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THE CONTRIBUTION OF *syn*- AND *anti*-ELIMINATION TO OLEFIN FORMATION IN BRANCHED OPEN-CHAIN SYSTEMS: THE EFFECT OF ALKYL STRUCTURE ON STERIC COURSE OF BIMOLECULAR ELIMINATION**

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Olefin formation from 2,2-dimethyl-4-nonyltrimethylammonium base (*V*, X = $\overset{(+)}{N}(CH_3)_3$), 2,2-dimethyl-3-nonyltrimethylammonium base (*VI*, X = $\overset{(+)}{N}(CH_3)_3$), and from their β-deuterium labelled derivatives (*threo*- and *erythro*-5-D-*V*, *erythro*-3-D-*V* and *erythro*-4-D-*VI*) has been investigated under Hofmann pyrolytic conditions and in several base–solvent systems. The deuterium isotope effects, k_H/k_D, for the formation of the individual isomeric olefins, supported by mass spectroscopic data, indicate that *trans*-olefins are formed by *syn*-elimination almost exclusively, under all conditions investigated. On the other hand, the *cis*-olefins were found to be formed almost exclusively by *anti*-elimination. Analogous data obtained for E2 reactions of the corresponding tosylates *V* and *VI* (X = OTs) and their β-deuterium labelled derivatives (*erythro*- and *threo*-5-D-*V*, *threo*-3-D-*V* and *threo*-4-D-*VI*) revealed a less pronounced contribution of the *syn*-mechanism. The analysis of the data obtained for some of the reactions afforded semiquantitative values (or their lowest limits) of the *trans*/*cis* ratios in the *syn*- and *anti*-components of the elimination indicating unusually high and "divergent" stereoselectivity of the two processes.

In preceding papers[2,3] of this series we reported a study of the steric course of the elimination in the open-chain systems *I* and *II* (X = $\overset{(+)}{N}(CH_3)_3$ and OTs), employing a wide range of base–solvent combinations. We found that in the reaction of the straight chain 'onium salt *I* with tert-butoxide in protic as well as aprotic solvents *syn*-elimination represents the principal reaction mode, the prevailing *trans*-isomer (*trans-III*) being formed predominantly by this mechanism, while the minor *cis*-isomer (*cis-III*) predominantly by *anti*-mechanism. By contrast, in the trisubstituted olefin formation (*trans*- and *cis-IV*) from the β-branched 'onium salts (*threo*- and *erythro-II*) as

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well as in the reactions of the corresponding *p*-toluenesulphonyl esters *I* and *II* (X = OTs), the principal reaction mode is *anti*-elimination in essentially* all the base–solvent combinations investigated.

From these data as well as from data published by other authors[4–10] it became clear that the choice of steric path (*syn* or *anti*) depends, in a more subtle way than one may have anticipated,** on the alkyl structure of the substrate. We have therefore investigated in a more detail the effect of alkyl branching on the steric course of the elimination reaction in open-chain systems. In the present paper we report a study on the quaternary 'onium bases and tosylates *V* and *VI* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs).

$C_4H_9.CH_2.CH(X).C_4H_9$ — *I*

$C_4H_9.CH(CH_3).CH(X).C_4H_9$ — *erythro-* and *threo-II*

$C_4H_9.CH = CH.C_4H_9$ — *cis-* and *trans-III*

$C_4H_9.C(CH_3) = CH.C_4H_9$ — *cis-* and *trans-IV*

$t\text{-}C_4H_9.CH_2CH(X).CH_2.C_4H_9$ — *V*

$t\text{-}C_4H_9.CH(X).CH_2.C_5H_{11}$ — *VI*

$t\text{-}C_4H_9.CH_2.CH = CH.C_4H_9$ — *cis-* and *trans-VII*

$t\text{-}C_4H_9.CH = CH.C_5H_{11}$ — *cis-* and *trans-VIII*

$X = \overset{(+)}{N}(CH_3)_3$ and OTs

For the determination of the steric course of the olefin formation we employed, as in previous studies[3,14,15], stereospecifically β-deuterium labelled derivatives, *i.e. threo-* and *erythro*-5-D-*V* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs), *threo*-3-D-*V* and *threo*-4-D-*VI* (X = OTs), *erythro*-3-D-*V* and *erythro*-4-D-*VI* ($X = \overset{(+)}{N}(CH_3)_3$). It was hoped that the olefinic products obtained from *V* (*cis-* and *trans-VII* and *cis-* and *trans-VIII*) as well as from *VI* (*cis-* and *trans-VIII*) would be more easily separated than in the case of the straight chain systems such as *I* so that otherwise formidable analytical problems would be simplified. As will be seen below, this expectation was fulfilled. The deuterium labelled derivatives of 2,2-dimethyl-4-nonanol, *threo-* and *erythro*-5-D-*V* (X = OH), were synthetised from *trans*-2,2-dimethyl-4-nonene (*trans-VII*), obtained by sodium–liquid ammonia reduction of the corresponding acetylene.

* The only base–solvent system in which the contribution of *syn*-elimination was significant was tert-butoxide–benzene.

** The fact that the choice of steric path is structure-dependent has been known for some time; this, however, concerned cyclic substrates[11–21] in which *anti*-elimination may be greatly handicapped through the geometry of the molecule.

$t\text{-}C_4H_9.CH_2.CH(X).CH(D).C_4H_9$ $t\text{-}C_4H_9.CH(D).CH(X).C_5H_{11}$

erythro- and *threo*-5-D-*V* *erythro-* and *threo*-3-D-*V*

$t\text{-}C_4H_9.CH(X).CH(D).C_5H_{11}$

erythro- and *threo*-4-D-*VI*

$X = \overset{(+)}{N}(CH_3)_3$ and/or OTs

Oxidative deuterioboration of the olefin gave two position isomeric alcohols from which the required alcohol, *threo*-5-D-*V*, was isolated by vapour phase chromatography. Reduction of the epoxide corresponding to the above olefin with lithium aluminium deuteride–aluminium chloride[22] (5 : 1) gave the other alcohol, *erythro*-5-D-*V* (X = OH), together with a position isomer from which it was separated by vapour phase chromatography.

Similarly, *threo*-2,2-dimethyl-4-nonanol-[3-D] (*threo*-3-D-*V*; X = OH) and *threo*-2,2-dimethyl-3-nonanol-[4-D] (*threo*-4-D-*VI*; X = OH) were synthesised from *trans*-2,2-dimethyl-3-nonene (*trans-VIII*) prepared again by sodium-liquid ammonia reduction of the corresponding acetylene. Oxidative deuteroboration of the olefin afforded a mixture of the two required alcohols which was separated by vapour phase chromatography.

The deuterium labelled alcohols were converted (with inversion of the configuration) into the quaternary salts by reaction of their *p*-toluenesulphonyl esters with sodium azide in dimethyl sulphoxide, followed by lithium aluminium hydride reduction and quaternisation. Of the four potential elimination products, two (*trans-VII* and *trans-VIII*) were available from the above syntheses. The remaining isomers, *cis-VII* and *cis-VIII*, were prepared from the corresponding acetylenes by reduction with diborane or by hydrogenation on the Lindlar catalyst.

EXPERIMENTAL

2,2-Dimethyl-4-nonyne

4,4-Dimethyl-1-pentyne[23] (50 g, 0·5 mol) was added to a solution of sodium amide (prepared *in situ* from 12 g of sodium) in 800 ml dry ammonia. The mixture was allowed to reflux for one hour under intense stirring, then treated with butyl bromide (70 g, 0·5 mol) and allowed to reflux for another two hours. Ether (600 ml) was added and the ammonia allowed to evaporate. The resulting ethereal suspension was stirred for 20 hours at the laboratory temperature and then at the reflux for 3 hours. Ice water (300 ml) was added, the ethereal layer washed with water, dilute hydrochloric acid and water to a neutral reaction, dried, the ether carefully driven off and the residue distilled, b.p. 105°C/100 Torr; yield 35 g (43%). For $C_{11}H_{20}$ (152·3) calculated: 86·76% C, 13·24% H; found: 86·98% C, 13·12% H.

2,2-Dimethyl-3-nonyne

The same procedure was applied to the alkylation of tert-butylacetylene[24] with n-pentyl bromide: 8 g of the former afforded 7·5 g (50%) of the title compound, b.p. 76°C/18 Torr, uniform by vapour phase chromatography. For $C_{11}H_{20}$ (152·3) calculated: 86·76% C, 13·24% H; found: 87·16% C, 13·24% H.

trans-2,2-Dimethyl-4-nonene

A solution of sodium (30 g, 1·3 gat) in ammonia (2 l) was treated with 2,2-dimethyl-4-nonyne (20·6 g, 0·135 mol) and the reaction mixture allowed to reflux for 5 h. The mixture was diluted with ether (600 ml), solid ammonium nitrate added to the disappearance of the blue colouration, followed by aqueous ammonium hydroxide (500 ml). The ammonia was allowed to evaporate freely overnight, the ethereal layer washed with water, dilute hydrochloric acid, and water, dried and the solvent distilled off. Vapour phase chromatography showed that the residue still contains about 10% of the starting acetylene. The residue was therefore subjected to another reduction (using 6 g sodium in 400 ml ammonia); this operation afforded 14·7 g (70%) of the title compound, uniform by vapour phase chromatography. For $C_{11}H_{22}$ (154·3) calculated: 85·63% C, 14·37% H; found: 85·61% C, 14·58% H.

trans-2,2-Dimethyl-3-nonene

2,2-Dimethyl-3-nonyne (2·2 g) was reduced with sodium (6 g) in ammonia (600 ml) as described above; in this smaller run a single "passage" was sufficient for complete reduction. Yield 1·7 g (77%), b.p. 68°3/15 Torr, uniform by vapour phase chromatography. For $C_{11}H_{22}$ (154·3) calculated: 85·63% C, 14·37% H; found: 85·40% C, 14·20% H.

cis-2,2-Dimethyl-4-nonene

A) *By hydrogenation on a Lindlar catalyst*: A solution of 2,2-dimethyl-4-nonyne (5 g) in hexane (15 ml) containing 0·3 g of palladium-on-charcoal catalyst was shaken with hydrogen at room temperature; the consumption of hydrogen ceased when approximately one equivalent had been taken up. The usual work-up afforded 3·4 g (67%) of a liquid (b.p. 70—75°C/20 Torr), consisting according to vapour phase chromatography of 94% *cis*- and 6% *trans*-olefin.

B) *By reduction with diborane*: A solution of 2,2-dimethyl-4-nonyne (1 g, 6·6 mmol) in ether (20 ml) was treated under ice cooling with 1M ethereal lithium aluminium hydride (1·7 ml) followed by boron trifluoride etherate (0·32 g, 2·2 mm), the mixture stirred for 1 h under nitrogen, treated with glacial acetic acid (3 ml) and allowed to stand overnight at room temperature. The solution was diluted with water (100 ml) and the product taken up in ether. The usual work-up afforded 0·55 g (54%) of a liquid, b.p. 70—75°C/20 Torr, which according to vapour phase chromatography consists of 85% *cis*-olefin, 7% *trans*-olefin and 8% starting acetylene.

cis-2,2-Dimethyl-3-nonene

A) *By hydrogenation on a Lindlar catalyst*: A solution of 2,2-dimethyl-3-nonyne (0·5 g) in pentane (30 ml) containing 0·2 g of the catalyst was shaken for 10 h with hydrogen at room temperature. The resulting mixture consisted according to vapour phase chromatography of 19% *cis*-olefin, 4% *trans*-olefin and 77% starting acetylene.

B) *By reduction with diborane*: 2,2-Dimethyl-3-nonyne (1·8 g) was treated with diborane under the same conditions as described above for the synthesis of the positional isomer. The resulting mixture, b.p. 70°C/18 Torr, consisted of 78% *cis*- and 22% *trans*-isomer.

trans-2,2-Dimethyl-4,5-epoxynonane

Oxidation of *trans*-2,2-dimethyl-4-nonene (23·0 g, 0·15 mol) with perphthalic acid (45 g, 0·25 mol) in ether (1 l) gave 21 g (83%) of the epoxide, b.p. 100°C/40 Torr, uniform by vapour phase chromatography. For $C_{11}H_{22}O$ (170·3) calculated: 77·58% C, 13·02% H; found: 77·44% C, 12·92% H.

2,2-Dimethyl-3-nonanol

A) A solution of tert-butylmagnesium chloride (4 mol) in ether (2 l) was added in the course of 6 h to heptanoic acid chloride[25]. The reaction mixture was allowed to stand overnight and then poured on ice (3 kg). The usual isolation procedure followed by careful distillation afforded 91 g (54%) of the alcohol, b.p. 90°C/13 Torr, pure by vapour phase chromatography. For $C_{11}H_{24}O$ (172·4) calculated: 76·67% C, 14·04% H; found: 76·89% C, 13·92% H.

B) A solution of *trans*-2,2-dimethyl-3-nonene (18·5 g, 0·12 mol) and sodium borohydride (2·7 g, 0·071 mol) in diglyme (450 ml) was treated in a stream of nitrogen under stirring and ice-cooling with boron trifluoride etherate (10·5 g, 0·074 mol) and the mixture kept under these conditions for 5 h. It was then treated, successively, with water (15 ml), 10M-NaOH (60 ml) and 30% hydrogen peroxide (80 ml), the mixture stirred for two hours at room temperature, diluted with 3 l of water and the product taken up in ether. The usual work-up yielded 15·5 g of a material distilling within a wide range 70—105°C/12 Torr. According to vapour phase chromatography, the distillate contains some unreacted olefin and the two position isomeric alcohols *V* and *VI* (X = OH) in a ratio of about 4 to 3, which were separated by preparative vapour phase chromatography (10% Apiezone on the ground unglazed porous tile support): 2·4 g (12%) of 2,2-dimethyl-3-nonanol (shorter retention time) and 3·9 g (19%) of 2,2-dimethyl-4-nonanol.

2,2-Dimethyl-4-nonanol

A) *By reaction of* trans-2,2-*dimethyl*-4,5-*epoxynonane* with $LiAlH_4$–$AlCl_3$: A solution of lithium aluminium hydride (0·4 g, 0·01 mol) in ether (15 ml) was treated under ice-cooling successively with a solution of aluminium chloride (0·25 g, 0·002 mol) in ether (5 ml) and the above epoxide (0·9 g, 0·005 mol), the mixture stirred for 8 h at room temperature, and the product isolated in the usual manner. Distillation afforded 0·7 g (77%) of an oil which, according to vapour phase chromatography, consists of a mixture of 2,2-dimethyl-4-nonanol and 2,2-dimethyl-5-nonanol in a 53 : 47 ratio.

B) *By oxidative hydroboration*: *trans*-2,2-Dimethyl-4-nonene afforded in 82% yield a mixture of 2,2-dimethyl-4-nonanol and 2,2-dimethyl-5-nonanol in a 3 : 2 ratio. *cis*-2,2-Dimethyl-4-nonene gave 2,2-dimethyl-4-nonanol and 2,2-dimethyl-5-nonanol in a 7 : 3 ratio.

The 2,2-dimethyl-4-nonanol was isolated from the above runs by preparative vapour phase chromatography using 5% poly(butylene adipate) on ground porous tile support. For $C_{11}H_{24}O$ (172·3) calculated: 76·67% C, 14·04% H; found: 76·85% C, 13·94% H.

Deuteriated Alcohols

erythro-2,2-Dimethyl-4-nonanol-[5-D] was prepared from *trans*-2,2-dimethyl-4,5-epoxynonane by the procedure *A*, described above for the synthesis of the deuterium-free compound,

using $LiAlD_4$—$AlCl_3$. *threo*-2,2-Dimethyl-4-nonanol-[5-D] was prepared from *trans*-2,2-dimethyl-4-nonene, by the procedure *B* described above, by reaction with $NaBD_4$—BF_3 in diglyme. *threo*-2,2-Dimethyl-3-nonanol-[4-D] and *threo*-2,2-dimethyl-4-nonanol-[3-D] was prepared from *trans*-2,2-dimethyl-3-nonene by reaction with $NaBD_4$—BF_3 in diglyme (procedure *B*). The resulting mixture was separated by preparative vapour phase chromatography.

2,2-Dimethyl-4-nonyl *p*-toluenesulphonate

A solution of 2,2-dimethyl-4-nonanol (3·5 g, 0·02 mol) and *p*-toluenesulphonyl chloride (4 g, 0·022 mol) in pyridine (20 ml) was allowed to stand for 48 h at 0°C. The usual work-up afforded 5·7 g (86%) of an oil which was dried *in vacuo*. For $C_{18}H_{30}O_3S$ (326·4) calculated: 66·23% C, 9·26% H; found: 66·24% C, 9·39% H.

The corresponding *erythro*- and *threo*-5-D and *threo*-3-D labelled compounds were synthesised by the same procedure, from the labelled alcohols.

2,2-Dimethyl-3-nonyl *p*-toluenesulphonate

The usual procedure (10 days at 0°C) gave the tosylate in 70% yield in the form of an oil which was dried *in vacuo*. For $C_{18}H_{30}O_3S$ (326·4) calculated: 66·23% C, 9·26% H; found: 66·40% C, 9·65% H. The corresponding *threo*-4-D labelled compound was prepared by the same procedure from the corresponding labelled alcohol.

2,2-Dimethyl-3-nonanone

A solution of 2,2-dimethyl-3-nonanol (67 g, 0·39 mol) in 85% aqueous acetone was treated in the course of 1 hour with a solution of chromium trioxide (37 g, 0·38 mol) in 2·5N-H_2SO_4 (200 ml), the mixture heated to 45°C for 2 h, diluted with water (1·5 l), the product taken up in ether and the extracts washed with 3% aqueous ferrous sulphate. The usual work-up afforded 56 g (83%) of the ketone, b.p. 85°C/12 Torr, homogeneous by vapour phase chromatography. For $C_{11}H_{22}O$ (170·3) calculated: 77·44% C, 13·02% H; found: 77·20% C, 12·80% H.

2,2-*Dimethyl*-3-*nonanone oxime*: A solution of the above ketone (42 g, 0·25 mol), sodium acetate trihydrate (68 g, 0·5 mol) and hydroxylamine hydrochloride (20 g, 0·33 mol) was refluxed for 2 h, diluted with water (1·5 l) and the product taken up in ether. The oxime was distilled, b.p. 94°C/l Torr, and a sample crystallised from light petroleum, m.p. 42—43°C. For $C_{11}H_{23}NO$ (185·3) calculated: 71·30% C, 12·51% H, 7·56% N; found: 71·51% C, 12·30% H, 7·64% N.

4-Amino-2,2-dimethylnonane

A solution of 2,2-dimethyl-4-nonyl *p*-toluenesulphonate (5·7 g, 0·0175 mol), sodium azide (6·5 g, 0·1 mol) and sodium hydrogen carbonate (2 g) in dimethyl sulphoxide (100 ml) was heated to 95°C for 4 h, the solution diluted with saturated sodium chloride solution and the product taken up in pentane. The usual work-up afforded 3·2 g of an oily azide which was taken up in ether (20 ml) and added to a suspension of 8 g (0·2 mol) of lithium aluminium hydride in ether (200 ml). The mixture was allowed to stand for 2 h at room temperature and decomposed by successive addition of water (10 ml), 15% aqueous sodium hydroxide (10 ml) and water (10 ml). The precipitate was filtered off and washed repeatedly with ether. The ethereal filtrates were dried over potassium hydroxide pellets, the solution saturated with hydrogen chloride and taken to dryness. This procedure afforded 3 g (71%) of a crystalline hydrochloride which was very soluble even in non-polar organic solvents. For $C_{11}H_{26}ClN$ (207·8) calculated: 63·58% C, 12·62% H, 17·06% Cl,

6·74% N; found: 63·92% C, 12·63% H, 16·75% Cl, 7·07% N. *erythro-* and *threo*-2,2-Dimethyl-4-aminononane-[5-D] was prepared by the same procedure starting, respectively, from the *threo-* and *erythro*-5-D labelled *p*-toluenesulphonyl ester. *erythro*-2,2-Dimethyl-4-aminononane-[3-D]: Prepared analogously from the *threo*-3-D labelled *p*-toluenesulphonyl ester.

2,2-Dimethyl-4-dimethylaminononane

A solution of 4-amino-2,2-dimethylnonane (2·25 g, 0·013 mol) in formic acid (50 ml) and 30% formaldehyde (50 ml) was refluxed for 24 h. The usual work-up[26] afforded 1·9 g (76%) of the base, b.p. 136—137°C/85 Torr, shown to be uniform by vapour phase chromatography. For $C_{13}H_{29}N$ (199·4) calculated: 78·31% C, 14·66% H, 7·03% N; found: 78·76% C, 14·66% H, 6·84% N.

Methoiodide: A solution of the above amine (1·7 g, 0·01 mol) and methyl iodide (2·8 g, 0·02 mol) in benzene (10 ml) was allowed to stand in the dark at room temperature for 24 h, diluted with pentane (20 ml), the crystals filtered off and washed with pentane. Yield 2·6 g (89%), m.p. 136—138°C. For $C_{14}H_{32}IN$ (341·3) calculated: 49·26% C, 9·45% H, 37·18% I, 4·10% N; found: 49·45% C, 9·38% H, 37·52% I, 4·17% N. The corresponding *threo-* and *erythro*-D labelled compounds were prepared analogously.

2,2-Dimethyl-3-dimethylaminononane

A) Sodium (50 g) was gradually added to a solution of the 2,2-dimethyl-3-nonanone oxime (40 g) in ethanol (600 ml), the solution made acid with hydrochloric acid and taken to dryness. The residue was dissolved in water (200 ml), the solution extracted with ether, made alkaline with solid potassium hydroxide, the amine set free, taken up in ether, the ether solution dried and distilled off. The residue was taken up in formic acid (200 ml) and 30% formaldehyde and refluxed for 20 h. The usual work-up procedure[26] afforded 18 g (42%) of the title compound, b.p. 105°C/15 Torr. For $C_{13}H_{29}N$ (199·4) calculated: 78·31% C, 14·66% H, 7·03% N; found: 78·75% C, 14·51% H, 7·12% N.

B) Sodium azide (1 g, 15 mmol) was dissolved at 90°C in dimethyl sulphoxide (15 ml) and to the solution was added under stirring 2,2-dimethyl-3-nonyl *p*-toluenesulphonate (2·4 g, 7·5 mmol). The mixture was kept at 95°C for 4 g, diluted with water and the product taken up in pentane. After usual work-up the crude azide was treated under reflux with an excess of lithium aluminium hydride in ether, the mixture decomposed by aqueous sodium hydroxide and the product isolated by standard procedure. Clark–Eschweiler methylation of the crude product afforded 0·32 g (22%) of the title compound. *erythro*-2,2-Dimethyl-3-dimethylaminononane-[4-D] was prepared by method *B* from the *threo*-4-D labelled *p*-toluenesulphonyl ester.

Methoiodide: The title amine (5 g) was dissolved in an excess of methyl iodide (15 ml) and the solution allowed to stand in dark for 2 weeks; the solvent was driven off on aspirator and the product repeatedly washed with pentane; m.p. 58—60°C. For $C_{14}H_{32}IN$ (341·3) calculated: 49·26% C, 9·45% H, 4·10% N; found: 49·30% C, 9·22% H. 3·80% N.

Quaternary Chlorides

The quaternary iodides were shaken in dark with an excess of silver chloride in aqueous methanol and the products isolated by the usual work-up[27]. The quaternary chlorides were obtained as dihydrates; dehydration could be achieved by prolonged drying *in vacuo* at 100—120°C.

N,N,N-*Trimethyl*-2,2-*dimethyl*-4-*nonylammonium chloride dihydrate*: M.p. 76—79°C. For $C_{14}H_{32}ClN.2\,H_2O$ (285·9) calculated: 58·90% C, 12·61% H, 4·92% N; found: 58·45% C, 12·71% H, 4·68% N.

N,N,N-*Trimethyl*-2,2-*dimethyl*-3-*nonylammonium chloride dihydrate*: M.p. 60–62°C. For $C_{14}H_{32}ClN.2\,H_2O$ (285·9) calculated: 58·90% C, 12·61% H, 4·92% N; found: 58·88% C, 12·62% H, 4·92% N.

Elimination Runs

The reactions were carried out in sealed tubes under nitrogen using samples of 60–300 mg of the reactant. The conditions are summarised in Table I. After heating for the time indicated, the tubes were cooled to −60°C and the contents acidified using 2M-HCl. The olefins were taken up in pentane, the organic layer washed with water, dried and pentane distilled off through a short column. The crude residue was directly analysed by vapour phase chromatography. In elimination runs

TABLE I

Conditions Employed in the Elimination Reactions of the Compounds *V* and *VI* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs) and Their Labelled Derivatives

X	Solvent[a]	Molarity		Temperature/time °C/h
		base	reactant	
$\overset{(+)}{N}(CH_3)_3$	methanol	2·0[b]	0·1	130/6
$\overset{(+)}{N}(CH_3)_3$	tert-butanol	0·5[c]	0·1	100/5
$\overset{(+)}{N}(CH_3)_3$	dimethyl sulphoxide	0·5[c]	0·1	40/0·5
OTs	dimethylformamide	0·5[c]	0·03	40/0·5
OTs	dimethyl sulphoxide	0·5[c]	0·02	40/0·5
OTs	tert-butanol	0·5[c]	0·03	110/5
OTs	benzene	0·2[c]	0·02	150/24

[a] Solvents were dried as reported previously[11,12]; [b] potassium methoxide; [c] potassium tert-butoxide.

involving *threo*-5-D-*V* derivative ($X = \overset{(+)}{N}(CH_3)_3$) trimethylamine was isolated from acidic aqueous layer using the procedure reported earlier[15]. Preparation and decomposition of the quaternary hydroxides was performed analogously as described previously[3]. Vapour phase chromatography was performed on Chrom-3 (Laboratorní potřeby, Prague) and/or Carlo Erba Fractovap GT instrument. The olefin and/or acetylene mixtures were separated on an Apiezon capillary (50 m) at 60°C. The values of apparent isotope effect, $(k_H/k_D)_{apparent}$, were evaluated on the basis of the olefin isomer composition data using the equation[28,29] (*I*):

$$(k_H/k_D)_{apparent} = \frac{(\%\, I_{exam}/\%\, I_{ref})_H}{(\%\, I_{exam}/\%\, I_{ref})_D}, \qquad (I)$$

where $\%\, I_{exam}$ and $\%\, I_{ref}$ is the percentage of the "examined" isomer and "reference" isomer, respectively, in the olefinic mixture from reaction of the unlabelled (*H*) and labelled (*D*) reactant.

In this procedure we are assuming that the formation of the olefin "allylic" to the deuterium labelled carbon (reference olefin) is not subjected to an isotope effect. In the calculation of k_H/k_D values the isomer formed in a greater amount was used as the reference olefin. The deuterium content in the starting alcohols, olefin mixtures obtained as well as in the trimethylamine produced was determined by mass-spectroscopy; reproducibility was better than 1%.

RESULTS

Semiquantitative information on the steric course is obtained from a comparison of the olefin composition in the reaction of the stereospecifically β-deuterium labelled compound with that of the deuterium-free "parent" compound[14,15,28]. This affords a value of a deuterium isotope effect, $(k_H/k_D)_{apparent}$, the value of which is close to unity when the reaction leading to the formation of the particular olefin has involved no C—D fission and has a value[14-21] about 2—6 when only C—D fission is involved. In the latter case, the value of $(k_H/k_D)_{apparent}$ is equivalent to the true isotope effect. Since olefin composition in the present systems is readily determined by vapour phase chromatography, the evaluation of $(k_H/k_D)_{apparent}$ is a relatively simple matter.

Complementary, and in some cases quantitative information on the steric course could be derived by mass spectroscopy determination of the deuterium content in the resulting olefin mixtures, without the need for additional separation. This approach involves some uncertainty, because the four olefin isomers do not necessarily afford the molecular ion with the same yield. This circumstance, however, does not affect seriously the accuracy of the results in those cases in which the olefin mixture produced was relatively uniform. On the other hand, only semiquantitative conclusions may be drawn from deuterium determination in the more homogeneous olefin mixtures.

'Onium Bases

Table II summarizes the olefin isomer composition in the eliminations from the 'onium bases *V* and *VI* and their deuterium β-labelled derivatives, *erythro*- and *threo*-5-D-*V*, *erythro*-3 D-*V*, and *erythro*-4-D-*VI*, using the base–solvent systems listed.

In the reactions of the unlabelled 'onium compound *V* the preferred orientation is, as was predictable[30], away from the tert-butyl group, *i.e.* the olefin *VII* is formed in preference to the olefin *VIII*. As regards *trans-cis* olefin composition this depends (both in reaction of *V* and *VI*) on the nature of the base and solvent; in the eliminations employing tert-butoxide in a protic or aprotic solvent, and also in the pyrolysis of the quaternary hydroxide, the *trans*-isomers (*trans-VII* as well as *trans-VIII*) greatly predominate over the corresponding *cis*-isomers (*cis-VII* and *cis-VIII*, respectively). On the other hand, in the case of the reactions employing methoxide in methanol it is the *cis*-isomer which predominates. This behaviour has been encountered previously[3-5,15] in other substrates, for which it could be shown that two stereochemically different *syn*- and *anti*-mechanisms operate side by side in the elimination process, the former leading predominantly or almost exclusively to the *trans*-olefins and the latter to the *cis*-olefins, again predominantly or almost exclusi-

vely. Consider first the elimination from the deuterium labelled derivatives of the 'onium base *V*. In all the base–solvent combinations investigated the value of $(k_H/k_D)_{apparent}$ found for the formation of both *trans*- and *cis*-*VII* olefin from the

TABLE II

Elimination of 2,2-Dimethyl-4-nonyltrimethylammonium Base (*V*; X = $\overset{(+)}{N}(CH_3)_3$), 2,2-Dimethyl-3-nonyltrimethylammonium Base (*VI*; X = $\overset{(+)}{N}(CH_3)_3$) and Their β-Deuterium Labelled Derivatives under Different Conditions: Olefin Composition and Values of k_H/k_D

Reactant	t-C_4H_9.CH_2.CH=CH.C_4H_9				t-C_4H_9.CH=CH.C_5H_{11}			
	trans-*VII*		*cis*-*VII*		*trans*-*VIII*		*cis*-*VIII*	
	%	k_H/k_D [a]	%	k_H/k_D [a]	%	k_H/k_D [a]	%	k_H/k_D [a]
Potassium methoxide–methanol								
V	40·5	—	53·2	—	5·2	—	1·1	—
erythro-5-D-*V*	40·4	1·0	53·5	1·0	5·1	—	1·0	—
threo-5-D-*V*	47·7	2·2	38·1	3·6	13·2	—	1·0	—
erythro-3-D-*V*	41·7	—	52·2	—	5·0	1·0	1·0	1·1
VI	—	—	—	—	46·1	—	53·9	—
erythro-4-D-*VI*	—	—	—	—	47·1	1·0	52·3	—
Potassium tert-butoxide–tert-butanol								
V	93·9	—	3·0	—	3·1	—	0·01	—
erythro-5-D-*V*	92·2	1·2	4·0	0·9	3·8	—	[b]	—
threo-5-D-*V*	89·5	2·9	1·8	4·7	8·7	—	[b]	—
erythro-3-D-*V*	94·0	—	2·9	—	3·1	1·0	[b]	—
VI	—	—	—	—	96·4	—	3·6	—
erythro-4-D-*VI*	—	—	—	—	96·4	1·0	3·6	—
Potassium tert-butoxide–dimethyl sulphoxide								
V	95·4	—	1·7	—	2·9	—	[b]	—
erythro-5-D-*V*	95·1	1·1	1·7	1·1	3·2	—	[b]	—
threo-5-D-*V*	86·8	4·2	2·0	3·3	11·2	—	[b]	—
Pyrolysis								
V	83·1	—	5·8	—	11·1	—	[b]	—
erythro-5-D-*V*	79·0	1·1	9·1	0·7	11·9	—	[b]	—
threo-5-D-*V*	70·8	2·6	4·2	3·1	25·0	—	[b]	—

[a] The values of k_H/k_D were not corrected for incomplete deuterium labelling in the reactant; for deuterium content of the starting alcohols see footnote *a* in Table III. [b] Only negligible amount of *cis*-*VIII* isomer was present and this was disregarded in the calculation of the product composition.

erythro-5-D-*V* derivative is very close or equal to unity. Similarly, less complete set of values of $(k_H/k_D)_{apparent}$ found for the formation of both *trans*- and *cis*-*VIII* olefin from the *erythro*-3-D-*V* derivative is also very close to unity. On the other hand, for the reaction of the *threo*-5-D-*V* isomer the corresponding values of $(k_H/k_D)_{apparent}$ are distinctly different from unity, ranging from 2·2–4·7. These findings strongly suggest that in the elimination of the 'onium base *V* the *trans*-olefins *VII* and *VIII* are formed predominantly by *syn*-elimination, whereas the *cis*-olefins *VII* as well as *VIII* are formed by *anti*-elimination.

Consider next the elimination from the position isomeric 'onium compound *VI* and from its β-deuterium labelled derivative, *erythro*-4-D-*VI*. Here, only two olefins (*trans*- and *cis*-*VIII*) are formed in the elimination process, the formation of both being potentially subjected to the operation of the deuterium isotope effect. Hence, the absence of the olefin having the label in the "allylic" position (reference olefin) in the mixture produced precludes the unambiguous calculation of the deuterium isotope effect by the same procedure as applied above for the derivatives of *V*. However, available data from the isomer *V* as well as from other 'onium compounds[3–5,15] indicate that *syn* → *cis* path plays generally negligible role in *cis*-olefin formation.* Assuming that *cis*-*VIII* formation from *erythro*-4-D-*VI* proceeded predominantly by *anti*-elimination (C—H fission) we used tentatively the isomer *cis*-*VIII* as the internal standard in the calculation of the deuterium isotope effect, $(k_H/k_D)_{apparent}$, in the formation of the corresponding *trans*-*VIII* isomer.

As may be seen from Table II, the values of the thus calculated deuterium isotope effect are equal to unity in methoxide–methanol as well as tert-butoxide–tert-butanol. This suggests that *trans*-olefin formation from 'onium compound *VI* proceeds also predominantly by *syn*-elimination.

The conclusions regarding the steric course of *trans*- and *cis*-olefin formation from the 'onium compounds *V* and *VI* are fully supported by the determination of the deuterium content in the olefin mixtures produced in the elimination of the deuterium labelled derivatives *erythro*- and *threo*-5-D-*V* as well as *erythro*-4-D-*VI* (Table III). From this Table it is apparent that the olefin mixtures obtained from the reactions of the *erythro*-deuterium labelled derivatives, *erythro*-5-D-*V* and *erythro*-4-D-*VI*, retained all the deuterium label practically under all conditions investigated. It follows from these findings that *syn* → *trans* and *anti* → *cis* routes (involving C—H fission) are the exclusive processes for the formation *trans*- and *cis*-olefins *VII* and *VIII* from *erythro*-5-D-*V* and *erythro*-4-D-*VI* derivatives, respectively. The only exception has been found in the olefin mixture obtained from the reaction of *erythro*-4-D-*VI* derivative with methoxide in methanol in which a small loss of the deuterium

* In *cis*-5-decene formation from unlabelled 5-decyltrimethylammonium base the contribution of the *syn*-path is less then 6% under comparable conditions[3]. Moreover, the *syn* → *cis* path in the elimination from *erythro*-deuterium labelled derivatives is considerably supressed by the operation of the deuterium isotope effect.

label (~3%) could be detected, indicating non-negligible incursion of *anti* → *trans* and/or *syn* → *cis* path in the elimination process. From analogy with other 'onium compounds investigated under comparable conditions[3] it is reasonable to assume that *anti* → *trans* path plays major role.

In contrast to the *erythro*-derivatives, the elimination of the corresponding *threo*-derivatives involves C—D fission in both *syn* → *trans* and *anti* → *cis* routes. The deuterium content found in the olefin mixtures obtained from the reaction of *threo*-5-D-*V* derivative corresponds very closely to the percentage of the "allylic" deuterium (*trans*- and *cis*-*VIII*), indicating again the dominant role of the *syn* → *trans** and *anti* → *cis* processes, in spite of the operation of the sizeable isotopic effect (Table II). Nevertheless, the operation of the alternative minor processes, *anti* → *trans* and/or *syn* → *cis*, involving C—H fisssion could be detected in the *threo*-isomer under all conditions investigated, as evidenced by the difference between the deuterium content values found and calculated. Taking into account the very small proportion of the *cis*-*VII* isomer produced under most conditions investigated** as well as the known very low propensity[3] of 'onium salts toward *syn* → *cis* elimination, it is reasonable to assume that the observed differencies are caused mainly by an incursion of the *anti* → *trans* path in the elimination process.

In Table IV are summarised the proportions of *syn*- and *anti*-elimination in the *trans*- and *cis*-olefin formation recalculated roughly for the unlabelled 'onium compounds *V* and *VI*.

Tosylates

The reaction of the tosylate *V* (X = OTs) leads to an olefin mixture in which the isomers are more equally represented (Table V). Two significant facts emerge. The first concerns orientation. Unlike in the case of the elimination of the corresponding 'onium base (*V*; X = $\overset{(+)}{N}(CH_3)_3$), the preferred orientation in the reaction of the tosylate *V* (X = OTs) is actually towards the tert-butyl group, under all conditions investigated. The second interesting feature concerns the *trans*–*cis* isomer composition. In the "neopentyl-amyl" olefin *VII* the *cis*-isomer is invariably formed in greater amount irrespective of the solvent used; by contrast, in "tert-butyl-hexyl" isomer *VIII* it is the *trans*-isomer which predominates. The more homogeneous composition of the olefin mixture arising from the elimination of the tosylate *V* precluded the quantitative evaluation of the data on the deuterium content in the mixture. For

* The trimethylamine isolated from the reaction of the *threo*-5-D-*V* derivative was found to be practically deuterium free under all conditions listed. It follows that the "ylide" reaction mode[21,31] does not contribute to the *syn*-process investigated.

** The sole exception is methoxide–methanol combination.

conclusions regarding the steric course of formation of the olefins *cis-* and *trans-VII* as well as *cis-* and *trans-VIII* we have therefore to rely mainly on the $(k_H/k_D)_{apparent}$ data deduced from a comparison of the olefin isomer composition obtained from the unlabelled and the labelled substrates (Table V).

The pattern found for the reaction of *erythro-* and *threo*-5-D-*V* tosylates with potassium tert-butoxide in dimethylformamide and in dimethyl sulphoxide indicates quite clearly that both *trans-* as well as *cis-VII* isomer are formed by *anti*-elimination. If the *syn* → *trans* reaction takes place at all, it does so to a small degree, not detectable by the procedure used.

The values of $(k_H/k_D)_{apparent}$ obtained for *cis*-olefin (*cis-VII*) formation in the reaction of the tosylate *erythro-* and *threo*-5-D-*V* (X = OTs) with potassium tert-butoxide in tert-butanol or benzene do not differ from those obtained in the corresponding reaction in the dipolar aprotic solvents, indicating once again a pre-

TABLE III

Elimination of β-Deuterium Labelled Derivatives of 2,2-Dimethyl-4-nonyltrimethylammonium Base (*V*; X = $\overset{(+)}{N}(CH_3)_3$ and 2,2-Dimethyl-3-nonyltrimethylammonium Base (*VI*; X = $\overset{(+)}{N}(CH_3)_3$ under Different Conditions: Deuterium Content (% d_1) in the Olefin Mixture and Percentage of *syn*-Elimination in *trans*-Olefin Formation

Reactant[a]	Conditions	% d_1 in olefin mixture		*trans*-Olefin[d] % syn
		found[b]	calc.[c]	
erythro-5-D-*V*	CH_3OK/CH_3OH	100	100	100
threo-5-D-*V*		28·6	13·2	68
erythro-5-D-*V*	t-C_4H_9OK/t-C_4H_9OH	100	100	100
threo-5-D-*V*		11·8	8·7	97
erythro-5-D-*V*	t-$C_4H_9OK/(CH_3)_2SO$	100	100	100
threo-5-D-*V*		12·3	11·2	99
erythro-5-D-*V*	pyrolysis	100	100	100
threo-5-D-*V*		27·6	25·0	96
erythro-4-D-*VI*	t-C_4H_9OK/t-C_4H_9OH	~99	100	~99
erythro-4-D-*VI*	CH_3OK/CH_3OH	97	100	94

[a] The starting *erythro*-5-D-*V* alcohol contained 96% d_1 species; *threo*-5-D-*V* alcohol contained 91% d_1 species. The starting dimethylamine, *erythro*-4-D-*VI*, contained 76·8% d_1 species. [b] Corrected for incomplete deuterium labelling in the reactant. [c] Calculated for exclusive *syn* → *trans* and *anti* → *cis* path. The isomers having the label in "allylic" position are assumed to retain all the deuterium label. Further, it is assumed that all the isomers afford the molecular ion in mass spectroscopy with the same yield. [d] Calculated (under assumption of an exclusive *anti* → *cis* route) from the equation (2): (% *syn* → *trans*) = 100 (1 − Δ/% *trans*-olefin), where Δ is the difference between % d_1 found and calculated.

dominance of the *anti*-elimination path in *cis*-olefin formation. By contrast, the values of $(k_H/k_D)_{apparent}$ found for *trans-VII* formation do not accord with an exclusive *anti*-elimination pathway. This would require (k_H/k_D) *erythro* $\geqq \sim 2$ and (k_H/k_D) *threo* ~ 1. However, the apparent isotope effects for the *trans-VII* formation from both *erythro*- and *threo*-derivatives have been found to be significantly different from unity, for the latter being in fact considerably greater. This indicates a sizeable contribution of *syn*-elimination to the formation of *trans-VII*. Taking into account the operation of the isotope effect one can estimate roughly that in the formation of *trans-VII* from the unlabelled "parent" substrate about or more than 70% would be due to *syn*-elimination.

On the other hand, the values of the apparent isotope effect found for the formation of *trans-VIII* olefin from the *threo*-3-D- labelled tosylate, *threo*-3-D-*V*, are very close to unity (1·2), regardless of the solvent used (dimethylformamide and benzene). This finding supported by the data on deuterium content in the olefin mixture

TABLE IV

Contribution of *syn*- and *anti*-Elimination in the Olefin Formation from the Unlabelled '(+)Onium Compounds *V* and *VI* (X = $\overset{(+)}{N}(CH_3)_3$)

Compound	Conditions	*trans-VII* % *syn*	*trans-VIII* % *syn*	*cis-VII* % *anti*	*cis-VIII* % *anti*
V	CH_3OK/CH_3OH	89[a]	$\geqq 90$[b]	$\geqq 90$[b]	$\geqq 90$[b]
V	t-C_4H_9OK/t-C_4H_9OH	99[a]	$\geqq 90$[b]	$\geqq 90$[b]	[c]
V	t-$C_4H_9OK/(CH_3)_2SO$	99·5[a]	[c]	$\geqq 90$[b]	[c]
V	pyrolysis	98[a]	[c]	$\geqq 90$[b]	[c]
VI	CH_3OK/CH_3OH	—	83[a]	—	$\geqq 90$[b]
VI	t-C_4H_9OK/t-C_4H_9OH	—	97[a]	—	$\geqq 90$[b]

[a] Calculated from the data for the labelled derivatives *threo*-5-D-*V* and *erythro*-5-D-*V* (Table III) using the values of isotope effects given in Table II. The value of the apparent isotope effect for the *trans*- olefin formation in reaction of *threo*-5-D-*V* with methoxide in methanol had to be corrected for incomplete *syn* → *trans* process. The corrected value (3·3) has been used for calculation of the corresponding process in *V* as well as *VI*. [b] The lowest value estimated on the basis of the corresponding deuterium isotope effect. [c] Not determined.

obtained (Table VI) indicates that *syn*-elimination does not contribute* considerably to the formation of *trans-VIII* from *V* (X = OTs) under the conditions investigated.

* The value found by mass spectroscopy for the proportion of *syn*-elimination is rather uncertain in the present case in view of the homogeneous character of the olefin mixture analysed; the value given for the reaction in benzene (Table VI) should be regarded as the highest limit.

TABLE V

Elimination of 2,2-Dimethyl-4-nonyl *p*-Toluenesulphonate (*V*; X = OTs), 2,2-Dimethyl-3-nonyl *p*-Toluenesulphonate (*VI*; X = OTs) and Their β-Deuterium Labelled Derivatives with Potassium Tert-butoxide in Different Solvents: Olefin Composition and Values of k_H/k_D

Reactant	t-C_4H_9.CH_2.CH=CH.C_4H_9				t-C_4H_9.CH=CH.C_5H_{11}			
	trans-VII		*cis-VII*		*trans-VIII*		*cis-VIII*	
	%	k_H/k_D[a]	%	k_H/k_D[a]	%	k_H/k_D[a]	%	k_H/k_D[a]
Dimethylformamide								
V	13·7	—	24·0	—	60·9	—	1·4	—
erythro-5-D-*V*	7·4	2·0	26·0	1·0	65·2	—	1·4	—
threo-5-D-*V*	19·3	0·8	9·2	3·1	70·4	—	1·4	—
threo-3-D-*V*	15·2	—	27·5	—	57·0	1·2	0·3	5·4
VI	—	—	—	—	98·2	—	1·8	—
Dimethyl sulphoxide								
V	16·3	—	27·9	—	53·9	—	1·9	—
erythro-5-D-*V*	6·3	3·0	28·1	1·2	62·8	—	2·8	—
threo-5-D-*V*	18·7	1·1	11·1	3·2	68·6	—	1·6	—
Tert-butanol								
V	18·7	—	49·8	—	27·6	—	3·9	—
erythro-5-D-*V*	14·4	1·4	54·0	1·0	28·6	—	3·0	—
threo-5-D-*V*	15·8	1·9	36·0	2·2	44·2	—	4·0	—
Benzene								
V	24·8	—	52·3	—	19·7	—	3·2	—
erythro-5-D-*V*	22·6	1·2	56·3	1·0	20·2	—	2·9	—
threo-5-D-*V*	24·2	2·1	31·7	3·3	39·5	—	4·5	—
threo-3-D-*V*	20·6	—	60·2	—	18·7	1·2	0·5	7·4
VI	—	—	—	—	96·6	—	3·6	—

[a] The values of k_H/k_D were not corrected for incomplete deuterium labelling in the reactant; for deuterium content of the starting alcohols see footnotes *a* in Table III and VI.

The reaction of the isomeric tosylate *VI* (X = OTs) with potassium tert-butoxide in dimethylformamide and in benzene afforded *trans-VIII* practically as the sole product. In the reaction of the *threo*-D-labelled tosylate, *threo*-4-D-*VI*, with tert-butoxide in dimethylformamide the olefin was found (Table VI) to have retained all the deuterium label; it follows that the reaction proceeds in the *threo*-labelled isomer exclusively by *anti*-elimination. On the other hand, the olefin obtained from

TABLE VI

Elimination of β-Deuterium Labelled *p*-Toluenesulphonates, *threo*-3-D-*V* and *threo*-4-D-*VI* (X = OTs), with Potassium Tert-butoxide in Different Solvents: Deuterium Content (% d_1) in the Olefin Mixture and Percentage of *syn*-Elimination in *trans*-Olefin Formation (% *syn* → *trans*)

Reactant[a]	Solvent	% d_1 in olefin mixture		% *syn* → *trans*[c]
		found[b]	calc.[c]	
threo-4-D-*VI*	dimethylformamide	99·4	0	~0
threo-4-D-*VI*	benzene	56·8	0	41
threo-3-D-*V*	dimethylformamide	100	42·7	~0
threo-3-D-*V*	benzene	95·0	80·8	24

[a] The starting alcohol *threo*-4-D-*VI* as well as *threo*-3-D-*V* contained 93·9% d_1. [b] Corrected for incomplete deuterium labelling in the reactant. [c] For calculation see footnotes *c* and *d* in Table III.

the reaction of the *threo*-D-labelled tosylate with tert-butoxide in benzene was found to contain only about 57% of the d_1 species. It follows that about 40% of the reaction of the *threo*-D isomer has taken place by *syn*-elimination. Since the *syn* → *trans* reaction in this isomer is slowed down by an isotope effect one can estimate that in the formation of *trans-VIII* from the parent compound some 2/3 would be due to *syn*-elimination.

DISCUSSION

The present results show that the *syn*-elimination operates also in the branched open-chain systems *V* and *VI* (X = $\overset{(+)}{N}(CH_3)_3$ and OTs) now investigated, the contribution of this reaction mode being greater in the reaction of the 'onium compounds.

Actually, in the reaction of the 'onium base *V* as well as *VI* with tert-butoxide and also in pyrolysis the *syn*-path represents (Table IV) invariably an almost exclusive path (98·0 to 99·5%) in the *trans*-olefin formation (*trans-VII* and/or *trans-VIII*). In contrast, the corresponding *cis*-isomers (*cis-VII* and/or *cis-VIII*) have been found to be formed predominantly or perhaps almost exlusively by *anti*-elimination. Thus, the dichotomous pattern (*syn* → *trans* and *anti* → *cis*) of bimolecular elimination processes which we have first observed in medium ring compounds[11–15] is re-encountered almost as pronouncedly in the open-chain branched 'onium compound *V* and *VI*, under practically all conditions investigated. On the other hand, in the reaction of the tosylates *V* and *VI* (X = OTs) with potassium tert-butoxide the previously[2,13,14,21] noted dependence of the steric course on the nature of the solvent is clearly apparent: in the dipolar aprotic solvents (dimethylformamide and dimethyl sulphoxide) *syn* → *trans* elimination appears to be completely absent; in the non-

dissociating solvents – both protic (tert-butanol) and aprotic (benzene) – the *syn* → → *trans* elimination makes a very appreciable contribution. About two third of the *trans-VIII* isomer has been formed by *syn*-elimination in the reaction of tosylate *VI* with potassium tert-butoxide in benzene. Similarly, about two third or more of the *trans-VII* isomer has been formed by *syn*-elimination in the reaction of the isomeric tosylate *V* with tert-butoxide in tert-butanol or benzene. Significantly, the other *trans*-olefin, *trans-VIII*, obtained from the same reaction of the tosylate *V* has been found to be formed mainly by *anti*-elimination, the contribution of the *syn*-path being only 10% or perhaps less. Hence, the *syn*-process appears to contribute in very different proportions to the formation of the position isomeric *trans*-olefins, *trans-VII* and *trans-VIII*, respectively, from the same substrate *V* (X = OTs). From the data obtained, one is tempted to conclude that *syn*-elimination prefers strongly the *trans*-olefin formation in the direction away from the branched tert-butyl group.

In accord with previous experience[2,14], the corresponding *cis*-olefins (*cis-VII* and *cis-VIII*) from the tosylate *V* and *VI* have been formed uniformly by *anti*-elimination in all the solvents investigated.

The observed trends with respect to the nature of the leaving group, the base and solvent correspond to those already found previously[3,12,13] for other substrates. Their implications have already been discussed and they require no further comment here.

The Effect of "Alkyl Structure" on the Proportion and Selectivity of the syn- *and* anti-*Processes in Bimolecular Elimination*

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 or more particularly as a criterion of the "double bond development"[22-35]. Even more significantly, values of the ratios of the alternative position isomers formed have been generally used in discussions concerning the origin of the Hofmann or Saytzeff orientation in those reactions[36-40]. As already pointed out[2,3,13], such discussions can be meaningful only if the separation into contribution of *syn*- and *anti*-processes is effected. This has now be carried out, approximately, for the compounds *V* and *VI* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs) and the data obtained compared with those available from analogous studies on structurally related open-chain derivatives.

Table VII summarises the quantitative or semiquantitative data on the steric course of the olefin formation in reactions of 2,2-dimethyl-3-nonyl (*VI*), 2,2-dimethyl-4-nonyl (*V*), 5-decyl (*I*), 3-hexyl and 2-hexyl 'onium compound[4,5] ($X = \overset{(+)}{N}(CH_3)_3$) with potassium tert-butoxide in tert-butanol and/or with potassium methoxide in methanol. In spite of the somewhat heterogeneous nature of the available data, several significant trends are immediately apparent from the inspection of the Table.

TABLE VII

The Proportion and Stereoselectivity of the *syn*- and *anti*-Processes in the Olefin Forming Reaction of the Open Chain 'Onium Compounds ($X = \overset{(+)}{N}(CH_3)_3$) with Tert-butoxide in Tert-butanol and with Methoxide in Methanol (in Parentheses): Effect of the Alkyl Structure

$R^1.\overset{(+)}{C}H(NMe_3).CH_2.R^2$		$R^1.CH{=}CH.R^2$ [a]			
				trans/*cis*	
R^1	R^2	% *syn*^{tot}	% *syn*^{trans}	*syn*	*anti*
C_5H_{11}	t-C_4H_9	90 (90)	≧90 (≧90)	3 000 (40)	(≦0·5)[b]
t-C_4H_9	C_5H_{11}	95 (44)	≧97 (83)	260 (7)	≦0·8 (≦0·2)
t-$C_4H_9.CH_2$	C_4H_9	96 (44)	99 (89)	310 (7)	≦0·4 (≦0·1)
C_4H_9	C_4H_9	65 (10)	89 (24)	45 (1·1)	0·3 (0·2)
C_2H_5	C_2H_5	59 (≦8)	83 (17)	17[b]	0·4 (0·3)
C_3H_7	CH_3	37[b]	70 (10)	6[b]	0·3 (0·3)
CH_3	C_3H_7	11[b]	15 (0)	b[b]	0·4 (0·3)

[a] The figures summarised in the Table were taken or calculated from the data given in this paper or in ref.[3-5]. The data available for the *syn* → *cis* elimination are based in most cases on the determination of the isotope effect only, indicating a "negligible" role of the process. Taking into account that less than 10% contribution of the *syn*-process could easily escape detection by this procedure we have calculated the *syn*-stereoselectivity for 10% contribution of *syn*-elimination in the *cis*-olefin formation. The figures obtained in this way represent thus the lowest limit of stereoselectivity. [b] Not determined.

TABLE VIII

Stereoselectivity (*trans-VII*/*cis-VII*) and Regioselectivity (*trans-VII*/*trans-VIII*) of the *syn*- and *anti*-Processes in the Elimination of 2,2-Dimethyl-4-nonyl *p*-Toluenesulphonate (*V*; X = OTs) with Potassium Tert-butoxide in Different Solvents

Solvent	*trans-VII*/*cis-VII*		*trans-VII*/*trans-VIII*	
	syn[a]	*anti*[a]	*syn*[a]	*anti*[a]
C_6H_6	≧3·1	≦0·18	≧8·4	≦0·46
t-C_4H_9OH	≧2·5	≦0·14	≧4·5	≦0·25
$(CH_3)_2SO$	[b]	0·58	[b]	0·30
$HCON(CH_3)_2$	[b]	0·57	[b]	0·22

[a] Calculated from the product composition data for the unlabelled tosylate and from the estimated contribution of *syn*- and *anti*-components. It is assumed[3] that less than 10% of the *cis*-olefin (*cis-VII*) arised by *syn*-elimination. [b] *syn*-Elimination is practically absent in the dipolar aprotic solvents.

The first concerns the relative proportions of *syn*- and *anti*-elimination. In both the base-solvent combinations listed, the proportion of *syn*-elimination, which is extremely strongly pronounced in the reaction of the now investigated compounds *VI* (R^1 = t-C_4H_9, R^2 = C_5H_{11}) and *V* (R^1 = C_5H_{11}, R^2 = t-C_4H_9; R^1 = t-$C_4H_9CH_2$, R^2 = C_4H_9), is somewhat less pronounced in the straight chain 5-decyl system (R^1 = R^2 = C_4H_9) reported in previous paper[2], decreases as demonstrated by Bailey and Saunders[4,5] on going to 3-hexyl system (R^1 = R^2 = C_2H_5; R^1 = C_3H_7, R^2 = CH_3) and, further still, almost vanishes in 2-hexyl system (R^1 = CH_3, R^2 = C_3H_7). Thus, the tendency towards *syn*-elimination appears to be closely related to the structural complexity of the substrate being the greater the more complex is the nature of the alkyl groups involved.

The next significant trend concerns the stereoselectivity of the *syn*-elimination. The estimated values of the $(trans/cis)_{syn}$ ratios are uniformly greater than unity (in most cases much greater than unity) indicating the pronounced *trans*-stereoselectivity of the *syn*-elimination process. In actual fact, the *trans*-stereoselectivity is the highest in the most branched systems *V* and *VI* and decreases, stepwise, on going to less complex 5-decyl, 3-hexyl and 2-hexyl systems. Thus, the extent of the *trans*-stereoselectivity in the *syn*-process appears also to be structure-dependent,* following the same structural pattern as observed above for the proportion of *syn*-elimination.

On the other hand, the corresponding *trans*/*cis* ratios for the *anti*-elimination, $(trans/cis)_{anti}$, are uniformly less than unity indicating, contrariwise, a remarkable *cis*-stereoselectivity of the *anti*-process. Surprisingly enough, the *cis*-stereospecificity remains unaltered or is perhaps even more pronounced** in the highly branched systems *V* and *VI*, in spite of the seemingly prohibitive alkyl-alkyl interactions involved in the *cis*-olefin (*cis-VIII*) formation. Indeed, the "divergent" stereoselectivity of the concurrent *syn*- and *anti*-processes appears to be a general feature in the bimolecular elimination of the 'onium compounds.

At present, the scarcity of the relevant data does not allow to make any general conclusions about the effect of alkyl branching on the steric course in the elimination of the open chain tosylates. However, the proportion of *syn*-elimination in the formation of *trans-VII* and *trans-VIII* from the tosylate *V* and *VI*, respectively, is considerably higher than that found by us previously[2] in the formation of *trans*-5-decene*** from the less branched 5-decyl tosylate. This is in accord with the trend observed

* Significantly, both the propensity towards *syn*-elimination and the *trans*-stereoselectivity are considerably more pronounced in tert-butoxide — tert-butanol combination.

** The values given were calculated under assumption of 10% contribution of *syn*-process to *cis*-olefin formation. It is almost certain[3] that the actual contribution of *syn* → *cis* path is considerably lower, at least in the branched systems *V* and *VI*.

*** About 15 and 27% of *trans*-5-decene arised by *syn*-elimination in the reaction of 5-decyl tosylate[3] with tert-butoxide in tert-butanol and benzene, respectively.

above for the corresponding 'onium compounds and suggests that similar factors operate in the reaction of the 'onium compounds as well as tosylates *V* and *VI*.

This view is further supported by the roughly estimated values of the stereoselectivity for the *syn*- and *anti*-process in the reaction of the tosylate *V* (Table VIII). Thus, the $(trans/cis)_{syn}$ ratios found for the formation of *VII* from the tosylate *V* are uniformly higher than unity, whereas the corresponding values for *anti*-elimination, $(trans/cis)_{anti}$ are invariantly lower than unity.*

Consider first the nature of the factors controlling the *syn*-elimination. As suggested by us previously[2], the preferential formation of *trans*-olefin (*trans*-stereoselectivity) in the *syn*-process may be explained reasonably in terms of the greater repulsive alkyl–alkyl interactions involved in the transition state (*syn* → *cis*) leading to *cis*-olefin. The unusually high *trans*-stereospecifity observed in the branched 'onium compound *V* and *VI* ($X = \overset{(+)}{N}(CH_3)_3$) now investigated lends further support to this view.

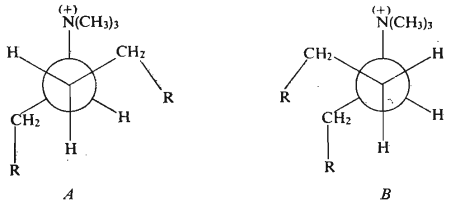
A less unambiguous explanation can be given for the observed regioselectivity[38] (Hofmann orientation) of the *syn*-process in the reaction of the system *V* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs). Both steric[38–40] and polar[30,36] explanation may be considered, however, some arguments are available to distinguish between the two. As follows from the papers[42,43] the amine oxide elimination (*syn*-elimination) is almost insensitive towards polar effects: the outcome of this reaction might hence afford information on the operation of steric factors. In the system *V* ($X = N(CH_3)_2O$), it is in fact the Saytzeff olefin (*trans-VIII*) which is formed in predominant amount[43]. It follows that the principal feature responsible for the Hofmann orientation in the *syn*-component of the bimolecular elimination of the derivatives *V* ($X = \overset{(+)}{N}(CH_3)_3$ and OTs) is not of steric origin. Consequently, a polar factor appears responsible, taking an advantage of the higher acidity of the hydrogen on the carbon located away from the tert-butyl group[30].

Consider next the nature of the factors controlling the *anti*-process,** namely the pronounced *cis*-stereoselectivity and the dependence of the *anti*-contribution on the

* In contrast, the corresponding ratio for the formation of the position isomer *VIII*, $(trans\text{-}VIII/cis\text{-}VIII)_{anti}$ is much greater than unity in the reaction of the tosylate *V* as well as tosylate *VI*. In this respect, the different behaviour of the 'onium compounds *V* and *VI* ($X = \overset{(+)}{N}(CH_3)_3$) might be a consequence of a more reactant-like[30,32,36] transition state in the reaction of the 'onium compounds.

** In the reaction of the corresponding 'onium compound *V* ($X = \overset{(+)}{N}(CH_3)_3$) *anti*-process appears to prefer the Hofmann olefin (*VIII*) formation. No satisfactory explanation can be given at present for the pronounced "Saytzeff" orientation in the *anti*-component of the reaction of the tosylate *V*. Any simple consideration taking into an account the polar[36] (inductive or hyperconjugative) or steric factors[39–41] would predict, contrariwise, the "Hofmann" orientation of the reaction.

substrate structure. For the reaction of the 'onium compounds and, less specifically, the tosylates as well, Saunders and his coworkers[4,5] proposed a scheme which is capable of accounting the features just mentioned (Scheme 1). In this arrangement the alkyl chain is oriented so as to be as far as possible from the bulky leaving group. Under these circumstances, it is assumed that the alkyl groups R could hinder the approach of the base to the hydrogen on C_β involved in *anti*-elimination, the hindrance being greater in the transition state leading to *trans*-olefin (*A*). Thus, the interpretation implies that the *cis*-stereoselectivity of the *anti*-process results from



A *B*

SCHEME 1

a slowing down of the *anti* → *trans* process by the more effective steric hindrance. At the same time, it implies that an overall decrease in the proportion of *anti*-elimination with the increasing "bulk" of R results from the gradual decrease in the rate of the *anti*-elimination.

In other words, this explanation implies that *syn*-elimination enters the picture only as a result of a slowing down of *anti*-elimination. An effect of the structural changes involved on the rate of *syn*-elimination is not taken into account in this scheme. We know, however, from elimination rate measurements in the cycloalkyl series[11–13] that very high *syn*/*anti* ratios (found *e.g.* in medium ring compounds) result both from a very low rate of *anti*-elimination as well as from greatly accelerated rates of *syn*-elimination. We therefore hesitate to accept the view that the high *syn*/*anti* ratios results from steric hindrance to *anti*-elimination alone. Rate data for open-chain systems are clearly required; such studies are at present under way.

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