

## ELIMINATION REACTIONS IN THE BICYCLO [4,2,1] NONAN-9-ONE DERIVATIVES

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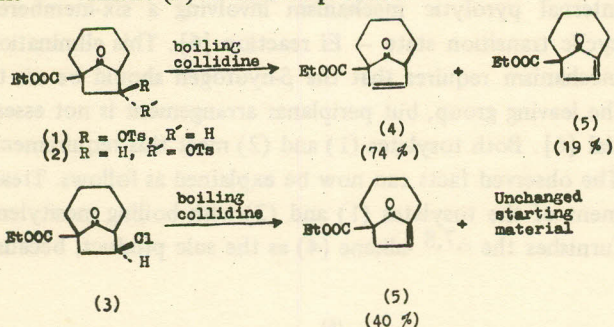
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Treatment of ethyl 9-oxo-7-*exo-p*-tolylsulphonyloxybicyclo-[4,2,1]nonane-1-carboxylate (1), or ethyl 9-oxo-7-*endo-p*-tolylsulphonyloxybicyclo[4,2,1]nonane-1-carboxylate (2), with boiling mesitylene furnished ethyl 9-oxobicyclo[4,2,1]non-7-ene-1-carboxylate (4) free from the  $\Delta^{6,7}$ -isomer (5). Under identical conditions, ethyl 7-*exo*-chloro-9-oxobicyclo[4,2,1]nonane-1-carboxylate (3) was unaffected. These results, together with the previously reported [1,2] elimination reactions of the above substrates in presence of boiling collidine, are interpreted as indicating that elimination by an E2 mechanism is prevented in these substrates due to unfavourable stereochemistry. A pyrolytic mechanism involving a six-membered cyclic transition state is suggested for the formation of the  $\Delta^{7,8}$ -alkene (4) from tosylates (1) and (2).

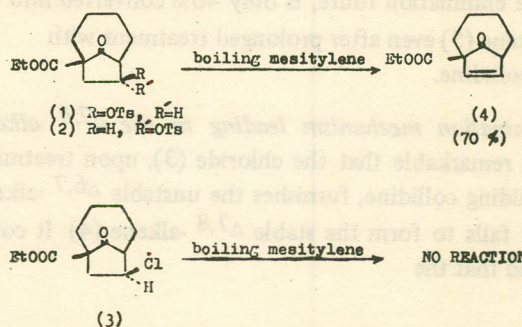
### INTRODUCTION

It has been previously reported [1,2] that the treatment of the *exo*-tosylate (1) or the *endo*-tosylate (2) with boiling collidine furnishes a mixture of two isomeric alkenes: the  $\Delta^{7,8}$ -alkene (4) and the  $\Delta^{6,7}$ -alkene (5), and that under identical conditions the *exo*-chloride (3) gives the  $\Delta^{6,7}$  alkene (5) as the sole product.



The  $\Delta^{6,7}$ -alkene (5) is an 'anti Bredt [3,4] bridgehead alkene with S number 7, and is an unstable compound that decomposes slowly at room temperature even under nitrogen atmosphere. Its formation in above elimination reactions was astonishing, for it was expected that the formation of this unstable bridgehead alkene would be so difficult as to force the above elimination reactions to exclusively take the alternate route to the stable  $\Delta^{7,8}$ -alkene (4). The fact that the  $\Delta^{6,7}$ -alkene (5) was formed in spite of its strained structure prompted a further study into these elimination reactions.

The present paper reports the elimination reactions of the tosylates (1) and (2), and the chloride (3) in the presence of boiling mesitylene. The boiling mesitylene was chosen as the reaction medium as it provides about the same reaction temperature as the boiling collidine did in the earlier studies [1,2], yet, unlike collidine, mesitylene is neutral and is not expected to promote elimination mechanisms requiring base catalysis. It was found that the treatment of the *exo*-tosylate (1), or the *endo*-tosylate (2), with boiling mesitylene gives the  $\Delta^{7,8}$ -alkene (4) free from the  $\Delta^{6,7}$ -isomer (5), and that the *exo*-chloride (3) remains unaffected under these conditions.



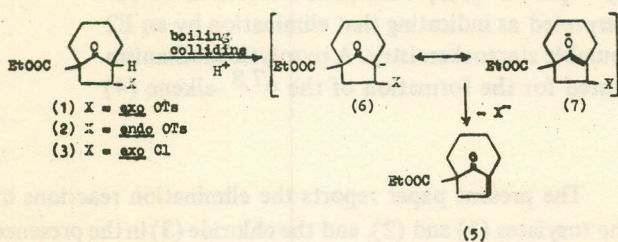
Pyrolysis of the tosylates (1) and (2) was also attempted by heating at 172°C without a solvent. This, however, gave complicated mixtures with signs of extensive decomposition.

The above results show that the  $\Delta^{6,7}$ -alkene (5) is obtained from all substrates, but only under basic conditions - i.e. upon treatment with boiling collidine. On the other hand, the  $\Delta^{7,8}$ -alkene (4) is obtained only from the tosy-

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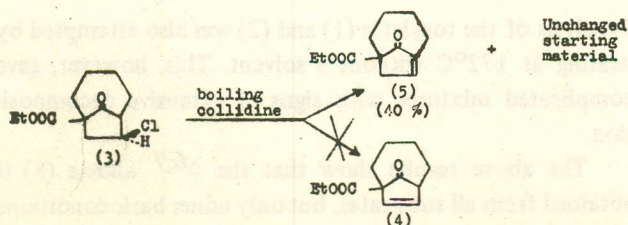
lates (1) and (2), and not from the chloride (3): interestingly, however, its formation does not require basic conditions. A possible mechanistic explanation of the above facts is presented in the following discussion.

**Elimination mechanism leading to the  $\Delta^{6,7}$ -alkene (5).** It is interesting to note that the formation of the  $\Delta^{6,7}$ -alkene (5) from two of the substrates, the *exo*-tosylate (1) and the *exo*-chloride (3), involves a *cis*-elimination. It has been previously proposed [2] that the formation of this alkene proceeds by an E1cB mechanism by way of the stabilized carbanion [6]. The present finding that the formation of this alkene requires basic conditions, supports this suggestion.



The resonance stabilization of the intermediate carbanion (6) is expected to be small, as the contributing structure (7) is a derivative of *trans*-cycloheptene and hence highly unstable [4]. It can be reasonably argued, therefore, that the formation of the carbanion (6), and consequently of the  $\Delta^{6,7}$ -alkene (5), would be a slow process. Support for this argument is provided by the fact that the chloride (3), which apparently can not taken an alternate elimination route, is only 40% converted into the  $\Delta^{6,7}$ -alkene (5) even after prolonged treatment with boiling collidine.

**Elimination mechanism leading to the  $\Delta^{7,8}$ -alkene (4)** it is remarkable that the chloride (3), upon treatment with boiling collidine, furnishes the unstable  $\Delta^{6,7}$ -alkene (5), but fails to form the stable  $\Delta^{7,8}$ -alkene (4). It could be argued that the

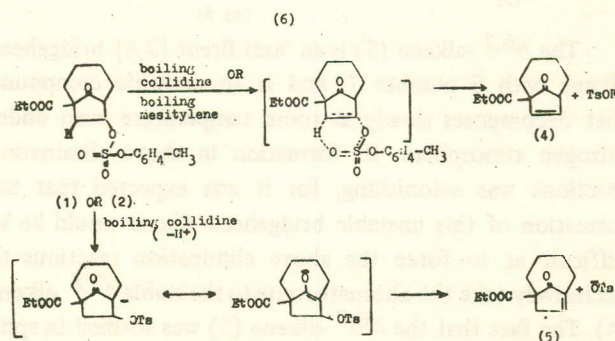


formation of the  $\Delta^{7,8}$ -alkene (4) is superseded by the

faster reaction leading to the  $\Delta^{6,7}$ -alkene (5). This possibility is, however, ruled out by the fact that a considerable amount of unchanged starting material is left at the end of the reaction. This clearly indicates that, under the reaction conditions, a reasonable elimination mechanism leading to the  $\Delta^{7,8}$ -alkene (4) is not available for the chloride (3). The obvious such mechanism, under the basic reaction conditions, would appear to be the E2 mechanism. An examination of models reveals, however, that the periplanar arrangement (*syn* or *anti*) of the involved atoms – a necessary condition for the E2 reaction is possible neither in the chloride (3) nor in the tosylates (1) and (2) – obviously due to rigidity of the five-membered ring. Numerous instances are known in the literature [5] where difficulty in achieving a periplanar arrangement rules out elimination by an E2 mechanism. It is not surprising therefore that the chloride (3) fails to form the  $\Delta^{7,8}$ -alkene (4) by an E2 mechanism.

The tosylates (1) and (2), however, furnish the  $\Delta^{7,8}$ -alkene upon treatment with boiling collidine as well as with boiling mesitylene. It is unlikely that these reactions proceed through an E2 mechanism, because, like the chloride (3), the tosylates (1) and (2) do not meet the stereochemical requirements of the E2 mechanism. Furthermore, the  $\Delta^{7,8}$ -alkene (4) is obtained from the tosylates (1) and (2) under basic as well as neutral conditions.

This paper proposes that the formation of the  $\Delta^{7,8}$ -alkene (4) from the tosylates (1) and (2) proceeds by an internal pyrolytic mechanism involving a six-membered cyclic transition state – E<sub>i</sub> reaction [6]. This elimination mechanism requires that the  $\beta$ -hydrogen should be *cis* to the leaving group, but periplanar arrangement is not essential [6]. Both tosylates (1) and (2) meet this requirement. The observed facts can now be explained as follows. Treatment of the tosylates (1) and (2) with boiling mesitylene furnishes the  $\Delta^{7,8}$ -alkene (4) as the sole product, because

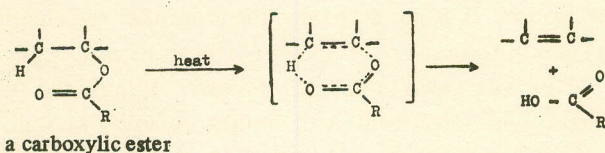


the E<sub>i</sub> mechanism is the only elimination mechanism possible under neutral conditions. However, upon treatment with boiling collidine – the basic reaction conditions

— the E1cB mechanism can compete with the E1 mechanism, and therefore a mixture of the two alkenes (4) and (5) is formed.

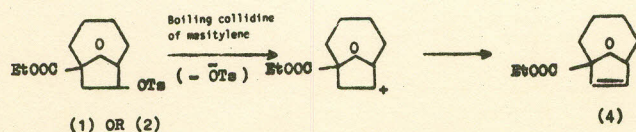
It is further proposed that, at the reaction temperature — the boiling point of collidine — the E1 reaction proceeds at a sufficiently slow rate such that the formation of the unstable "anti-Bredt"  $\Delta^{6,7}$ -alkene (5) by the E1cB mechanism is able to compete.

The E1 mechanism has been proposed [6] for a number of elimination reactions that proceed by the action of heat, usually in the absence of a solvent. Carboxylic esters are one of the common substrates that are known to undergo elimination by this mechanism. Analogous eliminations of tosylates have not been reported so far. This, in



the opinion of this author, may be due to the formation of *p*-toluenesulphonic acid during the pyrolysis of tosylates. *p*-Toluenesulphonic acid is a very strong acid, and, at the high pyrolysis temperatures, it can cause extensive decomposition of the olefinic products, especially when the reaction is carried out in the absence of a solvent. This was found to be the case with the tosylates (1) and (2). The attempted pyrolysis of these tosylates by heating at 172° — the boiling point of collidine — under nitrogen atmosphere, gave a complicated mixture from which no pure product could be isolated. The fact that heating the tosylates (1) and (2) with boiling mesitylene gave a good yield of the  $\Delta^{7,8}$ -alkene (4) may be attributed to the presence of mesitylene which separated the alkene from *p*-toluenesulphonic acid. Collidine, of course, has the further advantage that it can neutralize *p*-toluenesulphonic acid as it is formed.

Although the formation of the  $\Delta^{7,8}$ -alkene (4) by E1 mechanism explains the experimental results fairly well, the presently available evidence does not completely exclude the possibility of the formation of this alkene by solvolysis



of the tosylates (1) and (2) by way of a carbonium ion intermediate — E1 mechanism. This mechanism has been previously suggested for elimination reactions of tosylates,

taking place by action of heat in polar solvents such as DMSO or HMPT [7]. It seems unlikely, however, that the E1 mechanism would be favoured in presence of the non-polar solvent mesitylene.

## EXPERIMENTAL

IR spectra were recorded on a Unicam SP 1000 spectrophotometer and refer to thin films on NaCl discs unless stated otherwise.  $^1\text{H}$  NMR spectra were measured on a 60 MHz instrument using  $\text{CDCl}_3$  as solvent, and TMS as an internal reference.

Thin — (0.25 mm) and thick — (1.0 mm) layer chromatography plates were prepared from kieselgel DF (Riedel-De Haen). All organic extracts were dried over anhydrous magnesium sulphate. Throughout, ether refers to diethyl ether.

*Ethyl 9-oxo-7-exo-p-tolylsulphonyloxybicyclo [4,2,1] nonane-1-carboxylate* (1), *Ethyl 9-oxo-7-endo-p-tolylsulphonyloxybicyclo [4,2,1] nonane-1-carboxylate* (2), and *ethyl 7-exo-chloro-9-oxobicyclo [4,2,1] nonane-1-carboxylate* (3) were prepared and purified by the published procedure [2].

*Treatment of ethyl 9-oxo-7-exo-p-tolylsulphonyloxybicyclo[4,2,1]-nonane-1-carboxylate (1) with boiling mesitylene.* A solution of the above tosylate (380 mg) in mesitylene (10 ml) was heated under reflux for 20 hr. Work-up by washing with 5%  $\text{NaHCO}_3$  solution, drying and concentration gave a neutral oil (185 mg), T.L.C. (solvent ether) of which showed a single spot, RF 0.70. Purification by preparative T.L.C. followed by distillation gave a colourless oil (145 mg, 70%), b.p. 90° (air bath temperature) at 0.1 mbar, which was identified as *ethyl 9-oxobicyclo [4,2,1] non-7ene-1-carboxylate* (4) by comparison of  $R_f$  (Solvent ether), and IR and  $^1\text{H}$  NMR spectra with an authentic sample [2].

*Treatment of ethyl 9-oxo-7-endo-p-tolylsulphonyloxybicyclo [4,2,1]-nonane-1-carboxylate (2) with boiling mesitylene.* The reaction was carried out as described above for the *exo*-tosylate (1). The product was identical with the product given by the *exo*-tosylate (1).

*Treatment of ethyl 7-exo-chloro-9-oxobicyclo [4,2,1] nonane-1-carboxylate (3) with boiling mesitylene.* A solution of the above chloride (244 mg) in mesitylene (10 ml) was heated under reflux for 20 hr. Work-up by washing with 5%  $\text{NaHCO}_3$  solution, drying, and concentration gave a neutral oil (210 mg), which was identified as unchanged starting material by comparison of  $R_f$  (solvent ether), and IR and  $^1\text{H}$  NMR spectra.

*Attempted pyrolysis of 9-oxo-7-exo-p-tolylsulphonyloxybicyclo [4,2,1] - nonane-1-carboxylate (1).* The above tosylate was heated at 172° under nitrogen atmosphere for 20 hr. It was then cooled and taken up in ether. Washing with 5% NaHCO<sub>3</sub> solution followed by drying and concentration gave a brown oil (180 mg), the T.L.C of which showed several spots, None of these spots corresponded to the starting material, or the alkenes (4) or (5). This mixture was not further studied.

*Attempted pyrolysis of 9-oxo-7-endo-tolylsulphonyloxybicyclo [4,2,1]-nonane-1-carboxylate (2).* The pyrolysis of this tosylate was carried out as described above for the *exo*-tosylate (1). The product was a complicated mixture similar to the one obtained from tosylate (1).

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