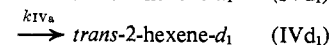
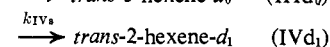
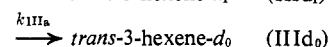
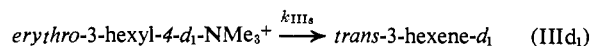
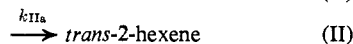
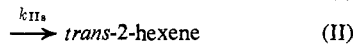
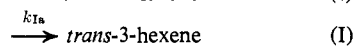
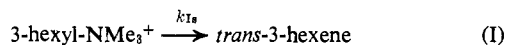


these values with the observed deuterium content of the fraction gave the per cent syn uncorrected values listed in Table II. These were converted to per cent syn corrected values (those values which would be found in the absence of an isotope effect) by means of $k_{\text{H}}/k_{\text{D}}$ values for the syn or anti elimination as described by Bailey and Saunders.⁹ The $k_{\text{H}}/k_{\text{D}}$ values used were average or compromise figures instead of those calculated from experimental data for the particular reaction (see the discussion). The values actually used are given in footnote *q* to Table II.

In the course of the work, we derived a modified version of the equation of Cooke and Coke¹⁶ which enabled us to estimate the error introduced by assuming no secondary isotope effect when hydrogen is removed from a deuterium-bearing carbon atom. The definitions of terms and the result are as follows (a refers to syn and a to anti):



We assume that $k_{\text{IIIa}} = k_{\text{IVa}}$ and that $k_{\text{IIIa}} = k_{\text{IVa}}$ (no secondary isotope effect on elimination into the branch away from that bearing deuterium) but let $k_{\text{Ia}}/k_{\text{IIIa}} = S$. We then define product ratios in terms of the relevant rate constants and solve for $k_{\text{Ia}}/k_{\text{IIIa}}$ (which is $(k_{\text{H}}/k_{\text{D}})_{\text{anti}}$).

$$\frac{k_{\text{Ia}}}{k_{\text{IIIa}}} = \frac{(\text{I})/(\text{II})}{(\text{III})/(\text{IV})} \left[1 + \frac{(\text{III d}_1)}{(\text{III d}_0)} \right] - \frac{(\text{III d}_1)}{(\text{III d}_0)} S$$

When the *threo*-3-hexyl-4-d₁ reactant is used, an analogous equation gives $(k_{\text{H}}/k_{\text{D}})_{\text{syn}}$. As an example of the expected influence of a secondary isotope effect of reasonable magnitude, we found $k_{\text{Ia}}/k_{\text{IIIa}}$ of 2.54 when $S = 1$ and 2.45 when $S = 1.1$. Consequently, we neglected S in our calculations.

Mechanisms of Elimination Reactions. XXIII. Stereochemistry of Elimination Reactions of 3-Hexyl Tosylate and Fluoride. The Role of Ion Pairing¹

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Abstract: 3-Hexyl tosylate with phenoxide bases in 95% dimethyl sulfoxide–5% *tert*-butyl alcohol gives *trans*-3-hexene predominantly *via* an anti route. The proportion of syn elimination runs PhOLi, 16.5%; PhOK, 9.3%; *p*-NO₂PhOK, 3.3%; PhOLi + NMe₄I, 0%. The order is also that of decreasing ion pairing of the base, indicating that ion-paired base favors syn elimination. 3-Hexyl fluoride gives only 14% syn → *trans* elimination with potassium *n*-butoxide in *n*-butyl alcohol but 68% with potassium *tert*-butoxide in *tert*-butyl alcohol. The latter figure shows that a large leaving group is not a necessary condition for obtaining substantial proportions of *syn* elimination from open-chain reactants.

Most of the examples of syn elimination from simple open-chain reactants are found with quaternary ammonium salts. Few comparisons with other substrates are available, but it has been established that tosylates show much less propensity for syn elimination than do alkyltrimethylammonium salts.^{2,3} We proposed that a key factor in this difference was the greater size of the trimethylammonio group, which forced the alkyl chain into a conformation that hindered approach to the anti β hydrogen.^{4,5} The trimethylammonio group is also a poor leaving group, and this property should contribute to the propensity for syn elimination by causing the transition state to be relatively reactant like. We suggested, however, that a poor leaving group that was not bulky, such as fluorine, should give much less syn elimination.⁴ The present work was

undertaken to test this prediction and also to compare some effects of ion pairing on stereochemistry of elimination with charged⁶ and uncharged substrates. It was predicted^{7,8} that a free anionic base should effectively promote syn elimination with charged substrates, and our results⁶ support this prediction. A base ion paired with a metal ion, however, was predicted to promote syn elimination with neutral substrates because of coordination of the metal ion with the leaving group as in **1**.^{9,10} Additional evidence on these points appeared in the literature during the course of these studies and will be discussed below along with our results.

Data on olefin proportions are given in Table I and on deuterium analyses in Table II for reactions of stereospecifically deuterated 3-hexyl-4-d fluorides and tosyl-

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(4) D. S. Bailey and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 6904 (1970).
(5) D. S. Bailey, F. C. Montgomery, G. W. Chodak, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 6911 (1970).

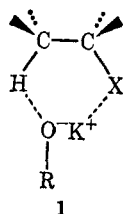


Table I. Product Proportions in Eliminations from 3-Hexyl Tosylate and Fluoride^a

Leaving group, X	Base	Reactant ^b	Hexenes, % ^c			
			<i>trans</i> -3	<i>cis</i> -3	<i>trans</i> -2	<i>cis</i> -2
OTs	PhOK	H	32.2	10.4	41.4	16.0
		er	15.6	13.2	51.3	19.8
OTs	<i>p</i> -NO ₂ PhOK	H	35.4	9.9	39.2	15.5
		er	22.0	9.7	50.5	17.8
OTs	PhOLi	H	34.0	10.5	38.3	17.2
		th	28.9	8.6	43.8	18.7
OTs	PhOLi + NMe ₄ I	H	37.0	9.3	37.9	15.8
		th	27.3	4.2	52.5	15.9
F	<i>t</i> -BuOK	H	31.4	7.3	43.8	17.5
		er	27.2	6.2	45.8	20.7
		th	21.4	4.4	51.5	22.6
F	<i>n</i> -BuOK	H	26.9	10.5	41.1	21.5
		er	6.9	12.6	53.1	27.4

^a The conditions were 95% dimethyl sulfoxide–5% *tert*-butyl alcohol at 60° for 24 hr with the tosylates, *tert*-butyl, and *n*-butyl alcohols, respectively, at 163° for 140 hr with the fluorides. ^b The erythro reactant contained 7.84% *d*₀ and the threo reactant 10.12% *d*₀ material. ^c Percentages for the deuterated compounds are corrected for contributions to the product from *d*₀ reactant. Observed percentages for the *d*₀ reactant were multiplied by the fraction of *d*₀ in the *d*₁ reactant, the resulting numbers subtracted from the corresponding percentages for the *d*₁ reactant, and the differences normalized to 100%.

Table II. Deuterium Analyses of Hexenes and Per Cent Syn Elimination from 3-Hexyl-4-*d*₁ Tosylate and Fluoride^a

Leaving group, X	Base	Reactant ^b	<i>d</i> ₀ , % Obsd	% syn	
				Uncorr	Corr
OTs	PhOK	er	25.69	23.5	9.3 ^c
OTs	<i>p</i> -NO ₂ PhOK	er	35.40	9.2	3.3 ^c
OTs	PhOLi	th	13.39	18.1	16.5 ^d
OTs	PhOLi + NMe ₄ I	th	9.64	ca. 0 ^e	ca. 0 ^e
F	<i>t</i> -BuOK	er	11.93	89.0	67.9 ^e
		th	24.02	47.9	68.0 ^f
F	<i>n</i> -BuOK	er	14.93	38.4	13.9 ^e

^a See footnote a, Table I. ^b See footnote b, Table I. ^c Corrected for assumed (*k*_H/*k*_D)_{anti} of 3.0. ^d Corrected for assumed (*k*_H/*k*_D)_{syn} of 2.2. ^e Corrected for (*k*_H/*k*_D)_{anti} of 3.84, calculated from data on this reaction. ^f Corrected for (*k*_H/*k*_D)_{syn} of 2.37, calculated from data on this reaction. ^g Apparent slight increase in deuterium content of olefin relative to reactant.

ates. From these data the proportions of syn elimination in the production of *trans*-3-hexene were determined as before^{4,6} and are recorded in Table II. The figures in the last column are corrected for the isotope effect and represent the values expected for the undeuterated substrate. The *cis*-3-hexene was not examined for deuterium content, but previous work has shown that the contribution of the syn → *cis* path is almost always small.^{2,3,6} The results with the fluorides are rendered somewhat uncertain by a small amount of isomerization (see Experimental Section) of the olefins which occurs under the strenuous conditions needed for the elimina-

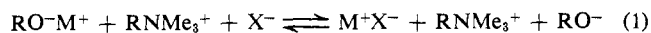
tion, but the close agreement of results from the erythro and threo isomers suggests that the error from this source is not large.

The results with the fluoride and potassium *tert*-butoxide in *tert*-butyl alcohol show clearly, contrary to our previous suggestion,⁴ that a large leaving group is not a necessary condition for syn elimination in open-chain systems. A similar observation has been made by Pánková, Svoboda, and Závada,¹¹ who found 90% syn elimination from 5-decyl-6-*d* fluoride with potassium *tert*-butoxide in benzene. The corresponding chloride gave less, but still substantial (62%), syn elimination under the same conditions. Whatever may be the effect of leaving-group bulk with quaternary ammonium salts, it is evidently not a decisive factor with neutral leaving groups. The most important property of the leaving group with the fluoride appears to be its low reactivity. A poor leaving group leads to a transition state with little double bond character and a consequent lack of the preference for anti elimination found with good leaving groups.⁴

Both of the media which give high proportions of syn elimination are strongly basic, but a much lower proportion of syn elimination (20%) is found in another strongly basic medium, potassium *tert*-butoxide in dimethyl sulfoxide.¹¹ Dimethyl sulfoxide differs from benzene and *tert*-butyl alcohol in that it promotes dissociation, while they promote pairing, of ionic solutes. Thus, ion-paired potassium *tert*-butoxide appears to favor syn elimination, probably *via* a transition state like 1.^{9,10} While strongly basic reagents may help to encourage syn elimination from fluorides by giving a more reactant-like transition state, the decisive factor is evidently ion pairing of the base.

The tendency of the tosylate to undergo syn elimination remains low under all of the conditions of the present study, but significant variations occur. Potassium phenoxide gives substantially more syn elimination than potassium *p*-nitrophenoxide. The greater tendency of salts of phenoxide than of *p*-nitrophenoxide ion to exist in the ion-paired form, as independently shown by uv spectra,¹² is very probably responsible for this difference. The greater proportion of syn elimination with lithium phenoxide, which is expected to be the most tightly ion paired of the first three bases in Table II,^{6,13} substantiates further the importance of an ion-paired base in these reactions.

The most striking evidence for the importance of ion pairing is afforded by the fourth entry in Table II, where addition of tetramethylammonium iodide to lithium phenoxide suppresses syn elimination completely. We have previously presented evidence for the ion-pair equilibrium of eq 1 in connection with



studies of eliminations from quaternary ammonium salts.^{6,13} It is clear that added tetramethylammonium iodide will shift this equilibrium to the right, thereby decreasing the proportion of ion-paired phenoxide and decreasing the proportion of syn elimination.

In conclusion, the present results have shown that a

(11) M. Pánková, M. Svoboda, and J. Závada, *Tetrahedron Lett.*, 2465 (1972).

(12) H. E. Zaugg and A. D. Schaefer, *J. Amer. Chem. Soc.*, 87, 1857 (1965).

(13) J. K. Borchardt and W. H. Saunders, Jr., *Tetrahedron Lett.*, 3439 (1972).

poor leaving group and an ion-paired base are conducive to syn elimination in E2 reactions of neutral substrates. Whether these are the only important factors, or whether base strength and solvent effects also affect the stereochemistry of elimination, cannot be judged from the present results. The effect of the structure of the alkyl group, which is important with quaternary ammonium salts,^{4,5} also remains to be established.

Experimental Section¹⁴

threo-3-Hexanol-4-*d*₁ was prepared in 29% yield from *trans*-3-hexene, sodium borodeuteride, and boron trifluoride etherate by the procedure of Brown and Zweifel.¹⁵

erythro-3-Hexanol-4-*d*₁ was prepared by the above procedure from *cis*-3-hexene.

3-Hexyl *p*-toluenesulfonate was prepared by the method of Tipson,¹⁶ and worked up as described by Bailey and Saunders⁴ to give an 85% yield of material of mp 25.5–26.5° (lit.⁴ 24–25°).

erythro- and *threo*-3-hexyl-4-*d*₁ *p*-toluenesulfonates were prepared by the same procedure from the corresponding hexanols.

3-Hexyl fluoride was prepared from 3-hexyl *p*-toluenesulfonate and potassium fluoride in diethylene glycol by the procedure of Edgell and Parts.^{17,18} Olefin (ca. 50% of crude product) was separated from 3-hexyl fluoride by glpc on a 20-ft column of di-*n*-decyl phthalate at 110° and then on a 20-ft column of 20% adiponitrile on Chromosorb P at room temperature. Injector and detector were kept at 100° to avoid thermal elimination from the fluoride. The proton nmr shows two multiplets centered at δ 4.45 and 1.5 ($J_{\text{HCF}} = 46$ Hz, $J_{\text{HCCF}} = 23$ Hz). The ¹⁹F resonance appears 16.38 ppm upfield from C₆H₆ with the same coupling constants.

erythro- and *threo*-3-hexyl-4-*d*₁ fluorides were prepared by the

(14) Melting points and boiling points are uncorrected.

(15) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 1241, 2544 (1961).

(16) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(17) W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, **77**, 4899 (1955).

(18) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 340 (1965).

same procedure from the *threo*- and *erythro*-*p*-toluenesulfonates, respectively.

Solvents. *n*-Butyl and *tert*-butyl alcohols were purified as described by Borchardt and Saunders.⁶ Tetrahydrofuran (for the deuteroboration reaction) was refluxed over and distilled from potassium hydroxide and redistilled from lithium aluminum hydride.

Base solutions were prepared as described by Borchardt and Saunders.⁶

Elimination Reactions. Fluoride solutions were prepared by collecting from the gas chromatograph directly in a 5.0-ml volumetric flask sufficient fluoride to give a 0.05–0.08 *M* solution when diluted with 0.33–0.38 *M* base. Tosylate solutions were 0.004 *M* in tosylate and 0.04–0.10 *M* in base. Reactions were carried out in stainless steel tubes and the products isolated as described by Borchardt and Saunders.⁶

Elimination product separation and analyses were performed essentially as described by Borchardt and Saunders.⁶ With the products from the fluorides, the injector and detector were kept at 100° to prevent formation of additional olefin from unreacted fluoride.

Control Experiments. Stability of the products to conditions more strenuous than those used for the tosylate reactions has already been demonstrated.^{4,6} The olefins were observed to undergo some isomerization with potassium *tert*-butoxide in *tert*-butyl alcohol at 163° for 140 hr, the conditions of the fluoride reactions. Pure *cis*-3-hexene gave 87.8% *cis*-3-hexene, 3.9% *trans*-3-hexene, 1.3% *cis*-2-hexene, and 7.0% *trans*-2-hexene. Pure *trans*-3-hexene gave 97.7% *trans*-3-hexene and 2.3% *cis*-2-hexene. Pure samples of *cis*- and *trans*-2-hexene were not available, but a mixture consisting mainly of *cis*-2-hexene could be estimated to give 96.6% *cis*-2-hexene, 3.2% *trans*-3-hexene, and 0.1% *cis*-3-hexene if isomerization of the *trans*-2-hexene is assumed to be negligible. (It probably is distinctly less than 1%, judging from the fact that *trans*-3-hexene isomerizes to only ca. one-fifth the extent of *cis*-3-hexene.)

Mass spectrometric analysis followed the procedures of Borchardt and Saunders.⁶

Calculations followed the methods of Borchardt and Saunders⁶ and Bailey and Saunders.⁴ The isotope effects used in correcting the per cent syn elimination to that expected in the absence of an isotope effect are given in footnotes *c–f* of Table II.