Mechanisms of Elimination Reactions. XIV. Stereochemistry and Isotope Effects in Eliminations from Cyclopentyl- and 3,3-Dimethylcyclopentyltrimethylammonium Salts[1]

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Abstract: *cis*-Cyclopentyl-2-*d*-trimethylammonium (I) and *cis*-3,3-dimethylcyclopentyl-5-*d*-trimethylammonium (II) ions were subjected to elimination reactions with various base–solvent combinations. The extent of deuterium loss in the product olefins from I and II, and the proportions of 3,3- and 4,4-dimethylcyclopentene from II were determined. With these data percentages of *syn* elimination and deuterium isotope effects for *syn* elimination were calculated. *syn* elimination was unimportant with hydroxide ion in dilute aqueous solution, but extensive under Hofmann conditions and with potassium *t*-butoxide in 50 mol % *t*-butyl alcohol–dimethyl sulfoxide. Isotope effects for *syn* elimination are all small ($k_H/k_D < 2$), and do not appear to vary significantly from one set of conditions to another. These results are consistent with ideas we have previously advanced on the stereochemistry of elimination reactions.

Until recently, elimination reactions of quaternary ammonium salts were believed to occur with *trans–anti* stereochemistry unless the reactant possessed special features such as activation of the β-carbon[2-4] or a carbon skeleton of sufficient rigidity to hinder *anti* orientation of the leaving group and β-hydrogen.[5] Recent work has shown that *syn* eliminations can occur under a variety of circumstances with unactivated cyclic[6-9] and acyclic[10-12] systems. The immediate aim of the present work was to clarify the meaning of studies in which we had determined deuterium isotope effects by intramolecular competition with cyclohexyl-, cyclopentyl- and 3-pentyltrimethylammonium salts.[13] To the extent that *syn* elimination occurred, the apparent isotope effects by our method were not true isotope effects for *anti* elimination. Preliminary results on stereochemistry[13] indicated that no major conclusions were vitiated, but we still wished to examine closely the effect of structure and reaction conditions on stereochemistry of elimination in a typical cyclic system which undergoes both *syn* and *anti* elimination. The study also afforded the opportunity of determining deuterium isotope effects for both *syn* and *anti* elimination in the same ring system, thereby giving information about differences in transition-state structures for the two modes of elimination.

The *cis*-cyclopentyl-2-*d*-trimethylammonium (I) and *cis*-3,3-dimethylcyclopentyl-5-*d*-trimethylammonium (II) ions were prepared in essentially the same manner as previously described.[9] Each was subjected to elimination reactions with various base/solvent combinations for comparison with the results obtained under the conditions of the Hofmann elimination[9] (pyrolysis of the quaternary hydroxide). The deuterium contents of the olefinic products from I and II, and the proportions of 3,3- and 4,4-dimethylcyclopentene from II were determined. Combination of the product proportions and deuterium contents from II yields isotope effects for *syn* elimination. These isotope effects permit the calculation of per cent *syn* elimination from undeuterated II, and also from undeuterated I, if the same isotope effects are assumed to apply to both I and II under the same conditions.[9] The percentages of *syn* elimination calculated in this manner are given in Table I, and the *syn* isotope effects in Table II. Tables II–IV give the product proportions and deuterium analyses upon which the calculations are based.

Table I. *syn* Elimination from Cyclopentyl- and 3,3-Dimethylcyclopentyltrimethylammonium Salts

Base/solvent, °C	Cyclopentyl, % *syn*[a]	Dimethylcyclopentyl, % *syn*[a]
NaOH/H_2O, 190	4 ± 3	10.0 ± 1.3
NaOH/H_2O–DMSO,[b] 130	1 ± 3	52.2 ± 2.5
t-BuOK/*t*-BuOH, 70	17 ± 2	63.4 ± 5.0
t-BuOK/*t*-BuOH–DMSO,[c] 70	45 ± 1	71.5 ± 4.0
Hofmann[d]	46[d]	76[d]

[a] Average and standard deviation. [b] Water containing 60 mol % dimethyl sulfoxide. [c] *t*-Butyl alcohol containing 50 mol % dimethyl sulfoxide. [d] Pyrolysis of quaternary ammonium salt. Values from ref 9.

In order to test the rather remote possibility that apparent *syn* elimination resulted from epimerization at the α-carbon prior to reaction, cyclopentyl-1-*d*-trimethylammonium hydroxide was prepared and subjected to elimination under Hofmann conditions. The deuterium content of the cyclopentene was the same as that of the reactant, demonstrating the absence of exchange at the α position.

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Table II. Product Ratios, Deuterium Contents, and Isotope Effects in Eliminations from Dimethylcyclopentyltrimethylammonium Salts

Solvent[a]	4,4-Ene/3,3-ene from H compd	4,4-Ene/3,3-ene from D compd[b]	4,4-Ene d_1/d_0[b]	k_H/k_D syn[b]
H_2O	2.65 ± 0.11	2.61 ± 0.15	10.5 ± 0.7	c
	2.65 ± 0.04			
H_2O–DMSO	1.66 ± 0.02	1.33 ± 0.01	1.49 ± 0.02	1.62 ± 0.08
t-BuOH	7.43 ± 0.09	5.26 ± 0.20	1.07 ± 0.02	1.85 ± 0.17
	7.38 ± 0.17	5.23 ± 0.16		
t-BuOH–DMSO	6.42 ± 0.07	4.22 ± 0.08	0.77 ± 0.02	1.92 ± 0.10
Hofmann	1.04 ± 0.03			
	1.07[d]	0.73[d]	0.55[d]	1.71[d]

[a] See Table I for details of conditions. [b] Average and standard deviation, minimum of six determinations on each sample. [c] A figure of 1.17 can be calculated, but the error is so large (because of the small amount of *syn* elimination) that it is undoubtedly meaningless. [d] Data from ref 9.

Table III. Deuterium Analyses of Cyclopentenes from *cis*-Cyclopentyl-2-*d*-trimethylammonium Salts

Solvent[a]	Salt[b]	Cyclopentene-d_1, %[c]
H_2O	Tosylate	97.2 ± 1.3[d,e]
	Tosylate	99.3 ± 1.0
	Av	98.2 ± 1.5
H_2O–DMSO	Tosylate	100.5 ± 2.0
	Iodide	99.3 ± 0.9
	Iodide	99.3 ± 0.9
	Av	99.7 ± 0.7
t-BuOH	Tosylate	95.0 ± 2.0
t-BuOH–DMSO	Tosylate	86.7 ± 3.0
	Tosylate	88.5 ± 5.0
	Tosylate	86.3 ± 1.4
	Iodide	87.3 ± 2.0
	Iodide	85.8 ± 1.4
	Iodide	86.9 ± 0.9
	Av	86.9 ± 0.9
Hofmann		86.0[f]

[a] See Table I for details of conditions. [b] See Experimental Section for differing syntheses of the two salts. [c] Each number is the average of at least six determinations at each of three ionizing voltages on a given sample. Different values represent samples from different reactions. Deviations are standard deviations. Deuterium content is corrected to per cent retention of deuterium content of reactant. [d] Average of determinations at ionizing voltages from 13 to 70 eV. [e] The tosylate sample here was not the same as that used in other runs. [f] Value from ref 9.

Table IV. Deuterium Analyses of Dimethylcyclopentenes from *cis*-3,3-Dimethylcyclopentyl-5-*d*-trimethylammonium Iodide

Solvent[a]	3,3-Olefin, % d_1[b]	4,4-Olefin, % d_1[b]	4,4-Olefin, % d_1, cor[c]
H_2O	94.4 ± 0.3	86.2 ± 0.3	91.3 ± 0.6
t-BuOH	*d*	45.8 ± 0.2	51.6 ± 0.8
H_2O–DMSO	92.4 ± 0.3	55.3 ± 0.2	59.8 ± 0.4
t-BuOH–DMSO	88.8 ± 0.6	38.7 ± 0.3	43.6 ± 0.9

[a] See Table I for details of conditions. [b] Each number is the average of at least four determinations each at 13 and 70 eV. Deviations are standard deviations. [c] Corrected to per cent retention of deuterium content of reactant, which was deduced from deuterium content of the 3,3-dimethylcyclopentene. [d] Could not collect because of low yield and an overlapping impurity peak. Used value obtained in *t*-BuOH–DMSO.

The major conclusions to be drawn from Table I are that the percentages of *syn* elimination vary over a wide range as the solvent–base system changes, and that *syn* elimination is consistently more important with II than with I. The latter effect has been observed in the Hofmann eliminations of I and II, and plausibly explained as a steric effect.[9] Attempts to force the trimethylammonio group and the β-*trans*-hydrogen into an *anti*-coplanar arrangement distort the cyclopentane ring in such a fashion as to increase steric interactions between the trimethylammonio group and the 3-methyl group *cis* to it.

The effect on stereochemistry of changing the base–solvent system is very similar to that noted with acyclic quaternary ammonium salts.[11,12] *t*-Butoxide in *t*-butyl alcohol gives a relatively high proportion of *syn* elimination, and addition of dimethyl sulfoxide to the solvent increases the importance of *syn* elimination (the failure of dimethyl sulfoxide to do so with I in aqueous solution probably reflects a proportion of *syn* elimination below detection by the experimental methods). Hofmann elimination conditions seem especially conducive to *syn* elimination. Qualitatively, there is an excellent correlation between the importance of *syn* elimination and the basicity of the medium.[14,15] While there are not quantitative data on the very concentrated syrups of quaternary hydroxides which constitute the reaction medium in Hofmann eliminations, they would be expected to be extremely basic by virtue of an insufficiency of water molecules for solvation of the hydroxide ion.

We have demonstrated that increasing basicity leads to a more reactantlike transition state in eliminations from ammonium[16] and sulfonium[17] salts. A more reactantlike transition state should show less stereoelectronic preference for *anti* elimination.[12] In the cyclopentyl system, the preference for *anti* elimination is further weakened by the distortion of the ring necessary for a completely *anti*-coplanar transition state. The result is a balance in which changes in the medium can affect dramatically the stereochemistry of the reaction.

Steric hindrance to abstraction of the *anti*-β-proton, which we postulated as a factor promoting *syn* eliminations in acyclic systems,[12] is probably not important here because the alkyl groups are tied back by the ring structure. The present system, in addition, is analogous to the formation of a *cis* olefin in the acyclic series, which is formed by very predominantly *anti* elimination under all conditions.[11,12] Thus, there is no single set of structural and environmental circumstances which can be said to be responsible for all cases of *syn* elimination.

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A final factor which may contribute in this and other cases of *syn* elimination from "onium" salts is attraction between the positive trimethylammonio group and the negative alkoxide ion.[18] The solvents which increase the basicity of the alkoxide also promote ion pairing, and an alkoxide ion associated with the trimethylammonio group would obviously attack more easily the *syn*-β proton. A possible objection to this argument is that association of the alkoxide with any metal ion present would be expected to be even stronger and strengthened more by the addition of dipolar aprotic solvents, making a geometrically specific association of the alkoxide with the quaternary ammonium ion less likely. A definitive answer on the role of coulombic attraction in determining stereochemistry must await further work.

The present data, along with the studies of Ashe[13] on isotope effects in eliminations from alicyclic quaternary ammonium salts, permit us to determine the true isotope effect for *anti* elimination from cyclopentyltrimethylammonium ion with *t*-butoxide in *t*-butyl alcohol. The isotope effect determined by the method of Ashe was, as we pointed out, not a true isotope effect for *anti* elimination if appreciable *syn* elimination was occurring. The apparent isotope effect under these conditions is given by [13]

$$\left(\frac{k_H}{k_D}\right)_{app} = \frac{(k_H)_{trans} + 2(k_H)_{cis}}{(k_D)_{trans}}$$

From Table I, $(k_H)_{cis}/(k_H)_{trans} = 17/83$. Substituting this figure and the $(k_H/k_D)_{app}$ of 6.71[13] into the equation, we find that $(k_H)_{trans}/(k_D)_{trans} = 4.75$. This isotope effect for *anti* elimination is to be compared with an isotope effect for *syn* elimination from the 3,3-dimethylcyclopentyltrimethylammonium ion of 1.85. The presence of the *gem*-dimethyl group probably does not have an appreciable influence on the *syn* isotope effect, which was found by Coke to be insensitive to wider variations in substrate structure than here.

The considerable difference in *syn* and *anti* isotope effects clearly points to a corresponding difference in extent of proton transfer in the two transition states. Since k_H/k_D is predicted to be at a maximum when the proton is half transferred to base,[19] the small value for the *syn* elimination shows that the proton is far from symmetrically located between the β-carbon and the base but does not tell whether it is more or less than half transferred. We have previously demonstrated[16,17] that increasing base strength of the attacking base leads to less complete proton transfer in eliminations (which are probably *anti*[20]) in the 2-arylethyl series. In the *syn* eliminations reported in Table II, however, the isotope effects do not change enough for one to decide whether they increase or decrease with changes in base strength. Consequently, the position of the proton cannot be fixed unambiguously by reference to the situation in *anti* elimination from 2-phenylethyltrimethylammonium ion,[16] where the proton is more than half-transferred and increasing the strength of the attacking base increase the isotope effect.

Nonetheless, we believe that by far the more likely interpretation is that the proton is more than half-transferred in both the *syn* and *anti* transition states and more so in the former than the latter. *syn* elimination appears to be favored when there is little or no double-bond character in the transition state,[12] suggesting that it gains less energetic advantage from concomitant double-bond formation than does *anti* elimination. Consequently, the β-carbon would be expected to have a higher electron density in a *syn* elimination transition state than in an otherwise identical (same base, substrate and conditions) *anti* elimination transition state. This greater "basicity" of the β-carbon in the *syn* elimination transition state should lead to more complete proton transfer to base.[16,21] A simpler way of stating the same argument is that the proton must be farther removed from the β-carbon at the energy maximum if there is no delocalization of the carbon–hydrogen bonding electrons (into a developing π bond) to promote its departure.

Superficially, this reasoning might seem to stand in contradiction to our argument that a reactantlike transition state favors *syn* elimination.[12] The contradiction is only apparent, however, for what is important is that the energetic advantage of *anti* elimination be reduced by lowering double-bond character in the transition state. One way of doing this is to increase the strength of the attacking base, thereby decreasing concomitantly the extent of proton transfer and the extent of carbon–nitrogen bond cleavage.[21] There is nothing in this process which requires that proton transfer be still less complete in the transition state of the *syn* elimination which begins to complete effectively with the *anti*. A number of energetic factors will differ between the *syn* and *anti* transition states, including nonbonded interactions, eclipsing effects, coulombic interactions, and electron delocalization. Thus, it is not unreasonable to conclude that proton transfer can be markedly greater but the degree of double-bond character less in the *syn* than in the *anti* transition state.

Experimental Section

Cyclopentyl-1-*d*-trimethylammonium Tosylate. Cyclopentanone was reduced with lithium aluminum deuteride and the resulting cyclopentanol-1-*d* converted to cyclopentanol-1-*d* tosylate.[22] The tosylate was treated with trimethylamine in nitromethane to give cyclopentyl-1-*d*-trimethylammonium tosylate.[13]

***cis*-Cyclopentyl-2-*d*-trimethylammonium Iodide.** Cyclopentene was deuterioborated and the reaction mixture treated with hydroxylamine-O-sulfonic acid by the general procedure of Brown.[23] The product was converted to *cis*-cyclopentyl-2-d_1-dimethylamine by treatment with formic acid and formaldehyde.[24] Mass spectrometric analysis showed the tertiary amine to be 95.6 ± 0.4% d_1. It was converted to *cis*-cyclopentyl-2-*d*-trimethylammonium iodide[9] by treatment with methyl iodide.

***cis*-Cyclopentyl-2-*d*-trimethylammonium Tosylate.** Treatment of cyclopentene oxide with lithium aluminum deuteride gave *trans*-cyclopentanol-2-*d*[22] containing 94.5 ± 1.3% d_1 by mass spectrometry. The alcohol was converted to the tosylate which was in turn treated with trimethylamine in nitromethane[13] to give *cis*-cyclopentyl-2-*d*-trimethylammonium tosylate.

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cis-3,3-Dimethylcyclopentyl-5-*d*-trimethylammonium Iodide. This compound and the corresponding undeuterated material were prepared by the method of Cooke and Coke.[9] The amine contained 89 ± 1% d_1 by mass spectrometry.

Elimination Reactions in Solution. Reactions were carried out in stainless steel ampoules[18] for at least ten half-lives. Rate constants were not known for the dimethylcyclopentyl salts, so reactions were run for twice to three times the period used for the cyclopentyl salts. An amount of the salt sufficient to give an approximately 0.1 *M* solution was weighed into the ampoule and 10 ml of 0.2 *M* base solution (at least a 100% excess) was added. The ampoule was heated in a thermostat for the specified time, cooled, and the contents were added to 10 ml of 2 *N* hydrochloric acid and 1 ml of *n*-pentane. In a few cases the reaction mixture was neutralized and analyzed directly by glpc.

Hofmann Elimination of Cyclopentyl-1-*d*-trimethylammonium Hydroxide. The aqueous solution of the hydroxide was evaporated *in vacuo* and the resulting syrup pyrolyzed at 120–130° in a stream of nitrogen. The products were collected in a Dry Ice trap. The cyclopentene was isolated and analyzed for deuterium at an ionizing voltage of 11 eV in the manner described below. It contained at least 0.99 atom of deuterium per molecule, thus demonstrating the absence of exchange at the α position prior to reaction.

Isolation and Analysis of Products. Cyclopentene from the Hofmann eliminations was purified by glpc on a 12 ft × 0.25 in. column of 20% tri-*o*-cresyl phosphate on Chromosorb P, using the gas inlet system. The olefin was collected in a liquid nitrogen trap. Cyclopentene from the reaction in dilute aqueous solution was distilled from the neutralized reaction mixture at −25° (carbon tetrachloride slush) to a liquid nitrogen trap on a high vacuum line. Cyclopentene was isolated from the reaction in *t*-butyl alcohol by neutralizing the reaction mixture, distilling 0.5–1.0 ml, and injecting the distillate on the glpc column described above. All other samples of cyclopentene were extracted into *n*-pentene (see above) and the extract injected on a 15 ft × 0.25 in. column of 20% adiponitrile on Chromosorb P. Under the conditions used (35°, 30 psi of helium), retention times were 3 min for *n*-pentane and 8 min for cyclopentene.

The dimethylcyclopentenes were in all cases extracted into *n*-pentane. Both collections and analyses (for the proportions of 3,3- and 4,4-dimethylcyclopentene) were performed on a 10-ft column of 40% silver nitrate–ethylene glycol on Chromosorb W. A 0.25-in. column at room temperature was used for collections, and a $^1/_8$-in. column at 50° for analyses. For analyses of products from reactions in *t*-butyl alcohol, a 10 ft × $^1/_8$ in. column of 20% Carbowax 20M on Chromosorb P was used in series with the silver nitrate column to hold back traces of *t*-butyl alcohol. All analyses were performed on a F & M Model 700 glpc equipped with a flame ionization detector and a Disc integrator. Measurement of relative peak areas with the integrator and with a planimeter gave the same results within experimental error.

Determination of Mass Spectra. The procedure was essentially the same as that previously described.[13] At least two ionizing voltages over the range of 70–13 eV (where no P − 1 peak is observed) were used and the spectra analyzed, according to standard methods.[25] Results at different ionizing voltages were indistinguishable. Appropriate corrections were made for the isotopic contents of the starting materials. In the case of the dimethylcyclopentenes, the deuterium content of the 3,3-dimethylcyclopentene (which cannot have lost deuterium during reaction) was used to correct the deuterium content of the 4,4-dimethylcyclopentene. The deuterium contents of the cyclopentenes and the dimethylcyclopentenes are given in Tables III and IV, respectively.

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Stereochemical Aspects of R_2O-3 Participation. Solvolytic Studies of the Epimeric 9-Oxabicyclo[4.2.1]nonan-2-yl Brosylates

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Abstract: Acetolysis of *endo*-9-oxabicyclo[4.2.1]nonan-2-yl *p*-bromobenzenesulfonate (**15**) is accompanied by direct interaction between the developing p orbital at C_2 and the lone pair orbital on oxygen. The oxonium ion so produced (**21a**) suffers ion-pair return to **15** and *endo*-9-oxabicyclo[3.3.1]nonan-2-yl brosylate (**17**) and concomitant passage to *endo* acetates **18** ad **19a**. The results are consistent with the observation that the first-order rate of solvolysis of **15** exhibits significant curvature through approximately one half-life whereupon the rate becomes steady. In the case of *exo*-9-oxabicyclo[4.2.1]nonan-2-yl brosylate (**16**), participation of the oxygen bridge by backside displacement is geometrically prohibited. Although its rate of solvolysis is steady, product analysis indicates that migration of the C_1–C_8 (which would provide the stereoelectronic backside shielding at C_2 in the manner truly characteristic of carbocyclic systems) does not occur because of the adverse inductive effect of the oxygen bridge. Rather, oxonium ion formation follows upon the rate-determining ionization. A number of other factors are organized and interpreted in terms of the high level of control exerted in unprecedented fashion by the oxygen atom in the solvolysis of **15** and **16**.

Because of the unique structural features associated with bridged bicyclic hydrocarbons, much attention has been given to solvolytic reactions of derivatives of such systems. The variety of available structural types has provided opportunity for assessment of the relative importance of participation by carbon–carbon σ electrons,[1] carbon–hydrogen σ electrons,[1] homoallylic π electrons,[1] remote π electrons,[2] and cyclopropane carbon–carbon σ electrons.[3] More recent develop-

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