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Steric Requirements in Base-Promoted Elimination Reactions

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The effect of the steric requirement of the attacking base in base-promoted elimination reactions was studied using a variety of pairs of diastereoisomeric bases. The pairs of diastereoisomeric alkoxide bases examined gave difinitely different *cis*-olefin to *trans*-olefin ratios from elimination reactions of secondary alkyl bromides and tosylates in dimethyl sulfoxide. The results indicate unambiguously that the steric requirement of the attacking base is an important controlling factor in determining the olefinic product distribution in these elimination reactions. The structural effect of the solvent molecule was also investigated using pairs of diastereoisomeric alcohols in base-promoted elimination reactions. Under a variety of conditions the effect upon the product distribution observed was rather small, as compared with those observed for the diastereoisomeric bases, to be an important contributing factor on the product distribution.

Extensive studies on the base-promoted elimination reactions have revealed that the olefinic product distribution (positional and geometrical isomers) is affected by various factors such as the structure of the substrate, the nature of the leaving group, the strength and the structure of the attacking base, and the nature of the reaction medium.[1] Since the structure of the substrate can be varied independently to the other variables such as the base, the solvent and the leaving group, the importance of this factor has easily been tested and clearly evidenced experimentally.[1] The effect of the base, on the other hand, are much more complicated because these must depend both on the structure and on the strength of the base and an ambiguity of many experimental works attempting to separate the factors arises mainly from the fact that the strength of the base is not an independent variable to the structure of the base. Moreover, since the effect of the base depends strongly on the solvent used, it is very difficult to separate the effects on the product distribution that are caused by intrinsic properties of the base from those they are the result of solvent effects. A metal alkoxide dissolved in the corresponding alcohol is the most common reagent for bringing about elimination reactions, so that much of the data available are on the results of simultaneous change in the base and the solvent.

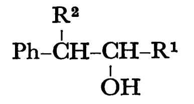
Intramolecular non-bonded interactions such as eclipsing effects are effectively able to alter the relative stereochemical stabilities between the possible conformers at the transition state in elimination reactions, so that it is reasonably anticipated that the intermolecular interactions between reactants or between reactants and the environment (such as the solvent molecule), though lesser extent than the intramolecular by virtue of the greater freedom with the intermolecular, will constitute a contributing factor on the product distribution.

To understand the effect of the attacking base on the product distribution in base-promoted elimination reactions, it is, therefore, desired to determine the effects of the strength and of the structure of the attacking base separately. The present work was undertaken to make this point clear, and also to examine the effect of the molecular structure of the solvent as one of the effects of the environment in elimination reactions. For the examination of the structural effect of the base it is necessary to use such bases that the variation of the structure should have little effect upon the base strength. A pair of diastereoisomeric alkoxide bases that differ only in the spatial alignment of the substituents around the basic center would satisfy the requisite, because the electronic effect of the substituents may cause little differences in the base strength between the pair. With such a pair of bases, the transition states are diastereoisomeric in each other, so that they should give different product distributions.

In a similar sense, the parent diastereoisomeric alcohols can also be utilized as solvent for the elucidation of the structural effects of the environment in elimination reactions.

Results and Discussion

Effects of Diastereoisomeric Alkoxide Bases. The effect of pairs of diastereoisomeric alkoxides, the conjugate bases of *dl-threo-* and *dl-erythro-*alcohols, **1—6**, was examined for the product distribution from base-promoted elimination reactions of secondary alkyl bromides and tosylates. Since the nature of the transition state is affected by the solvent, the steric requirement of the attacking base must also be dependent on the nature of the solvent used. With changing the polarity the influence of the solvent upon the steric requirement of the base was first examined using two pairs of alkoxides, **1** and **2**, and the results are given in Table 1. The solvents used in these runs were mixtures of the solvent in question and 3-methyl-3-pentanol which was added to make all the base solutions easily homogeneous. Though the reaction temperatures were different, little differences were observed in the product distributions between a pair of the diastereosiomeric alkoxides **1** or **2** in dimethyl sulfoxide-methylpentanol system (Table 1) and in the pure dimethyl sulfoxide system (Table 3),[2] so that the equilibrium between an alkoxide



$$\mathrm{Ph{-}\overset{R^2}{\overset{|}{C}H}{-}\underset{\underset{OH}{|}}{C}H{-}R^1}$$

1,	R^1=Me	R^2=Me
2,	R^1=Et	R^2=Me
3,	R^1=^{n}Bu	R^2=Me
4,	R^1=Et	R^2=Et
5,	R^1=Et	R^2=^{n}Bu
6,	R^1=Ph	R^2=Me

Table 1. Effects of the solvent on the product distribution from elimination reactions of 4-heptyl-X with diastereoisomeric pairs of alkoxides **1** and **2** in the dipolar aprotic solvent (75 v/v %)–3-methyl-3-pentanol (25 v/v %) mixture at 60 °C

X in subst.[a]	Base[b]	Dipolar aprotic component[c]	$\left(\frac{cis}{trans}\right)_E$ [d]	$\left(\frac{cis}{trans}\right)_T$ [e]	$\frac{(cis/trans)_E}{(cis/trans)_T}$
Br	**1**	DMSO	0.150	0.131	1.15
Br	**1**	DMF	0.157	0.135	1.16
Br	**1**	ACN	0.196	0.184	1.07
Br	**1**	Diglyme	0.190	0.181	1.05
Br	**2**	DMSO	0.250	0.165	1.52
Br	**2**	DMF	0.269	0.177	1.52
Br	**2**	ACN	0.281	0.229	1.23
Br	**2**	Diglyme	0.277	0.222	1.25
OTs	**1**	DMSO	0.376	0.334	1.13
OTs	**1**	DMF	0.380	0.354	1.07
OTs	**1**	ACN	0.506	0.492	1.03
OTs	**1**	Diglyme	0.558	0.560	0.996
OTs	**2**	DMSO	0.539	0.414	1.30
OTs	**2**	DMF	0.550	0.437	1.26
OTs	**2**	ACN	0.590	0.536	1.10
OTs	**2**	Diglyme	0.664	0.599	1.11

a) $[\mathrm{subst.}]_i$≒0.1 M. b) $[\mathrm{alkoxide}]_i$≒0.2 M. c) DMSO=dimethyl sulfoxide; DMF=dimethylformamide; ACN=acetonitrile; Diglyme=diethyleneglycol dimethyl ether. d) E=*erythro*-alkoxide. e) T=*threo*-alkoxide.

base and the added alcoholic component, $\mathrm{ROH}+\mathrm{R'O^-} \rightleftharpoons \mathrm{RO^-}+\mathrm{R'OH}$, seems to contribute little in the mixed solvent systems.[3] Though the factors attributable to the apparent trend in the product distribution were not clear, the results indicated that the larger the polarity of the solvent used, the larger the difference in the product distribution between a pair of the diastereoisomeric alkoxides. Hence dimethyl sulfoxide was the prefered solvent throughout the studies of the structural effect of the attacking base.

Table 2. Effects of diastereoisomeric pairs of alkoxides **1** and **2** on the product distribution from elimination reactions of 2- and 3-pentyl-X in dimethyl sulfoxide at 35 °C

Subst.[a]	Base[b]	$\frac{\text{1-ene}}{\text{2-ene}}$	$\frac{cis}{trans}$ [c]	$\frac{(cis/trans)_E}{(cis/trans)_T}$
2-Br	E-**1**	0.396	0.166	1.07
2-Br	T-**1**	0.407	0.155	
2-Br	E-**2**	0.574	0.258	1.29
2-Br	T-**2**	0.584	0.200	
3-Br	E-**1**		0.182	0.978
3-Br	T-**1**		0.186	
3-Br	E-**2**		0.235	1.12
3-Br	T-**2**		0.209	
2-OTs	E-**1**	1.48	0.318	1.11
2-OTs	T-**1**	1.47	0.286	
2-OTs	E-**2**	1.82	0.457	1.29
2-OTs	T-**2**	1.85	0.353	
3-OTs	E-**1**		0.293	0.983
3-OTs	T-**1**		0.298	
3-OTs	E-**2**		0.382	1.16
3-OTs	T-**2**		0.328	

a) $[\mathrm{subst.}]_i$≒0.1 M. b) E=*erythro*-alkoxide, T=*threo*-alkoxide. $[\mathrm{alkoxide}]_i$≒0.2 M. c) 2-pentenes.

Table 3. Effects of diastereoisomeric pairs of alkoxides **1**—**6** on the product distribution from elimination reactions of 4-heptyl-X in dimethyl sulfoxide at 35 °C

X in Subst.[a]	Base[b]	$\left(\frac{cis}{trans}\right)_E$ [c]	$\left(\frac{cis}{trans}\right)_T$ [d]	$\frac{(cis/trans)_E}{(cis/trans)_T}$
Br	**1**	0.161	0.132	1.22
Br	**2**	0.248	0.182	1.36
Br	**3**	0.263	0.183	1.44
Br	**4**	0.273	0.186	1.47
Br	**5**	0.274	0.179	1.53
Br	**6**	0.107	0.146	0.733
OTs	**1**	0.374	0.319	1.17
OTs	**2**	0.508	0.388	1.31
OTs	**3**	0.564	0.422	1.34
OTs	**4**	0.533	0.409	1.30
OTs	**5**	0.554	0.411	1.35
OTs	**6**	0.247	0.285	0.867

a) $[\mathrm{subst.}]_i$≒0.1 M. b) $[\mathrm{alkoxide}]_i$≒0.2 M. c) E=*erythro*-alkoxide. d) T=*threo*-alkoxide.

The product distributions from elimination reactions of 2-, 3-pentyl and 4-heptyl bromides and tosylates with pairs of diastereoisomeric sodium alkoxides, **1**—**6**, in dimethyl sulfoxide are given in Tables 2 and 3. In these runs the results are much less complicated than those in Table 1, because neither an alcoholic cosolvent was present nor the polarity of the solvent varied. The remarkable feature of the results is that all the pairs of diastereoisomeric alkoxides examined gave definitely different product distributions. With 4-heptyl systems the *erythro*-alkoxides always produced larger *cis* to *trans* ratios than the *threo*-alkoxides except for the diastereoisomeric diphenylpropoxides **6** with which the ratios were just the opposite to those for the other members.[4] Generally the larger the steric bulk of the attacking base, the larger the difference in the product distribution between the pair of diastereoisomeric bases. By comparing the results of 2- and 3-pentyl systems with those of 4-heptyl system, the alkyl substituents on the α and the β′ carbons of the substrate seems to play a certain role in controlling the steric interactions between the substrate and the attacking base, that is, the larger the alkyl substituents on the substrate, the larger the ratio of $(cis/trans)_E$ to $(cis/trans)_T$ with a given pair of diastereoisomeric alkoxides.

As mentioned, since the base strength should be of little difference between a pair of diastereoisomeric bases, it must contribute little to the variation of the product distribution, so that a steric factor must be the controlling one. The relationship generally observed between the reactivity and the selectivity[5] will also ascertain steric factors to be responsible for the variation of the product distribution. Though, strictly speaking, the comparison of the product distributions should be limited within a given pair of diastereoisomeric bases only where the strength of the bases is held constant, the apparent trend of the change in the product distribution with different pairs of bases is opposite to that predicted by the change in the base strength, that is, the variation of the alkyl substituents R^1 or R^2 in the alkoxide from methyl to ethyl to *n*-butyl (from **1** to **2** to **3** or from **2** to **4** to **5**) should make the alkoxide base stronger, so that a decrease in selectivity (expressed in $(cis/trans)_E/(cis/trans)_T$) would be anticipated in this order. The selectivity observed, however, is just the opposite (Table 3).

The contribution of the parent alcohol produced during reaction to the variation of the product distribution appears to be negligible, since no effect of a pair of diastereoisomeric alcoholic solvent was observed when a large amount of dimethylformamide, as a cosolvent, was present (see below).

Recent studies on the stereochemistry of the base-promoted elimination reactions have revealed that a *syn-anti* dual mechanism of elimination prevails a wide range of conditions of the base and the solvent properties and the substrate structure.[6)] In general, a *syn* mechanism appears to become important when the substrate carries large alkyl substituents on the both α positions to the leaving group and a poor leaving group such as trimethylammonio, and when the elimination is effected by a bulky and strong base in a poor ion dissociating solvent such as *tert*-butoxide in *tert*-butanol or in benzene. With the systems examined here, incursion of a *syn* mechanism seems unlikely to be a significant factor to the *cis* to *trans* ratio. A *syn* mechanism accounts for only 10 per cent of the overall reaction in the reaction of 5-decyl tosylate with *tert*-butoxide in *tert*-butanol,[6f)] and even smaller contributions of the mechanism with the same substrate have been reported when a good ion dissociating solvent was used (5.2 and 4.2 per cent of the overall reaction with *tert*-butoxide in dimethylformamide[6f)] and in dimethyl sulfoxide[6i)] respectively). With secondary alkyl bromides the mechanism seems to contribute to the *cis* to *trans* ratio even lesser extent than with secondary alkyl tosylates.[6g)]

These results confirm unambiguously that the steric requirement of the attacking base to be an important contributing factor to the product distribution in base-promoted elimination reactions.

Effects of Diastereoisomeric Solvents. Using pairs of diastereoisomeric alcohols **1**, **2** and **3** as solvent, the olefinic product distributions from elimination reactions of 4-heptyl bromide and tosylate were examined under a variety of conditions, and the results are collected in Tables 4 and 5. As anticipated, the effect of the diastereoisomeric solvent, *i.e.*, the steric requirement for solvation, upon the product distribution was less pronounced compared to that of the diastereoisomeric attacking base in Tables 2 and 3. From the Tables it is clearly seen that the effect of the steric requirement for solvation upon the product distribution changes in a complex manner by the nature of the reaction medium and by the attacking base. With the bicyclic amine base known as a very efficient dehydrohalogenating agent,[7)] the difference in the product distribution, *i.e.*, the selectivity, between a given pair of diastereoisomeric solvents gradually decreased with increasing the steric bulk of the solvent molecule, whereas complex changes in the product distributions were observed with phenoxide base. In the presence of 18-Crown-6 ether which has been believed to make an alkoxide base reactive by dissociating ion paired species,[6g,6h)] a maximum selectivity was observed in the diastereoisomeric phenylheptanols **3**. When 25 volume per cent of dimethylformamide was present as a cosolvent,[8)] a maximum selectivity was obtained from the eliminations of the bromide in the diastereoisomeric phenylpentanols **2**. The tosylate, though only two pairs of diastereoisomeric alcohols **1** and **2** were examined, showed a similar change to that of the bromide. In the presence of 50 and 75 volume per cent of the cosolvent, no selectivity between a given pair of diastereoisomeric solvents could be observed from elimination reactions of either the bromide and the tosylate.

Neither the stereochemistry of these elimination reactions nor the details of the interactions between the reactants and the solvent molecules are known, but these results show definitely that it is necessary to take into account the structural effects of the solvent molecule as well as the polarity of the solvent,[9)] when

Table 4. Product distributions from elimination reactions of 4-heptyl bromide with DBU[a)] in diastereoisomeric alcoholic solvents at 50 °C[b)]

Solvent	$\frac{cis}{trans}$	$\frac{(cis/trans)_{erythro}}{(cis/trans)_{threo}}$
erythro-**1**	0.0768	1.08
threo-**1**	0.0708	
erythro-**2**	0.0760	1.06
threo-**2**	0.0716	
erythro-**3**	0.0692	1.03
threo-**3**	0.0674	

a) 1,8-Diazabicyclo[5.4.0]undec-7-ene. b) $[\text{subst.}]_i=$ 0.1 M. $[\text{DBU}]_i=0.5$ M. Reaction period, 50 hr.

Table 5. Product distributions from elimination reactions of 4-heptyl-X with sodium phenoxide[a)] in diastereoisomeric alcoholic solvents

X in Subst.[b)]	Solvent[c)]	$\frac{cis}{trans}$	$\frac{(cis/trans)_E}{(cis/trans)_T}$
Br	E-**1**+DMF[d)]	0.153	1.02
Br	T-**1**+DMF[d)]	0.150	
Br	E-**2**+DMF[d)]	0.139	0.921
Br	T-**2**+DMF[d)]	0.151	
Br	E-**3**+DMF[d)]	0.143	0.947
Br	T-**3**+DMF[d)]	0.151	
OTs	E-**1**+DMF[d)]	0.405	0.998
OTs	T-**1**+DMF[d)]	0.406	
OTs	E-**2**+DMF[d)]	0.369	0.932
OTs	T-**2**+DMF[d)]	0.396	
Br	E-**1**+Crown[e)]	0.167	1.03
Br	T-**1**+Crown[e)]	0.162	
Br	E-**2**+Crown[e)]	0.161	1.01
Br	T-**2**+Crown[e)]	0.159	
Br	E-**3**+Crown[e)]	0.176	0.941
Br	T-**3**+Crown[e)]	0.187	

a) $[\text{phenoxide}]_i \fallingdotseq 0.2$ M. b) $[\text{subst.}]_i \fallingdotseq 0.1$ M. c) E=*erythro*-alcohol, T=*threo*-alcohol. DMF=dimethylformamide, 25 v/v%. Crown=18-Crown-6 ether, 0.2 M. d) at 40 °C for 15 hr. e) at 50 °C for 2 hr.

the solvent effects upon the product distribution in the elimination reactions are considered.

Experimental

Materials. *2-Pentyl, 3-Pentyl, and 4-Heptyl Bromides*: The bromides were prepared by treating the corresponding alcohols with triphenyl phosphite dibromides at −10—0 °C.[10)] 2-Pentyl bromide, bp 117—118 °C, $n_{\rm D}^{20}$ 1.4409 (lit.,[9a)] bp 58.4—58.8 °C/100 mmHg, $n_{\rm D}^{20}$ 1.4412); 3-pentyl bromide, bp 47 °C/60 mmHg, $n_{\rm D}^{20}$ 1.4454 (lit.,[9a)] bp 59—59.5 °C/100 mmHg, $n_{\rm D}^{20}$ 1.4444); 4-heptyl bromide, bp 64—65 °C/24 mmHg, $n_{\rm D}^{20}$ 1.4501 (lit.,[11)] bp 75—75.5 °C/38 mmHg, $n_{\rm D}^{25}$ 1.4478).

2-Pentyl, 3-Pentyl, and 4-Heptyl Tosylates: The tosylates were prepared by the standard method.[12)] 2-Pentyl tosylate, $n_{\rm D}^{20}$ 1.5008 (lit.,[9e)] $n_{\rm D}^{20}$ 1.4995); 3-pentyl tosylate, mp 44.6—44.8 °C (lit.,[9a)] mp 42—44 °C); 4-heptyl tosylate, $n_{\rm D}^{20}$ 1.4978. Found: C, 62.33; H, 8.44%. Calcd for $C_{14}H_{22}O_3S$: C, 62.20; H, 8.20%.

18-Crown-6 Ether: This macrocyclic polyether was prepared according to Greene.[13)] mp 39.7—40.7 °C, PMR ($CDCl_3$) δ 3.7 (s) (lit.,[13)] mp 39.5—40.5 °C, PMR ($CDCl_3$) δ 3.67 (s)).

1,8-Diazabicyclo[5.4.0]undec-7-ene: A commercial sample was dried over potassium hydroxide and distilled under reduced pressure. bp 96—97 °C/3 mmHg.

*Diastereoisomeric Alcohols, **1**—**6***: The alcohols **1**, **2**, **4**, and **6** were prepared and separated into the diastereomers according to Cram *et al.*[14)] The alcohol **3** obtained by the action of *n*-butyl-magnesium bromide upon 2-phenylpropionaldehyde, bp 137—140 °C/14 mmHg (lit.,[15)] bp 156—160 °C/30 mmHg), was separated into the diastereomers *via* their ester derivatives. 4-Phenyl-3-octanone obtained by *n*-butylation of ethyl benzyl ketone, bp 142—145 °C/14.5 mmHg, semicarbazone, mp 105—106 °C (lit.,[15)] bp 147—150 °C/16 mmHg, semicarbazone, mp 104—105 °C) was reduced to **5** by sodium borohydride, bp 146.5—147.5 °C/15 mmHg. The diastereomers were separated *via* their ester derivatives. The properties of the alcohols and their derivatives are collected in Table 6.

Purification of Solvents. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure. Dimethylformamide was first dehydrated by distilling with anhydrous benzene, dried over Driereit and then redistilled under reduced pressure. Acetonitrile was distilled from phosphorus pentoxide. Diethyleneglycol dimethyl ether was distilled from lithium aluminum hydride under reduced pressure. 3-Methyl-3-pentanol was purified by distilling twice from sodium metal.

Preparation of Base Solutions. A. Sodium hydride (Ventron Co., dispersed in mineral oil) was washed three to four times with anhydrous *n*-pentane, weighed and dissolved in an appropriate amount of anhydrous dimethyl sulfoxide or a solvent mixture. The resulting solution was converted into the desired alkoxide solution by adding a slightly excess of the calculated amount of an alcohol.

B. Phenoxide solutions were prepared by dissolving sodium hydride into an appropriate solvent mixture containing a calculated amount of phenol. All the preparations were operated under dry nitrogen atmosphere.

Procedure for Elimination Reactions. An appropriate amount (2 to 5 ml) of the base solution was pipetted into an ampoule with a serum stopper under dry nitrogen atmosphere. The substrate was added by a syringe through the stopper just before the reaction. The ampoule was sealed and reacted in a thermostated bath.

Analysis of the Reaction Mixtures. The reaction mixture was poured into about 100 ml of cold water and extracted with 1 to 1.5 ml of *n*-pentane when the reaction was fast. With slow reactions 1 ml of *n*-pentane was added to the reaction mixture and the low boiling fractions were distilled into a dry ice–acetone trap under reduced pressure (about 30 mmHg) at room temperature. The pentane solutions were analyzed for the olefins produced by glpc on JEOL Model JGC 20K or JGC 1100 instruments. The pentenes were analyzed on a 3 m×3 mm column of silver nitrate in *p*-methoxybenzyl cyanide on Celite 545 at 25 °C. The heptenes were analyzed on a 2 m×3 mm column of silver nitrate in benzyl cyanide on Celite 545 at 35 °C (JGC 1100) or on 3 m×3 mm column of silver nitrate in *p*-nitrobenzyl cyanide on Celite 545 at 35 °C (JGC 20K). The *cis* to *trans* ratios obtained from the peak heights were calibrated by the standard curves prepared by analyzing the *cis-trans* mixtures of known compositions under the same conditions.

Control Experiments. Neither synthetic *cis*- nor *trans*-3-heptenes were isomerized on exposure to the reaction condition, 0.2 M of sodium 3-phenyl-2-butoxide (a mixture of *threo*- and *erythro*-isomers) in dimethyl sulfoxide at 35 °C for 60 min.

No isomerizations between the pairs of diastereoisomeric alkoxides could be detected for the recovered alcohols, **1** and **2**, from the elimination reactions carried out in dimethyl

Table 6. Properties of the alcohols **1**—**6** and their derivatives

Alcohol[a)]	Bp (mp) (°C)	Isomeric[b)] Purity (%)	Deriv.[c)]	Recrystn.[d)] Solvent	mp (°C)
1 T	103.5—104/15[e)]	97.8	AP	AcOEt-PE	130—131.3[e)]
1 E	107.8—108/16[e)]	98.5	ANP	AcOEt-PE	160—161[e)]
2 T	125/20[f)]	97	AP	AcOEt-PE	137—138[f)]
2 E	127—127.2/22[f)]	98.6	ANP	AcOEt-PE	155—157[f)]
3 T	136.3—137.7/13.5[g)]	96	AP	E-PE	95—96
3 E	138—140/14.5[g)]	99.6	PNB	EtOH	39—39.2
4 T	134—134.8/22[h)]	96.1	AP	E-P	126—127[h)]
4 E	(44.8—45)[h)]	98.3			
5 T	112—113/3.5	99.8	AP	E-PE	122—123
5 E	110/3, (46—46.5)	99.8	DNB	MeOH	61—62
6 T	136—136.5/3[i)]	—[j)]	PNB	Benzene	142—143[i)]
6 E	(50—51)[i)]	—[j)]			

a) T=*threo*, E=*erythro*. b) The purity was estimated by the relative glpc peak heights. PEG 20 M on Diasolid L 2 m. c) AP=acid phthalate, ANP=acid 3-nitrophthalate, PNB=*p*-nitrobenzoate, DNB=3,5-dinitrobenzoate. d) PE=petroleum ether, E=ether, P=*n*-pentane. e) ref. 14a. f) ref. 14b. g) ref. 15. h) ref. 14c. i) ref. 14d. j) No separation could be attained on glpc.

sulfoxide.

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2) A similar tendency was observed between the diglyme–methylpentanol and the pure diglyme systems. In diglyme, the diastereoisomeric alkoxides **2** gave the ratios, $(cis/trans)_E/(cis/trans)_T$, of 1.16 and 1.24 with 4-heptyl bromide and tosylate respectively.

3) Ref. 1a. p. 190.

4) The irregularity is only a superficial, *i.e.*, the configuration of the *threo*-alcohol **6** corresponds to those of the *erythro*-alcohols **1**—**5**.

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