Although the overall yield of **19** is rather low from this multistep procedure, other approaches failed to give any of the desired product (or intermediates).[86]

Spiro[4.5]decan-8-one (20). The procedure of Baird and Winstein[87] was modified slightly to accommodate a preparative scale reaction. In several experiments, attempted distillation of the spiro[4.5]deca-6,9-dien-8-one lead to the dienone–phenol rearrangement product. Consequently, it proved simpler to reduce the dienone directly without purification. The isolated product, **20**, had bp 90° (4 mm),[87] and showed no impurities by vpc.

Spiro[5.5]undecan-3-one (21). The procedure of Burnell and Taylor[88] was used to form cyclohexane-1,1-di-2-propionic acid, which was cyclized to **21** using the KF method described by Helmkamp and Johnson.[89] The product had bp 128° (11 mm), and was 98.3% pure by vpc; 2,4-dinitrophenylhydrazone, mp 127–128° (lit.[88] mp 121°).

4-Methylenecyclohexanone (22). The monobenzoate of 1,4-cyclohexanediol was prepared as described earlier.[90] Oxidation gave 4-benzoyloxycyclohexanone,[90] mp 62–63°. Hydrolysis gave 4-hydroxycyclohexanone,[90] bp 90–92° (0.8 mm).

Triphenylmethylenephosphorane was generated from 170 g (0.42 mol) of phosphonium iodide in *tert*-butyl alcohol with potassium *tert*-butoxide, following the procedure of Schlosser and Christmann.[91] The 4-hydroxycyclohexanone, 47.9 g (0.42 mol), was added to the refluxing ylide solution, and the resulting mixture stirred overnight at *ca.* 45°. The pale orange solution was taken up in 3 l. of ice–water and extracted five times with ether. The combined organic solution was then washed with water, saturated salt solution, and dried with sodium sulfate. The ether was evaporated, and about 300 ml of *tert*-butyl alcohol then removed by distillation at 150 mm. At this point 200 ml of triethyleneglycol was added to maintain the triphenylphosphine oxide in solution, and the residue distilled giving 40.1 g (0.36 mol, 85%) of 4-methylenecyclohexanol as a colorless oil, bp 58.5° (1.8 mm).

Jones oxidation of 38.1 g (0.34 mol) of this material gave 33.5 g of a pale yellow oil, which on spinning band distillation gave 27.2 g (0.25 mol, 73%) of very pure **22**: bp 70° (21 mm); ir 900 (s), 1140, 1230, 1305, 1325 (w), 1350 (w), 1430 (w), 1445, 1655, 1730 (vs), C–H str. 3070 cm^{-1}; nmr 2.44 (m, 8 H), 4.92 (s, 2 H).

Anal. Calcd for $C_7H_{10}O$: C, 76.3; H, 9.2. Found: C, 76.0; H, 9.2.

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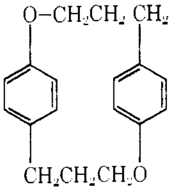
(86) For example, treatment of 1,1-di(mesyloxymethyl)cyclobutane with diethyl sodiomalonate gave as the only isolable product 53% diethyl spiro[3.3]heptane-2,2-dicarboxylate. Attempted intramolecular cyclization of the tosylate of 4-(3-hydroxypropyl)-3-cyclohexenone (as in the preparation of 20) gave no detectable spiro[3.5]non-5-en-7-one, but instead the major product appeared to be the dioxa[4.4]paracyclophane,



Attempted condensation of cyclobutanecarboxaldehyde with methyl vinyl ketone, following the procedure in the preparation of 17 gave very low yields, if any, of the spiro enone. If view of the difficulty experienced in preparing and handling this aldehyde, this line was abandoned.

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Mechanisms of Elimination Reactions. XVI. Stereochemistry of Elimination from 2- and 3-Hexyltrimethylammonium Ions. An Explanation of the Syn–Anti Dichotomy[1]

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Abstract: Stereospecifically deuterated 3-hexyl-*4-d*-, 3-hexyl-*2-d*-, and 2-hexyl-*3-d*-trimethylammonium iodides were prepared and subjected to elimination reactions under a variety of conditions. The product proportions, deuterium contents of products, and assumed isotope effects were combined to calculate the amount of syn elimination expected in the absence of the deuterium label. Syn elimination is important only in the production of *trans*-olefin, and increases with increasing strength of the attacking base. Under any given set of conditions, the importance of the syn → trans route increases in the order 2-hexyl → 2-ene < 3-hexyl → 2-ene < 3-hexyl → 3-ene. These results are shown to be consistent with a steric theory of syn elimination in which the key assumption is that the bulky trimethylammonio group forces the γ and β' groups on the alkyl chain into conformations where they hinder approach of base to the anti β-hydrogen, thereby raising the energy of the anti → trans above that of the syn → trans route. The range of applicability of the theory is discussed.

Until a few years ago, it was generally believed that bimolecular elimination reactions showed a strong preference for trans–anti departure of the leaving group and the β-hydrogen.[3-6] Exceptions to this rule were attributed to special circumstances such as strong activation at the β-carbon[7-12] or a rigid ring

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(1) This work was supported by the National Science Foundation.

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system which hindered attainment of the trans–anti conformation.[13–16] The presumption in favor of anti elimination was sufficiently strong that an apparent syn elimination (in a group of results that were otherwise exclusively anti) was assumed without an experimental test to result from epimerization prior to or during reaction.[17]

In recent years, the elegant studies of Sicher and his coworkers on medium-ring compounds have provided a strong impetus for reevaluation of accepted theories and generalizations concerning stereochemistry of elimination. They reported an intriguing pattern of results in which *cis*-olefin was formed by anti elimination, but *trans*-olefin by syn elimination, which they called the "syn–anti dichotomy." The propensity toward the syn–anti dichotomy was strongest with onium salts,[18–21] but was also observed with bromides[22] and tosylates.[23] While special conformational features of the medium rings can be invoked[21] to explain these results, the discovery by Coke of substantial syn elimination with cyclobutyl-, cyclopentyl-, and cycloheptyl- (but not cyclohexyl-) trimethylammonium ions[24] made it evident that syn elimination was by no means a rare or unusual occurrence.

It had been suggested some time ago that anomalously high cis:trans ratios in the olefinic products from quaternary ammonium salt eliminations might be the result of syn elimination,[25] but this suggestion received little general credence until positive evidence with stereospecifically deuterium-labeled reactants was adduced.[26,27] Surprisingly, the same syn–anti dichotomy was observed as with the medium-ring compounds, though in some cases not all of the *trans*-olefin resulted from syn elimination. Some speculation about the nature of the problem was presented,[28] but no satisfactory general theory of syn elimination could be said to exist. About the same time, we proposed a steric theory[29] to explain the syn–anti dichotomy in open-chain compounds. We wish now to develop further the evidence for and the consequences of our theory.

Results

Our approach was designed to determine the effect of reaction conditions and reactant structure on stereochemistry of elimination for simple quaternary ammonium salts. To this end, we prepared three stereospecifically β-deuterated hexyltrimethylammonium ions: the 3-hexyl-*4-d*, 3-hexyl-*2-d*, and 2-hexyl-*3-d*. The erythro and threo isomers of the former were prepared by deuteroboration of *cis*- and *trans*-3-hexene followed by treatment with hydroxylamine-*O*-sulfonic acid,[30] and then by conversion of the resulting amines to the 3-hexyl-*4-d*-trimethylammonium salts by standard procedures.[31,32] The same procedure was applied to

Table I. Product Proportions from Elimination Reactions of the Hexyltrimethylammonium Iodides

Reaction condn[c]	Reactant[d]	Hexenes, %[a,b] *trans*-3-	*cis*-3-	*trans*-2-	*cis*-2-
	A. From 3-Hexyltrimethylammonium Iodide				
NaOH, 190°	H	10.9	20.5	22.5	46.1
	er-4-d	4.9	20.6	24.6	50.2
	th-4-d	11.0	8.6	26.7	53.8
MeOK, 135°	H	6.4	19.1	19.3	55.3
	er-4-d	3.4	18.3	22.3	56.1
	th-4-d	6.0	6.0	22.7	65.3
n-BuOK, 85°	H	6.1	17.1	19.0	57.8
	er-4-d	2.1	16.0	19.6	62.3
	th-4-d	5.5	4.6	20.4	69.5
sec-BuOK, 85°	H	12.6	11.7	25.5	50.1
	er-4-d	9.5	11.1	27.7	51.8
	th-4-d	8.7	2.9	32.0	56.4
tert-BuOK, 70°	H	17.4	8.7	33.5	40.8
	er-4-d	14.4	8.4	36.0	41.2
	th-4-d	11.4	3.6	39.9	45.2
tert-PeOK, 85°	H	18.7	6.9	36.4	38.0
	er-4-d	15.6	7.8	35.5	41.1
	th-4-d	9.8	2.0	42.7	45.5
Pyrol[e]	H	19.5	16.4	28.3	35.8
	er-4-d	14.4	15.5	30.6	39.5
	th-4-d	16.4	6.7	34.0	42.9
NaOH, 130°[f]	H	14.6	19.2	25.9	40.3
	er-4-d	9.9	17.1	28.2	44.9
	th-4-d	12.7	6.5	31.5	49.4
NaOH, 190°	H	10.9	20.5	22.5	46.1
	er-2-d	13.4	24.6	10.3	51.8
	th-2-d	16.0	29.7	30.3	24.0
n-BuOK, 85°	H	6.1	17.1	19.0	57.8
	er-2-d	7.5	18.9	8.5	65.1
	th-2-d	11.9	30.1	28.6	29.5
tert-PeOK, 85°	H	18.7	6.9	36.4	38.0
	er-2-d	22.2	8.8	27.7	41.3
	th-2-d	32.2	13.7	37.6	16.5
Pyrol[e]	H	19.5	16.4	28.3	35.8
	er-2-d	23.3	19.8	19.0	37.9
	th-2-d	28.7	24.3	29.2	17.8
	B. From 2-Hexyltrimethylammonium Iodide				
n-BuOK, 85°	H			0.84	2.95
	er-3-d			0.25	2.94
	th-3-d			0.89	0.91
tert-BuOK, 85°	H			0.60	1.40
	er-3-d			0.29	1.41
	th-3-d			0.52	0.38

[a] Corrected for 5% of undeuterated material in deuterated reactants. [b] Determined by glpc on a column of 20 ft of 20% adiponitrile on Chromosorb P plus 1.5 ft of silver nitrate–ethylene glycol on Chromosorb P (for products from the 3-hexyl system), or on a column of 50 ft of 5% Ucon 50 HB 100 on Chromosorb P (for products from the 2-hexyl system). [c] Except as otherwise noted, the solvent is the conjugate acid of the base; *e.g.*, NaOH in H_2O, *n*-BuOK in *n*-BuOH, etc. [d] H refers to undeuterated reactant, *er-4-d* to *erythro-4-d*, *th-4-d* to *threo-4-d*, etc. [e] Aqueous solution of the quaternary hydroxide concentrated by distillation until olefin distilled (usual Hoffmann conditions). [f] Solvent was 62 mol % dimethyl sulfoxide in water.

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Table II. Deuterium Analyses of Hexenes and Per Cent Syn–Anti Dichotomy in Elimination Reactions of the 3-Hexyltrimethylammonium Iodides

Reaction cond[a]	Reactant[b]	Olefin frac[c]	d_0, % obsd	d_0, % calcd[d] Syn	Anti	syn, %[e]
n-BuOK	*er-2-d*	*t*-2,3; *c*-3	5.27	0.00	24.36	21.6
n-BuOK	*th-2-d*	*t*-2,3; *c*-3	2.05	40.6	0.00	5.04
n-BuOK	*er-4-d*	*t*-2,3; *c*-3	3.57	0.00	5.57	36.0
n-BuOK	*th-4-d*	*t*-2,3; *c*-3	16.68	15.08	33.14	8.69
NaOH[f]	*er-4-d*	*t*-3	25.69	0.00	100.0	74.3
NaOH[f]	*er-4-d*	*t*-2,3; *c*-3	2.69	0.00	17.90	85.0
NaOH[f]	*er-4-d*	All	2.45	0.00	9.87	75.2
NaOH[f]	*th-4-d*	*t*-3	33.92	100.0	0.00	33.9
NaOH[f]	*th-4-d*	*t*-2,3; *c*-3	20.07	37.77	12.73	29.3
tert-PeOK	*er-2-d*	*t*-2; *c*-3	9.67	0.00	75.89	87.3
tert-PeOK	*er-2-d*	*t*-2,3; *c*-3	5.81	0.00	47.19	87.8
tert-PeOK	*th-2-d*	*t*-2,3; *c*-3	23.30	45.02	0.00	51.8
tert-PeOK	*er-4-d*	*t*-2,3; *c*-3	2.27	0.00	26.49	91.4
tert-PeOK	*er-4-d*	All	0.96	0.00	15.60	93.8
tert-PeOK	*th-4-d*	*t*-2,3; *c*-3	16.58	21.65	3.67	71.8
sec-BuOK	*er-4-d*	*t*-3	12.80	0.00	100.0	87.2
sec-BuOK	*er-4-d*	*t*-2,3; *c*-3	3.52	0.00	19.88	82.3
sec-BuOK	*th-4-d*	*t*-3	51.23	100.0	0.00	51.2
sec-BuOK	*th-4-d*	*t*-2,3; *c*-3	19.11	25.46	12.38	51.4
Pyrol[g]	*er-2-d*	*t*-2; *c*-3	17.05	0.00	49.05	65.2
Pyrol[g]	*th-2-d*	*t*-2; *c*-3	16.50	53.51	0.00	30.8
Pyrol[g]	*th-2-d*	*t*-2,3; *c*-3	11.78	35.54	0.00	33.2
Pyrol[g]	*er-4-d*	*t*-3	21.72	0.00	100.0	78.3
Pyrol[g]	*th-4-d*	*t*-3	46.14	100.0	0.00	46.1
Pyrol[g]	*th-4-d*	*t*-2,3; *c*-3	24.10	40.41	11.69	50.2
NaOH	*er-2-d*	*t*-2; *c*-3	25.5	0.00	29.54	13.7
NaOH	*er-2-d*	*t*-2,3; *c*-3	19.9	0.00	21.34	6.7
NaOH	*er-2-d*	All	9.67	0.00	10.29	6.1
NaOH	*th-2-d*	*t*-2; *c*-3	0.95	49.65	0.00	1.9
NaOH	*th-2-d*	*t*-2,3; *c*-3	0.00	39.52	0.00	0.0
NaOH	*er-4-d*	*t*-3	74.83	0.00	100.0	25.2
NaOH	*er-4-d*	*t*-2,3; *c*-3	7.52	0.00	9.25	18.7
NaOH	*th-4-d*	*t*-3	4.04	100.0	0.00	4.0
NaOH	*th-4-d*	*t*-2,3; *c*-3	18.06	37.19	17.33	3.8

[a] See Table I, column 1 and footnote *c* for details of conditions. [b] See footnote *d*, Table I. [c] *t*-2 refers to *trans*-2-hexene, etc. All refers to total olefinic product. [d] Data from Table I used to calculate expected deuterium contents for production of all *trans*-olefin by syn elimination (*i.e.*, pure syn–anti dichotomy), and all anti elimination, respectively. [e] Calculated by comparing d_0 obsd (column 4) with d_0 calcd for all syn–anti dichotomy (column 5) and all anti (column 6). Not corrected for isotope effects. [f] See footnote *f*, Table I. [g] See footnote *e*, Table I.

Table III. Mass Spectral Analysis of Trimethylamine from Elimination Reactions of 3-Hexyl-*4-d*-trimethylammonium

Reaction condn[a]	Reactant	$(P + 1)/P \times 100$[b]
n-BuOK	erythro	3.55 ± 0.09
tert-PeOK	erythro	3.44 ± 0.15
tert-PeOK	threo	3.60 ± 0.12
		3.57 ± 0.11[c]

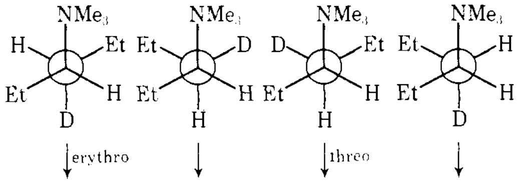
[a] See Table I, column 1 and footnote *c* for details of conditions. [b] Intensity of *m/e* 60 peak divided by intensity of *m/e* 59 peak, run at 11.0 eV or less to suppress *m/e* 58 (P − 1) peak. Errors are average deviations for three or more scans on a single sample. [c] Value for an undeuterated sample of trimethylamine, run by Mr. F. J. Romano and Mr. J. K. Borchardt.

cis- and *trans*-2-hexene to obtain mixtures of the 3-hexyl-*2-d* and 2-hexyl-*3-d* systems. The position isomers were separated by preparative glpc at the alkyldimethylamine stage and then each converted to the corresponding hexyltrimethylammonium salt.

The quaternary ammonium salts were subjected to elimination reactions with a variety of bases and solvents. The olefin proportions of the products from deuterated and undeuterated reactants were determined by glpc, and the deuterium contents of the products determined by mass spectrometry. The product analyses are recorded in Table I and the deuterium analyses in Table II. In a few cases the trimethylamine produced in the elimination was subjected to isotopic analysis to determine whether any of the syn elimination occurred *via* an α′-β mechanism.[33] The results are given in Table III.

Calculation of the percentage of syn elimination can be done in a number of ways, all of which amount to deciding whether hydrogen or deuterium was lost in the formation of a given product. The possibilities are illustrated with the 3-hexyl-*4-d* system in Scheme I. The simplest approach, which gives semiquantitative answers, is to calculate apparent isotope effects on the formation of each product by comparing olefin proportions from deuterated and undeuterated reactants.[18,26] The ideal approach is to separate all product olefins completely and analyze each for deuterium. Because really quantitative separation is not simple, and because some products are formed in too small yields for ready isolation, we chose to combine product analyses with deuterium analyses on partially separated olefin fractions. We also assumed the syn → cis path to be negligible in all cases. Earlier studies with the 5-decyl system gave only 5–7% syn → cis path under conditions similar to ours.[27] The details of the methods of calculation are given in the Experimental Section.

Scheme I



anti:	trans-h	cis-d	trans-d	cis-h
syn:	trans-d	cis-h	trans-h	cis-d
syn–anti:	trans-d	cis-d	trans-h	cis-h

The percentages of syn elimination which we arrive at are thus per cent syn → trans, and measure the extent to which the syn–anti dichotomy operates. To make the data really useful a further calculation is necessary, for the per cent syn → trans will be different for the two diastereomers because of isotope effects. Apparent isotope effects can be calculated from product proportions,[26,29] but are composite figures except when all anti or all syn–anti elimination occurs. Deuterium analyses and product proportions taken together can be used to calculate true isotope effects,[24] but the calculated isotope effects are rather sensitive to error in the deuterium analyses for reactions where there are either large or small amounts of syn–anti dichotomy. The more reliable isotope effects cluster in the range 1.9–2.3 for syn and 2.6–3.4 for anti elimination. We chose the average of these, 2.2 for syn and 3.0 for anti elimination, and used the approach of Cooke and Coke[24] to calculate the per cent syn → trans elimination in the absence of isotope effects. Although there is doubtless some variation of the isotope effects with

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[33] G. Wittig and R. Polster, *Justus Liebigs Ann. Chem.*, **599**, 1 (1956).

reaction conditions, we concluded that an attempt to allow for the variation would introduce more uncertainty than the assumption of constancy. If our assumed values are correct, both threo and erythro reactants should give the same corrected percentages of syn → trans elimination. The error limits in Table IV show that the agreement is good in most cases. Furthermore, the calculated percentages of syn → trans elimination are not very sensitive to the assumed values of the isotope effects. With the 2-hexyl system, the yield of 2-hexene was too small to isolate and obtain reliable deuterium analyses. Consequently, the per cent syn → trans elimination was estimated by comparing apparent isotope effects from product proportions[26,29] with values expected for all anti and all syn–anti elimination, respectively (see Table IV for details).

Table IV. Percentages of Syn–Anti Dichotomy in Elimination Reactions of Hexyltrimethylammonium Iodides

Reaction condn[a]	Reaction[b]	Syn, %[c]
n-BuOK	3 → 3-ene	16.6 ± 0.7
	3 → 2-ene	9.5 ± 1.1
	2 → 2-ene	0[f]
tert-PeOK	3 → 3-ene	83.0 ± 2.0
	3 → 2-ene	69.5 ± 0.5
NaOH–H_2O	3 → 3-ene	9.4 ± 1.1
	3 → 2-ene	2.2 ± 0.1
Pyrol[d]	3 → 3-ene	59.8 ± 5.2
	3 → 3-ene	43.7 ± 5.3
NaOH–DMSO[e]	3 → 3-ene	53.0 ± 1.5
MeOK	3 → 3-ene	20[h]
sec-BuOK	3 → 3-ene	67.5 ± 2.5
tert-BuOK	3 → 3-ene	80[i]
	2 → 2-ene	15[g]

[a] See Table I, column 1 and footnote *c* for details of conditions. [b] 3 → 3-ene refers to 3-hexyl-*4-d*-trimethylammonium ion yielding 3-hexene, etc. [c] Calculated per cent of syn → trans path (out of total trans product of elimination into the indicated branch), *i.e.*, per cent of syn–anti dichotomy. Calculation was by the method of Coke[24] assuming $(k_H/k_D)_{syn} = 2.2$ and $(k_H/k_D)_{anti} = 3.0$ throughout. [d] See footnote *e*, Table I. [e] See footnote *f*, Table I. [f] Yield of 2-hexene (Table I) was too low to isolate material for deuterium analysis. Apparent isotope effects from product proportions[18,26,29] were 3.38 for threo and 0.96 for erythro, indicating essentially all anti elimination. [g] Apparent isotope effects (footnote *f*) were 2.09 for erythro and 1.17 for threo, indicating *ca.* 15% syn elimination. [h] Apparent isotope effects (footnote *f*) were 2.1 for erythro and 1.2 for threo, indicating *ca.* 20% syn elimination. [i] Apparent isotope effects (footnote *f*) were 1.3 for erythro and 1.8 for threo, indicating *ca.* 80% syn elimination.

Two patterns are apparent in the results in Table IV. First, the importance of syn elimination for any one reactant increases as the chain branching of the alkoxide–alcohol pair increases. Considering the whole range of base–solvent combinations, there is an excellent qualitative correlation between increasing basicity of the medium and increasing syn elimination. While the alkoxide–alcohol results alone are consistent with an effect arising from the steric requirements of the base,[34] the relative importance of syn elimination in two cases where the base is hydroxide, the Hoffmann elimination, and the reaction in water–dimethyl sulfoxide, makes it apparent that the steric requirements of the base do not correlate with all of the results. The strength of the attacking base is also a key factor in syn elimination from medium-ring compounds.[21]

The second pattern is that there are distinct differences in propensity toward syn elimination among the three isomeric reactants. The per cent syn → trans elimination decreases in the order 3-hexyl → 3-hexene > 3-hexyl → 2-hexene > 2-hexyl → 2-hexene. The suspicion that this is in some way related to the steric requirements of the alkyl chain is strengthened by recalling that the 2,2-dimethyl-4-nonyl-*5-d*-trimethylammonium ion, a more congested system than any of ours, gives mainly or entirely syn → anti dichotomy with all base–solvent systems tried.[26]

Before discussing the causes of these patterns, the results of trimethylamine analyses in Table III should be recalled. It is evident that all three samples have a deuterium content within experimental error of natural abundance of the *m/e* 60 species, so that the α'–β mechanism[33] cannot be an important path for the syn elimination. With the *threo*-3-hexyl-*4-d* compound in *tert*-pentoxide–*tert*-pentyl alcohol, nearly 10% deuteration of the trimethylamine would be expected by this path, yet none is detectable.

Discussion

The strength of the attacking base is obviously a key factor in the propensity toward syn elimination. Sicher and Závada[21] argued that a stronger base should lead to more extensive stretching of the β-carbon–hydrogen bond. They proposed that a relatively well-developed p orbital on the β-carbon resulted, and that the lobe opposite to the breaking carbon–hydrogen bond performed a backside displacement of the leaving group (the "double inversion" mechanism). While this is an intuitively attractive picture, the basic assumption of increased carbon–hydrogen stretching with increased base strength is supported neither by experimental evidence nor by more sophisticated theory.

The hydrogen isotope effect in proton-transfer reactions is expected to be at a maximum when the proton is half transferred in the transition state and to be smaller when it is either more or less than half transferred.[35] The isotope effect for the reaction of 2-phenylethyltrimethylammonium ion with ethoxide in ethanol is distinctly below the expected maximum, and *increases* when the reaction medium is changed to *tert*-butoxide–*tert*-butyl alcohol.[36] The accompanying decrease in the Hammett ρ value[36] makes it clear that a decrease in the extent of proton transfer is occurring. Evidence that this results specifically from increasing base strength is afforded by the fact that the deuterium isotope effect at first increases and then decreases as dimethyl sulfoxide is added to the medium in the reaction of 2-phenylethyldimethylsulfonium[37] and -trimethylammonium[38] ions with hydroxide ion in water. A decrease in the extent of proton transfer with increasing strength of the attacking base is also predicted by Thornton's theory of the effect of substituents on transition-state geometry.[39,40]

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(34) H. C. Brown, I. Moritani, and Y. Okamoto, *J. Amer. Chem. Soc.*, **78**, 2193 (1956).

(35) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(36) W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).

(37) A. F. Cockerill, *J. Chem. Soc. B*, 964 (1967).

(38) K. C. Brown, unpublished results in these laboratories.

(39) L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 6149 (1967).

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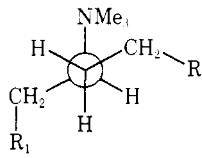
Although the transition state for syn elimination may well have a higher degree of proton transfer than that for anti elimination,[41] it does not seem reasonable to maintain that the changeover from anti to syn with increasing base strength results from a steady increase in the extent of proton transfer with base strength. There must instead be a steady decrease up to the point of change of stereochemistry, with a probably discontinuous increase at this point.[41] Increasing base strength, then, cannot promote syn elimination by increasing the ease of the double-inversion mechanism as postulated by Sicher and Závada,[21] but must operate in some other way.

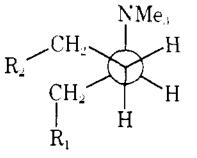
We propose that increasing base strength leads to less stretching of both the carbon–hydrogen and carbon–nitrogen bonds,[39] and hence to a transition state with less double-bond character. It is evident that many E2 reactions still show a rather strong tendency toward anti elimination.[3–6] The cause of this tendency is not known with certainty. It is probably not electrostatic repulsion of the anionic base and leaving group, both because estimated electrostatic effects are too small,[42] and because the phenomenon persists to at least some extent when the base is negatively and the leaving group positively charged (as in quaternary ammonium salts). It has been shown to be predicted by the principle of least motion, which states that reaction paths involving the least change in atomic positions will be favored.[43] Perhaps the most consistently accepted theory has been that the preference for anti elimination is stereoelectronic. In simplest terms, the carbon–hydrogen bonding electrons are considered to "displace" the leaving group from the α-carbon *via* a backside attack, so that concerted elimination is facile only when the carbon–hydrogen and carbon–X bonds are anti to each other.[42]

Either a stereoelectronic or a least-motion preference for anti elimination should be weaker when the transition state resembles reactant. Under such circumstances, a relatively minor effect could tip the balance in favor of syn elimination. We believe this effect is predominantly if not exclusively steric in origin.

An examination of models of the transition states for anti elimination reveals that the bulky trimethylammonio forces alkyl groups attached to the β′ and γ positions (the unprimed letter refers to the branch into which elimination occurs) as far away from itself as possible. This situation is illustrated for the 3-hexyl → 3-hexene system in **1a** (production of *trans*-olefin) and **2a** (production of *cis*-olefin). The β′- and γ-methyl groups provide significant hindrance to approach to the anti β-hydrogen. The mode of operation of this hindrance is better appreciated in **3**, which is simply a different projection of the anti → trans transition state shown in **1a**. It is then evident that the hydrogens of the β′-methyl group introduce two 1,4 interactions with the β-hydrogen, and that the hydrogens of the γ-methyl group introduce a single 1,3 interaction. The combination of these two interactions shields the β-hydrogen from approach by base. While the same interactions are present in the anti → cis transition state (**2a**), they are less effective in shielding the β-hydrogen because it is still relatively open to approach from the side opposite that on which the two methyl groups are found.

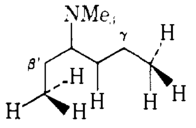


1



2

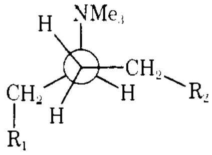
a, $R_1 = R_2 = CH_3$
b, $R_1 = C_2H_5$; $R_2 = H$
c, $R_1 = H_1$; $R_2 = C_2H_5$



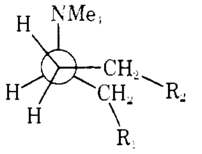
3

Thus, one expects the anti → cis path to be more facile than the anti → trans path. Examination of cis:trans ratios in the products of predominant anti elimination (Table I, reactions utilizing *n*-alkoxides in *n*-alcohols) reveals that this is indeed the case. One requirement for the incursion of syn elimination, increased difficulty of the normal anti → trans elimination, is fulfilled. The fact that syn elimination becomes important in the production of *trans*- but not of *cis*-olefin requires another factor.

This factor is almost certainly a simple eclipsing effect. While one cannot be sure that the groups on the α- and β-carbon are precisely eclipsed in the syn transition state, a tendency toward eclipsing would seem reasonable because of the increased orbital overlap it affords. If this is the case, it is evident that **4a** will be markedly preferred over **5a**. Such conformational preferences can be very large if the transition states are similar in bond angles to the reactants, giving **4** an advantage of some 1.0–2.7 kcal/mol over **5**.[44] Consequently, it is not unreasonable to find a ratio of *trans*- to *cis*-olefin that approaches two powers of ten from syn elimination.[28]



4



5

a, $R_1 = R_2 = CH_3$
b, $R_1 = C_2H_5$; $R_2 = H$
c, $R_1 = H$; $R_2 = C_2H_5$

In order to test our hypothesis that the syn–anti dichotomy arises from steric hindrance to the anti → trans route of elimination, we next decided to vary the reactant structure so as to vary this hindrance. Examination of models leads to the conclusion that more serious hindrance is exerted by the β′ (R_1 in **1**) than by the γ substituent (R_2 in **1**), an observation which is also apparent in **3**. Consequently, replace-

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(41) K. C. Brown and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 4292 (1970).

(42) S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951).

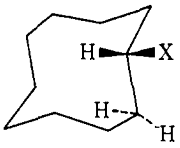
(43) J. Hine, *ibid.*, **88**, 5525 (1966); O. S. Tee, *ibid.*, **91**, 7144 (1969).

(44) E. L. Eliel, N. L. Allinger, S. J. Angyal, and and G. A. Morrison, "Conformational Analysis," Wiley-Interscience, New York, N. Y., 1965, Chapter 1.

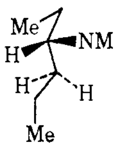
ment of R_2 by hydrogen should decrease the tendency toward syn elimination, and the decrease should be still more marked when R_1 is replaced by hydrogen. Under any given set of reaction conditions, the per cent syn → trans elimination should decrease in the order 3-hexyl → 3-hexene (**1a**) > 3-hexyl → 2-hexene (**1b**) > 2-hexyl → 2-hexene (**1c**). Table IV shows that this is indeed the case.

Additional evidence on the role of the β' and γ substituents is furnished by a reexamination of the original example of the syn–anti dichotomy in an open-chain system.[26] The reactant in that case was the 2,2-dimethyl-4-nonyl-*5-d*-trimethylammonium ion, where R_1 = *tert*-Bu and R_2 = *n*-Pr, and apparently pure syn–anti dichotomy was observed even with methoxide ion in methanol, a medium which gives only 20% syn → trans elimination in the 3-hexyl → 3-hexene system. A *tert*-butyl group instead of a methyl group in the β' position should greatly increase hindrance to approach to the anti β-hydrogen (see **3**), and thereby give syn elimination the opportunity to predominate under conditions where it cannot in a reactant with an unbranched carbon chain.

Our theory also explains the prevalence of the syn–anti dichotomy in medium-ring systems. The stable conformation[45] of a substituted cyclodecane is shown in **6**, and a redrawn version of structure **3** in **7**. The extraannular β-hydrogen in **6** is clearly more subject to attack than the intraannular, and such attack will lead to *trans*-olefin by a syn elimination. Structure **7** is closely analogous in conformation to the right-hand half of structure **6**, and it is to be expected that both will follow the syn–anti dichotomy if conformation is an important factor. The difference is that the ring structure enforces the conformation favorable to syn elimination in **6**, while the bulk of the trimethylammonio group enforces it in **7**. Hence, the syn–anti dichotomy is observed with a number of different leaving groups in medium-ring compounds,[18,23] but has so far been shown to be of importance only with quaternary ammonium salts in open-chain systems. Our theory predicts that there should be much less tendency toward the syn–anti dichotomy with poor leaving groups that are not bulky (such as fluorine) than with the trimethylammonio group.



6



7

This conformational explanation of the syn–anti dichotomy in medium rings was considered by Sicher,[21] but he concluded that it could not be "the sole or even the main cause" because he believed it to be inapplicable to open-chain compounds. Our evidence, however, strongly supports the contention that the syn–anti dichotomy is produced by conformational effects in both open-chain systems and medium rings. Syn elimination in rigid rings[13,16] and smaller rings[24] must result from different, though probably still steric, effects. A relatively reactant-like transition state seems likely to be a prerequisite for most if not all syn eliminations.

We should emphasize that our discussion of conformational effects refers to transition-state conformations. The analogy to ground-state conformations is valid only as long as the two states are geometrically similar, and there is no strong stereoelectronic factor affecting the stabilities of the transition-state conformations. The discussion of the medium rings, incidentally, was based on the cyclodecyl system because it has a single most stable conformation.[45] The other medium rings are conformationally more complicated, but they all possess partial structures similar to the right-hand side of **6**.

Experimental Section

3-Hexyl-*p*-toluenesulfonate was prepared by the method of Tipson.[46] The crude tosylates were taken up in ligroin, filtered through activated charcoal, and recrystallized at *ca.* −80°. The product had mp 24–25° (lit.[47] room temperature).

2-Hexyl-*p*-toluenesulfonate was prepared as above. The product had $n^{20}\mathrm{D}$ 1.4978.

3-Hexyldimethylamine was prepared by the substitution of dimethylamine for the tosylate group following the procedure of Cram, *et al.*[17] The product had bp 35° (10 mm), $n^{20}\mathrm{D}$ 1.4144.

2-Hexyldimethylamine was prepared from the corresponding *p*-toluenesulfonate as described above. The amine was separated from the 1- and 3-hexyldimethylamines by preparative glpc collection from a 15 ft × 0.375 in. column of 12% Carbowax 20M, 3% tetraethylenepentamine, and 4% potassium hydroxide on Chromosorb W.[48] The purified 2-hexyldimethylamine was shown to contain less than 0.03% of the 3 isomer by injection on an analytical column of the same packing.

3-Hexyltrimethylammonium iodide was prepared by addition of a 1.5-molar excess of methyl iodide to a solution of 3-hexyldimethylamine[49] in acetonitrile. After 20 hr, the mixture was poured into ether to precipitate the salt. The product was obtained in 89% yield and had mp 195–197° dec. *Anal.* Calcd for $C_9H_{22}NI$: C, 39.86; H, 8.18; N, 5.17. Found: C, 40.09; H, 8.11; N, 5.22.

2-Hexyltrimethylammonium iodide was prepared as above. The product had mp 200° dec. *Anal.* Calcd for $C_9H_{22}NI$: C, 39.86; H, 8.18; N, 5.17; I, 46.80. Found: C, 39.90; H, 8.14; N, 5.04; I, 46.74.

***erythro*-3-Hexylamine-*4-d*$_1$.** *cis*-3-Hexene (Chemical Samples Co.) was deuteroborated and converted to the corresponding amine with hydroxylamine-*O*-sulfonic acid by the procedure of Rathke, *et al.*[30] The crude product distilled at 110–130°.

***erythro*-3-Hexyldimethylamine-*4-d*$_1$** was prepared from the corresponding primary amine by the Eschweiler–Clark reaction following the procedure of Icke and Wisegarver.[31]

***erythro*-3-Hexyldimethylamine-*2-d*$_1$ and *erythro*-2-Hexyldimethylamine-*3-d*$_1$.** *cis*-2-Hexene (Chemical Samples Co.) was deuteroborated and converted to the primary amine as above.[6] The crude mixture of deuterio-2- and -3-hexylamines was converted to the hexyldimethylamines.[7] The products were distilled and the isomeric tertiary amines were preparatively separated by gas chromatography on the column described above.

Deuterated Hexyltrimethylammonium Iodides. The following hexyltrimethylammonium iodides were prepared from the corresponding olefins by the methods given above: *threo*-2-hexyl-*3-d*$_1$, mp 197–199° dec; *threo*-3-hexyl-*2-d*$_1$, mp 195–197° dec; *threo*-3-hexyl-*4-d*$_1$, mp 195–197° dec; *erythro*-2-hexyl-*3-d*$_1$, mp 197–200° dec; *erythro*-3-hexyl-*2-d*$_1$, mp 195–197° dec; *erythro*-3-hexyl-*4-d*$_1$, mp 193–194° dec.

Hexyltrimethylammonium hydroxides were prepared following the procedure of Cope.[50] Hexyltrimethylammonium iodide (100–300 mg) was dissolved in 5 ml of distilled water and passed through

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[46] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[47] P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 5834 (1960).

[48] Y. L. Sze, M. L. Burke, and D. M. Ottenstein, *Anal. Chem.*, **35**, 240 (1963); E. D. Smith and R. D. Radford, *ibid.*, **33**, 1160 (1961).

[49] M. Kohn and J. Giaconi, *Monatsh. Chem.*, **28**, 461 (1961).

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35 g of amberlite IRA-400 anion resin in the hydroxide form. Water (20 ml) containing the ammonium salt was collected and subjected to standard Hoffman elimination conditions (see below).

Solvents. Methanol and ethanol were distilled twice from the corresponding magnesium alkoxides;[51] *n*-, *sec*- and *tert*-butyl alcohols and *tert*-pentyl alcohol were distilled twice from calcium hydride,[52,53] the middle 80% of the distillate being used for elimination reactions. Water was distilled from potassium permanganate, pyridine from barium oxide,[54] dimethyl sulfoxide from calcium hydride,[52] and acetonitrile from phosphorus pentoxide.[54]

Base Solutions. Sufficient amounts of sodium or potassium were cleaned in pentane, washed twice in dried alcohol, and added to the alcohol under an atmosphere of dry nitrogen. Upon completion of reaction the normality of the base was determined by titration and adjusted if necessary by addition of alcohol. Sodium hydroxide solutions were prepared by addition of reagent grade sodium hydroxide to water. Mixtures of dimethyl sulfoxide and water were prepared gravimetrically from sodium hydroxide solutions of known normality, correcting the weight of sodium hydroxide in a known volume of water. All solutions for product studies were prepared at room temperature and no correction was made for higher temperatures.

Elimination Reaction Procedures. The hexyltrimethylammonium iodides were weighed in volumetric flasks to produce 0.05–0.08 *M* solutions when filled to the mark with 0.2–0.3 *M* base solutions. The solutions were transferred to stainless steel reaction tubes[56] and run to completion.

The reactions in alcohol were quenched and subjected to short-path distillation to remove the base prior to analysis. The distilled reaction mixture was either analyzed as such or was extracted into pentane from an aqueous solution, dried, and analyzed. Products of reactions in water and dimethyl sulfoxide–water were extracted directly into pentane.

Hoffmann pyrolytic eliminations were performed as follows: 20 ml of water containing the ammonium hydroxide was subjected to short-path distillation at atmospheric pressure to remove the water and the resulting syrup was pyrolyzed in a stream of dry nitrogen at *ca.* 120°. The products were collected in 2 ml of pentane cooled in an ice–salt bath.

Elimination Product Analysis. The four isomeric olefins resulting from elimination of the 3-hexyltrimethylammonium salts were analyzed on a 20 ft × 0.250 in. column of 20% adiponitrile adjoining a 1.5 ft × 0.250 in. column of silver nitrate in ethylene glycol using an Aerograph A-90-P gas chromatograph equipped with thermal conductivity detectors. The retention times of the olefinic products relative to pentane (1.00) were: *trans*-3-hexene, 3.64; 1-hexene and *trans*-2-hexene, 4.00; *cis*-3-hexene, 4.37; and *cis*-2-hexene, 4.88. The absence of significant amounts of 1-hexene, the major elimination product from 2-hexyltrimethylammonium salt,[56,57] was established by analysis on a 20 ft × 0.250 in. column of adiponitrile on Chromosorb P. Since 1-hexene and *trans*-3-hexene have nearly the same retention time on this column, changes in the proportion of *trans*-3-hexene would have revealed the presence of 1-hexene.

The three isomeric olefins resulting from the elimination of the 2-hexyltrimethylammonium iodides were analyzed on a 50 ft × 0.125 in. column of 5% Ucon 50 HB 100 on Chromosorb P using an F and M Model 700 gas chromatograph with flame ionization detectors.[58] The retention times of the olefinic products relative to *n*-pentane are: 1-hexene, 1.92; *trans*-2-hexene, 2.08; *cis*-2-hexene, 2.24.

The detector responses to the isomeric olefins were assumed to be equal. The areas of the peaks were determined by the use of a polar planimeter, by the method of cutting and weighing, or by the peak height times width at half-height method.[59] All three methods gave similar results. The reported per cent ether is uncorrected for detector response. The relative proportions of the olefins are corrected for incomplete deuterium content by subtracting 5% of the undeuterated product proportions from the observed product proportions and recalculating the results to total 100%.

Mass Spectral Analysis. a. Sample Preparation. The products of the elimination reaction were subjected to short-path distillation to remove the base and then were extracted into *n*-pentane from a cold aqueous solution of the alcohol. The extract was washed several times with cold distilled water and dried over magnesium sulfate. The olefins were collected by injecting 20–150-μl portions of the pentane extract onto a 21 ft × 0.25 in. column of 21% adiponitrile on Chromosorb P-AW and trapping in a glass tube cooled in either Dry Ice–acetone or liquid nitrogen. The sample was then degassed, dried over phosphorus pentoxide and calcium sulfate, and condensed in a mass spectrometer gas-sample tube on a vacuum line. The trimethylamine from elimination reactions and the deuterated hexyldimethylamines were collected from the Carbowax–KOH column used for amines.

b. Isotopic Analysis. The analyses were performed on an Atlas CH-4 mass spectrometer at an ionizing voltage that was consistent with reasonable peak heights and minimum fragmentation. The hexanes were analyzed at 15.0 eV, although there is no fragmentation to produce a significant P − 1 fragment even at 70.0 eV.[60] The amines were analyzed at 11.0 eV, or lower, to suppress the P − 1 ionization.[61]

The reported values of undeuterated material are given as percentages of the total hexene sample calculated as described by Bieman.[62] The per cent undeuterated values reported for the hexenes are corrected for the amount of undeuterated material present in the ammonium salt. These values, 5.2% for both 3-hexyl-*4-d*-, and 5.5% for the 3-hexyl-*2-d*-trimethylammonium iodides were determined on the hexyldimethylamine precursor.

The K_H/K_D values were calculated using the equation derived by Coke.[24,63] The per cent syn elimination values of the undeuterated parent compounds were calculated using an anti K_H/K_D of 3.0, and a syn K_H/K_D of 2.2 with the following equations

$$\text{threo } K_{\text{syn-H}} = \%\ \text{syn-D}(K_H/K_D)_{\text{syn}}$$

$$100\% = \%\ \text{syn-D} + \%\ \text{anti-D}$$

$$\%\ \text{anti-D} = K_{\text{anti-H}}$$

$$\text{erythro } K_{\text{syn-H}} = \frac{\%\ \text{syn-D}}{(K_H/K_D)_{\text{anti}}}$$

$$\%\ \text{syn-H} = \frac{K_{\text{syn-H}}}{K_{\text{syn-H}} + K_{\text{anti-H}}}$$

following Coke, *et al.*[64] The assumed values of K_H/K_D are supported by the calculated K_H/K_D when the measured deuterium ratios are not sensitive to error (between 25 and 75 % syn loss of deuterium as in the cases of hydroxide pyrolysis, *sec*-butoxide–*sec*-butyl alcohol, and dimethyl sulfoxide–hydroxide, and by values determined by the method of Závada, *et al.*,[19] for systems with large amounts of syn–anti dichotomy).

Control Experiments. The *n*-hexene products were shown to be stable under the reaction conditions employed. The work-up of product olefins (above) was shown to involve no changes in product ratios relative to the untreated reaction product mixture. The *n*-pentane used to extract the hexenes from base solutions was shown to possess no peaks in the region of the hexenes on both the adiponitrile and the adiponitrile–silver nitrate columns used for product analysis. Collection of the regions where the hexenes appeared on glpc yielded no peaks in the region *m/e* 83–88 at 70 eV from a sample of 200 μl of *n*-pentane.

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