

STEREOCHEMICAL STUDIES. LXI.*

THE CONTRIBUTION OF *syn*- AND *anti*-ELIMINATION TO OLEFIN FORMATION IN OPEN-CHAIN SYSTEMS: 5-DECYL AND 5-NONYL TRIMETHYLAMMONIUM BASES AND TOSYLATES**

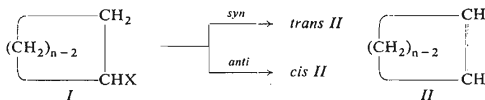
†J. SÍCHER, J. ZÁVADA and M. PÁNKOVÁ

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, Prague 6

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The steric course of olefin formation in the reaction of the title compounds with a wide range of base-solvent systems has been investigated with the aid of stereospecifically β -deuterated, and of $\beta, \beta, \beta', \beta'$ -tetradeuterated, substrates. In the reaction of the 'onium bases with potassium tert-butoxide in protic as well as aprotic solvents, and also on pyrolysis, the *trans*-olefin (*trans*-5-decene or *trans*-4-nonene) is formed mainly by *syn*-elimination; only when methoxide in methanol is used does *trans*-olefin formation proceed mainly by *anti*-elimination. In the reaction leading to the *cis*-olefin, *anti*-elimination represents the predominant reaction path under all the reaction conditions investigated. In the reaction of the tosylates, *syn*-elimination contributes only to a minor extent.

In several papers published in the years 1966–1968 we reported⁴⁻⁸ the finding that bimolecular eliminations of cycloalkyl 'onium bases (*I*, X = N⁽⁺⁾(CH₃)₃; n = 8–16) to give *cis*- and *trans*-cycloalkenes (*II*, *cis* and *trans*) exhibit an unusual and till then unrecognized reaction pattern, the *cis*-cycloalkenes being formed largely by the



SCHEME 1

* Part LX: This Journal 36, 3128 (1971).

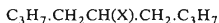
** The results contained in this paper have, in part, been communicated in preliminary form^{1,2}. This is the twentieth of a series of papers dealing with the mechanism of elimination reactions; for previous paper see ref.³.

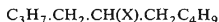
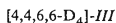
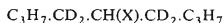
† Deceased September 8th, 1970.

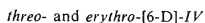
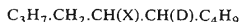
“usual” *anti*-elimination mechanism but the *trans*-cycloalkenes by the “stigmatized” *syn*-elimination mechanism* (Scheme 1).

Subsequent work on cycloalkyl tosylates¹⁰ (I , $X = \text{OTs}$) and bromides^{11,12} (I , $X = \text{Br}$) showed that with these leaving groups the *syn*-mechanism also operates in *trans*-cycloalkene formation but that this reaction mode is here less general than in the case of the 'onium base eliminations.

Medium rings are well known in many respects to exhibit unusual reactivity behaviour¹³. The question posed itself whether the massive contribution of *syn*-elimination to medium ring cycloalkene formation noted in the above studies is not another manifestation of the unique position of compounds of this class. In particular, it was necessary to find out whether, and to what extent, the *syn*-mechanism will also be encountered in eliminations in simple open chain systems. In the past, it has been assumed¹⁴⁻¹⁷ that the sole mechanism operating in such systems is *anti*-elimination. An inspection of the literature reveals, however, that the experimental evidence on which this view is based is not very substantial. In fact, for the reaction of the open chain 'onium compounds the above view is based entirely on analogy. For the case of alkene formation from alkyl bromides and alkyl tosylates there is some direct evidence provided by the pioneering studies of Skell and his coworkers¹⁸⁻²⁰ on the reaction of 2-butyl tosylate and 2-butyl bromide with potassium ethoxide in ethanol using derivatives stereospecifically deuterium labelled on $C_{(3)}$; both *trans*- and *cis*-2-butene were found to be formed exclusively by *anti*-elimination. It should be noted that in the case of the elimination of 2-butyl bromide the *anti* steric course was only assumed. It was on the basis of this assumption that it was concluded that the steric course of photo-addition of deuterium bromide to the 2-butenes proceeds in a *trans* fashion. Recent investigations^{7,11,12,21} have revealed that primary alkoxide systems such as ethoxide-ethanol favour *anti*-relative to *syn*-elimination. Again, therefore, it appeared that the generalisations commonly drawn from Skell's results may not be fully justified. At any rate, corresponding studies in which a greater range of base-solvent systems would be employed appeared to be necessary.



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* Coke and Mourning⁹ have subsequently examined the steric course of the elimination of cycloöctyltrimethylammonium hydroxide under pyrolytic conditions; they found that *trans*-cycloöctene is indeed formed by *syn*-elimination exclusively; *cis*-cycloöctene is formed in practically equal proportions by *syn*- and *anti*-elimination.

Two such investigations are reported in the present paper. The first is a qualitative study on the open-chain system *III* ($X = \overset{(+)}{N}(\text{CH}_3)_3$ and OTs), using the 4,4,6,6-tetra-deuterated derivatives. The other is a quantitative study on the open-chain system *IV* ($X = \overset{(+)}{N}(\text{CH}_3)_3$ and OTs) employing reactants stereospecifically deuterium labelled on carbon 6.

SYNTHESIS

The 4,4,6,6-tetradeuterated derivatives of *III* were prepared from 5-nonanone by six times repeated treatment with a 1 : 1 mixture of heavy water and dioxane, containing a catalytic amount of sodium deuterioxide. The tetradeuterated ketone was converted into the labelled tosylate *III* ($X = \text{OTs}$) and the quaternary base *III* ($X = \overset{(+)}{N}(\text{CH}_3)_3$) by standard procedures described in the Experimental.

The *threo*-6-deuterated 5-decanol was obtained from *trans*-5-decene by reaction with perdeuterated diborane²². This procedure was not applied to the synthesis of the corresponding *erythro*-isomer because of difficulties in the preparation of pure *cis*-5-decene from 5-decyne (cf. Experimental). We therefore again set out from *trans*-5-decene, converted this to the epoxide which on reaction with lithium aluminium deuteride- AlCl_3 ²³ gave *erythro*-6-deuterio-5-decanol. Conversion of the two labelled alcohols to the corresponding inverted amines was carried out by treating their *p*-toluenesulphonyl esters with sodium azide in dimethyl sulphoxide and subsequent reduction with lithium aluminium hydride. Clarke-Eschweiler methylation followed by reaction with methyl iodide in benzene gave the required quaternary salts. The corresponding unlabelled compounds were prepared by analogous procedures.

EXPERIMENTAL

trans-5-Decene

5-Decyne²⁴ (138 g, 1 mol) was added under intense stirring to a solution of sodium (230 g, 10 gat) in liquid ammonia (7 l), the reaction mixture kept at a mild reflux for 5 h, diluted with ether (2 l) and the excess sodium destroyed by careful addition of ammonium nitrate. The decolourised solution was treated with conc. ammonium hydroxide solution (2 l), followed by water (1.5 l). The excess ammonia was driven off, the ethereal layer separated and worked up in the standard manner^{25,26}. Distillation afforded 124 g (90%) of *trans*-5-decene (homogeneous by v.p.c.), b.p. 75°C/12 Torr. For $\text{C}_{10}\text{H}_{20}$ (140.3) calculated: 85.63% C, 14.37% H; found: 85.43% C, 14.40% H.

cis-5-Decene-[5-D]

A solution of 5-decyne (2.8 g, 20 mmol) in diglyme (20 ml) was treated with sodium borodeuteride (260 mg, 6 mmol). The flask was placed into an ice-bath and boron trifluoride etherate (1.1 g,

8 mmol) was added dropwise under intense stirring under a slow stream of nitrogen. The reaction mixture was allowed to stand for 1 h at 5°C, treated with acetic acid (4 ml), allowed to stand overnight, diluted with water (100 ml) and extracted with pentane. The pentane extracts were repeatedly washed with water, dried over magnesium sulphate and pentane slowly distilled off. The crude product (2.4 g, 85%) contained, according to v.p.c., 72% *cis*-olefin, 9% *trans*-olefin and 31% starting compound. The pure *cis*-5-decene was obtained by preparative v.p.c. and found to contain 16.6% d_0 and 83.4% d_1 .

trans-5,6-Epoxydecane

Prepared from the *trans*-olefin and perphthalic acid by the described procedure²⁷ in 91% yield.

5-Decanol

A. Boron trifluoride etherate (22.9 g, 0.161 mol) was added in the course of 30 minutes to an ice-cooled and stirred solution of sodium borohydride (5 g, 0.123 mol) and *trans*-5-decene (61.25 g, 0.441 mol) in diglyme (500 ml). The reaction mixture was allowed to stand at 0°C for 5 h under nitrogen and treated successively with water (22 ml), 3*N*-NaOH (115 ml) and 30% hydrogen peroxide (100 ml), and stirring continued for 2 h at room temperature. The mixture was then diluted with about 2 l of water and then extracted with pentane. The pentane extracts were washed with water, dried with magnesium sulphate and taken down. Distillation of the residue at reduced pressure afforded 60 g of the crude product which contained some starting olefin and which was purified by fractionation through a column. The yield of the v.p.c. pure alcohol was 40.6 g (59%), b.p. 123°C/30 Torr. For C₁₀H₂₂O (158.3) calculated: 75.88% C, 14.01% H; found: 75.88% C, 13.96% H.

B. *trans*-5,6-Epoxydecane (71 g, 0.45 mol) in ether (300 ml) was added to a solution of lithium aluminium hydride (15 g, 0.4 mol) and aluminium chloride²³ (15 g, 0.11 mol) in ether (300 ml) under ice cooling. The reaction mixture was stirred for 15 minutes, then treated with water, followed by 25% sulphuric acid. The ethereal layer was separated off, washed with water, dilute sodium hydroxide, water, dried and the ether distilled off. Distillation of the residue afforded 70 g (97%) 5-decanol pure by v.p.c.

threo-5-Decanol-[6-D]

trans-5-Decene (123.5 g, 0.88 mol), sodium borodeuteride (10 g, 0.245 mol) and boron trifluoride etherate (45.8 g, 0.322 mol) by procedure A (above) on distillation afforded 73 g (52%) of the title compound; it contains, according to mass spectroscopy, 6% d_0 and 94% d_1 .

erythro-5-Decanol-[6-D]

trans-5,6-Epoxydecane (71 g, 0.45 mol), lithium aluminium deuteride (16 g, 0.4 mol) and aluminium chloride (15 g, 0.11 mol) afforded by procedure B (above) 69.5 g (97%) of the title compound, pure by v.p.c.; it contains, according to mass spectroscopy, 4% d_0 and 96% d_1 .

5-Decyl *p*-Toluenesulphonate

A solution of 5-decanol (34 g, 0.22 mol) and *p*-toluenesulphonyl chloride (50 g, 0.26 mol) in pyridine (300 ml) was allowed to stand at 0°C for 4 h, the reaction mixture poured on ice and the product taken up in ether. The usual work-up afforded an oil which was purified by recrystallisa-

tion at -40°C . For $\text{C}_{17}\text{H}_{29}\text{O}_3\text{S}$ (313.5) calculated: 65.36% C, 9.03% H, 10.24% S; found: 65.28% C, 9.05% H, 10.07% S. The corresponding *threo*- and *erythro*-deuterium labelled compounds were prepared analogously from the corresponding alcohols.

5-Decyldimethylamine

A solution of sodium azide (40 g, 0.62 mol) and 5-decyl *p*-toluenesulphonate (58 g, 0.19 mol) in dimethyl sulphoxide (600 ml) containing sodium carbonate (24 g) was heated to $85-90^{\circ}\text{C}$ for 4 h under continuous stirring, the cold mixture diluted with water (3 l) and the product taken up in ether. The ethereal extracts were washed repeatedly with water, carefully dried, the ether distilled off and the residue added to a solution of lithium aluminium hydride (10 g, 0.25 mol) in ether (300 ml). The reaction mixture was refluxed for one hour and then treated, successively, with water (19 ml), 15% aqueous sodium hydroxide (19 ml) and water (56 ml). The precipitated inorganic hydroxides were filtered off and the precipitate further extracted by boiling with ether. The combined extracts were dried over solid potassium hydroxide and the ether distilled off.

The residue was taken up in formic acid (300 ml) and 30% formaldehyde (300 ml) and the mixture refluxed 24 h. The cooled reaction mixture was treated with conc. hydrochloric acid (35 ml) and the solution taken down on the aspirator. The residue was taken up in hot water (200 ml), the insoluble material filtered off and the filtrate extracted with ether. The aqueous layer was made strongly alkaline and the liberated amine taken up in ether. The extracts were dried over solid potassium hydroxide, the ether driven off and the residue distilled, b.p. $112^{\circ}\text{C}/20$ Torr. Yield 30 g (87.5%). For $\text{C}_{12}\text{H}_{27}\text{N}$ (185.3) calculated: 77.75% C, 14.68% H, 7.56% N; found: 78.14% C, 14.60% H, 7.67% N. *erythro*- and *threo*-5-Decyldimethylamine-[6-D] was prepared by an analogous procedure from the appropriately labelled tosylates.

5-Decyltrimethylammonium Iodide

A solution of 5-decyldimethylamine (30 g, 0.16 mol) in benzene (250 ml) was treated with methyl iodide (45 g, 0.32 mol) under ice cooling. The mixture was allowed to stand in the ice-bath for two hours and then at room temperature for 24 h, diluted with light petroleum and cooled. The crystals which separated were filtered off and washed with light petroleum, m.p. $215-216.5^{\circ}\text{C}$ (decomp.), yield 52 g (98%). For $\text{C}_{13}\text{H}_{30}\text{N}$ (327.3) calculated: 47.70% C, 9.24% H, 4.28% N; found: 47.95% C, 9.21% H, 4.36% N. The labelled compounds were prepared in an analogous manner.

TABLE I

Conditions Employed in the Elimination Reaction of the ⁽⁺⁾Onium Bases III and IV ($\text{X} = \text{N}(\text{CH}_3)_3$)

Base/solvent ^a	Molarity of substrate	Molarity of base	Temperature/time $^{\circ}\text{C}/\text{h}$
$\text{CH}_3\text{OK}/\text{CH}_3\text{OH}$	0.60M ^b	1.80M	130/24
<i>t</i> - $\text{C}_4\text{H}_9\text{OK}/t\text{-C}_4\text{H}_9\text{OH}$	0.40M ^c	1.20M	100/10
<i>t</i> - $\text{C}_4\text{H}_9\text{OK}/(\text{CH}_3)_2\text{SO}$	0.28M ^c	0.44M	40/0.5
<i>t</i> - $\text{C}_4\text{H}_9\text{OK}/\text{C}_6\text{H}_6$	0.13M ^c	0.44M	80/8

^a Alkoxide solutions were prepared as reported previously^{6,7}; ^b quaternary iodides, ^c quaternary chlorides.

5-Nonanone-[4,4,6,6-D₄]

A solution of 5-nonanone²⁸ (6.5 g, 0.05 mol) in 0.5M sodium deuteroxide in 1:1 deuterium oxide-dioxane (200 ml) was refluxed for 3 h under exclusion of atmospheric moisture. The cooled reaction mixture was treated with 0.1M aqueous acetic acid and the product taken up in pentane. The pentane extracts were repeatedly extracted with water, dried and the pentane carefully distilled off. The residue was subjected to the same treatment and the entire procedure was repeated five times. The product (4.4 g, 66%) thus obtained contained 97.3% *d*₄ and 2.7% *d*₃.

5-Nonanol-[4,4,6,6-D₄]

A solution of the above ketone (3.8 g, 0.027 mol) by reduction with lithium aluminium hydride in ether gave 3.8 g (100%) of the alcohol, b.p. 95°C/18 Torr. It contains 97.4% *d*₄ and 2.7% *d*₃.

5-Nonanol-[5-D]

5-Nonanone (3.8 g, 0.027 mol) was reduced with lithium aluminium deuteride in ether (54 ml of an 0.5M solution). The alcohol contained 97.0% *d*₁.

Deuterium Labelled 5-Nonyl *p*-toluenesulphonates were prepared from the corresponding alcohols by the procedure described here for the corresponding 5-decyl derivatives.

TABLE II

Composition of Products Obtained from the Reaction of 5-Decyltrimethylammonium Bases (+) (IV, X = N(CH₃)₃) under Different Conditions

Compound	Conditions	% 4- and 5-Decenes ^b	% <i>trans</i> -Olefines in <i>cis-trans</i> mixture ^a	% 5-Decyl-N(CH ₃) ₂ ^b
5-Decyl	CH ₃ OK/CH ₃ OH	33	21.0	60
<i>erythro</i> -6-D		34	19.4	50
<i>threo</i> -6-D		37	28.0	62
5-Decyl	<i>t</i> -C ₄ H ₉ OK/ <i>t</i> -C ₄ H ₉ OH	37	71.0	58
<i>erythro</i> -6-D		34	68.3	46
<i>threo</i> -6-D		29	71.6	49
5-Decyl	<i>t</i> -C ₄ H ₉ OK/(CH ₃) ₂ SO	63	80.0	^c
<i>erythro</i> -6-D		71	79.9	^c
<i>threo</i> -6-D		71	82.1	^c
5-Decyl	<i>t</i> -C ₄ H ₉ OK/C ₆ H ₆	52	90.0	^c
<i>erythro</i> -6-D		92	92.4	^c
<i>threo</i> -6-D		85	93.4	^c
5-Decyl	pyrolysis of	76	71.0	^c
<i>erythro</i> -6-D	quaternary hydroxide	70	69.2	^c
<i>threo</i> -6-D		71	75.5	^c

^a Determined by v.p.c. analysis; ^b yield of isolated product; ^c not determined.

Deuterium labelled 5-nonyltrimethylammonium iodides were prepared from the above tosylates *via* the corresponding dimethylamino derivatives, exactly as reported above for the corresponding 5-decyl derivatives. The melting points agree with that found previously^{2,9} for the non-deuterated compound.

Conversion of the Quaternary Iodides to the Chlorides

The quaternary chlorides were shaken with an excess of silver chloride in methanol under standard conditions^{5,29}. The chlorides are hygroscopic and melt over a broad range at temperatures above 200°C. Before further use they were dried at the oil pump at 70–80°C for 5 h.

Elimination Reactions

A. *Quaternary bases*: The conditions used are summarised in Table I. The reactions were invariably carried out in sealed tubes which had been flushed with dry nitrogen previous to the reaction. After completed heating, the ampoules were cooled to –60°C and, when convenient, stored at this temperature. The contents were acidified with 15% hydrochloric acid, then quantitatively transferred into a separatory funnel, diluted with a ten-fold amount of water and taken up in pentane. The pentane extract was repeatedly washed with water, dried and the pentane carefully distilled off through a short column. The residue was distilled on the aspirator. The yields of the olefins and product composition are given in Table II.

The acid aqueous layer was taken down to a small volume on the aspirator, the residue made alkaline and the amines set free isolated in the usual manner. The yields of the isolated 5-decyl-dimethylamines are summarized in Table II. In the elimination reaction involving 4,4,6,6-tetra-deuterio-5-nonyltrimethylammonium chloride with tert-butoxide in tert-butanol and in dimethyl sulphoxide we also isolated the trimethylamine formed, using the procedure reported earlier⁸. The deuterium content in the trimethylamine was in both cases less than 0.5% d_1 .

Pyrolysis of 5-decyltrimethylammonium hydroxide: A solution of the quaternary iodide (8.5 g) in a minimum amount of water was filtered through a column of Zerolith-FF (150 ml) which was then washed with carbon dioxide free distilled water. The solution was taken to dryness on the rotatory evaporator at 40°C, the residue transferred into a Hickman flask (equipped with

TABLE III

Conditions Employed in the Elimination Reaction of the Tosylates III and IV (X = OTs) with Potassium tert-Butoxide

Solvent ^a	Molarity of tosylate	Molarity of base	Temperature/time °C/h
HCON(CH ₃) ₂	0.20	0.9	40/2
(CH ₃) ₂ SO	0.20	0.9	40/2
t-C ₄ H ₉ OH	0.27	1.3	100/2
C ₆ H ₆	0.12	0.3	125/25

^a Alkoxide solutions were prepared as described previously^{6,7}.

a reflux condenser cooled to -70°C), dried on the oil pump for 2 h at laboratory temperature, and then very slowly heated on the water pump up to 170°C (bath temperature). The distillate was taken up in pentane and the pentane solution extracted with 1M-HCl. The usual work-up of the pentane fraction afforded 3 g of an olefin mixture; the acid extracts afforded 70 mg of 5-decyl-dimethylamine. The pyrolysis of the deuterium labelled 'onium bases was carried out in the same manner.

B. p-Toluenesulphonates: The conditions used are summarised in Table III. The reactions were carried out in sealed ampoules under nitrogen. The contents of the ampoules were transferred into a separatory funnel using pentane, diluted to a ten-fold volume with water and extracted with pentane. The extracts were repeatedly washed with water, dried over magnesium sulphate and the pentane carefully distilled off. The composition of the products obtained from the reaction of the 5-decyl *p*-toluenesulphonates is shown in Tables IV and V. As may be seen from Table IV, the olefins are accompanied by small amounts of other products. These were separated as follows. The crude product (4–5 g) was placed on a column of neutral alumina (act. II, 500 g) and eluted with pentane, fractions of 200 ml being collected. The olefin mixture was contained

TABLE IV

Composition (%) of Products Obtained from the Reaction of 5-Decyl *p*-Toluenesulphonate (IV; X = OTs) with Potassium tert-Butoxide in Different Solvents

Product ^a	C ₆ H ₆	t-C ₄ H ₉ OH	HCON(CH ₃) ₂
4- and 5-Decenes	77.3	91	95
tert-Butyl 5-decyl ether ^b	3.4	5.5	1
5-Decanone ^c	2.3	0	0.5
5-Decanol ^c	15.2	3.5	3.5

^a Determined by v.p.c. analysis using 5% 1,2,3-tris-β-cyanoethoxypropane on ground unglazed porous tile at 140°C ; ^b assignment of the structure follows from NMR data and elemental analysis; ^c tentative structure deduced from the identity of v.p.c. retention data.

TABLE V

Percentage of *trans*-Olefin in *cis-trans* Olefinic Mixture Obtained from the Reaction of 5-Decyl *p*-Toluenesulphonates (IV, X = OTs) with Potassium tert-Butoxide in Different Solvents

Solvent	5-Decyl	<i>erythro</i> -[6-D]	<i>threo</i> -[6-D]
HCON(CH ₃) ₂	76.0	68.3	82.4
t-C ₄ H ₉ OH	29.0	22.2	31.5
C ₆ H ₆	46.0	41.9	49.4

in fractions 2 and 3; fraction 5 contained the tert-butyl ether. 5-Decanone and 5-decanol were eluted with a pentane-ether (2 : 1) mixture. The olefins were thus obtained in a yield of 50–80%.

Separation of the 4- and 5-Decenes

The mixture of 4- and 5-decenes (3–4 g), obtained as indicated in the preceding paragraph, was placed on a column prepared from 500 g neutral alumina containing 30% AgNO_3^{30} . Elution with pentane-ether (99 : 1) afforded a mixture of the two *trans*-olefins (4- and 5-decenes) (fractions 1–8, 600 ml each); pentane-ether (97 : 3) eluted the corresponding *cis*-olefins (fractions 10–20, 600 ml each). The individual fractions were carefully taken down, the residues combined and distilled. The isomer purity of the two fractions was better than 99%. The deuterium content found in the separated *cis*- and *trans*-fractions is summarised in Tables VI and VII.

*Ozonisation*³¹: The above olefin fraction (0.3 g) in pentane (10 ml) was cooled to -60°C and at this temperature treated with ozone till the solution attained a permanent blue colouration. The excess ozone was then driven out with nitrogen, and the ozone free solution, still at -60°C ,

TABLE VI

Reaction of *erythro*- and *threo*-6-D-Labelled 5-Decyltrimethylammonium Bases IV under Different Conditions: Deuterium Isotope Composition Data

Compound	Reaction conditions	% d_1 in <i>trans</i> -Fraction ^a		% d_1 in <i>cis</i> -Fraction ^a	
		4- and 5-decenes	pentanol ^b	4- and 5-decenes	n-pentanol ^b
<i>erythro</i> ^c	$\text{CH}_3\text{OK}/\text{CH}_3\text{OH}$	83.5	24.9	99.0	48.7
<i>threo</i> ^d		93.4	43.2	80.4	9.8
<i>erythro</i> ^c	$t\text{-C}_4\text{H}_9\text{OK}/t\text{-C}_4\text{H}_9\text{OH}$	97.4	47.7	98.6	48.8
<i>threo</i> ^d		79.4	13.9	86.6	11.2
<i>erythro</i> ^e	$t\text{-C}_4\text{H}_9\text{OK}/(\text{CH}_3)_2\text{SO}$	98.2	48.8	99.9	50.0
<i>threo</i> ^d		78.0	9.8	88.3	15.3
<i>erythro</i> ^c	$t\text{-C}_4\text{H}_9\text{OK}/\text{C}_6\text{H}_6$	99.0	49.5	92.0	41.4
<i>threo</i> ^d		79.9	11.8	90.0	29.1
<i>erythro</i> ^c	pyrolysis	97.9	47.8	99.5	49.0
<i>threo</i> ^d		76.2	6.1	82.7	7.9

^a Values given in the Table were corrected for incomplete labelling; ^b n-butanol contained invariantly less than 0.5% d_1 species, whereas deuterium content in n-hexanol was in all cases practically identical with that of the starting substrate. Similarly, deuterium content of 5-decyltrimethylamine isolated from the reaction of the two substrates in methoxide-methanol and tert-butoxide-tert-butanol was identical with those of corresponding starting compounds. The recovered amines were used in further E2 reactions; identical results were obtained using either authentic or recycled substrates; ^c starting 5-decyltrimethylamine contained 94% d_1 species; ^d starting 5-decyltrimethylamine contained 96% d_1 species; ^e starting 5-decyltrimethylamine contained 80% d_1 species.

treated with 1M ethereal lithium aluminium hydride (10 ml). The mixture was allowed to attain room temperature, allowed to stand for 4 h and treated with water (10 ml). The organic layer was separated off, dried, the solvent driven off and the residue distilled. The mixture of n-butanol, n-pentanol and n-hexanol thus obtained was separated by preparative gas chromatography: the alcohols thus obtained were better than 99% pure. The deuterium content of the alcohols is given in Tables VI and VII.

Control Experiments

A mixture (2 g) containing equal parts of *trans*-5-decene and *cis*-5-decene-[5-D] (83.4% d_1) was placed on a silver nitrate-aluminium oxide column, exactly as in the preparative scale separations described above. The *trans*-olefin isolated was found to contain 1.4% d_1 ; the *cis*-olefin 82.7% d_1 . This result shows that there is about 1% scrambling during the passage of the olefins through the silver nitrate column. When the *trans*-olefin was subjected to ozonisation followed by reduction as indicated in the preceding paragraph, n-pentanol, containing less than 1% of n-butanol and n-hexanol, was obtained. An analogous treatment of the *cis*-olefin obtained above afforded n-pentanol of comparable purity which, according to mass spectroscopy, contained 41.5% d_1 , in almost perfect agreement with theory (41.7%).

Gas Chromatography

The analyses were performed on CHROM-3 (Laboratorní potřeby, Prague) instrument using a flame ionisation detector. The analytical separation of the *cis*- from the *trans*-olefins was performed using 2% saturated silver nitrate in triethylene glycol on the ground unglazed porous plate at 40°C. The preparative separation of n-butanol, n-pentanol and n-hexanol was carried out on the Beckmann GC2 instrument using 10% diethylene glycol succinate on the same support at 130°C.

TABLE VII

Reaction of *erythro*- and *threo*-6-D-Labelled 5-Decyl *p*-Toluenesulphonates IV with Potassium tert-Butoxide in Different Solvents: Deuterium Isotope Composition Data

Compound	Solvent	% d_1 in <i>trans</i> -Fraction ^a		% d_1 in <i>cis</i> -Fraction ^a	
		4- and 5-decenes	n-pentanol ^b	4- and 5-decenes	n-pentanol ^b
<i>erythro</i> ^c	HCON(CH ₃) ₂	81.8	7.0	100.0	49.5
<i>threo</i> ^d		99.6	48.6	81.0	9.7
<i>erythro</i> ^c	t-C ₄ H ₉ OH	76.6	14.6	100.0	50.0
<i>threo</i> ^d		97.2	46.9	72.6	7.0
<i>erythro</i> ^c	C ₆ H ₆	85.0	27.3	100.0	49.4
<i>threo</i> ^d		93.0	41.1	75.6	8.1

^a Values given in the Table were corrected for incomplete labelling; ^b n-butanol contained uniformly less than 0.5% d_1 species. Deuterium content of n-hexanol was in all cases the same as in the corresponding starting alcohol; ^c starting 5-decanol contained 96.0% d_1 species; ^d starting 5-decanol contained 94.0% d_1 species.

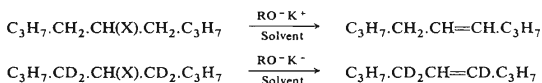
RESULTS

THE 5-NONYL SYSTEM

It has been noted on previous occasions^{9,32} that the values of (k_H/k_D) found for concurrent *anti*- and *syn*-elimination reactions are not identical, the isotope effect for the former process being significantly higher than for the latter, *i.e.* $(k_H/k_D)_{anti} > (k_H/k_D)_{syn}$. It should be possible to make use of this fact for obtaining qualitative information on the steric course of a bimolecular elimination reaction, for, if a system reacts according to the *syn* → *trans*, *anti* → *cis* dichotomy pattern, the *trans-cis* isomer ratio obtained from a substrate in which all the β-hydrogen atoms have been replaced by deuterium should be notably higher than that obtained from the non-deuterated parent compound. On the other hand, when both isomeric olefins are formed by the same mechanism (*e.g.* both by *anti*-elimination), one might expect the values of $(k_H/k_D)_{cis}$ and $(k_H/k_D)_{trans}$ to be closely similar; in such a case the pre-

TABLE VIII

The *cis-trans* Olefin Composition from the Reactions:



X	Base/solvent	<i>trans/cis</i>	$\frac{(k_H/k_D)_{cis}}{(k_H/k_D)_{trans}}$	
(+) N(CH ₃) ₃	$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{t-C}_4\text{H}_9\text{OK}/(\text{CH}_3)_2\text{SO}$	4.55	1.9	
	$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{t-C}_4\text{H}_9\text{OK}/\text{t-C}_4\text{H}_9\text{OH}$	2.79		
	$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{CH}_3\text{OK}/\text{CH}_3\text{OH}$	0.305	1.15	
	$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\}$	0.353		
	OTs	$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{t-C}_4\text{H}_9\text{OK}/\text{HCON}(\text{CH}_3)_2$	3.06	1.0
		$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\}$	3.08	
$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{t-C}_4\text{H}_9\text{OK}/\text{t-C}_4\text{H}_9\text{OH}$		0.50	0.9	
$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\}$		0.44		
$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\} \text{t-C}_4\text{H}_9\text{OK}/\text{C}_6\text{H}_6$		1.08	1.0	
$\left. \begin{array}{l} d_0 \\ d_4 \end{array} \right\}$		1.07		

sence of the deuterium atoms on the β -carbons will have little or no effect on the *cis-trans* ratio in the product.

The *cis-trans* olefin composition obtained from trimethyl-5-nonylammonium base III ($X = N^{(+)}(CH_3)_3$) and 5-nonyl tosylate III ($X = OTs$) and from the corresponding 4,4,6,6-tetradeuterated derivatives are listed in Table VIII together with the calculated values of $(k_H/k_D)_{cis}/(k_H/k_D)_{trans}$. The value of this ratio for the reactions of the 'onium bases with potassium tert-butoxide in tert-butanol and in dimethyl sulphoxide is very high, *i.e.* 1.9 and 1.7, respectively; by contrast, in the case of the reaction with methoxide in methanol its value is close to unity. This suggests that in the reaction of the 'onium bases with tert-butoxide in the two solvents the elimination proceeds largely according to the *anti* \rightarrow *cis*; *syn* \rightarrow *trans* pattern, whereas in the reaction with methoxide in methanol both olefins are largely formed by the same mechanism, presumably *anti*-elimination.

The values for $(k_H/k_D)_{cis}/(k_H/k_D)_{trans}$ for the reaction of the 5-nonyl tosylates with potassium tert-butoxide in all the three solvents examined are close to unity. This suggests again that the formation of *cis*- and *trans*-4-nonene in these reactions proceeds largely (though not necessarily entirely) by one mechanism, presumably *anti*-elimination. As will be shown in the subsequent part of this paper, the conclusions drawn from this qualitative but relatively simple and rapid approach are indeed correct.

Griffith and Singerman³³ have recently studied the reaction of the 3-pentyl halides and the corresponding 2,2,4,4-tetradeuterio derivatives and found — for some of the base-solvent combinations — an analogous though much less pronounced situation as we have now found for the 'onium base eliminations using tert-butoxide as base. As the American authors have already noted, these results might be consistent with a dichotomous reaction pattern. Our present findings lend weight to this conclusion.

THE 5-DECYL SYSTEM

To obtain more definitive and quantitative information it is necessary to investigate the behaviour of stereospecifically β -deuterium labelled substrates. This procedure was now applied to the 5-decyl system IV ($X = N^{(+)}(CH_3)_3$ and OTs).

The elimination in the 5-decyl system IV can give rise to two pairs of position isomeric olefins, the *cis*- and *trans*-4-decenes and the *cis*- and *trans*-5-decenes (*cf.* Scheme 2). In view of the position of the label, only the 5-decenes can afford information on the steric course of the elimination reaction. Since isolation of *cis*- and *trans*-5-decene from the olefin mixture would be very difficult, an approach not requiring this operation was devised. This consisted in a separation of the olefins produced into a *cis*-4- and 5-decene fraction and a *trans*-4- and 5-decene fraction by elution chromatography on alumina coated with silver nitrate³⁰. The *cis*-olefin fraction and

the *trans*-olefin fraction thus obtained were then individually subjected to ozonisation, followed by reduction with lithium aluminium hydride³¹. This procedure resulted in the formation of two sets of mixtures each consisting of butanol, pentanol and hexanol. The alcohols were separated from each other by preparative vapour phase chromatography and the individual alcohols were subjected to mass spectrometry to determine the deuterium content.

In the absence of complications, the butanol produced by this sequence will be deuterium free, the hexanol will contain the same percentage of deuterium as the reactant; finally, the percentage of deuterium in the pentanol will indicate the contributions of *syn*- and *anti*-elimination involved in the particular reaction. The argument involved in this assignment regarding *threo*-6-D-labelled derivative *IV* should be evident from Scheme 2. Analogous scheme can be obtained for the corresponding *erythro*-derivative simply by interchanging the indices *s* and *a* in partial rate constants involved in reaction paths (*A*), (*B*) and (*A'*), (*B'*) (Scheme 2) leading to *trans*- and *cis*-5-decene formation, respectively.

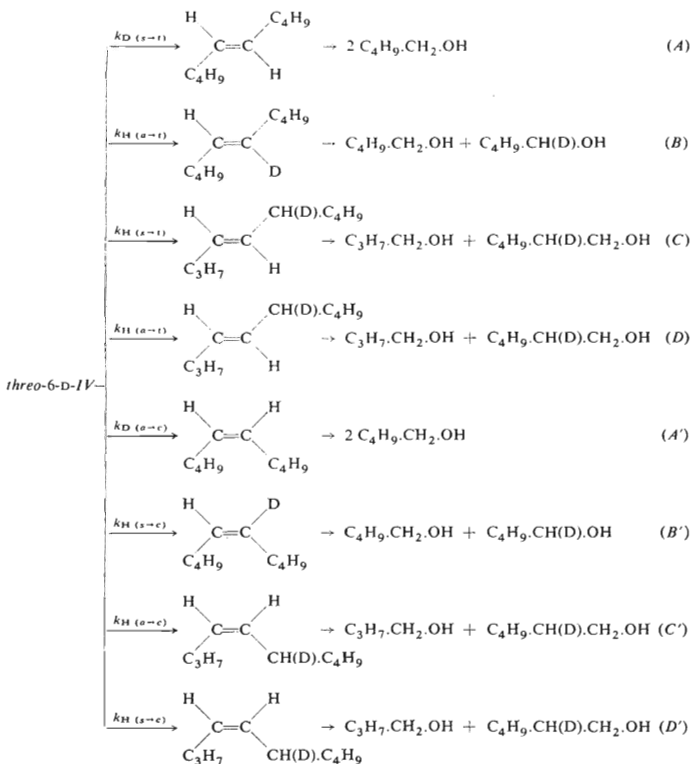
The experimental data for the deuterium labelled 'onium bases *IV* ($X = N(CH_3)_3$)⁽⁺⁾ show (Table VI) that the pentanol obtained from the *trans*-olefin mixture produced in the reaction of the "*threo*-deuterated" reactant with potassium tert-butoxide in tert-butanol contains 13.9% of the d_1 species, showing that only 27.8% of *trans*-5-decene formation has taken place by *anti*-elimination, whereas the predominant part (72.2%) of the olefin has been formed by *syn*-elimination. The pentanol obtained from the complementary run involving the "*erythro*-deuterated" diastereoisomer contained 47.7% of the d_1 species indicating that here 95.4% of *trans*-5-decene formation has taken place by *syn*-elimination and only 4.6% by "usual" *anti*-elimination.

Corresponding data for the steric course of the formation of *cis*-5-decene reveal a quite different situation: in the run involving the "*threo*-labelled" diastereoisomer the pentanol contains 11.2% of the d_1 species indicating only a minor contribution (22.4%) of *syn*-elimination, the predominant part of the olefin being formed by *anti*-elimination. Analogous data obtained for "*erythro*-labelled" reactant show the same pattern even more pronouncedly: the pentanol contains 48.8% of the d_1 species indicating 97.6% and 2.4% contribution of *anti*- and *syn*-elimination, respectively. The other data in the Table VI will be interpreted analogously.

The results of the elimination reactions of the labelled 5-decyl tosylates (Table VII) may next be considered. The pentanol obtained from the *trans*-olefin fraction – by the sequence indicated – from the *threo*-6-D-*IV* ($X = OTs$) in the reaction with potassium tert-butoxide in dimethylformamide contains 48.6% of d_1 species; the pentanol obtained from the corresponding run involving *erythro*-labelled reactant contains 7.0% of the d_1 species. The results thus indicate a predominance of *anti*-elimination, 97.2 and 86%, respectively. The analogous data for the reaction in tert-

butanol and especially in benzene reveal a somewhat higher contribution of *syn*-elimination in the formation of *trans*-5-decene. On the other hand, the corresponding data for the formation of the *cis*-isomer show invariably an overwhelming importance of the *anti*-elimination regardless of the solvent used.

The different contributions of *syn*-elimination found for reactions of the diastereoisomerically labelled substrates result from the operation of the deuterium isotope effect. For a systematic discussion of the dependence of steric course on the "variables"



SCHEME 2

(such as leaving group, base, solvent and alkyl structure) it is necessary to have values for the parent (undeuterated) substrate. These are most conveniently expressed as the partial relative rate constants of the reaction of the undeuterated substrate, *i.e.* $k_{H(s \rightarrow t)}$, $k_{H(a \rightarrow t)}$, $k_{H(s \rightarrow c)}$ and $k_{H(a \rightarrow c)}$. The values of these rate constants could be directly calculated from the data given in Tables VI and VII provided the values of $(k_H/k_D)_{syn}$ and $(k_H/k_D)_{anti}$ were known with some confidence. However, the magnitude of these isotope effects seems to vary from one base-solvent system to another and a reliable choice of values from available evidence did not appear to be feasible. A calculation would also be possible if we could make the assumption that $(k_H/k_D)_{syn} = (k_H/k_D)_{anti}$. However, earlier evidence^{9,32,33} as well as data discussed in this paper show that this assumption would not be warranted.

For these reasons we made use of the following procedure.

It may readily be deduced from equations (A)–(D) in Scheme 2 that for the *threo*-D-labelled reactant we have

$$(d_0/d_1)_{olef}^{trans} = [k_{D(s \rightarrow t)}]/[k_{H(s \rightarrow t)} + 2k_{H(a \rightarrow t)}] \quad (1)$$

and

$$(d_0/d_1)_{pent}^{trans} = [2k_{D(s \rightarrow t)} + k_{H(a \rightarrow t)}]/[k_{H(a \rightarrow t)}], \quad (2)$$

where $(d_0/d_1)_{olef}^{trans}$ is the experimental mass spectrometrically determined value of the ratio of the d_0 to d_1 species in the mixture of *trans*-4- and *trans*-5-decene; and $(d_0/d_1)_{pent}^{trans}$ is, correspondingly, the ratio of the d_0 to the d_1 species determined spectrometrically in the pentanol obtained by ozonisation of the *trans*-olefin mixture. Analogously, use was made of the experimentally determined values* of $(d_0/d_1)_{olef}^{cis}$ and $(d_0/d_1)_{pent}^{cis}$.

From (1) and (2) we get

$$\frac{k_{H(s \rightarrow t)}}{k_{H(a \rightarrow t)}} = \left[\frac{(d_0/d_1)_{pent}^{trans} - 4(d_0/d_1)_{olef}^{trans} - 1}{2(d_0/d_1)_{olef}^{trans}} \right]_{threo} \quad (3)$$

and analogously

$$\frac{k_{H(a \rightarrow c)}}{k_{H(s \rightarrow c)}} = \left[\frac{(d_0/d_1)_{pent}^{cis} - 4(d_0/d_1)_{olef}^{cis} - 1}{2(d_0/d_1)_{olef}^{cis}} \right]_{threo} \quad (4)$$

Similarly, corresponding expressions may be deduced for the reaction of the *erythro*-6-D-labelled reactant:

$$\frac{k_{H(a \rightarrow t)}}{k_{H(s \rightarrow t)}} = \left[\frac{(d_0/d_1)_{pent}^{trans} - 4(d_0/d_1)_{olef}^{trans} - 1}{2(d_0/d_1)_{olef}^{trans}} \right]_{erythro} \quad (5)$$

$$\frac{k_{H(s \rightarrow c)}}{k_{H(a \rightarrow c)}} = \left[\frac{(d_0/d_1)_{pent}^{cis} - 4(d_0/d_1)_{olef}^{cis} - 1}{2(d_0/d_1)_{olef}^{cis}} \right]_{erythro} \quad (6)$$

* The assumption is implicit in these derivations that any secondary deuterium isotope effects will be negligibly small.

We further have, by definition,

$$k_{H(s \rightarrow t)} + k_{H(a \rightarrow t)} + k_{H(a \rightarrow c)} + k_{H(s \rightarrow c)} = 100 \quad (7)$$

and, also, from the assumption* that the values of corresponding partial relative rate constants for the formation of the 4- and 5-position isomers from the parent unlabelled 5-decyl derivatives are identical, we have

$$\frac{k_{H(s \rightarrow t)} + k_{H(a \rightarrow t)}}{k_{H(s \rightarrow c)} + k_{H(a \rightarrow c)}} = \frac{\% \text{ trans-4- and 5-decene}}{\% \text{ cis-4- and 5-decene}} \quad (8)$$

Values of the partial rate constants may, in principle, be calculated from data for either or both the diastereoisomeric reactants. However, more reliable results will be obviously obtained from that diastereoisomer in which both competing processes (*syn* and *anti*) operate in more comparable proportions. Thus, in our case, the values obtained for the *threo*-isomer were used invariably for the quantitative evaluation of the processes contributing to the *cis*-5-decene formation. Similarly, the analogous data were used also in the corresponding calculation regarding *trans*-5-decene formation in the reactions of the 'onium bases, except for methoxide-methanol base-solvent combination. On the other hand, data obtained for *erythro*-isomer were used for the evaluation of the processes leading to *trans*-5-decene formation from the corresponding tosylate under all reaction conditions investigated.

The values of the partial rate constants of *trans*- and *cis*-5-decene formation as evaluated for the unlabelled 'onium compound and the tosylates *IV* using relationships (3) – (8), are given in the Table IX.

EVIDENCE AGAINST ALTERNATIVE TWO-STEP α -MECHANISMS

In order to be able to exclude the possibility that under some of the conditions employed the elimination could proceed by a two step α -mechanism, reaction of α -deuterium labelled derivatives of the 'onium base *III* ($X = \overset{(+)}{N}(\text{CH}_3)_3$) and the tosylate *III* ($X = \text{OTs}$) were run. The olefin produced and, in the case of the 'onium base reactions, also the 5-dimethylaminononane, were examined for deuterium content. As may be seen from the data in Table X, the deuterium is completely retained both in the olefins and the amine. A two-step α -elimination mechanism, which *a priori* was rather improbable, is thus excluded.

In the elimination reaction involving 4,4,6,6-tetradeuterio-5-nonyltrimethylammonium chloride with tert-butoxide in tert-butanol and in dimethyl sulphoxide the

* Since we have been unable to separate the position isomers we have no direct information on the ratio of the 4- to 5-position isomeric olefins. However, the ratios of the rates of elimination into the two different directions are probably very close to unity as shown by the fact that the amount of pentanol formed on ozonization of the olefin mixture obtained by elimination of the (undeuterated) derivatives *IV* ($X = \overset{(+)}{N}(\text{CH}_3)_3$, OTs) was equal — within the limit of experimental error — to the sum of the amounts of butanol and hexanol.

trimethylamine formed was also examined for deuterium content and found to contain in both cases less than 0.5% of the d_1 species. Another remote possibility regarding the operation of an alternative "ylide" mechanism in the present systems is thus also safely excluded.

DISCUSSION

THE *syn-anti* ELIMINATION DICHOTOMY

In the case of the eliminations of the *onium compounds III and IV* ($X = \overset{(+)}{N}(\text{CH}_3)_3$) with tert-butoxide *trans*-olefin formation takes place largely by *syn*-elimination, irrespective of the solvent (tert-butanol, dimethyl sulphoxide or benzene) employed.

TABLE IX

Relative Rate Constants of *syn*- and *anti*-Elimination Leading to *trans*- and *cis*-5-Decene from Unlabelled 5-Decyl Compounds *IV* ($X = \overset{(+)}{N}(\text{CH}_3)_3, \text{OTs}$)

X	Reaction conditions	<i>trans</i> -5-Decene ^a		<i>cis</i> -5-Decene ^a	
		$k_{\text{H}(s \rightarrow t)}$	$k_{\text{H}(a \rightarrow t)}$	$k_{\text{H}(a \rightarrow c)}$	$k_{\text{H}(s \rightarrow c)}$
Onium compounds					
$\overset{(+)}{N}(\text{CH}_3)_3$	t-C ₄ H ₉ OK/C ₆ H ₆	82.4	7.6	8.2	1.8
$\overset{(+)}{N}(\text{CH}_3)_3$	t-C ₄ H ₉ OK/(CH ₃) ₂ SO	74.7	5.3	18.8	1.2
$\overset{(+)}{N}(\text{CH}_3)_3$	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	63.1	7.9	27.6	1.4
$\overset{(+)}{N}(\text{CH}_3)_3$	Pyrolysis	67.8	3.2	27.8	1.2
$\overset{(+)}{N}(\text{CH}_3)_3$	CH ₃ OK/CH ₃ OH	5.1	15.9	74.0	5.0
Tosylates					
OTs	t-C ₄ H ₉ OK/C ₆ H ₆	12.4	33.6	50.4	3.6
OTs	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	4.2	24.8	68.2	2.8
OTs	t-C ₄ H ₉ OK/HCON(CH ₃) ₂	2.8	73.2	22.6	1.4

^a Data corrected for incomplete labelling of the starting compounds have now been used (cf. Table VI and VII) for the calculation of the figures given in Tables IX, XI and XII, in contrast to the corresponding figures reported in the preliminary form^{1,2,50}. However, the resulting differences are mostly insignificant and do not change the situation substantially.

TABLE X
Reaction of α -D-Labelled 5-Nonyl Derivatives III (X = N(CH₃)₃, OTs): Deuterium Isotope Composition Data

X	Base/solvent	% d_1 in 4-Nonene ^a	% d_1 in 5-Nonyl- dimethylamine
(+) N(CH ₃) ₃ ^b	CH ₃ OK/CH ₃ OH	97.7	97.5
(+) N(CH ₃) ₃ ^b	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	97.4	97.4
(+) N(CH ₃) ₃ ^b	t-C ₄ H ₉ OK/(CH ₃) ₂ SO	97.2	^d
OTs ^c	t-C ₄ H ₉ OK/HCON(CH ₃) ₂	96.5	—
OTs ^c	t-C ₄ H ₉ OK/(CH ₃) ₂ SO	96.9	—
OTs ^c	t-C ₄ H ₉ OK/C ₄ H ₉ OH	95.5	—

^a Determined in the resulting *cis-trans* isomeric mixture; ^b starting 5-nonyldimethylamine contained 97.3% d_1 ; ^c starting 5-nonanol contained 97.0% d_1 ; ^d not determined.

TABLE XI
Contributions of *syn*- and *anti*-Elimination in the *trans*- and *cis*-5-Decene Formation from Unlabelled 5-Decyl Compounds IV (X = N(CH₃)₃, OTs)

X	Reaction conditions	<i>trans</i> -5-Decene ^a		<i>cis</i> -5-Decene ^a		Overall
		% <i>syn</i>	% <i>anti</i>	% <i>syn</i>	% <i>anti</i>	% <i>syn</i>
(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/C ₆ H ₆	91.6	8.4	18.0	82.0	84.2
(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/(CH ₃) ₂ SO	93.4	6.6	6.0	94.0	75.9
(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	88.9	11.1	4.7	95.3	64.5
(+) N(CH ₃) ₃	Pyrolysis	95.5	4.5	4.1	95.9	69.0
(+) N(CH ₃) ₃	CH ₃ OK/CH ₃ OH	24.3	75.7	6.3	93.7	10.1
OTs	t-C ₄ H ₉ OK/C ₆ H ₆	27.0	73.0	6.6	93.4	16.0
OTs	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	14.5	85.5	3.9	96.1	7.0
OTs	t-C ₄ H ₉ OK/HCON(CH ₃) ₂	3.7	96.3	5.8	94.2	4.2

^a cf. footnote^a in Table IX.

As follows from the quantitative data obtained for non-deuterated γ -onium base IV (Table XI), 89–93% of *trans*-5-decene is formed under these conditions by *syn*-elimination. By contrast, with the same base-solvent combinations, *cis*-olefin formation takes place predominantly (82–95%) by *anti*-elimination; a non-negligible contribution (18%) of *syn*-elimination is found only with benzene as solvent. It should be noted, however, that under these conditions the *cis*-isomer accounts for only about 10% of the olefin formed so that no more than about 2% of the total olefin forming reaction can be allotted to the *syn* \rightarrow *cis* process. A closely similar behaviour was found for the reaction of the quaternary base under pyrolytic conditions.

It follows clearly from these findings that two stereochemically distinct mechanisms are operating in the present reactions, the one being responsible for *trans*-olefin formation, the other for *cis*-olefin formation. Therefore, the dichotomous behaviour we found previously in the elimination reaction of medium ring compounds is now observed – under quite common conditions – in the simple open-chain γ -onium compound. Moreover, since the *trans*-isomer is formed in predominant amount in the reactions considered above, it follows that *syn*-elimination is the principal process in these reactions.

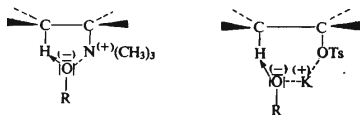
A different situation is encountered in the case of the reaction with methoxide in methanol. Here, *anti*-elimination has become the principal process even in *trans*-olefin formation.

In the elimination reaction of the *tosylates* (III and IV, X = OTs) some *syn*-elimination is also found; however, its contribution is considerably smaller than in the reaction of the γ -onium compounds under corresponding conditions. Moreover, the nature of the solvent employed (with *tert*-butoxide as base) here appears to be more critical: in *trans*-5-decene formation there is a drop in the contribution of *syn*-elimination from 27 to 14.5 and 3.7% on going from benzene to *tert*-butanol and dimethylformamide (Table XI).

The same trend has been found in the elimination reactions of the cyclododecyl *tosylates*¹⁰ and the bicyclo[2.2.2]octyl *tosylates*^{2,3}. This dependence on the nature of the solvent (and base) may, in part, explain the discrepancy between our present results and the exclusive *anti*-elimination found by Skell and Hall²⁰ for the reaction of 2-butyl *tosylates* with ethoxide-ethanol, as well as the recent results of Froemsdorf and his colleagues³⁴ who found that the reaction of this *tosylate* with *tert*-butoxide in dimethyl sulphoxide proceeds practically exclusively by the *anti*-elimination mechanism. Another factor may contribute to the complete absence of *syn*-elimination: as the results of Saunders³⁵, Froemsdorf³⁶ and Bartsch³⁷ suggest, *anti*-elimination is extremely facile in the 2-alkyl systems which may thus represent a “limiting” rather than a “typical” case.

The observed dependence on base and solvent has been commented before^{7,10,12,21}. The fact that *syn*-elimination is favoured in solvents which support ion pair formation

and suppressed in ion pair dissociating solvents has led to the suggestion^{10,12} that the ion-paired base is more efficiently utilized in *syn*- than *anti*-mechanism. The favourable charge-charge or charge-dipole interactions present in the transition state of the former mechanism (Scheme 3) may play an important role. The smaller tendency towards *syn*-elimination in tosylates than in 'onium bases under corresponding reaction conditions has also already been noted^{3,10}. It is in line with the concept that the transition states of *syn*-elimination possesses some carbanion character^{7,32}.



SCHEME 3

Summing up, we may say that the dual pathway (*syn* and *anti*) in bimolecular elimination processes which we have first observed in medium ring compounds is re-encountered in the unbranched straight chain systems *III* and *IV* ($X = \overset{(+)}{N}(\text{CH}_3)_3$ and OTs) now studied. However, the dichotomous situation is here less general and the contribution of *syn*-elimination less pronounced than in the case of the ring compounds just referred to.

Some explanations for the very high tendency towards *syn*-elimination in the medium rings has already been considered previously⁷. We shall return to the problem of the effect of alkyl structure on the choice of the steric path of elimination in the following papers.

SIGNIFICANCE OF THE *trans-cis* OLEFIN RATIOS

Values of the ratios of *trans*-to-*cis* olefin formed in elimination reactions have frequently been used in discussions concerning the nature of the transition state (more particularly the extent of "double bond development")³⁷⁻⁴⁴. As already pointed out¹² such values can be meaningful only if a separation into contributions of *syn*- and *anti*-elimination is effected. This has now been carried out for the 5-decyl system *IV*.

The ratio of $k_{(s \rightarrow t)}/k_{(s \rightarrow c)}$ is invariably greater than unity (Table XII). The explanation that first suggests itself for this finding is that the preferred formation of *trans*-olefin in *syn*-elimination is a consequence of the greater non-bonded interactions (C_4H_9 vs C_4H_9) involved in the transition state of the *syn*-process leading to the *cis*-isomer. It is generally argued^{45,46} that, if, in olefin formation, the

TABLE XII

trans- to *cis*-Decene Ratios in the *syn*- and *anti*-Components of the Elimination of the Unlabelled 5-Decyl Compounds $IV(X = N(CH_3)_3, OTs)$

Run	X	Reaction conditions	Overall <i>trans</i> / <i>cis</i>	<i>syn</i> -Route ^a $k_{H(s \rightarrow t)}/k_{H(s \rightarrow c)}$	<i>anti</i> -Route ^a $k_{H(a \rightarrow t)}/k_{H(a \rightarrow c)}$
1	(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/C ₆ H ₆	9.0	45.7	0.93
2	(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/(CH ₃) ₂ SO	4.0	62.2	0.28
3	(+) N(CH ₃) ₃	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	2.4 ₅	45.0	0.29
4	(+) N(CH ₃) ₃	Pyrolysis	2.4 ₅	56.6	0.11 ₅
5	(+) N(CH ₃) ₃	CH ₃ OK/CH ₃ OH	0.27	1.02	0.21 ₅
6	OTs	t-C ₄ H ₉ OK/C ₆ H ₆	0.85	3.45	0.67
7	OTs	t-C ₄ H ₉ OK/t-C ₄ H ₉ OH	0.41	1.5	0.36
8	OTs	t-C ₄ H ₉ OK/HCON(CH ₃) ₂	3.17	2.0	3.24

^a cf. footnote^a in Table IX.

transition state is "olefin-like", the ratio of *trans*- to *cis*-olefin obtained should be large, approaching the value of the *trans* ⇌ *cis* olefin equilibrium. Now, in the runs 1–4 (onium bases) the values of $k_{(s \rightarrow t)}/k_{(s \rightarrow c)}$ range from 45–62, corresponding to a difference in free energy of activation of about 2.5 kcal mol⁻¹; however, the free energy difference between the *trans*- and the *cis*-5-decenes themselves is of the order of only about 1 kcal mol⁻¹. The *trans-cis* ratio in the product of *syn*-elimination thus considerably exceeds the equilibrium value.* Analogous argumentation in terms of a "ground state like" transition state is possible.** The *trans-cis* olefin ratio might then be expected to depend on the difference between the strains in the 0 and 120° eclipsed conformations. Recent data are available for the case of butane; there, at any rate, the difference between the free energies of the above two conformations is only small, *i.e.* about 0.6 kcal mol⁻¹.

* The ratio of *trans* to *cis*-4-nonene obtained on pyrolysis of 5-nonyldimethylamine oxide⁴⁷ (an intramolecular *syn*-elimination process) is indeed about 5.5, corresponding to approximately 1 kcal mol⁻¹.

** This may, indeed, appear more appropriate since other evidence^{12,32} suggests that in bimolecular *syn*-elimination the transition state does not possess much double bond character.

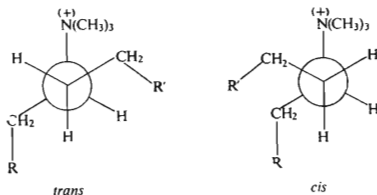
In the elimination runs 6–8 (tosylates) the value of $k_{(s \rightarrow t)}/k_{(s \rightarrow c)}$ is very much smaller than in the case of the 'onium base eliminations just discussed, *i.e.* 1.5–3.4. The contribution of *syn*-elimination in most of these reactions is, however, only very small and the significance of the above values hence less certain.

Consider next the corresponding ratios for the *anti*-elimination component of the reaction. With the exception of the reaction of the tosylate IV ($X = \text{OTs}$) with tert-butoxide in dimethylformamide (run 8) the values of $k_{(a \rightarrow t)}/k_{(a \rightarrow c)}$ are actually smaller than unity. In other words, in seven out of the eight processes examined, *anti*-elimination gives rise to the less stable isomer preferentially, the preference for this isomer in most cases being very strong. Thus, while, in the *syn*-elimination, the proportion of *trans*- to *cis*-olefin was – so to speak – “better than thermodynamic”, in the concurrent *anti*-elimination it is evidently “antithermodynamic”. The conclusion seems inescapable that interpretations in terms of R *vs* R' interactions alone are not applicable to our results.

Conformational considerations of a more complex nature may be necessary: differences in the ease of approach of the base, or differences in the interactions between the leaving group and the alkyl group R' on C_β in the transition states leading to the two isomers may have to be taken into account.

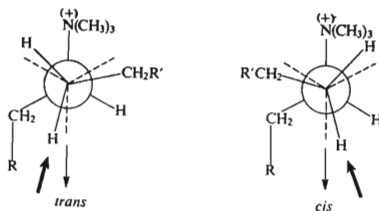
A transition state model for *anti*-elimination taking some of these factors into account has been put forward by Bailey and Saunders²¹ for *anti*-elimination of 'onium bases (Scheme 4). They suggest that in the transition state leading to the *trans*-olefin the *anti*-periplanar hydrogen on C_β is “shielded on both sides”, whereas in the corresponding transition state leading to the *cis*-olefin, the hydrogen in question “while still hindered on one side, is relatively open to attack on the other”. If now “non-linear approach of the base is energetically feasible, *cis*-olefin should form faster than *trans*-olefin, especially with the bulkier bases”.

In a detailed conformational analysis it is necessary to enquire whether the optimal arrangements for elimination in the systems presently examined indeed correspond to exact *anti*- or *syn*-periplanarity. It has been estimated some time ago⁴⁸ that for *anti*-elimination a deviation of some 10° would not produce a noticeable energy



SCHEME 4

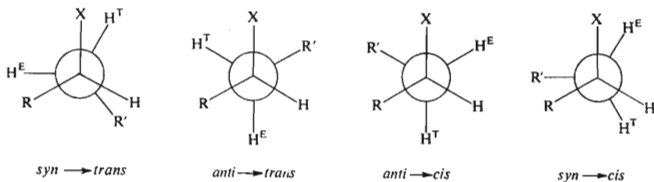
effect. In our systems there will clearly be a tendency for the dihedral angle between $C_{\alpha}-N^{(+)}(CH_3)_3$ and $C_{\beta}-R'$ to widen beyond the 60° value in order to reduce the gauche interactions between the extremely large trimethylammonium group and the alkyl residue R' .



SCHEME 5

Felkin⁴⁹ has pointed out that if such a rotation about the $C_{\alpha}-C_{\beta}$ bond takes place, the *anti*-periplanar hydrogen (H^e) in the transition state leading to the *trans*-isomer will move into the very congested environment about $C_{\beta}-C_{\alpha}-R$, whereas in the transition state leading to the *cis*-isomer the rotation will move the hydrogen (H^i) from a crowded position into a more free one (Scheme 5). The hydrogen H^i in this somewhat "shifted" *anti* \rightarrow *cis* transition state should hence be more open to attack by base than the hydrogen H^e in the corresponding *anti* \rightarrow *trans* transition state.

Some time ago, we have proposed a different interpretation for the observed stereoselectivity of the two alternative elimination modes^{7,50} (Scheme 6). This sets out from the recognition that the two "important" processes, *i.e.* *syn* \rightarrow *trans* and *anti* \rightarrow *cis*, involve the removal of the same hydrogen, namely H^i . This has led us to



SCHEME 6

suggest that the two diastereotopic hydrogens⁵¹ on C_p differ in their readiness to undergo reaction with base, having been rendered nonequivalent by induction from the chiral α -carbon atom.

The tentative character of the above speculations is obvious. It seems necessary to obtain further quantitative data on the steric course of elimination reaction for other structurally related compounds before more definite explanation of the challenging problem can be given.

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