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# ACETOLYSIS OF THUJYL p-TOLUENESULPHONATES

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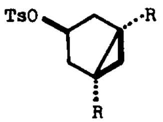
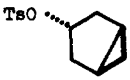
A symmetrical non-classical ion, the tris-homocyclopropenyl cation (I), has been proposed by Winstein et al.[1,2] to be the intermediate in the acetolysis of cis-3-bicyclo[3.1.0]hexyl p-toluenesulphonate (IIa).

Corey and co-workers[3,4] have recently reported the deamination of the cis- and trans-3-bicyclo[3.1.0]hexyl amines and the acetolysis of 1,5-diphenyl-cis-3-bicyclo[3.1.0]hexyl p-toluenesulphonate (IIb). The results of the deamination experiments spoke against a mechanism based on an intermediate tris-homocyclopropenyl cation[3] and those of the acetolysis experiments seemed to contradict the assumption of direct ionisation to a stabilised ion of this type.[4] Further knowledge about the chemistry of the intermediate cations in the bicyclo[3.1.0]hexyl system is obviously desirable.

I



II a R=H
b R=$C_6H_5$



III

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[1] S. Winstein and J. Sonnenberg, J.Am.Chem.Soc. **83**, 3235 (1961).

[2] ibid. **83**, 3244 (1961).

[3] E.J. Corey and R.L. Dawson, J.Am.Chem.Soc. **85**, 1782 (1963).

[4] E.J. Corey and H. Uda, J.Am.Chem.Soc. **85**, 1788 (1963).

TABLE 1. Acetolysis rates of some 3-bicyclo[3.1.0]hexyl p-toluenesulphonates.

| p-Toluene-sulphonates | [ROTs] $10^2$M | Temp. °C | [NaOAc] $10^2$M | $10^5 k$ $sec^{-1}$ | Ref. |
|---|---|---|---|---|---|
| Unsubstituted (IIa) | 1.26 | 50 | 3.05 | 4.6[a] | 1 |
| 1,5-Diphenyl-substituted (IIb) | 1.95 | 55 | 3.27 | 1.87[a] | 4 |
| (-)-Neothujyl-(Vb) | 10.0 | 50 | 10.0 | 66.2[b] | |
| | 3.3 | 50 | 3.3 | 50.2[b] | |
| (+)-Neoisothujyl-(VIIb) | 10.0 | 50 | 10.0 | 53.0[b] | |
| Unsubstituted (III) | 0.83 | 50 | 3.05 | 0.295[a] | 1 |
| (-)-Thujyl- (IVb) | 10.0 | 50 | 10.0 | < 0.07[c] | |
| (+)-Isothujyl-(VIb) | 10.0 | 50 | 10.0 | < 0.07[c] | |

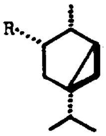
[a] Titrimetric method. [b] Polarimetric method. [c] Calculated from a more than 90 % recovery of unchanged starting material after 50 h reaction time.

TABLE 2. Acetolysis products of thujyl p-toluenesulphonates.

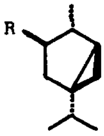
| p-Toluene-sulphonates | Temp. °C | Reaction time h. | Products % Acetates | Products % Olefins |
|---|---|---|---|---|
| (-)-Neothujyl- (Vb) | 50 | 47 | 94 | 6 |
| (+)-Neoisothujyl-(VIIb) | 50 | 47 | 95 | 5 |
| (-)-Thujyl- (IVb) | 95 | 21 | a | |
| (+)-Isothujyl- (VIb) | 95 | 28 | a | |

[a] According to infrared spectrum the dark coloured reaction mixture still contained small amounts of p-toluenesulphonate ester. According to gas liquid chromatography the reaction mixture was mainly a complex mixture of olefins and acetates.

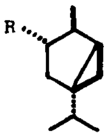
The four thujyl alcohols provide suitable optically active model compounds for studies in this field. The stereochemistry of the compounds has been carefully studied[5,6] and the configurations are indicated in the formulae (IVa), (Va), (VIa) and (VIIa).


IV

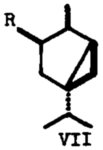
(-)-Thujyl-


V

(-)-Neothujyl-


VI

(+)-Isothujyl-


VII

(+)-Neoisothujyl-

a) R=OH b) R=OTs

In this communication the acetolysis of the four thujyl *p*-toluenesulphonates will be briefly discussed. The toluenesulphonates were prepared in the usual way (*p*-toluenesulphonyl chloride/pyridine). They were all crystalline and gave correct analyses. Acetolysis rates were measured and compared with those of some related compounds (Table 1) and the products of acetolysis were analysed by means of gas liquid chromatography (G.L.C.) (Table 2).

The homogeneous optically inactive acetate from the acetolysis of (-)-neothujyl *p*-toluenesulphonate (Vb) was treated with lithium aluminium hydride. The high boiling alcohol thus obtained was found to be racemic neothujyl alcohol, which was further characterised by the preparation of its crystalline *p*-nitrobensoate.

According to G.L.C. the optically inactive acetate fraction from the acetolysis of (+)-neoisothujyl *p*-toluenesulphonate (VIb) was a mixture of two compounds (Ratio 93:7). After treatment with lithium aluminium hydride the main reaction component was identified as racemic neoisothujyl alcohol. The minor constituent was not identical with any of the thujyl alcohols.

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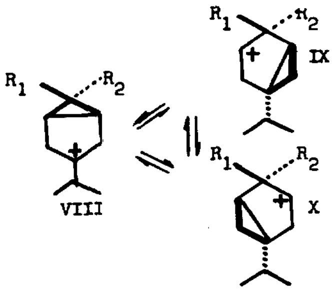
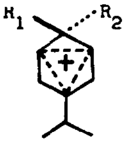
[5] T. Norin, Acta Chem.Scand. **16**, 640 (1962).

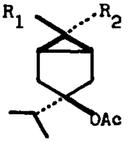
[6] T. Norin and M.S. Bergqvist, Arkiv Kemi. In press.

Winstein and Sonnenberg[2] reported that the acetolysis of cis-3-bicyclo[3.1.0]hexyl p-toluenesulphonate (IIa) with deuterium in the 3-position gave the corresponding acetate with an equal distribution of deuterium over carbon atoms 1, 3 and 5. Similarly, the acetolysis of (-)-neo- and (+)-neoisothujyl p-toluenesulphonates gave the corresponding racemic acetates. To account for this phenomenon the reactions must proceed via a set of rapidly equilibrating classical (or "essentially classical"[4]) ions, as (VIII), (IX), and (X), or lead directly to a symmetrical non-classical intermediate, e.g. of the tris-homocyclopropenyl type (XI). The above classical and non-classical intermediates may also operate together.





XI



XII

Derived from:
(-)-neothujyl-OTs, $R_1$=H, $R_2$=$CH_3$
(+)-neoisothujyl-OTs, $R_1$=$CH_3$, $R_2$=H.

Whether the present acetolysis results are interpreted on the basis of classical or non-classical intermediates, it is remarkable that the solvent anion does not attack the most substituted position leading to the tertiary acetate (XII) as the main product. Assuming the classical mechanism, referred to above, the secondary ions (IX) and (X) must be the more stable intermediates under the present experimental conditions, or these ions would be more reactive towards acetate anions than the tertiary ion (VIII). The products formed when the solvolysis is carried out using other solvents are presently under investigation.

The low acetolysis rate constants ($k_{50^\circ} < 0.07 \times 10^{-5}$ sec$^{-1}$) of the compounds (IVb) and (VIb), compared with that of the corresponding unsubstituted "trans"-compound (III) ($k_{50^\circ} = 0.295 \times 10^{-5}$ sec$^{-1}$)[1], are remarkable. However, most significant is the difference between the rate of acetolysis of a cis-isomer (Vb or VIIb) and that of the corresponding trans-isomer (IVb and VIb, respectively). This may be interpreted according to Winstein and Sonnenberg[1], who suggested that the anchimeric acceleration in the acetolysis of the cis-isomer indicates the direct formation of a tris-homocyclopropenyl cation. However, direct formation of the tertiary ion (VIII) with participation of the C(1)-C(5) bond of the cyclopropane ring would also account for the enhanced acetolysis rates of the "cis"-series.

The acetolysis of (-)-neo- and (+)-neoisothujyl p-toluenesulphonate proceeds with significant stereospecificity. The solvent anion attacks the intermediate ion from the same side as the cyclopropane $CH_2$-group. The same stereospecificity was reported by Winstein and Sonnenberg[1] in the acetolysis of cis-3-bicyclo[3.1.0]-hexyl p-toluenesulphonate and taken as an indication that ionization leads to a tris-homocyclopropenyl cation (I). To account for this stereospecificity Corey and Uda[4] proposed an "essentially classical" intermediate cation with weak interaction involving the part of the C(3) p-orbital trans to the cyclopropyl $CH_2$-group and the delocalised electrons of the three-membered ring.

At the present stage it appears premature to decide whether classical or non-classical intermediates operate in the above acetolysis reactions. Further investigations concerning the chemistry of bicyclo[3.1.0]hexyl cations are presently being carried out in this Laboratory.

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