Remote Sulphur Participation in the Solvolysis of *endo*-4-Thiatricyclo[5,2,1,$0^{2,6}$]dec-8-yl *p*-Nitrobenzoate

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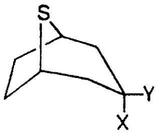
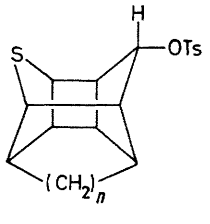
Summary *endo*-4-Thiatricyclo[5,2,1,$0^{2,6}$]dec-8-yl *p*-nitrobenzoate is solvolysed 752 times faster than *endo*-tricyclo[5,2,1,$0^{2,6}$]dec-8-yl *p*-nitrobenzoate and 955 times faster than *exo*-4-thiatricyclo[5,2,1,$0^{2,6}$]dec-8-yl *p*-nitrobenzoate; this rate enhancement has been attributed to remote sulphur participation.

REPORTS of intramolecular participation by remote sulphur in the solvolysis of esters and/or halides are limited[1] although the phenomenon of anchimeric assistance by neighbouring sulphur is well known.[2,3] In an early test for transannular participation, Ireland and Smith[4] found that 8-thiabicyclo[3,2,1]hept-3-*endo*-yl tosylate (**1a**) was only 2·2 times more reactive than the *exo*-tosylate (**1b**), indicating that sulphur was not participating in the rate-determining step. On the other hand, Paquette and his co-workers[1d] found tosylate (**2b**) to be 173 times more reactive than tosylate (**2a**). In (**2b**), the ethano-bridge causes the ring sulphur to be forced closer to the developing positive charge resulting in anchimerically assisted solvolysis. We report a new example of transannular participation by sulphur in a solvolysis reaction.



(1a) X = OTs, Y = H
(1b) X = H, Y = OTs



(2a) *n* = 1
(2b) *n* = 2

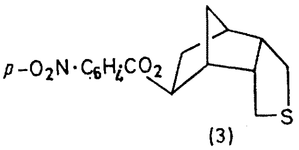
The rate data for the solvolysis of *endo*- and *exo*-4-thiatricyclo[5,2,1,$0^{2,6}$]dec-8-yl *p*-nitrobenzoates (**3**, **4**) and for the solvolysis of the carbocyclic analogues (**5**, **6**) are summarized in the Table.

Hydrolysis rates of p-*nitrobenzoate esters* (**3**), (**4**), (**5**), *and* (**6**)[a]

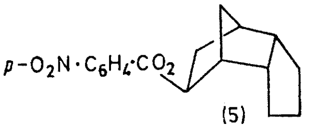
Compound	10^6k, min.$^{-1}$	k_{rel}
(3)	$4{\cdot}37 \times 10^3$	752
(4)	4·57	0·8
(5)	5·81	1·0
(6)	3·90	0·7

[a] The solvent was dioxan : water (75 : 25, by weight) and the temperature was 148·8°.

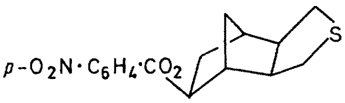
Inductive or steric effects alone cannot account for the 752-fold increase in rate in going from the *endo*-carbocyclic (**5**) to the *endo*-sulphide (**3**), and, in fact, the inductive effect of the sulphur atom should lead to rate retardation. Thus, the unshared electrons of sulphur must assist in "pushing off" the leaving group in the transition state, and an intermediate such as (**7**), with the positive charge delocalized to sulphur, must intervene. When the five-membered sulphide ring is in the *exo*-configuration, the sulphur is unavailable for participation. The factor of 955 between the solvolysis rates of (**3**) and (**4**) is further evidence for sulphur participation in (**3**). This latter rate ratio may be compared to the factor of 1·5 observed for the carbocyclic analogues (**5**) and (**6**) and to the factor of 3·8 observed by Takeuchi and co-workers in the methanolysis of *endo*- and *exo*-tricyclo[5,2,1,$0^{2,6}$]dec-8-yl tosylates.[6]



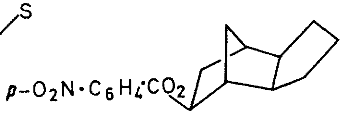
(3)



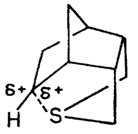
(5)



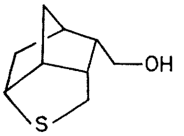
(4)



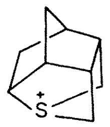
(6)



(7)



(8)



(9)

Although sulphur participation is indicated, the exact nature of the intermediate cannot be determined from the rate data alone. The only solvolysis product of (**3**) was the *endo*-8-ol and none of the rearranged alcohol (**8**) was present. This rules out the possibility of σ-bond formation since intervention of sulphonium ion (**9**) should lead to formation of some (**8**).[7] The absence of the *exo*-8-ol strongly indicates that the intermediate is sufficiently immobile to preclude rearrangement to the thermodynamically more stable *exo*-skeleton.

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