STEREOCHEMICAL STUDIES. LXIX.*

CONTRIBUTION OF *syn-* AND *anti*-ELIMINATION TO THE MONOSUBSTITUTED OLEFIN FORMATION FROM 1-DECYLTRIMETHYLAMMONIUM BASE**

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The steric course of 1-decene formation from the reaction of 1-decyltrimethylammonium base has been studied in four base–solvent combinations with the aid of the corresponding *erythro-* and *threo*-1,2-dideuterio derivatives and infra-red spectrometry. Both *syn-* and *anti*-processes have been found to participate in 1-decene formation, the latter being of a greater importance (79—93%) under all conditions investigated. All the deuterium isotope isomers of 1-decene due to the labelling on $C_{(1)}$ and/or $C_{(2)}$ were prepared from 1-decyne or 1-decyne-[1-D] by hydro-(deuterio)-boration procedure in a completely stereospecific manner.

Recent work from This as well as other Laboratories demonstrated[2–8] that in bimolecular elimination of the open-chain 'onium compounds *I* (R^1, R^2 = alkyl group) participate, in greatly varying proportions, two stereochemically distinct *syn-* and *anti*-processes, the former being an important path[2–7] for the disubstituted *trans*-olefin (*trans-II*) formation but, by contrast, the latter an almost exclusive path[2–7] for the corresponding *cis*-olefin (*cis-II*) formation. A less pronounced situation was found in the formation of the trisubstituted olefins[8], *cis-* and *trans-IV*, from the quaternary base *III*; here the contribution of *syn*-elimination is small to appreciable, depending very strongly on the configuration of the reactant as well as on the base–solvent combination used.

The question arose from these findings, whether the *syn*-elimination participates also in the formation of the monosubstituted (terminal) olefins. This question is not only interesting on its own right but also important in connection with the not yet fully understood relationship[2,6,7] between the alkyl structure of the reactant and the steric course of the bimolecular elimination.

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** This is the twenty-seventh of a series of papers dealing with the mechanism of elimination reactions; for previous paper see ref.[1].

$R^1.CH(\overset{(+)}{N}(CH_3)_3).CH_2.R^2$ *I*

$R^1.CH{=}CH.R^2$ *cis-* and *trans-II*

$R^1.CH(\overset{(+)}{N}(CH_3)_3).CH(CH_3).R^2$ *erythro-* and *threo-III*

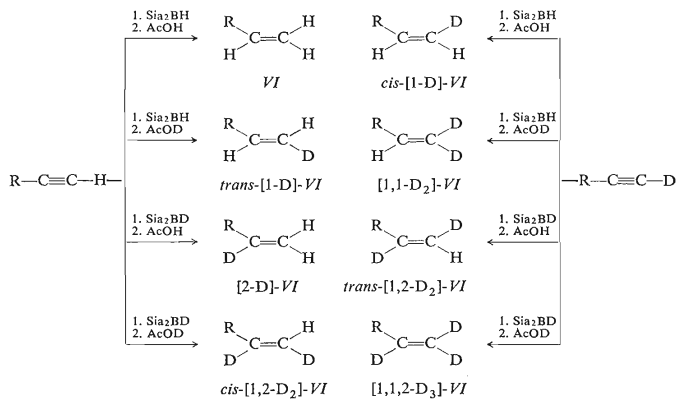
$R^1.CH{=}C(CH_3).R^2$ *cis-* and *trans-IV*

$C_8H_{17}.CH_2.CH_2\overset{(+)}{N}(CH_3)_3\ Cl^{(-)}$ *V*

$C_8H_{17}.CH{=}CH_2$ *VI*

We have therefore investigated the 1-decene (*VI*) formation from 1-decyltrimethylammonium chloride (*V*) in four different base–solvent combinations using the stereospecifically deuterium labelled derivatives *erythro-* and *threo*-1,2-D_2-*V* as the tool for elucidation of the steric course. To obtain information on the steric course of elimination in these compounds, it was necessary to determine the isotope isomer composition in the resulting olefin mixtures. For this purpose, a new procedure had to be devised for analysis of the complex isotope isomer mixtures of 1-decenes. Infra-red spectra of individual 1- and/or 2-deuterio-1-alkenes had been known[9–11] to differ each from other profoundly; therefore, it was hoped that the infra-red spectrometric analysis of the complex olefin mixtures could be feasible. As will be shown below, this expectation has been fulfilled.

Individual isomers of 1-decene having the deuterium label on the vinyl were required as the standards for the study. These were synthetised, uniformly, according



R = n-C_8H_{19}; Sia = 2-Methyl-2-butyl AcOH = CH_3COOH; AcOD = CH_3COOD

SCHEME 1

to Scheme 1, in a one-step reaction of 1-decyne (or 1-decyne-[1-D] with disiamylborane[12] and acetic acid (or with their deuterio derivatives). All possible mono-, di- and tri-1- and/or 2-deuterio substituted 1-decenes were prepared in good yields by this procedure in a completely stereospecific manner, as evidenced by careful analysis of their infra-red spectra[11]. *threo*- and *erythro*-1-Decanol-[1,2-D_2] were prepared, respectively, by treatment of *cis*- and *trans*-1-decene-[1-D] with perdeuteriated diborane[13] followed by alkaline hydrogen peroxide. Conversion of the two labelled alcohols into 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 of the amines followed by reaction with methyl iodide in benzene gave the required quaternary salts.

EXPERIMENTAL

1-Decyne-[1-D]

1-Decyne[14] (50 g, 0·36 mol) was added dropwise to a stirred solution of propyllithium (0·4 mol) in ether (600 ml) under nitrogen at −42°C, the reaction mixture kept at this temperature for 5 min and decomposed under cooling by careful addition of an excess of deuterium oxide (240 ml). After standing overnight at room temperature the ethereal layer was separated, dried over calcium sulphate and taken down. Distillation of the residue *in vacuo* afforded 50·4 g (100%) of the oily product, b.p. 62—63°C/12 Torr. The deuterium isotope composition was determined by infra-red spectrometry (ν(C≡C—H) 3315 cm^{-1}, ν(C≡C—D) 2598 cm^{-1}). The product was found to contain 99% of the deuterium label.

Deuterated 1-Decenes

1-Decyne (or 1-decyne-[1-D]) was treated with disiamylborane[10,12] (or its deuterated analogue) under nitrogen and the adduct decomposed by acetic acid (or deuterioacetic acid[10]). The crude product contained invariantly a great amount of unidentified boronic compounds and, in some cases, traces of the starting acetylene. The boronic impurities were destroyed by treatment of the crude product with alkaline solution of hydrogen peroxide in methanol; the starting acetylene (if any) was separated by filtration through a column containing neutral alumina coated with silver nitrate[15]. A standard procedure used for these preparations is exemplified for the synthesis of *trans*-1-decene-[1-D]: A solution of sodium borohydride (32 g, 0·84 mol) in diglyme (1 l) in a nitrogen atmosphere was treated with 2-methyl-2-butene (143 g, 2·04 mol). The flask was placed into an ice-bath and boron trifluoride etherate (145 g, 1·02 mol) was added dropwise to a stirred solution under nitrogen. The reaction mixture was allowed to stand for 3 h at 0°C, cooled down to −12°C and treated with 1-decyne (70 g, 0·51 mol). Stirring was continued for 2 h at 20°C, the mixture treated with an excess of acetic acid-[O-D] (375 ml), allowed to stand overnight at room temperature, diluted with water (10 l) and the product taken up in pentane. The pentane extracts were washed, successively, with 2M-KOH, solution of sodium chloride and water, dried with magnesium sulphate and taken down. The residue was dissolved in methanol (1·2 l), the stirred solution placed into an ice-bath and treated with 3M-NaOH (350 ml), followed by 30% hydrogen peroxide (350 ml). After 4 h stirring at room temperature the reaction mixture

was diluted with water (5 l) and the product taken up in pentane, the pentane extracts were washed with 1M-HCl and water, dried and taken down. The oily residue was placed on a column prepared from 50 g of neutral alumina containing 30% of silver nitrate[15]. Filtration through the column followed by elution with pentane–ether (95 : 5) afforded after the usual work-up the olefin (55 g, 78%), b.p. 62°C/12 Torr.

The samples of 1-decenes for infra-red and mass spectrometry were purified by preparative vapour phase chromatography before the measurements; the purity* was uniformly better than 99%. The deuterium content in the individual olefins was determined by mass spectrometry: *cis*-1-D-*VI*: 0·6% d_0, 99·4% d_1; *trans*-1-D-*VI*: 20·0% d_0, 80·0% d_1; 2-D-*VI*; 6·6% d_0, 93·4% d_1; *cis*-1,2-D_2-*VI*: 0·6% d_0, 26·8% d_1, 72·6% d_2; *trans*-1,2-D_2-*VI*: 0·7% d_0, 9·3% d_1, 90·0% d_2; 1,1-D_2-*VI*: 0·3% d_0, 22·4% d_1, 77·3% d_2; 1,1,2-D_3-*VI*: 0·9% d_0, 1·3% d_1, 25·7% d_2, 72·1% d_3.

erythro-1-Decanol-[1,2-D]

A solution of sodium borodeuteride (3·5 g, 0·083 mol) in diglyme (400 ml) was treated under nitrogen with *trans*-1-decene-[1-D] (27·5 g, 0·195 mol). The flask was placed into an ice-bath and boron trifluoride etherate (15 g, 0·106 mol) was added dropwise to the stirred solution under nitrogen and the reaction mixture was allowed to stand for 4—5 h at 0°C. It was then treated, under cooling, with water (15 ml) and 3M-NaOH (80 ml), followed by 30% H_2O_2 (80 ml), permitted to stand at room temperature overnight and the product taken up in light petroleum (2 × 600 ml). The combined extracts were washed with water, dried and taken down. Distillation of the residue under reduced pressure afforded 24·3 g (78%) of the crude product which contains, according to vapour phase chromatography, about 3% of the position isomer (2-decanol). The separation was achieved by careful rectification on the spinning band column. Yield 21·2 g (69%). *threo*-1-Decanol-[1,2-D_2] was prepared analogously from *cis*-1-decene-[1-D] by reaction with $NaBD_4$–BF_3 in diglyme.

erythro-1-Decyl *p*-Toluenesulphonate-[1,2-D_2]

A solution of *erythro*-1-decanol-[1,2-D_2] (10 g, 0·063 mol) in pyridine (100 ml) was placed into an ice-bath and treated with *p*-toluenesulphonyl chloride (26 g, 0·14 mol). The reaction mixture was allowed to stand at 0°C for 2 h and diluted with ice-cooled water (600 ml). The product was taken up in pentane, extracted with 3M-HCl, water, dried with magnesium sulphate and the solvent distilled off on the rotatory evaporator at room temperature. It was obtained 18 g (90%) of the oily product which was immediately used in the further reaction. *threo*-1-Decyl *p*-toluenesulphonate-[1,2-D_2] was prepared analogously from the corresponding *threo*-alcohol.

threo-1-Dimethylaminodecane-[1,2-D_2]

Sodium azide (12 g, 0,185 mol) was dissolved in dimethylsulphoxide (180 ml) at 90°C and to the stirred hot solution was added dropwise *erythro*-1-decyl *p*-toluenesulphonate-[1,2-D_2]. The reaction mixture was kept for 3 h at this temperature, cooled down and diluted with water (1 : 1). The product was taken up in pentane, the extracts washed with water, dried with magnesium sulphate and the solvent distilled off on aspirator at room temperature. The residue was dissolved in ether (20 ml) and added dropwise to 1M ethereal solution of lithium aluminium hydride (50 ml).

* Position isomers were completely absent even in the crude products. The parent un-deuterated 1-decene was commercial sample (Lachema, Brno) and contained about 1% of the *cis*- and *trans*-2-isomer, detectable by the strong IR absorption at 957 cm^{-1}.

The reaction mixture was heated under reflux until the evolution of nitrogen ceased, cooled in an ice-bath and decomposed by addition of water (3·5 ml), 3M-NaOH (3·5 ml) and water (8 ml). The precipitate was filtered off and washed with ether. The ethereal filtrates were dried over potassium hydroxide pellets, taken down and the crude residue treated with formic acid–formaldehyde mixture in the usual manner[2]. It was obtained 7·2 g (71%; based on the starting alcohol) of the title compound, b.p. 100°C/15 Torr. The deuterium content was determined by mass spectrometry; the product was found to contain 0·7% of the d_0, 21·7% of the d_1 and 77·5% of the d_2 species. *erythro*-1-Dimethylaminodecane-[1,2-D_2] was prepared analogously from the corresponding *threo*-tosylate. The product was found to contain 12·7% of the d_1 and 87·3% of the d_2 species.

Quaternary Salts

Quaternary iodides were prepared from the labelled dimethylaminodecanes by a reaction with methyl iodide in benzene in the usual manner[2]. Quaternary chlorides were prepared from the corresponding iodides by shaking with silver chloride in methanol by standard procedures[16]. The quaternary chlorides are very hygroscopic; before further use they were dried *in vacuo* at 70°C/1 Torr for 10 h.

Elimination Runs

A) *Homogenous conditions*: 600—1 000 mg of the quaternary chloride was dissolved in 0·5M solution of potassium tert-butoxide in the solvent listed (threefold excess) and heated in sealed tubes under nitrogen. The conditions are summarised in Table I. The mixtures were diluted with tenfold volume of water and the products taken up in pentane. The pentane extracts were washed with 1M-HCl, water, dried over magnesium sulphate and the solvent carefully distilled off through a short column. The residue was distilled under reduced pressure. Yields are summarised in the Table I. Position isomers are, according to vapour chromatography, completely absent in the products indicating that isomerisation did not occur under condition used. Under more forcing conditions, however, the isomerisation does occur in tert-butoxide–dimethylformamide combination; in preliminary runs performed at elevated temperature or even on prolonged standing at room temperature a considerable proportion of the *cis*- and *trans*-2-isomers was found in the product.

TABLE I

Elimination of *erythro*- and *threo*-1-Decyltrimethylammonium Base

Base/Solvent	°C/h	Yield[a], %
t-C_4H_9OK/C_6H_6	80/5	40
t-C_4H_9OK/H.CO.N(CH_3)$_2$	25/1	47
t-C_4H_9OK/t-C_4H_9OH	100/4	22
Pyrolysis	150/0·5	20

[a] Yield of isolated 1-decene mixtures. Yields from the *erythro*- and *threo*-derivatives were uniformly almost identical.

TABLE II

Elimination of *erythro*- and *threo*-1,2-Dideuterio-1-decyltrimethylammonium Base under Different Conditions: Isomer Composition Data (%) with Standard Deviations (1σ) in Parentheses

VI	tert-Butoxide Benzene		tert-Butoxide Dimethylformamide		tert-Butoxide tert-Butanol		Pyrolysis	
	erythro	*threo*	*erythro*	*threo*	*erythro*	*threo*	*erythro*	*threo*
cis-1-D	20·2^a (1·5)	6·9^s (1·4)	20·3^a (1·4)	7·2^s (1·4)	24·2^a (1·5)	5·8^s (1·5)	27·5^a (1·4)	6·4^s (1·5)
cis-1,2-D_2	54·5^a (1·8)	11·2^s (1·8)	59·6^a (1·8)	8·3^s (1·7)	59·5^a (1·8)	3·7^s (1·8)	51·0^a (1·7)	5·5^s (1·8)
trans-1-D	9·6^s (2·3)	12·5^a (2·2)	9·1^s (2·2)	13·3^a (2·1)	7·9^s (2·3)	17·7^a (2·3)	10·0^s (2·2)	20·6^a (2·3)
trans-1,2-D_2	13·8^s (1·6)	48·6^a (1·6)	9·3^s (1·6)	49·7^a (1·5)	5·1^s (1·6)	50·3^a (1·6)	8·3 (1·6)	45·4^a (1·6)
VI	0·0 (2·9)	5·9 (2·8)	0·0 (2·7)	6·1 (2·6)	0·0 (2·8)	7·1 (2·8)	0·4 (2·7)	8·0 (2·9)
2-D	1·9 (3·4)	14·9 (3·2)	1·7 (3·2)	15·4 (3·1)	3·3 (3·3)	15·4 (3·3)	2·8 (3·2)	14·2 (3·4)

^{a} Produced by *anti*-elimination; ^{s} Produced by *syn*-elimination.

B) *Pyrolysis of the quaternary hydroxide.* Synthesis of the quaternary hydroxides as well as the pyrolytic decomposition was performed in the same manner as described previously[2] for the position isomers.

Vapour Phase Chromatography

The analyses were performed on the CHROM-3 (Laboratorní potřeby, Prague) and/or Carlo Erba Fractovap GT 4 instrument. The olefins were analysed using a capillary (50 ml) coated with Apiezone or di-n-butyl tetrachlorophthalate at 60°C. The alcohols and amines were analysed at 100–120°C using Apiezone on the porous tile support pre-treated with sodium hydroxide. Preparative vapour phase chromatography of the olefins was performed at 100°C using Apiezone on porous tile support.

Evaluation of the Infra-red Spectra of the Deuterium Labelled 1-Decene Mixtures

The infra-red spectra of the individual 1- and/or 2-deuterium labelled 1-decenes were measured in a broad region (1000–600 cm^{-1}) and the results were reported in a separate paper[11]. The important finding that any of the deuterium labelled 1-decenes exhibits characteristic absorptions in this region distinguishing it from the other labelled isomers as well as from the parent

un-deuterated 1-decene made it possible to evaluate, quantitatively, spectra of the complex mixtures containing all the 1-decene isomers due to deuterium label on the vinyl. Use was made of the following procedure: The absorbance $A_0(\nu_i)$ at a particular point in the spectrum of a mixture of m components, measured in a cell with path length d_0 and in concentration c_0, can be expressed as

$$A_0(\nu_i) = (\sum_{j=1}^{m} [n_j \cdot A_j(\nu_i)/(c_j d_j)] + n_{m+1}) \cdot c_0 d_0 ,$$

TABLE III

Proportions of the *syn*- and *anti*-Processes in 1,2-Dideuterio-1-decenes (*V*) Formation from the Reaction of *erythro*- and *threo*-1,2-Dideuterio-1-decyltrimethylammonium Base under Different Conditions

Conditions	*erythro*-1,2-D_2-*V*		*threo*-1,2-D_2*V*	
	% *syn*	% *anti*	% *syn*	% *anti*
t-C_4H_9OK/C_6H_6	20·2	79·8	18·7	81·3
t-C_4H_9OK/H.CO.$N(CH_3)_2$	13·5	86·5	14·3	85·7
t-C_4H_9OK/t-C_4H_9OH	7·9	92·1	6·9	93·1
Pyrolysis	14·0	86·0	10·8	89·2

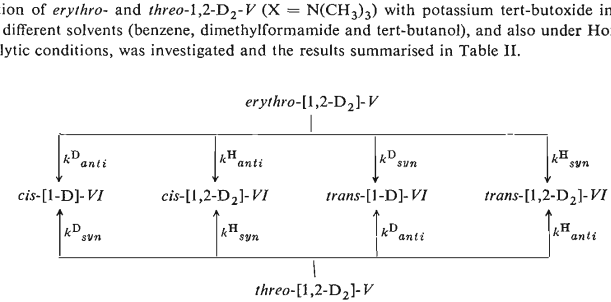
Calculated from the equations: $\%\ syn^{erythro} = \%(trans\text{-}1,2\text{-}D_2\text{-}VI) \times 100/((\%\ trans\text{-}1,2\text{-}D_2\text{-}VI) + (\%\ cis\text{-}1,2\text{-}D_2\text{-}VI))$,
$\%\ syn^{threo} = \%(cis\text{-}1,2\text{-}D_2\text{-}VI) \times 100/((\%\ trans\text{-}1,2\text{-}D_2\text{-}VI) + (\%\ cis\text{-}1,2\text{-}D_2\text{-}VI))$,
$\%\ syn + \%\ anti = 100$.

where $A_j(\nu_i)$ is the absorbance of the j-th component present in the mixture, measured separately in a cell with path length d_j and in concentration c_j. The value of n_j represents the mole fraction of the j-th component in the mixture; n_{m+1} is the background term. Those equations were solved for n in the sense of the least squares. The pertinent algorithm was written for the digital computer Gier in the Gier Algol III language and together with the solution it yields also an estimate of standard deviations (1σ) for the computed mole fractions. As many as 16 points of absorbance measurements were used for the computations (the Table of the wavenumbers ν_i ref.[11]). The mole fractions with negative values (if any) were deleted from the solution and the sum of remaining ones was normalised to the unity.

The reliability of the procedure was checked by two independent control experiments. In the first, a composition of two multicomponent artificial mixtures was calculated from IR-data and a surprisingly good agreement was found between the amounts weighted and calculated with the difference not exceeding the value of $1{\cdot}3\sigma$. In the second experiment, deuterium isotope composition of the olefin mixtures resulting from the elimination runs was determined by mass spectrometry and the data compared with those obtained by calculation of the corresponding infrared spectra. Again, an excellent agreement has been found invariantly between the data obtained by the two different procedures.

RESULTS

Information concerning the steric course of elimination of the stereospecifically β-deuterium labelled compounds can be obtained from the determination of the isotope isomer olefin composition. As follows from the configurational correlations between reactant and products (Scheme 2), the elimination of the *erythro*- as well as the *threo*-derivative can each give rise to four isotope isomer olefins. In addition, two other olefins (2-D-*VI* and *VI*) are expected to be present (in a minor amount) in the resulting olefin mixture, due to the incomplete labelling of the reactants on $C_{(1)}$. Hence, the determination of the six-component isotope isomer mixtures of 1-decene was required, and this was accomplished by the infrared spectrometry. By this procedure, the reaction of *erythro*- and *threo*-1,2-D_2-*V* ($X = \overset{+}{N}(CH_3)_3$) with potassium tert-butoxide in three very different solvents (benzene, dimethylformamide and tert-butanol), and also under Hofmann pyrolytic conditions, was investigated and the results summarised in Table II.



For incomplete labelling:

SCHEME 2

As a cursory inspection of the Table II immediately shows, the *cis*- as well as the *trans*-olefins (*cis*-1,2-D_2-*VI*, *cis*-1-D-*VI* and *trans*-1,2-D_2-*VI*, *trans*-1-D-*VI*, respectively) are invariantly present in the resulting olefin mixtures from reactions of both the *erythro*- and *threo*-derivatives. It follows from this finding that *anti*- and *syn*-elimination took part simultaneously in all the reactions investigated: their contributions in the individual runs can be calculated, according to Scheme 2, from the proportions of the appropriate mono- and/or di-deuterated *cis*- and *trans*-olefins.

The incomplete labelling of the reactants has to be considered before the calculation; as evidenced by mass spectrometry of the starting dimethylamines, both the *erythro*- as well as *threo*-reactant contained a non-negligible proportion of the d_1 species (12·7 and 21·7%, respectively). As shown in the Scheme 2, the deficiency of the label on the $C_{(1)}$ leads exclusively to the formation of the additional olefins 2-D-*VI* and *VI* (Table II) and does not, therefore, affect the reliability of the calculation. On the other hand, a lack of label on the $C_{(2)}$ would lead (Scheme 2) to the formation of the monodeuterated olefins *cis*- and *trans*-1-D-*VI* by *syn*- as well as *anti*-

elimination. This circumstance makes, obviously, any conclusions concerning the steric course of formation of the two monodeuterated olefins from derivatives *erythro*- and *threo*-1,2-D_2-*V* less reliable. For this reason, only the steric course of the dideuterated olefins *cis*- and *trans*-1,2-D_2-*VI* will be analysed in the Discussion. For the same reason, any attempts to calculate the deuterium isotope effects for the *syn*- and *anti*-elimination would be unwarranted.

DISCUSSION

For a systematic discussion of the dependence of the steric course on "variables" (such as base–solvent combination or alkyl structure) it is convenient to have contributions of the *syn*- and *anti*-processes unaffected by an operation of a sizeable deuterium isotope effect. This has been, in the present case, approached most closely* by the evaluation of the *syn*- and *anti*- contributions in the formation of the 1,2-dideuterio labelled olefins (*cis*- and *trans*-1,2-D_2-*VI*). The results obtained are summarised in Table III.

As the data of Table III show, *syn*-elimination contributes to the 1,2-dideuterio-1-decene formation from *erythro*- as well as *threo*-reactant in all reactions investigated in proportions varying between 6·9 – 20·2%, in dependence on the conditions used. In accord with expectation, the contributions from the two diastereoisomeric reactants are practically identical, indicating that the configurational difference due to the deuterium labelling does not affect measurably the steric course of the reaction. By contrast, the proportions of the *syn*- and *anti*-elimination depend considerably on the base–solvent combination used. The proportion of *syn*-elimination is the greatest in reaction with tert-butoxide in the non-polar aprotic solvent benzene (18·7 – 20·2%) and decreases, gradually, on going to the dipolar aprotic solvent dimethylformamide (13·5 – 14·3%) and to the protic solvent tert-butanol (6·9 – 7·9). The observed trend corresponds – by and large – to that found previously[2,5,8,17,18] for other 'onium compounds. Its implications have already been discussed[18] and it requires no further comments here.

Extensive studies of the steric course in bimolecular elimination of several open-chain quaternary bases revealed that the contributions of the two mechanistic pathways depend also, very sensitively, on the alkyl structure of the reactant[2–8]. The most complete set of data on the effect of the alkyl structure on the steric course is available for the formation of the *trans*-disubstituted olefins, *trans-II*, from the quaternary compounds *I* in the reaction with potassium tert-butoxide in tert-butanol. The pertinent data are summarised in Table IV and compared with the present ones concerning the monosubstituted olefin formation from 1-decyltrimethylammonium base under analogous conditions.

A very clear-cut pattern of elimination behaviour is immediately apparent from

* The secondary deuterium effect in the 1-decenes formation due to the labels on $C_{(1)}$ as well as $C_{(2)}$ is assumed to be negligibly small.

TABLE IV

The Proportions of the *syn*- and *anti*-Processes in the Olefin (*II*) Formation from the Open-Chain Quaternary Chlorides *I* in the Reaction with Potassium tert-Butoxide in tert-Butanol: The Effect of the Alkyl Structure

R^1	R^2	% *anti*	% *syn*	R^1	R^2	% *anti*	% *syn*
H	C_8H_{17}	92·4[a]	7·4[a]	C_4H_9	C_4H_9	11[c]	89[c]
CH_3	C_3H_7	85[b]	15[b]	t-$C_4H_9.CH_2$	C_4H_9	1[d]	99[d]
C_2H_5	C_2H_5	17[b]	83[b]	t-C_4H_9	C_5H_{11}	$\ll 3$[d]	$\gg 97$[d]

[a] The average from the values found for the deuterium labelled 1-decene formation from *erythro*- and *threo*-1,2-D_2-*V*. The secondary deuterium isotope effect is assumed to be negligible. [b] The value for the *trans*-olefin from ref.[6,7]. [c] The value for the *trans*-olefin from ref.[2]. [d] The value for the *trans*-olefin from ref.[5].

these data. The proportion of *anti*-elimination which prevails in 1-decene formation from the now investigated compound *VI* becomes somewhat less pronounced on introduction of the methyl group[6,7] into $C_{(\alpha)}$ position ($R^1 = CH_3$) and decreases, stepwise, on lengthening[2,7] the R^1 group ($C_2H_5 > C_4H_9$), and, further still, almost vanishes on alkyl branching[5] of the R^1 group (R^1 = t-$C_4H_9.CH_2$ or t-C_4H_9).

Thus, the present results appear to be in good accordance with the recent proposal by Saunders and his coworkers[6,7], suggesting that the steric bulk of the R^1 (and less pronouncedly of the R^2) group is responsible for the changes in the steric course. These authors proposed tentatively that the extremely bulky trimethylammonium group forces the R^1 and R^2 substituents into positions, where they can hinder access of the attacking base to the *anti*-β-hydrogen. Accordingly, a gradual decrease of the rate of the *anti*-process with the increasing steric bulk of the R^1 and R^2 group is assumed to result from the steric hindrance, allowing thus a better chance for the unaffected *syn*-process to enter the picture.

However, there are some arguments available, speaking strongly against such a simple explanation. Recently, we have investigated[19] the effect of alkyl structure on the course of *syn*-elimination (Cope elimination) in a closely related series of the open-chain amine oxides, $R^1.CH(N(CH_3)_2O).CH_2 . C_5H_{11}$, and found a very remarkable increase of the rate of elimination on increasing, gradually, the steric bulk of the R^1 group in order $H < CH_3 < C_2H_5 < C_3H_7 < i\text{-}C_3H_7 < t\text{-}C_4H_9$, the rate difference between the two extremes being 10^6. Clearly, a similar factor may be envisioned to operate in the *syn*-component of bimolecular elimination* of the quaternary com-

* In a cycloalkyl series we have found that structural changes exert an almost identical rate effect in the intramolecular reaction of the amine oxides[21] and in the bimolecular *syn*-elimination of the quaternary compounds[20].

pounds *I*; accordingly, a steric acceleration of the *syn*- instead of a retardation of the *anti*-elimination, or perhaps a combination of both of them may be responsible for the observation listed in Table IV.

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