The Steric Course of Eliminations in Simple Open-chain 'Onium Compounds: the Contributions of *syn*- and *anti*-Elimination Mechanisms[1]

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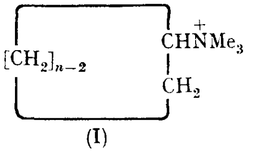
OLEFIN-forming eliminations of the type (1) in open-chain systems are believed to proceed exclusively by an *anti*-elimination mechanism.[2]

$$\mathrm{R^1CH\cdot\overset{+}{N}Me_3\cdot CH_2R^2} + \mathrm{B^-} \rightarrow$$
$$(\textit{cis}\text{ and }\textit{trans})\mathrm{R^1CH{=}CHR^2} + \mathrm{BH} + \mathrm{X^-} \qquad (1)$$

We have shown[1,3] that in alkene formation in the cycloalkyl compounds (I; n = 8—14, 16), as well as in the open-chain system (II), *syn*-elimination is a common and, often preferred course of, reaction. Moreover, we suggested that in processes in which *syn*-elimination operates extensively it usually does so largely to give *trans*-olefin, while *anti*-elimination gives mainly the *cis*-isomer.



(I)

$Bu^tCH_2{\cdot}CH(\overset{+}{N}Me_3){\cdot}CH_2Bu^n$

(II)

$Bu^nCH(\overset{+}{N}Me_3){\cdot}CH_2Bu^n$

(III)

In order to determine the contributions of *anti*- and *syn*-elimination, and the stereoselectivity of these two reaction modes in a quantitative manner and on a simple and generally valid model, we have made a detailed study of the elimination behaviour, under a wide range of experimental conditions, of 1-butylhexyltrimethylammonium chloride (III). The procedure consisted of the determination of the deuterium content of the *cis*- and *trans*-dec-5-enes, obtained from the reaction of *threo*- and *erythro*-2-deuterio-derivatives of (III) {*e.g. threo*- and *erythro*-[2-^{2}H]-(III)} as illustrated for the reaction of *threo*-[2-^{2}H]-(III) in Scheme I. {The [6-^{2}H]-labelled decan-5-ols were obtained, respectively, from *trans*-dec-5-ene by reaction with B_2D_6 (*threo*-isomer), and from the corresponding epoxide by treatment with $LiAlD_4$–$AlCl_3$ (*erythro*-isomer)}. The corresponding quaternary salts (of inverted configuration) were obtained from the toluene-*p*-sulphonate esters by reaction with sodium azide, followed by hydride reduction and quaternization. The two isomeric *cis*-olefins (*cis*-dec-4- and -5-ene) formed in the elimination process can be separated from the two corresponding *trans*-olefins on a preparative scale;[4] separation of the *cis*-dec-4-ene from the *cis*-dec-5-ene (or of the corresponding *trans*-isomers) could not be achieved. The determination of the deuterium content in the olefins produced was therefore carried out as follows. Mixtures of the *cis*-dec-4- and -5-enes (and, separately, of the *trans*-dec-4- and -5-enes) were analyzed for deuterium content and subjected to ozonization, followed by reduction with lithium aluminium hydride: the resulting mixtures of butanol, pentanol, and hexanol were then separated by preparative v.p.c. and each analyzed for deuterium content. (It is invariably found that the butanol is deuterium free and the hexanol has retained all the label: this forms evidence for the correctness of the methods employed.) From these findings it was possible to evaluate the relative rate constants $k_{s\to t}$, $k_{a\to t}$, $k_{a\to c}$, and $k_{s\to c}$ for the reaction of the parent (unlabelled) 'onium compound (III), as detailed in footnote *a* to the Table.

The results (Table) show that *syn*- and *anti*-

Relative rate constants[a] *of* syn- *and* anti-*elimination leading to* trans- *and* cis-*dec-5-ene from* 1-*butylhexylltrimethylammonium chloride* (III)

		trans-Dec-5-ene			*cis*-Dec-5-ene			% *syn*
Reaction	Base/solvent[b]	$k_{s\to t}$	$k_{a\to t}$	% *syn*	$k_{a\to c}$	$k_{s\to c}$	% *anti*	overall
1	Pyrolysis	67·4	3·6	95	27·6	1·4	95	68·8
2	Bu^{t}OK/DMSO	72·9	7·1	91	18·4	1·6	92	74·5
3	Bu^{t}OK/benzene	82·4	8·6	90	6·7	2·3	75	84·7
4	Bu^{t}OK/Bu^{t}OH	61·8	9·2	87	26·3	1·7	94	63·5
5	MeOK/MeOH	6·7	14·3	32	73·2	5·8	93	12·5

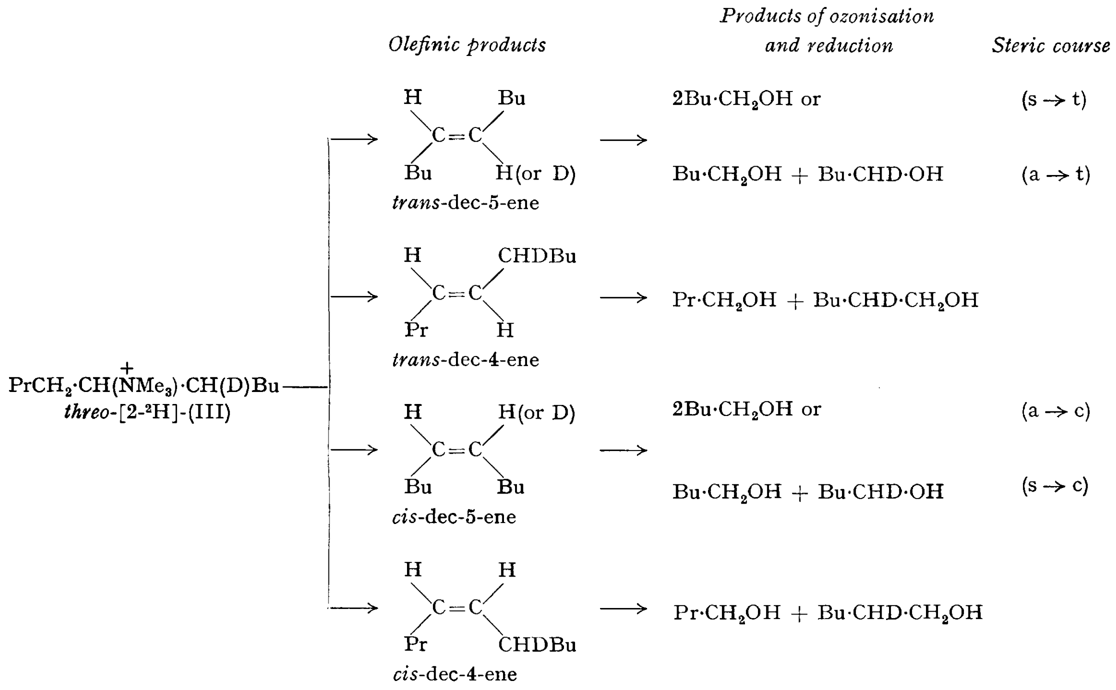
[a] The values of the relative rate constants, $k_{s\to t}$, $k_{a\to t}$, $k_{s\to c}$ and $k_{s\to c}$, were evaluated assuming (a) that the rates of formation of the 4- and 5-position isomeric decenes from (III) are identical and (b) that *threo*- and *erythro*-[2-^{2}H]-(III) are completely mono-deuteriated; the actual deuterium content of the two diastereoisomers is about 95% per mole. The following relationships were used: (1) $k_{s\to t} + k_{a\to t} + k_{a\to c} + k_{s\to c} = 100$ (by definition); (2) $(k_{s\to c} + k_{a\to c})/(k_{s\to t} + k_{a\to t})$ = (% *cis*-dec-4- and-5-ene)/(% *trans*- dec-4- and-5-ene) [*cf.* assumption (a) above]; (3)$(k_{a\to c}/k_{s\to c}) = [(D_0/D_1)^{cis}_{pent} - 4(D_0/D_1)^{cis}_{olef} - 1]/2(D_0/D_1)^{cis}_{olef}$; and (4) $k_{s\to t}/k_{a\to t} = [(D_0/D_1)^{trans}_{pent} - 4(D_0/D_1)^{trans}_{olef} - 1]/2(D_0/D_1)^{trans}_{olef}$, where $(D_0/D_1)^{cis}_{olef}$ and $(D_0/D_1)^{trans}_{olef}$ are values of the ratio of the d_0 to the d_1 species, as determined by mass spectroscopy, in the mixture of *cis*-dec-4- and-5-ene, and *trans*-dec-4- and-5-ene, respectively; and $(D_0/D_1)^{cis}_{pent}$ and $(D_0/D_1)^{trans}_{pent}$ pent *trans* are the corresponding values for the pentanol fractions obtained, respectively, from the above *cis*- and *trans*-decene mixtures. The experimental values substituted into equation (2) refer to the "parent" compound (III), those used in equations (3) and (4) to the *threo*-deuteriated diastereoisomer, *threo*-[2-^{2}H]-(III).

In view of the high degree of stereoselectivity of both the *syn*- and the *anti*-elimination reactions, reinforced by the deuterium isotope effect, it is not possible for purely numerical reasons, to use analogous experimental data from the reaction of *erythro*-[2-^{2}H]-(III). Nevertheless, these data serve to confirm qualitatively and in some cases semi-quantitatively, the correctness of the conclusions drawn.

The mass spectroscopic determinations were kindly obtained by Dr. L. Dolejš and his staff.

[b] The conditions of concentration, temperature, and reaction time were as reported previously (ref. 3).

elimination operate side by side under most conditions; *syn*-elimination[†] being the principal process in all reactions except that using methoxide–methanol.



SCHEME 1

Moreover, *syn*- as well as *anti*-elimination may, in most cases, be seen to possess a considerable degree of stereo-selectivity, in the direction anticipated from our earlier work involving the compounds (I) and (II).[1,3] Thus, with one exception, *cis*-dec-5-ene arises by over 90% by the *anti*-elimination route; correspondingly, *trans*-dec-5-ene is formed preponderantly (87—95%) by *syn*-elimination, except for the reaction in methoxide–methanol.

These results establish that the conclusions regarding the steric course of 'onium base eliminations reached on the basis of studies employing the compounds (I) and (II) apply also to the simple open-chain case (III). The view that *anti*-elimination is the preferred, or even the sole, route in these reactions[2] must therefore definitely be abandoned: a dichotomous situation prevails over a wide range of conditions of base and solvent properties and substrate structure.

The recent important finding by Coke, Cooke, and Manning[6] that the formation of cyclobutene, cyclopentene, and cycloheptene, as well as *cis*-cyclooctene from the 'onium salts under Hofmann (pyrolytic) conditions in part proceeds by *syn*-elimination (*i.e. syn* → *cis*) further emphasizes the importance of the *syn*-mechanism in 'onium-base eliminations. Our present results suggest, however, that in the absence of specific steric features, such as torsional constraint, the *syn* → *cis* path is not important. The results of Coke *et al.*[6] may thus be accommodated in our general picture of the

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[†] Trimethylamine formed from 1-([1-$^{2}H_{2}$]butyl)[2-$^{2}H_{2}$]pentyltrimethylammonium chloride under conditions of th reactions 2 and 4 (Table) was found to be deuterium free; this excludes the unlikely possibility that *syn*-elimination here proceeds by way of an ylid intermediate (α′β-elimination).[5] The equally remote possibility of an α-elimination mechanism was excluded by showing that the non-4-ene, obtained from 1-butyl[1-H^{2}]pentyltrimethylammonium chloride under the conditions of reactions 2, 4, and 5, contains all the deuterium present in the starting compound.

steric course of bimolecular eliminations and no substantial modification of our earlier views[1,3] is necessary.

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[1] This is the fifteenth of a series of papers dealing with the mechanism of elimination reactions; for previous paper see J. Závada, M. Svoboda, and J. Sicher, *Coll. Czech. Chem. Comm.*, in the press.

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[6] J. L. Coke, M. P. Cooke, and M. C. Mourning, *Tetrahedron Letters*, 1968, 2247; J. L. Coke and M. P. Cooke, *ibid.*, p. 2253.