of 4β*H*- (85%) and 4α*H*-thujan-3α-ol (15%), an improvement in stereoselectivity on the 68 : 32 mixture obtained by hydrogenation over a heterogeneous catalyst.[7] The alcohol was obtained from the acetate by lithium aluminium hydride reduction. The alcohols were converted into acetates and toluene-*p*-sulphonates by conventional methods.[8]

Kinetics.—Ester acetolyses were followed by titration of the acid produced, and alcohol heterolyses by isolation of reaction mixtures followed by g.l.c. analysis. Analyses were carried out on a Perkin-Elmer F 11 Chromatograph using either a 14 ft packed glass capillary column, 15% Carbowax 20M on Chromosorb W at 170°, or a similar 27 ft column at 190°.

Product Studies.—Products were isolated by preparative g.l.c. using a Pye 105 chromatograph with a 30 ft × ⅜ in column, 25% Carbowax 20M on Chromosorb W at 210°. Products were then identified spectroscopically, using i.r., ^{1}H n.m.r., and ^{13}C n.m.r. spectra. The ^{13}C n.m.r. spectra of some of the products are reported in Table 2.

Spectra.—^{1}H N.m.r. spectra were recorded on a Varian HA 100 spectrometer for $CDCl_3$ solutions. ^{13}C N.m.r. spectra were recorded on a Varian XL-100-15 spectrometer, operating in the Fourier transform mode for $CDCl_3$ solutions.

Studies of Cations.—The solutions of cations for ^{13}C n.m.r. studies were made up by slow addition of a solution of fluorosulphonic acid, to which antimony pentafluoride was added in some cases, in sulphur dioxide at −72° to a solution of the alcohol in sulphur dioxide at −72°.

The alcohol solution was cooled throughout in a dry ice–alcohol bath, and shaken gently to aid mixing. Precautions to exclude air or moisture were not taken during the mixing process. A 3—4M excess of acid over alcohol was used, so that any water condensing into the mixture would bond to surplus acid. The solution was then transferred to a 12 mm n.m.r. tube, and sealed with plastic film.

Solutions in concentrated sulphuric acid were made up by slow direct addition of the alcohol to acid, the mixture being cooled in ice throughout the addition.

RESULTS AND DISCUSSION

Since Norin[5] did not determine either the rates or products of acetolysis of the toluene-*p*-sulphonates of (IIa and c), we first studied the acetolysis of this ester of (IIc). Acetolysis of 4β*H*-thujan-3β-yl toluene-*p*-sulphonate (0.03M) in the presence of sodium acetate (0.04M) at 90° gave first-order kinetics with k_1 6.3 × 10^{-5} s^{-1}, and the product composition listed in Table 1.

TABLE 1
Products of decomposition of thujanyl cations

	Product (mole %)										
Reaction	α-Terpinene	γ-Terpinene	*p*-Cymene	Terpinolene	Acetate of (VI)	Unknown acetate	Unknown acetate	Acetate of (IIc)	Acetate of (VII)	Acetate of (IId)	Terpinen-4-yl acetate
Acetolysis of toluene-*p*-sulphonate of (IIc) in the presence of excess of sodium acetate at 90°	14	22	18	8						38	
Acetolysis of toluene-*p*-sulphonate of (IIc) in the absence of sodium acetate at 90°	21	10	14	14	4			11	19	6	
Heterolysis of acetate of (IIc) in acetic acid containing 0.105M-H_2SO_4 at 70°	6	4	7	4	28	3	13		34		
Heterolysis of acetate of (IId) in acetic acid containing 0.105M-H_2SO_4 at 70°	12	5	4	8	10			34	27		
Reaction of α-thujene in acetic acid containing 0.000 1M-sulphuric acid at 25°	21	30	8	6							24

Comparison of the rate of acetolysis with the data reported by Norin for acetolysis of 4β*H*-thujan-3α-yl toluene-*p*-sulphonate suggests a rate difference of the order of 10^2 between the isomers, which is rather less than the figure estimated by Norin, but similar to the figure of 119 reported by Winstein[3] between the rates

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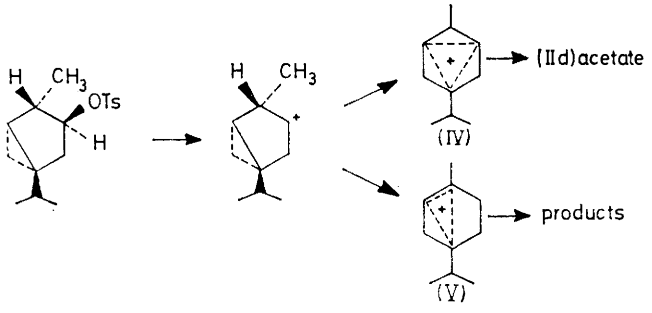
[6] S. Forsen and T. Norin, *Tetrahedron Letters*, 1966, 4183.

[7] D. V. Banthorpe and H. ff. S. Davies, *J. Chem. Soc.* (*B*), 1968, 1356.

[8] R. Tipson, *J. Org. Chem.*, 1944, **9**, 235.

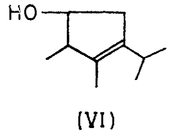
for *cis*- and *trans*-1,5-dimethylbicyclo[3.1.0]hexan-3-yl toluene-*p*-sulphonates.

The products of the reaction, listed in Table 1, are similar to those reported earlier[9] for the hydration of sabinene and α-thujene, except that terpinen-4-ol derivatives are not observed under the more vigorous conditions required for the toluene-*p*-sulphonate acetolysis, and 38% of the acetate of (IId) is formed. It seems probable, then, that the solvolysis of the toluene-*p*-sulphonate of 4β*H*-thujan-3β-ol (IIc) proceeds *via* the route in Scheme 1.

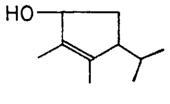


Scheme 1

This relatively simple mixture of products seems inconsistent with Norin's report of a complex mixture,[5] so we repeated the experiment in the absence of sodium acetate, permitting toluene-*p*-sulphonic acid generated by ester acetolysis to catalyse product interconversion. The results of this product study, shown in Table 1, are clearly more complex than those obtained previously, and now include the acetates of the iridane derivatives (VI) and (VII). Since (VI) and (VII) do not arise from the reaction with acids of thujene or sabinene, and are not observed when the terpinenes are reacted with acid,[10] we suggest that they probably arise from the trishomocyclopropyl cation (IV) by nucleophilic attack at position 3 or 5 [these are identical, since (IV) has a plane of symmetry]. In the presence of acid, an equilibrium would be set up between the acetate of (IId) and (IV), which would permit the observation of slow reactions of (IV).



(VI)



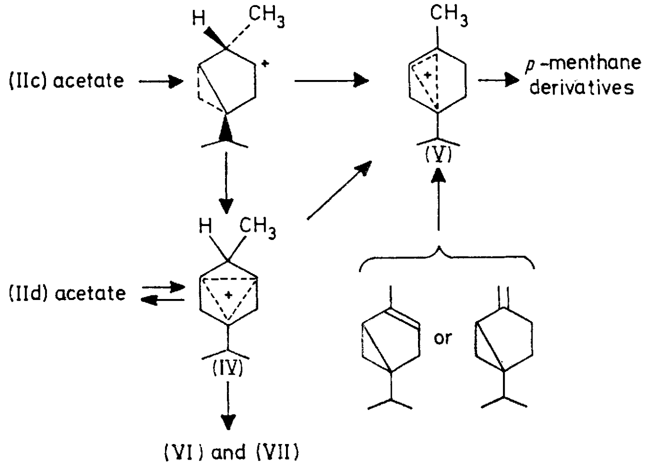
(VII)

We next examined the reactions of the alcohols (IIc and d) with sulphuric acid in acetic acid, a reaction which, in the pinane series,[11] yielded an ion pair in close association with a water molecule. In this case, however, both thujan-3-ols yielded their acetates without loss of optical activity, from which we conclude that the reaction is a bimolecular acid-catalysed acetylation, with rate constants k_1 in 0.105M-acid at 25° of 1.15×10^{-4} for (IIc) and 0.37×10^{-4} s^{-1} for (IId). In the same solvent, but at higher temperature, the acetates of (IIc and d) undergo a slow heterolysis to yield mixtures of products which are given in Table 1. For this reaction, the rate constants k_1 in 0.105M-H_2SO_4 at 70° are 1.37×10^{-5} for (IIc) and 85.0×10^{-5} s^{-1} for (IId).

In this case, (IId) reacts faster by a factor of 62, approximately half the rate difference observed between acetolysis of the toluene-*p*-sulphonate esters. In both cases, however, the effects of internal pair return to the starting material are ignored, so the rate differences should be considered with caution.

The products of reaction of the two acetates, listed in Table 1, show qualitative similarity, but differ in the production of 16% of unidentified acetates from (IIc) and 34% of the acetate of (IIc) from (IId). Any acetate of (IId) formed from (IIc) would not, of course, be stable under the reaction conditions.

The difference in rates of product formation is consistent with reaction of the acetate of (IId) forming (IV), while the acetate of (IIc) forms a classical ion. To explain the product similarities this classical ion must be capable of forming (IV), to yield iridane derivatives, and (V), to yield menthane derivatives. However, since (V) cannot yield (IV), the overall reaction cannot be a simple equilibrium of ions, but must be that outlined in Scheme 2. Scheme 2 does not explain the formation of the acetate of (IIc) from (IId), but it could arise from bimolecular attack of acetic acid on protonated (IId).



Scheme 2

Scheme 2, while consistent with the observed products, involves the assumption that the bishomocyclopropyl cation (V) is more stable than the trishomocyclopropyl cation (IV). This assumption is supported by the experimental data of Freeman,[12] who reacted bicyclo-[3.1.0]hex-2-ene with HCl in methanol, and observed only products of reaction *via* the bishomocyclopropyl cation, not the trishomocyclopropyl cation. In our case, introduction of the methyl group on C-4 would

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[9] M. A. Cooper, C. M. Holden, P. Loftus, and D. Whittaker, *J.C.S. Perkin II*, 1973, 665.

[10] C. M. Williams and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 668.

[11] H. Indyk and D. Whittaker, *J.C.S. Perkin II*, 1974, 313.

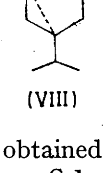
[12] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, 1965, **30**, 771.

undoubtedly stabilise the former relative to the latter, and so increase the energy difference.[7]

The formation of iridane derivatives (VI) and (VII) as products of a slow reaction of the less stable ion seems unlikely to account for the report of Norin[6] that (III) is the sole product of reaction of any of the thujanols (II) with concentrated sulphuric acid at room temperature, unless the *p*-menthane derivatives can undergo a ring contraction reaction. We therefore set out to investigate the mechanism of formation of (III) from (II).

Following the route outlined by Norin,[6] we were able to obtain the ion (III) from 4β*H*-thujan-3β-ol (IIc) in concentrated sulphuric acid at room temperature. The ^{13}C n.m.r. spectrum of this ion, given in Table 2, was consistent with structure (III),[6] in which the charge was spread over the three substituted carbon atoms in the cyclohexane ring.

It seems unlikely that a structure such as (III) would be formed directly from (IIc), so we examined the effect of forming an ion from (IIc) under conditions more likely to favour ion stability, in the hope of observing an ion intermediate between (IIc) and (III). We therefore slowly added a solution of (IIc) in sulphur dioxide to a sulphur dioxide solution of fluorosulphonic acid containing 25% antimony pentafluoride (' magic acid '), at −72° and observed the spectrum of the mixture at −52°. The spectrum, given in Table 2, is clearly different from that of (III), and comparison of the spectrum with that of known thujanes[13] suggests a structure such as the ion (V), or an ion such as (VIII). However, CNDO calculations on an ion obtained by heterolysis of (IIc) show a charge spread over C-1, -4, and -5, as observed, and indicate the presence of partial bonds from C-5 to both C-1 and -4. Alternatively, Sorensen[14] has pointed out that a structure isomeric to (III) is consistent with these data.



(VIII)

TABLE 2

^{13}C Chemical shifts (δ values downfield from Me_4Si)

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
Terpinolene	134.2	120.8	31.5	127.7	29.6	26.7	23.4	121.6	20.1	19.7
Terpinen-4-ol	133.8	118.4	34.7	71.7	30.9	27.1	23.2	36.8	16.9	16.9
(VI)	137.0	35.9	79.9	50.1	130.8	16.5	26.6	20.9	20.9	11.4
(VII)	42.2	35.9	78.8	135.3	122.6	19.8 *	38.4	12.6	14.1	21.0 *
4β*H*-Thujan-3β-ol[13]	30.1	73.0	77.0	42.7	26.7	11.0	33.1	19.7	19.7	15.9
4β*H*-Thujan-3α-ol[13]	33.1	38.6	74.4	40.4	28.8	13.3	32.8	19.9	19.9	12.1
(III) in H_2SO_4	247.0	150.6	238.9	39.2	43.9	21.6	7.3	34.7	17.8	17.8
(III) in HSO_3F–SO_2	247.6	151.6	240.7	40.6	45.3	23.1	8.7	35.8	19.1	19.1
(V) in HSO_3F–SbF_5–SO_2	260.7	45.2	22.5	158.3	219.8	12.2	68.4	16.4 *	25.7 *	33.7

* These assignments may be reversed.

Repetition of the above experiments with 4β*H*-thujan-3α-ol (IId) gave similar results, both in sulphuric acid at room temperature, and in SO_2–SbF_5–HSO_3F at −72°.

On removal of the solvent from the solution of (V), followed by warming the solution to room temperature, its ^{13}C n.m.r. spectrum was unchanged, even on leaving overnight. However, preparation of the ion under similar conditions to those described above, but in the absence of antimony pentafluoride, gave at −60° a spectrum of a mixture of the ions. On removal of sulphur dioxide and warming to room temperature the spectrum changed to that of (III), given in Table 2, and remained unchanged overnight at room temperature.

Antimony pentafluoride clearly plays an important part in stabilising ion (V), since in its absence the rate of rearrangement of the ion is increased by several powers of ten. There is no reason to suppose that this stabilisation, presumably by electron supply to the ion, has any large conformational effect on the ion, since the spectrum is not significantly changed.

Our spectroscopic studies of ions provided no evidence for the existence of the trishomocyclopropyl cation (IV). A similar study by Olah[15] on the unsubstituted bicyclo[3.1.0]hexan-3-yl system failed to show either the bis- or tris-homocyclopropyl cations, giving only the methylcyclopentyl cation. Recently, Masamune[16] has claimed formation of the trishomocyclopropyl cation under very mild conditions by treating the chloride of bicyclo[3.1.0]hexan-3-ol with antimony pentafluoride at −120°, but we have found[17] that reaction of the alcohol under the conditions described above does not give this ion. Since the substitution of the system would favour the bis- over the tris-cation, we should not have expected to observe the latter from thujanols under our conditions.

Product studies on the reaction of the 4β*H*-thujan-3-yl esters suggest formation of the iridane skeleton by attack of a nucleophile on (IV). This reaction is, however, very much faster than the slow formation of (III) from (V) observed in strong acid, and we suggest that this

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[13] R. J. Abraham, C. M. Holden, P. Loftus, and D. Whittaker, *Org. Magnetic Resonance*, 1974, **6**, 184.

[14] T. S. Sorensen, *J.C.S. Comm.*, 1976, 45.

[15] G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, 1972, **94**, 3544.

[16] S. Masamune, M. Sakai, A. V. Kemp-Jones, and T. Nakashima, *Canad. J. Chem.*, 1974, **52**, 855.

[17] P. Buttrick, C. M. Holden, and D. Whittaker, *J.C.S. Chem. Comm.*, 1975, 534.

latter reaction provides a second route to the iridane skeleton by opening of the C-1–C-6 bond of (IV). Reactions of this type are well known in the thujane system.

We conclude that the reaction pathway shown in Scheme 2 provides a possible explanation of the reactions of the carbonium ions generated by the 4α*H*-thujan-3-ols and their esters, but that in strong acid conditions, ion (V) undergoes further slow decomposition to yield (III).

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