Tetrahedron Letters No. 8, pp 699 - 702, 1972. Pergamon Press. Printed in Great Britain.

SOLVOLYSIS OF 4-TOSYLOXYTWISTANES: THE RELATIONSHIP BETWEEN 4-TWISTYL AND 10-PROTOADAMANTYL CATIONS

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(Received in UK 3 January 1972; accepted for publication 19 January 1972)

Twistane is one of the few hitherto described systems belonging to the large family of adamantane isomers. Whereas it is known that indiscriminative generation of carbonium ions by Lewis acids leads to rearrangement of twistane to adamantane[1], only little is known about the behaviour of this system under solvolytic conditions. Thus, Whitlock and Siefken[1] found that acetolysis of 2-tosyloxytwistane resulted in a mixture of six principal compounds, none of them being 2-twistyl acetate or 1- or 2-adamantyl acetate.

We studied the solvolysis of the exo- and endo-4-tosyloxytwistanes, Ib (m.p. 58-60°C) and IIb (m.p. 61-62°C), respectively. The alcohol Ia, m.p. 202-203°C, was obtained as the main product of $LiAlH_4$ reduction of 4-twistanone[2]; its endo-epimer IIa, m.p. 142-143°C, was prepared by equilibration of Ia with aluminium isopropoxide.

Ia : R^1 = H, R^2 = OH ; IIa : R^1 = OH, R^2 = H
Ib : R^1 = H, R^2 = OTs; IIb : R^1 = OTs, R^2 = H

The alcohols Ia and IIa were assigned unequivocally the configuration exo- and endo-, respectively, on the basis of their chemical behaviour and coupling constants of the carbinol proton in their NMR spectra[3].

In 70% aqueous ethanol, the rates of solvolysis at 50.0°C are $k = 23.1 \cdot 10^{-5} sec^{-1}$ for the first and $k = 3.99 \cdot 10^{-5} sec^{-1}$ for the second isomer.

Solvolysis of Ib and IIb in 70% aqueous acetone in the presence of calcium carbonate or sodium hydrogen carbonate gave very similar mixtures of alcohols together with only 1.5 - 3% of olefinic products. Oxidation of the alcohol portion afforded a mixture of ketones consisting (as shown by gas liquid chromatography) in both cases of two ketones, one of which was 4-twistanone. Wolf-Kishner reduction of the ketones led to hydrocarbons which were analysed by IR-spectroscopy. The g.l.c. as well as IR-spectroscopic analysis showed that the solvolysis of both Ib and IIb gives predominantly derivatives of protoadamantane, the only other detected products being twistane derivatives (TABLE 1). The IR spectra of the Wolf-Kishner products were completely identical with that of synthetic mixtures of pure twistane and protoadamantane.

The acetolysis of Ib and IIb resulted again in formation of protoadamantyl and twistyl derivatives in proportions similar to that arising in the solvolysis in 70% acetone (Table 1).

TABLE 1

Percentage of Protoadamantyl and Twistyl Derivatives in the Solvolysis of Ib and IIb

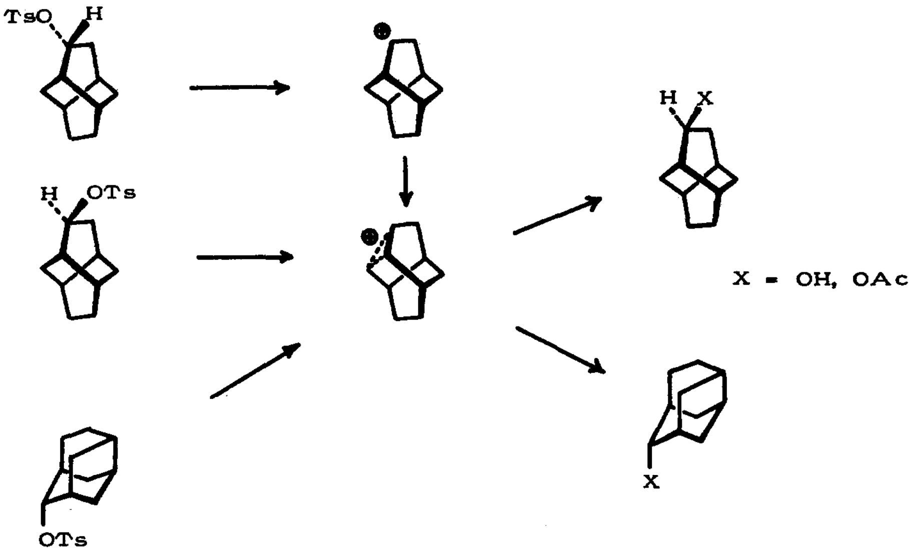
Tosylate	70% aqu. acetone[a] (90°C)	AcOH/AcOK[b] (90°C)
Ib	70% protoadamantyl 30% twistyl	82% protoadamantyl 18% twistyl
IIb	61% protoadamantyl 39% twistyl	79% protoadamantyl 21% twistyl
(93% 10-protoadamantyl + 7% Ib)	70% protoadamantyl 30% twistyl	83% protoadamantyl 17% twistyl

[a] Analysed as ketones by g.l.c. and as hydrocarbons by IR-spectra. [b] The mixture of acetates was reduced with $LiAlH_4$ and the resulting alcohols were treated in the same manner as described for the products of solvolysis in 70% acetone.

The slightly higher protoadamantane : twistane ratio in the acetolysis may be ascribed to lower nucleophility of acetic acid as compared with 70% aqueous acetone.

The absence of any adamantyl derivatives was proved by gas chromatography where the authentic 1- and 2-adamantanols had clearly distinct peaks from the peaks of the reaction mixture. This indicates that there is no extensive rearrangement (involving e.g. bridgehead ions).

In order to obtain further information about the nature of the rearrangement, the mixture of alcohols from the solvolysis of Ib was enriched in protoadamantyl derivative by crystallisation (it contained 93% of protoadamantanol and 7% of Ib) and was quantitatively tosylated and then subjected to acetolysis. If the product composition were controlled kinetically then the amount of twistane derivatives in this second solvolysis should be about $0.07 \cdot 20 = 1.4\%$. However, the products contained again about 20% of twistane derivative, i.e. their composition was practically the same as in the acetolysis of Ib or IIb.



Scheme 1

Although we did not succeed as yet in ascertaining the configuration of the 10-protoadamantanol formed in the solvolysis, we found that the 4-twistanol arising from the tosylates Ib and IIb as well as from the "enriched" protoadamantanol sample, has in all cases the exo-configuration (Ia). All these facts may indicate an equilibrium between the 4-twistyl and 10-protoadamantyl ions or the existence of a common bridged ion involved in a reaction pattern such as depicted in Scheme 1. The stereospecific formation of Ia supports the second alternative.

Further studies of the detailed nature of the rearrangement are in progress.

We are indebted to Professor P. von R. Schleyer and to Dr D. Lenoir for very valuable comments and for the kind gift of a sample of protoadamantane.

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