The Operation of *syn*- and *anti*-Mechanisms in Base-promoted Toluene-*p*-sulphonate Eliminations in Open-chain Systems

By J. ZÁVADA, M. PÁNKOVÁ, and J. SICHER*

(*Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, Prague*)

RECENTLY,[1,2] we showed that in base-induced eliminations of cyclodecyl and cyclododecyl toluene-*p*-sulphonates a *syn*- and an *anti*-mechanism operate side by side: the *trans*-cycloalkenes arise by *syn*-elimination, practically exclusively in the former system and largely in the latter. Evidence on the steric course of *cis*-cycloalkene formation was less detailed but it appeared that, in contrast to the corresponding *trans*-isomers, these are formed largely or even exclusively by *anti*-elimination.

Froemsdorf and his colleagues[3] have now examined the steric course of the elimination of 1-methylpropyl toluene-*p*-sulphonate. They argued that since our observations[1] were made "under conditions that emphasize the carbanionic character of the transition state, competing *syn*- and *anti*-elimination might occur under the strongly basic conditions using dimethyl sulphoxide with alkoxide bases". However, under these reaction conditions they found practically no *syn*-elimination and concluded that "in acyclic systems which allow the stereoelectronic requirements of both *syn*- and *anti*-elimination to be met, *anti*-elimination occurs preferentially with almost total exclusion of *syn*-elimination".† We present evidence showing that this conclusion is not justified.

It must be stressed that a strong base represents a necessary but not a sufficient condition for ready *syn*-elimination. This point, which we emphasized on a previous occasion,[2,4] is evident from the data on the steric course of formation of *trans*-cyclododecene[2] and bicyclo[2,2,2]octene from the corresponding toluene-*p*-sulphonate esters (Table 1).

The percentage of *syn*-elimination contributing to the overall reaction may be seen to decrease significantly on going from ion-pair supporting solvents benzene (or t-butyl alcohol)[2] to dissociating solvents such as dimethylformamide or dimethyl sulphoxide. We have suggested that this may be accounted for in terms of a "cyclic" mechanism of the *syn*-elimination process, involving a $K^+ \ldots OR^-$ ion pair as the effective basic species (1).

Irrespective of whether this represents the correct interpretation, our data on *trans*-cyclododecene formation and those given in Table 1 show that t-butoxide–dimethyl sulphoxide is *a priori* not a suitable system for testing whether a *syn*-mechanism operates in the elimination of the open-chain toluene-*p*-sulphonates.

We have examined the steric course of *trans*- and *cis*-dec-5-ene formation from stereospecifically [2-^{2}H]-labelled 1-butylhexyl toluene-*p*-sulphonates with potassium t-butoxide using benzene, t-butyl

† The dual elimination behaviour observed by us in cyclic compounds[1,2,4] was thought to stem from "the inability of these systems to satisfy the requirements (of *anti*-elimination) without creating a prohibitive amount of conformational strain".[4]

TABLE 1

Bicyclo[2,2,2]*octene formation from* cis- *and* trans-[3-^{2}H]-*bicyclo*[2,2,2]*oct-2-yl toluene*-p-*sulphonate*[a] *and potassium t-butoxide*: % syn-*elimination in the unlabelled compound*

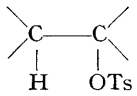
Solvent	% Deuterium in bicyclo-octene[d] From *cis*-OTs,D	From *trans*-OTs,D	% *syn* Elimination[e]
Benzene[b]	16·9	94·75	90
DMF[c]	67·5	87·4	65
DMSO[c]	81·1	73·7	45

[a] The labelled bicyclo-octanols were prepared by standard procedures[2] from bicyclo-octene; [b] three-fold excess of 0·5M-base at 130° for 100 hr.; [c] 0·5M-base at 75° for 8 hr.; [d] determined by mass spectroscopy and corrected for incomplete deuteriation (~95%) of the starting toluene-*p*-sulphonates; [e] the data refer to the steric course in the parent (unlabelled) compound and have been calculated on the assumption that $(k_H/k_D)_{syn} = (k_H/k_D)_{anti}$; actually, the former is likely to be smaller:[2,4] consequently the figures given represent maximum values.

alcohol, and dimethylformamide as solvents. The synthesis of the *threo*- and *erythro*-6-[^{2}H]-labelled decan-5-ols, and the principles of the procedure are reported in the preceding Communication.

The results (Table 2) show that the total amount of *syn*-elimination in dec-5-ene formation (% *syn* overall) decreases, in the order anticipated, from 19·4 and 10·1% in benzene and t-butyl alcohol to only 5·4% in dimethylformamide. Considering the mode of formation of the *trans*-isomer (where our earlier findings[1,2,4] on the steric course of cycloalkene formation lead us to expect *syn*-elimination to operate more extensively) we see that in benzene *syn*-elimination indeed accounts for 33% of the reaction and in t-butyl alcohol for 16%; in dimethylformamide this figure is only 4·5%. It is hence not surprising that Froemsdorf *et al.*[4] found practically no *syn*-elimination in the even more strongly dissociating dimethyl sulphoxide.

We may conclude that in the t-butoxide-induced eliminations of toluene-*p*-sulphonate esters of the open-chain secondary alcohols, at any rate in the solvents benzene and t-butyl alcohol, *syn*- and *anti*-elimination do operate side by side. The fact that the contribution of *syn*-elimination is not as extensive as in the case of the cyclodecyl or cyclododecyl toluene-*p*-sulphonates[1,2] is due to the relative slowness of *anti*-elimination in the ten- and the twelve-membered ring, as correctly implied by Froemsdorf *et al.*,[3] and also to the greatly accelerated rates of *syn*-elimination of rings of this size.[4]



RO^- K^+

(1)

TABLE 2

Relative rate constants of syn-*elimination* ($k_{s\to t}$, $k_{s\to c}$) *and* anti-*elimination* ($k_{a\to t}$, $k_{a\to c}$) *leading to* trans- *and* cis-*dec-5-ene from* 1-*butylhexyl toluene*-p-*sulphonate*[a] *and potassium t-butoxide*[b]

Solvent	*trans*-Dec-5-ene $k_{s\to t}$	$k_{a\to t}$	% *syn*	*cis*-Dec-5-ene $k_{a\to c}$	$k_{s\to c}$	% *anti*	% *syn* overall
Benzene[c]	15·1	30·9	33	49·7	4·3	92	19·4
Bu^{t}OH[d]	4·7	24·3	16	65·6	5·4	92	10·1
DMF[e]	3·4	72·6	4·5	22·2	1·8	92	5·2

[a] The method of evaluation of the relative rate constants $k_{a\to t}$, *etc.*, was that described in the preceding Communication for the reaction of the corresponding 'onium salts; [b] a three-fold excess of base was employed; [c] 0·3M-base at 125° for 25 hr.; [d] 1·3M-base at 100° for 10 hr.; [e] 0·9M-base at 40° for 2 hr.

(*Received, June 11th*, 1968; *Com.* 765.)

[1] J. Závada, M. Svoboda, and J. Sicher, *Tetrahedron Letters*, 1966, 1626.
[2] M. Svoboda, J. Závada, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1415.
[3] D. H. Froemsdorf, W. Dowd, W. A. Gifford, and S. Meyerson, *Chem. Comm.*, 1968, 449.
[4] J. Sicher, J. Závada, and J. Krupička, *Tetrahedron Letters*, 1966, 1619; J. Závada, J. Krupička, and J. Sicher, *Chem. Comm.*, 1967, 66; J. Závada, J. Krupička, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1393; J. Sicher and J. Závada, *ibid.*, 1967, **32**, 2122; J. Závada and J. Sicher, *ibid.*, p. 3701; J. Sicher and J. Závada, *ibid.*, 1968, **33**, 1278.