Stereochemistry of Hydrolysis and Elimination Reactions of Toluene-*p*-sulphonate Esters on Alumina

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Summary A stereochemical preference for *trans*-1,2-elimination and hydrolysis with inversion of configuration has been found when solutions of toluene-*p*-sulphonate esters are stirred over alumina, but *exo*-norbornyl toluene-*p*-sulphonate undergoes 1,3-elimination and hydrolysis with retention of configuration.

Treatment of several steroidal toluene-*p*-sulphonate esters with alumina giving mixtures of alcohols and olefins has been studied mainly with the aim of developing a reliable method for epimerization of alcohols from the more to the less thermodynamically stable epimer.[1] We have begun an examination of the mechanistic and synthetic aspects of the chemistry of sulphonate esters on alumina, and we now report preliminary results on interaction of Activity I Woelm Alumina with representative primary and secondary acyclic and cyclic toluene-*p*-sulphonate esters.

The experimental procedure involves dissolving *ca.* 1 mmol of toluene-*p*-sulphonate in 4—5 ml of CCl_4† followed by adding 4—5 g of Activity I neutral, acidic, or basic Woelm Alumina; fast stirring is continued at 25° for 24 h in most cases. Aliquot portions taken periodically during this time and analysed by n.m.r. indicate that only for the least reactive toluene-*p*-sulphonates, n-octadecyl and menthyl toluene-*p*-sulphonates, is 24 h actually needed for essentially complete reaction. Product isolation is done by extracting the alumina repeatedly with CCl_4 which elutes all elimination products and then with diethyl ether which elutes the alcoholic products.

When neutral, acidic, and basic aluminas are each used [see

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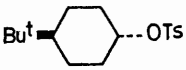
† This solvent was chosen to aid following the reaction by n.m.r.; virtually the same results have been obtained in several experiments with diethyl ether as solvent.

(**1**) and (**2**), Table], the distribution of products is found to change by less than 10%, and there is no change [see (**2**)] in the stereochemical course of the reaction. Although menthyl toluene-*p*-sulphonate, (**4**), also gives the same ratio of hydrolysis to elimination products on neutral, acidic, and basic aluminas (8—3% neomenthol and 90—95% menthenes), the ratio of *trans*-menth-2-ene : menth-3-ene varies reproducibly as follows: 1·5 : 1 (neutral alumina), 2 : 1 (acidic alumina), and 4 : 1 (basic alumina). Control experiments indicate that *trans*-menth-2-ene does not isomerize to menth-3-ene under the standard reaction conditions.

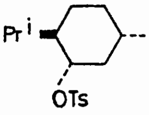
Reaction of toluene-p-*sulphonate esters in* CCl_4 *with neutral Activity I Woelm Alumina at* 25°

	Toluene-*p*-sulphonate (ROTs)	% Yield[a] Alcohol (ROH)	Olefin [R(–H)]
(1)	n-$C_{18}H_{37}OTs$	75[b]	0
(2)	s-$C_{14}H_{29}OTs$	30	65[c]
(3)		5[d]	90—95[e]
(4)		8—3[f]	90—95[g,h]
(5)		35—45[i]	45[e,j]

[a] Of isolated product. [b] Di-n-octadecyl ether was isolated in 20% yield. [c] *cis*-Tetradec-2-ene, *trans*-tetradec-2-ene, and tetradec-1-ene in 2 : 1 : 1 ratio. [d] *cis*-4-t-Butylcyclohexanol. [e] Yield determined by analytical gas chromatography. [f] Neomenthol. [g] 1·5 : 1 *trans*-Menth-2-ene : menth-3-ene. [h] Yield determined using internal n.m.r. standard. [i] *exo*-Norborneol. [j] Nortricyclane.



(3)



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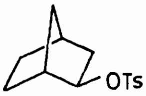

(5)

The amount of elimination increases and the amount of hydrolysis decreases on going from primary, (**1**), to secondary acyclic, (**2**), to secondary cyclic, (**3**) and (**4**), toluene-*p*-sulphonate. The high yield of olefin from the substituted cyclohexyl toluene-*p*-sulphonates and the simplicity and mildness of this procedure compare favourably with other methods for dehydration of alcohols.[2]

2-Tetradecyl toluene-*p*-sulphonate reacts with alumina to give tetradecan-2-ol in 30% yield and a mixture of tetradecenes in 65% yield. The distribution of olefins (*cis*-tetradec-2-ene, *trans*-tetradec-2-ene, and tetradec-1-ene in 2 : 1 : 1 ratio) parallels that found by Pines and Haag[3] in the dehydration of secondary alcohols over alumina and indicates a kinetic preference for *cis*- over *trans*-olefin formation in this acyclic system.

trans-4-t-Butycyclohexyl and menthyl toluene-*p*-sulphonates both undergo little hydrolysis, but the alcohols which are formed are the epimeric *cis*-4-t-butylcyclohexanol and neomenthol. Furthermore, like menthol,[4] menthyl toluene-*p*-sulphonate over alumina undergoes predominantly a *trans*-1,2-elimination to give *trans*-menth-2-ene as the major olefinic product.

exo-Norbornyl toluene-*p*-sulphonate reacts with alumina to form nortricyclene as the only elimination product and *exo*-norborneol as the only hydrolysis product. This is the first reported example of alumina promoted toluene-*p*-sulphonate hydrolysis with complete retention of configuration, and it suggests that the norbornyl system might undergo hydrolysis by a mechanism different from that operating in alumina hydrolysis (with inversion) of all other secondary cyclic toluene-*p*-sulphonates which have been studied.

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