The Question of a Dual Mechanism in Base-promoted Toluene-*p*-sulphonate Eliminations

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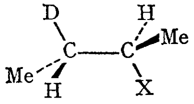
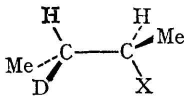
Base-promoted *cis*- and *trans*-eliminations occur simultaneously in certain systems.[1–4] Whereas in some systems the relative rates differ by no more than one power of ten,[5] recent studies show that the *cis*-olefin is produced exclusively by *trans*-elimination, and the *trans*-olefin exclusively by *cis*-elimination. The evidence was obtained by stereochemical labelling with deuterium in alkyltrimethylammonium salts,[4] cyclodecyl trimethylammonium chlorides,[1,2] and cyclodecyl toluene-*p*-sulphonates.[2] Consideration of relative rate versus ring-size suggested that cycloalkyl bromides (C_8–C_{10}) also react in this manner when treated with potassium t-butoxide in t-butyl alcohol but not with potassium ethoxide in ethanol.[3] These authors have suggested[2,4] that the simultaneous operation of *cis*- and *trans*-eliminations leading respectively to *trans*- and *cis*-olefin from one single substrate may be more common than has been believed.

In the reaction of *trans*-2-phenylcyclopentyl toluene-*p*-sulphonate with potassium t-butoxide in t-butyl alcohol, *cis*-elimination competes effectively with *trans* by virtue of the built-in geometric preference for the former and of the enhanced acidity of the β-hydrogen as a result of β-phenyl substitution.[5] Similarly, [2,3-*exo*-$^2H_2$]bicyclo-[2,2,1]heptan-2-*endo*-yl chloride when reacted with potassium t-hexyl oxide undergoes both *cis*- and *trans*-elimination.[6] The pyrolysis of *trans*-2-phenylcyclohexytrimethylammonium hydroxide undergoes predominantly *cis*-elimination to give 1-phenylcyclohexene, though the corresponding *cis*-isomer gives the same product by *trans*-elimination at 133 times the rate.[7] Pyrolysis of [3-*exo*-$^2H_2$]-bicyclo[2,2,1]heptan-2-*exo*-yltrimethylammonium hydroxide and [3-*cis*-^{2}H]bicyclo[2,2,2]octan-2-yl-trimethylammonium hydroxide at 100—130° and 40—60 torr[8] and the reaction of [3-*exo*-^{2}H]bicyclo-[2,2,1]heptan-2-*exo*-ylbromide with potassium t-hexoxide[9] all give the corresponding olefins by exclusive *cis*-elimination.

In view of these findings and of the fact that Sicher and Zavada's[1–4] observations were made under conditions that emphasize the carbanionic character of the transition state,[10] we felt that competing *cis*- and *trans*-eliminations might occur under the strongly basic conditions realized in our studies[11] of eliminations in dimethyl sulphoxide with alkoxide bases. Although earlier work on a cyclohexyl system[11a] had given no evidence for *cis*-elimination, we felt it necessary to check an acyclic system as well since *cis*-elimination in cyclohexyl systems may require prior conversion into the boat conformer.[5]

Our data from the elimination of *erythro*-(Ia) and *threo*-[3-^{2}H]2-butyl toluene-*p*-sulphonate (IIa) in dimethyl sulphoxide reveal no evidence for the simultaneous occurrence of *cis*- and *trans*-eliminations.[12] Comparison of the isotopic compositions of the but-1-ene and the *cis*- and *trans*-but-2-enes† formed from the *erythro*-compound (Table 1) reveals that *cis*-but-2-ene was formed without loss of deuterium while *trans*-but-2-ene was formed with loss of deuterium; from the *threo*-compound, *trans*-but-2-ene was formed without loss of deuterium. Comparison of the isotopic compositions of the butenes from each of the diastereoisomers (Table 1) and those of the trimethylsilyl ethers (Ib and IIb) of the corresponding precursor alcohols (Table 2) reveals no more than a possible minor contribution from an *E*1*cb* mechanism.‡ Therefore, the above results are consistent only with a *trans*-elimination of the *E*2 type in all cases reported herein.





(Ia) $X = OSO_2{\cdot}C_7H_7$ (IIa)
(Ib) $X = OSiMe_3$ (IIb)

These results demonstrate that in acyclic systems that allow the stereoelectronic requirements of both *cis*- and *trans*-eliminations to be met,[5] *trans*-eliminations occur preferentially with almost

TABLE 1

Deuterium content of the olefinic products from the elimination of erythro- *and* threo-[3-^{2}H]2-*butyl toluene*-p-*sulphonates*

			Isotopic composition of olefinic products, %*					
Compound	Solvent	Base	but-1-ene		*trans*-but-2-ene		*cis*-but-2-ene	
(Ia)	DMSO	KOBu^t	$^2H_0$	2·1	$^2H_0$	94·2	$^2H_0$	2·8
			$^2H_1$	96·3	$^2H_1$	3·9	$^2H_1$	96·4
			$^2H_2$	1·6	$^2H_2$	1·9	$^2H_2$	0·8
(IIa)	DMSO	KOBu^t			$^2H_0$	6·0		
					$^2H_1$	91·1		
					$^2H_2$	2·9		
(IIa)	DMSO	KOEt			$^2H_0$	5·8		
					$^2H_1$	91·3		
					$^2H_2$	2·9		

* Measured by mass spectrometry.

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† Since the formation of but-1-ene does not involve the deuterium label in the 3-position, the isotopic distribution in but-1-ene is a direct measure of the amount of label in the starting toluene-*p*-sulphonate unless exchange occurs before elimination. Such exchange should effect a proportionate decrease in the deuterium content of all the resultant butenes.

total exclusion of *cis*-elimination. The unique results obtained by Sicher and Zavada[1–4] apparently stem from the inability of their systems to satisfy these requirements without creating a prohibitive amount of conformational strain.

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TABLE 2

Isotopic composition of trimethylsilyl ethers‡

	(Ib)	(IIb)
$^2H_0$	1·2%	0·8%
$^2H_1$	97·4%	92·7%
$^2H_2$	1·4%	6·5%

‡ Measured by mass spectrometry.

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