Orientation of Olefin-Forming Elimination in Reactions of 2-Substituted Hexanes with Potassium *t*-Butoxide–*t*-Butyl Alcohol and Sodium Methoxide–Methanol[1,2]

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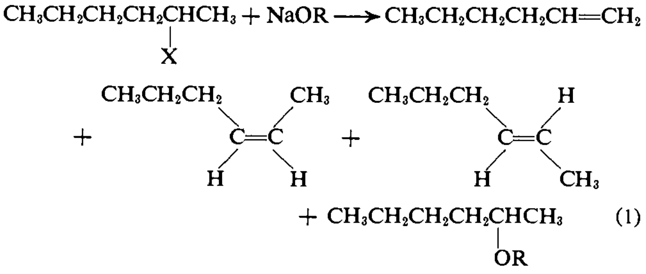
Abstract: Reactions of 13 2-substituted hexanes with *t*-BuO$^-$K$^+$–*t*-BuOH and of 10 of the same substrates with $NaOCH_3$–CH_3OH are studied. Compositions of the olefin mixtures formed under conditions in which olefin isomerization is negligible are determined. In *t*-BuO$^-$K$^+$–*t*-BuOH, three 2-hexyl arenesulfonates, 2-hexyl 2,4,6-trimethylbenzoate, 2-hexyl phenyl sulfone, and 2-hexyl diphenyl phosphate give more *cis*- than *trans*-2-hexene, but all substrates studied give more *trans*- than *cis*-2-hexene in $NaOCH_3$–CH_3OH. Hofmann orientation predominates with all substrates in *t*-BuO$^-$K$^+$–*t*-BuOH, and is more accentuated from the 2-hexyl halides than from the 2-butyl halides in the same base–solvent system. Most of the observations of both positional and geometrical orientation are in accord with the theory of the variable E2 transition state, but the preferential formation of *cis*- over *trans*-2-hexene from certain substrates is thought to be of steric origin.

Although orientation of olefin-forming elimination has long been a problem,[5–7] and although there has been considerable activity in this area in recent years,[8–10] the effects of certain variables are incompletely explored.

In the present research, the effects of varying the leaving group are studied in two base–solvent systems. Leaving-group influences are prominent in all modern discussions of the orientation problem, but little attention has been given to leaving groups outside a familiar set of old favorites: the halogens, arenesulfonoxy groups, trialkylammonio, dialkylsulfonio, and sulfonyl groups.

Results

Reactions with Sodium Methoxide–Methanol. Reactions of several 2-substituted hexanes with $NaOCH_3$–CH_3OH occur according to eq 1, in which R = CH_3. In this base–solvent system, elimination rates are very slow when the leaving group is a poor one, and it was practical to study only ten of our substrates. Results are set forth in Table I. The leaving groups represented are the halogens, three arenesulfonoxy groups, and the phenylseleno, 2,4,6-trimethylbenzoyloxy, and phenylsulfonyl groups. All olefin yields were determined by glpc.



The data for the 2-hexyl halides and 2-hexyl *p*-bromobenzenesulfonate in Table I are selected from an earlier publication,[11] which should be consulted for more extensive detail. The total hexenes yield data for the four 2-hexyl halides and the three 2-hexyl arenesulfonates are yields at completion of reaction; the differences between the figures listed and 100% represent 2-hexyl methyl ether. However, the total hexenes yield data for the last three substrates are merely the yields which were formed during the reaction times indicated. Nonolefinic products from those three reactions were not determined. The last three substrates react very sluggishly, and the differences between the tiny olefin yields and 100% represent mainly unreacted starting materials.

The hexene product ratios in Table I are kinetically determined. Isomerization of 1-hexene is negligible and 2-hexyl methyl ether is unreactive under the most strenuous conditions involved in Table I.[11]

Reactions with Potassium *t*-Butoxide–*t*-Butyl Alcohol. In this base–solvent system, elimination rates were greater and measurable amounts of olefins could be obtained even from quite unreactive substrates. The results obtained are listed in Table II. In cases where the total hexenes yield is 80% or greater, the discrepancy from 100% probably represents by-products and/or error of measurement, but in other cases a large part of it is ascribed to incompleteness of reaction.

In *t*-BuO$^-$K$^+$–*t*BuOH, olefin isomerization rates

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[1] Based on the Ph.D. Dissertation of R. A. Bartsch, June 1967; *Diss. Abstr.*, **28**, 3212-B (1968).

[2] Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

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[5] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

[7] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **78**, 2203 (1956).

[8] J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); *Angew. Chem. Int. Ed. Engl.*, **1**, 225 (1962).

[9] W. H. Saunders, Jr., in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 149.

[10] J. F. Bunnett, *Surv. Progr. Chem.*, in press.

[11] R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968).

Table I. Products from Reactions of 2-Substituted Hexanes with Sodium Methoxide in Methanol

Leaving group, X	Leaving group no.	Temp, °C	Time, min	Total hexenes yield, %	Per cent of total hexenes			2:1	*trans*:*cis*	Reactivity index
					1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene			
I	1	100	*a*	84.0	19.3	63.0	17.6	4.2	3.6	−1.94
Br	2	100	*a*	75.0	27.6	54.5	17.9	2.6	3.0	−2.54
Cl	3	100	*a*	65.4	33.3	49.5	17.1	2.0	2.9	−4.12
F	4	100	*a*	56	69.9	21.0	9.1	0.43	2.3	−6.96
OBs[b]	5	100	*a*	36	41.7	36.3	22.0	1.4	1.7	−1.67
OSO_2Ph[c,d]		29.7	1153	10	30.5	46.2	23.2	2.3	2.0	
		44.3	1153	16	31.8	44.8	23.5	2.2	1.9	
		59.8	133	20	32.9	43.2	23.9	2.0	1.8	
OTs[d,e]		44.3	1085	14	32.8	44.4	22.9	2.0	1.9	
		59.8	150	15	34.5	42.6	22.9	1.9	1.9	
OTMB[f]	6	164.4	150	0.20	63.2	24.8	12.0	0.59	2.1	−9.6
SeC_6H_5	9	164.4	150	2.0	52.6	30.4	17.1	0.90	1.8	−8.6
$SO_2C_6H_5$	11	164.4	150	3.8	87.2	7.0	5.8	0.15	1.2	−8.1

[a] Data at completion of reaction, selected from ref 11. [b] *p*-Bromobenzenesulfonoxy group; the data listed are corrected for the contribution of solvolysis, and represent only reaction with $NaOCH_3$. [c] Benzenesulfonoxy group. [d] The data listed are composite, representing both solvolysis and reaction with $NaOCH_3$. [e] *p*-Toluenesulfonoxy group. [f] 2,4,6-Trimethylbenzoyloxy group.

Table II. Products from Reactions of 2-Substituted Hexanes with 1.03 *M* Potassium *t*-Butoxide in *t*-Butyl Alcohol

Leaving group, X	Leaving group no.	Temp, °C	Time, min	Total hexenes yield, %	Per cent of total hexenes			2:1	*trans*:*cis*	Reactivity index
					1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene			
I	1	29.7	1030	78	77.8	14.8	7.4	0.29	2.0	
		50.8	985	92	74.8	16.4	8.7	0.34	1.9	
		75.8	940	92	73.0	17.6	9.4	0.38	1.9	
		99.0	130	87	69.0	19.8	11.1	0.45	1.8	−1.8
Br	2	29.7	1460	46	89.2	6.2	4.6	0.11	1.3	
		50.8	1460	91	86.6	7.3	6.0	0.15	1.2	
		75.8	1460	89	83.6	9.3	7.2	0.20	1.3	
		99.0	130	94	80.2	11.5	8.3	0.25	1.4	−2.4
Cl	3	50.8	2225	21	91.1	4.5	4.4	0.10	1.0	
		75.8	1115	64	90.8	4.9	4.3	0.10	1.1	
		99.0	1175	90	87.6	6.6	5.8	0.14	1.1	−3.8
F	4	99.0	1440	6.8	97.4	1.4	1.2	0.027	1.2	−6.1
OBs[a]	5	29.7	227	50	84.2	2.6	13.2	0.18	0.20	
		44.3	180	77	83.2	3.2	13.6	0.20	0.24	
		50.8	132	83	82.5	3.6	13.9	0.21	0.26	
		99.0	155	82	80.0	5.7	14.4	0.25	0.40	−1.5
OSO_2Ph[b]		50.8	410	80	82.7	3.6	13.7	0.21	0.26	
		75.8	369	86	81.8	4.4	13.9	0.22	0.32	
		99.0	448	78	81.1	5.0	13.9	0.23	0.36	
OTs[c]		50.8	285	89	82.9	4.1	13.0	0.21	0.31	
		75.8	255	82	80.3	5.2	14.4	0.24	0.36	
		99.0	215	83	81.8	4.8	13.5	0.22	0.35	
OTMB[d]	6	99.0	3600	2.7	92.6	2.2	5.2	0.080	0.41	−6.9
		129.5	390	3.7	91.7	2.7	5.6	0.090	0.48	
OC_6H_5	7	129.5	316	0.48	82.0	10.3	7.7	0.22	1.35	−8.1
SC_6H_5	8	129.5	425	0.10	69.0	20.2	10.8	0.45	1.87	−9.0
SeC_6H_5	9	129.5	235[e]	0.65	77.5	14.6	7.9	0.29	1.8	
		129.5	1370[e]	2.3	80.5	10.0	9.4	0.24	1.1	−8.0
ODPP[f]	10	99.0	750	2.6	89.4	3.6	7.0	0.12	0.52	−6.8
		129.5	320	3.9	89.0	3.6	7.4	0.12	0.48	
$SO_2C_6H_5$	11	99.0	1298	3.7	98.9	0.4	0.7	0.011	0.63	−6.3
		129.5	135	12	97.9	0.8	1.4	0.022	0.55	

[a] *p*-Bromobenzenesulfonoxy group. [b] Benzenesulfonoxy group. [c] *p*-Toluenesulfonoxy group. [d] 2,4,6-Trimethylbenzoyloxy group. [e] Data at two intermediate times (Dissertation, R. A. B.) suggest that the apparent trend of olefin product ratios with time is real. [f] $OPO(OC_6H_5)_2$; see text regarding complications in this case.

must be taken into account. Table III summarizes the results of two experiments in which 1-hexene was exposed to 1.0 *M* $t\text{-BuO}^-K^+$ in *t*-BuOH for various periods of time. At 99°, 1.6% of the 1-hexene was isomerized to 2-hexenes in 60 hr. Only one experiment at 99° in Table II involved a reaction time as long as 60 hr, and the small fraction of isomerization of the predominant 1-hexene product that occurred in that experiment is at the level of experimental error. Product isomerization was negligible in all the other experiments at 99° or lower.

At 129.5°, isomerization of 1-hexene was faster.

Table III. Isomerization of 1-Hexene by 1.0 *M* Potassium *t*-Butoxide in *t*-Butyl Alcohol

Temp, °C	Reaction time, hr	Per cent of total hexenes 1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene
99.0	0	100		
99.0	60.0	98.4	0.3	1.3
129.5	0	100		
129.5	4.5	97.9	0.2	1.9
129.5	6.7	96.8	0.6	2.8
129.5	20.0	90.8	1.6	7.6
129.5	26.2	86.8	2.2	9.7
129.5	28.5	86.6	2.3	11.2

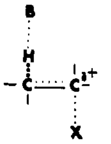
When per cent of any hexene from Table III is plotted against time, a linear plot is obtained.[12] On the assumption that isomerization is first order in t-BuO$^-$K$^+$, the approximate rate coefficients are: 1-hexene to *cis*-2-hexene, 1.1×10^{-6} M^{-1} sec^{-1}, 1-hexene to *trans*-2-hexene, 2.1×10^{-7} M^{-1} sec^{-1}. Other workers have previously observed that base-catalyzed isomerization of 1-alkenes forms *cis*-2-alkenes preferentially.[13]

In most of the 129.5° experiments of Table II, the reaction time was 425 min (7.1 hr) or less, and Table III indicates that less than 3% of the 1-hexene initially formed was isomerized to 2-hexenes. The considerable agreement between the product ratios at 99 and 129.5° for three substrates suggests that the small amount of isomerization which occurred at 129.5° was of little consequence. In the one case (2-hexyl phenyl selenide) where a long (22.8 hr) reaction time was used at 129.5°, the measured proportion of 1-hexene was actually higher than after a shorter time! We suspect that a trace of impurity in that substrate may be responsible for this minor irregularity.

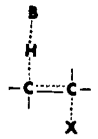
Potassium *t*-butoxide induced elimination from *sec*-alkyl halides and arenesulfonates has been studied by other workers in recent years.[14-16] The trends in the *trans*/*cis* and 2-hexenes/1-hexene ratios which are evident among the halides in Table II are similar to those recorded by other investigators.[15b] Also, the predominance of *cis*- over *trans*-2-alkenes from *sec*-alkyl arenesulfonates has been noted previously.[15a,16b] However, Hofmann orientation is more accentuated in the 2-hexyl than in the 2-pentyl or 2-butyl series.

Discussion

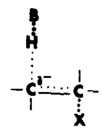
Theory of the Variable E2 Transition State. This theory[17a] has proven useful for interpretation and prediction of orientation phenomena and other aspects of E2 reactions. It postulates that the relative degrees of breaking of the C_α–X and C_β–H bonds vary, at the transition state, from an extreme in which the former is extensively and the latter but slightly broken to an opposite extreme in which the C_α–X bond is almost but not wholly intact and the β-H is extensively transferred to the base. The former extreme approaches in character the transition state for the carbonium ion forming step of the E1 mechanism, but differs in that it includes the base in a functional role, and is represented by structure **1**. In earlier discussions it was called the "nearly E1" extreme, but we now propose to call it the *paenecarbonium*[17b] extreme. The opposite paenecarbanion (earlier designated as "nearly carbanion") extreme, represented by structure **3**, approaches in character the transition state for the first step of the carbanion or E1cb mechanism of elimination. Between these extremes lies a continuum of transition states of intermediate character; in a strictly "central" transition state (**2**), the degrees of C_α–X and C_β–H rupture are equal, and double-bond character in the developing double bond is maximum.



1
paenecarbonium



2
central



3
paenecarbanion

The theory further postulates that the character of an E2 transition state is governed by a number of structural and environmental factors, and that tangible expression of transition-state character may be found in rate data or in product ratios. For present purposes, the determinants of transition state character of chief interest are the leaving group (a poorer leaving group causes greater paenecarbanion character), the solvent (a solvent of lower dielectric constant and lesser tendency to hydrogen bond to anions causes greater paenecarbanion character when the leaving group is initially neutral and the base is an anion), and the base (a stronger base probably causes greater paenecarbanion character[17c]).

The experimental consequences of transition-state character of present interest are *positional orientation*, that is, the relative rates of double bond formation to alternative β-carbons differently substituted with alkyl groups, and *geometrical orientation*, referring to the relative proportions of *trans* and *cis* isomeric olefins formed. A β-alkyl substituent has an energetically favorable (inductive and hyperconjugative) interaction with paenecarbonium and central transition states, but an unfavorable (inductive) interaction with a partial negative charge of C_β in paenecarbanion transition states, and therefore positional orientation shifts gradually from favoring to disfavoring double bond formation toward a β-alkyl group (that is, from Saytzeff to Hofmann orientation) as the transition state changes from a paenecarbonium or central type toward the paenecarbanion extreme. Eclipsing of *cis*-destined alkyl groups, with resultant steric crowding, is greater the greater the degree of double bond character, and therefore higher *trans*/*cis* ratios are expected from central transition states than from those toward either extreme.

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(12) See the Dissertation of R. A. Bartsch.

(13) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **83**, 3731 (1961).

(14) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956).

(15) (a) H. C. Brown and R. L. Klimisch, *ibid.*, **87**, 5517 (1965); (b) *ibid.*, **88**, 1425 (1966).

(16) (a) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965); (b) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966).

(17) (a) See ref 8 and 10 and references cited therein. (b) From the Latin *paene*, "almost." (c) The evidence on the effect of base strength is not wholly consistent. *Cf.* D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967); W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *ibid.*, **90**, 1775 (1968).

Reactions with Sodium Methoxide–Methanol. The olefin product ratios obtained from the 2-hexyl halides in this system are in excellent accord with the theory of the variable E2 transition state, providing that the 2-hexyl iodide transition states are "central" or somewhat toward the paenecarbanion side. As the leaving group becomes worse, the transition states shift ever more toward the paenecarbanion extreme, with consequent decrease in both the 2-hexenes/1-hexene and *trans*/*cis* ratios. These effects are evident in the 2-hexyl halide data of Table I. The 2-hexyl *p*-bromobenzenesulfonate product ratios conform approximately but not exactly to that pattern, and there are indications that formation of both 2-hexenes, but especially the *trans* isomer, are retarded by what is presumed to be a steric effect.[11] The olefin ratios from the 2-hexyl halides and *p*-bromobenzenesulfonate are discussed more fully elsewhere.[11]

The predictions of the theory, that both the 2-hexenes/1-hexene ratio and the *trans*/*cis* ratio should be low when the leaving group is a very poor one, are qualitatively satisfied by the data displayed in Table I. A more quantitative examination of these effects is provided by plotting logarithms of product ratios against a logarithmic measure of reactivity in forming 1-hexene, which we call the *reactivity index*. This index is, roughly speaking, the logarithm of the pseudo-first-order rate coefficient for the 1-hexene-forming reaction with 2 *M* $NaOCH_3$ at 100°.[18] Plots of log (*trans*/*cis* ratio) and log (2-hexenes/1-hexene ratio) against reactivity index are presented as Figures 1 and 2, respectively. The lines drawn are based mainly on the halogen points.

The plot in Figure 1 shows that the *trans*/*cis* ratios from 2-hexyl phenyl selenide and 2-hexyl 2,4,6-trimethylbenzoate are in fair accord with extrapolation from the 2-hexyl halides. However, the phenyl sulfone and *p*-bromobenzenesulfonate give exceptionally low proportions of *trans*-2-hexene.

As to the 2-hexenes/1-hexene ratio (Figure 2), the phenyl sulfone gives relatively more 1-hexene than extrapolated from the halide data, while the phenyl selenide and 2,4,6-trimethylbenzoate give less than expected.

Over-all, the product ratios in methanol are somewhat as expected from the theory of the variable E2 transition state and the ease or difficulty of breaking the various C–X bonds. The imperfections of correlation in Figures 1 and 2 may perhaps be attributed to neglect of other factors, of which the inductive effects of the leaving groups and steric interactions come immediately to mind.

Reactions with Potassium *t*-Butoxide–*t*-Butyl Alcohol. Two features of the data in Table II that catch the eye are the strong predominance of Hofmann elimination from the halides (around 90% of 1-hexene even from the bromide and chloride) and the formation of *cis*-2-hexene in excess of its *trans* isomer from several substrates. The latter include not only arenesulfonate esters, for which the preferential formation of *cis*-2-alkene has previously been noted in the 2-butyl and 2-pentyl series,[15a,16b,19] but also 2-hexyl 2,4,6-trimethylbenzoate, 2-hexyl phenyl sulfone, and 2-hexyl diphenyl phosphate.

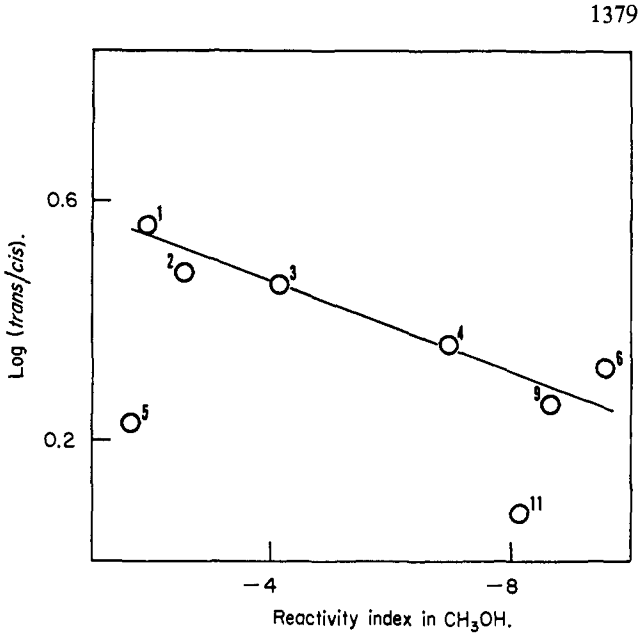

Figure 1. Relation of log (*trans*/*cis* 2-hexenes ratio) to reactivity index, for reactions in $NaOCH_3$–CH_3OH. Leaving groups are identified by number; see Table I.

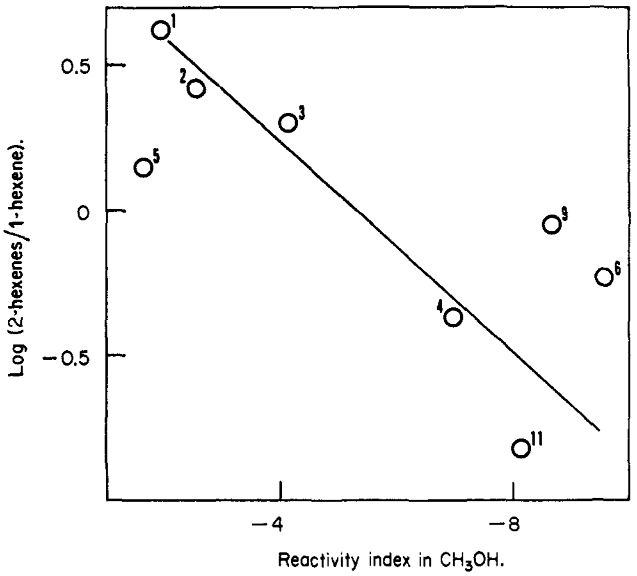

Figure 2. Relation of log (2-hexenes/1-hexene ratio) to reactivity index, for reactions in $NaOCH_3$–CH_3OH. Leaving groups are identified by number; see Table I.

The preponderance of 1-hexene from 2-hexyl chloride and t-BuO^-K^+–BuOH is of possible preparative interest. Potassium triethylmethoxide has been reported to surpass t-BuO^-K^+ in causing a predominance of Hofmann elimination from alkyl chlorides, and has been advocated for use as a preparative reagent,[20] but for some purposes the economy and convenience of *t*-butoxide may make it the reagent of choice.

[18] For the first five substrates in Table I, the reactivity index was calculated from accurate kinetic data,[11] but for the last three it was estimated from yield data on incomplete reactions by the formula: *reactivity index* = log [(fractional yield of 1-hexene)/(time in seconds)]/(temperature correction factor). The temperature correction factors (chosen by rule of thumb) were, respectively, 500 and 25 for data at 164.4 and 129.5°.

[19] R. L. Klimisch, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1964.

[20] D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem. Commun.*, 90 (1968); S. P. Acharya and H. C. Brown, *ibid.*, 305 (1968).

Hofmann elimination is more accentuated with the 2-hexyl halides in this base–solvent system than with the 2-butyl halides. For example, the olefin mixture formed from 2-butyl bromide at 50° is only 54% 1-butene,[15b] whereas that from 2-hexyl bromide at the same temperature is 87% 1-hexene. This dependence of Hofmann elimination on alkyl chain length is much sharper than in the $NaOCH_3$–CH_3OH system: the 1-alkene/2-alkenes ratio changes from 0.17 (2-butyl bromide)[21] to 0.28 (2-hexyl bromide) in $NaOCH_3$–CH_3OH and from 1.17 to 6.46 in t-BuO^-K^+–t-BuOH. The increase in this ratio is 1.6-fold in $NaOCH_3$–CH_3OH, between 2-butyl and 2-hexyl bromide, and 5.5-fold in t-BuO^-K^+–BuOH.

The explanation is undoubtedly steric: problems arise in the 2-hexene-forming transition states stemming from interaction between the *n*-propyl group on C_β and the large *t*-butoxide ion, problems which do not arise or are less serious when the base is smaller (methoxide ion), when the β-alkyl substituent is smaller (methyl instead of *n*-propyl), or when the base attacks an alternative β-H to form 1-hexene. Two kinds of steric interaction are conceivable: compressions arising from unavoidable crowding of the *n*-propyl chain against the *t*-butoxide moiety,[7] and restrictions on rotational freedom which might arise if the transition state were obliged to assume a specific strain-free conformation, or one of a very few strain-free conformations, in order to avoid such crowding. The present results do not allow a decision between these possibilities.

Let us now consider the extent to which the data in Table II are in accord with the theory of the variable E2 transition state. Of first interest are the four 2-hexyl halides, and specifically the trends in the *trans/cis* and 2-hexenes/1-hexene ratios within the t-BuO^-K^+–t-BuOH system and between it and $NaOCH_3$–CH_3OH. At 99°, both ratios decrease regularly from the iodide to the fluoride, just as they did in $NaOCH_3$–CH_3OH, and in accord with expectations from the theory. (The *trans/cis* ratios for the chloride and fluoride, which seem to be slightly irregular, are actually the same within experimental error.) Moreover, comparison of corresponding ratios between $NaOCH_3$–CH_3OH (Table I) and t-BuO^-K^+–t-BuOH (Table II) shows that in every case the ratio is lower in the latter system. This is also as anticipated from the theory, because t-BuO^- is a stronger base than CH_3O^-, and *t*-BuOH is a poorer ionizing solvent than CH_3OH.

Plots analogous to Figures 1 and 2 are presented as Figures 3 and 4. In this case, the reactivity index represents a crude estimate of log k_ψ for formation of 1-hexene in 1 M t-BuO^-K^+ solution at 100°.[22]

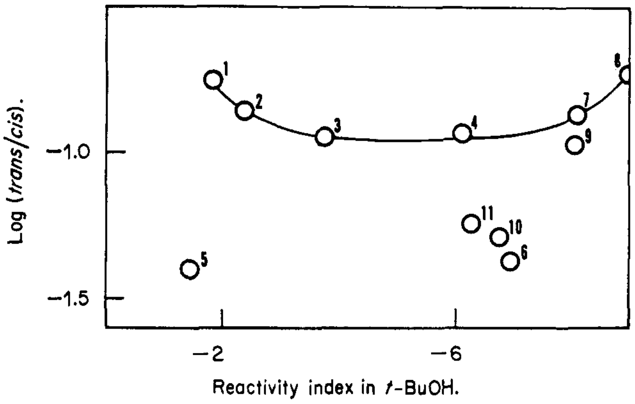

Figure 3. Relation of log (*trans/cis* 2-hexenes ratio) to reactivity index, for reactions in t-BuO^-K^+–t-BuOH. Leaving groups are identified by number; see Table II.

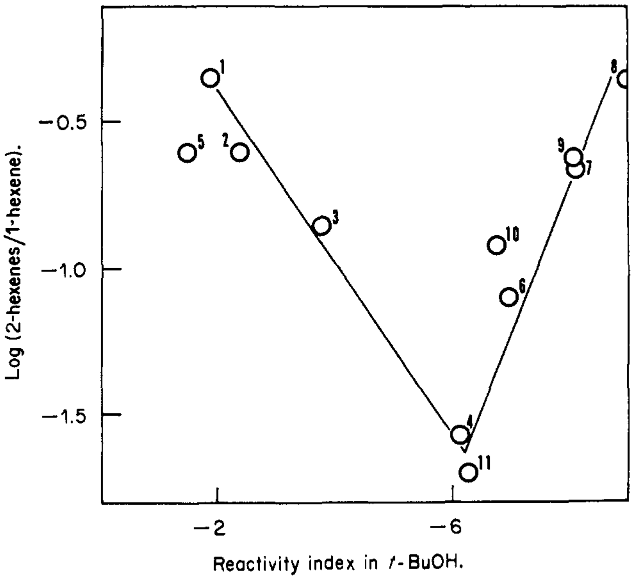

Figure 4. Relation of log (2-hexenes/1 hexene ratio) to reactivity index, for reactions in t-BuO^-K^+–t-BuOH. Leaving groups are identified by number; see Table II.

The plots in Figures 3 and 4 are both remarkable in that they appear to have a minimum at a reactivity index of about −6. The *trans/cis* plot (Figure 3) is saucer shaped, dipping at its shallow minimum to near-equality of *cis* and *trans* rates, except that four substrates give more *cis*- than *trans*-2-hexene, as mentioned above. The 2-hexenes/1-hexene plot (Figure 4) falls nearly linearly to a nadir at the phenyl sulfone, and then rises to almost its original level at the least reactive substrate.

In the case of 2-hexyl diphenyl phosphate, there is evidence that the actual leaving group is not $-OP(OC_6H_5)_2O$, but rather either $-OP(OC_6H_5)O_2^-$ or $-OPO_3^{2-}$. In addition to small amounts of hexene products, reaction of 2-hexyl diphenyl phosphate with t-BuO^-K^+–t-BuOH formed large amounts of a low-boiling substance. A similar product was formed by reaction of the same substrate and base in dimethyl sulfoxide solution,[23] and in that case the low-boiling product was shown to have an infrared spectrum identical with that of 2-methylpropene. The low-boiling products formed in both solvents had the same glpc retention time. We hypothesize that *t*-butoxide ion displaced phenoxide ion from phosphorus, and that E2

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(21) R. A. Bartsch, unpublished observations.

(22) In most cases the reactivity indices were reckoned as with $NaOCH_3$–CH_3OH[18] but with 2-hexyl iodide, bromide, chloride, and *p*-bromobenzenesulfonate the formula used was: reactivity index = log {(2.3/t) × (fraction of 1-hexene in hexenes formed) × log [(total hexenes yield at completion of reaction)/(total hexenes yield at completion of reaction less hexenes yield at time t)]}. Reactivity indices measured at 29.7° were increased by 7 log 2.5, and those measured at 50.8° by 5 log 2.5 to adjust them to 100°.

(23) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1382 (1969).

elimination from the resulting *t*-butyl phosphate ester occurred rapidly. These reactions would form either 2-hexyl phosphate dianion or 2-hexyl phenyl phosphate monoanion, depending on whether the pair of reactions occurred twice or once.

Insofar as Figures 3 and 4 are concerned, the significance of these side reactions is that the rate of reaction of *t*-butoxide ion with an anionic substrate was retarded by perhaps two to four orders of magnitude owing to the electrical charge situation.[24] Accordingly a corrected reactivity index, increased by perhaps two to four units, should be used to represent the inherent reactivity of the phosphate leaving group. Moving the phosphate point (no. 10) in Figure 4 four units to the left would bring it close to the bromine point, and thus essentially on the line which has been drawn. However, such a move for the phosphate point in Figure 3 would not bring it any closer to the saucer-shaped curve which has been drawn.

In Table II or Figure 3, the preponderance of *cis*- over *trans*-2-hexene from certain substrates can probably be associated with the steric characteristics of the leaving groups concerned.[25] Those leaving groups are either bulky because of substitution at their first atom (as with phenylsulfonyl) or they have oxygen as their first atom with bulkiness about their second atom (as with the arenesulfonoxy, phosphoryloxy, and 2,4,6-trimethylbenzoyloxy groups). Explanations for the preponderant formation of *cis*-2-alkenes from *sec*-alkyl arenesulfonates have been proposed by Brown and Klimisch[15a] and by Froemsdorf, Dowd, and Leimer;[16b] those explanations should be given careful consideration with respect to the other leaving groups now shown to have similar geometrical orientation effects.

The left segments of the two plots in Figures 3 and 4 are, as discussed above, in agreement with expectations from the theory of the variable E2 transition state. But the right segments, beyond the minima, are not in accord with that theory if, as we have assumed, the relative ease or difficulty of breaking the C–X bond is the major influence of the leaving group on transition-state character. It is possible that we have incorrectly assessed the effects of leaving groups on the character of the transition state. Another possibility is that some new variety of mechanism begins to play an important role when the leaving group is particularly sluggish, a mechanism which involves new orientation rules. But it is not clear what that new variety of mechanism might be.

As we show in the accompanying paper,[23] orientation effects in the $t\text{-BuO}^-\text{K}^+\text{-(CH}_3)_2\text{SO}$ system have many novel features, and some of them rather clearly suggest a change of mechanism.

Experimental Section

The 2-hexyl halides and 2-hexyl *p*-bromobenzenesulfonate were made as previously described.[11]

2-Hexyl Benzenesulfonate. A mixture of 15.3 g of 2-hexanol, 17.7 g of benzensulfonyl chloride, 7.9 g of pyridine, and 25 ml of benzene was stirred overnight at room temperature under nitrogen. The reaction mixture was vigorously stirred with 30 ml of hot concentrated NaOH solution for 5 min, then poured into cold 10% HCl and extracted with pentane. The pentane solution was washed with cold 5% HCl, saturated $NaHCO_3$, and water, dried with $MgSO_4$, and concentrated *in vacuo*. The residual liquid was pulled through a column of alumina using aspirator vacuum, with pentane as eluent. Evaporation of pentane *in vacuo* gave 10.3 g (43%) of clear, colorless liquid with $n^{27.5}$D 1.5070 and characteristic strong infrared absorptions at 1348 and 1176 cm^{-1} (S=O stretch). *Anal.* Calcd for $C_{12}H_{18}O_3S$: C, 59.45; H, 7.49. Found:[26] C, 59.45; H, 7.46.

2-Hexyl *p*-toluenesulfonate, prepared in 41% yield in the same manner as the benzenesulfonate, had $n^{27.5}$D 1.4944 and strong infrared absorptions at 1350 and 1175 cm^{-1} (S=O stretch). *Anal.* Calcd for $C_{13}H_{20}O_3S$: C, 60.88; H, 7.87. Found:[26] C, 60.21; H, 7.92.

2-Hexyl Phenyl Ether. A mixture of 18.8 g of phenol, 12.5 g of crushed KOH pellets, and 100 ml of dimethylformamide was heated at 100° for 0.5 hr. 2-Hexyl *p*-toluenesulfonate (40.9 g) was added, and the mixture was heated for 2.5 hr at 100°. After addition of cold water, the organic layer was separated and chromatographed on alumina, using pentane as eluent. Evaporation of pentane *in vacuo* and fractional distillation gave 10.7 g (38%) of colorless liquid with bp 231–232° (lit.[27] 129–132° (29 mm)) and n^{25}D 1.4877 (lit. [27] n^{20}D 1.4901, 1.4964). The liquid was shown to be isomer free by glpc.[28] *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found:[26] C, 80.71; H, 10.01.

1- and 3-hexyl phenyl ethers were prepared for gas chromatographic comparison purposes in the same manner as the 2-hexyl isomer. 1-Hexyl phenyl ether had bp 246.5–247.5° (lit.[29] 244.5° (761 mm)) and n^{25}D 1.4882 (lit.[29] n^{20}D 1.4920). 3-Hexyl phenyl ether had bp 228–229° and n^{25}D 1.4874 and gave the following analysis. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found:[26] C, 80.68; H, 10.18.

2-Hexyl Phenyl Sulfide. Benzenethiol (3.75 g) was added to 56 ml of 0.66 *M* sodium methoxide in methanol under nitrogen. After 0.5 hr, 8.0 g of 2-hexyl benzenesulfonate was added in small portions. After 8 hr at room temperature, water was added, and the mixture was extracted with pentane. Evaporation of pentane *in vacuo* left a colorless liquid which was pulled through a column of alumina using aspirator vacuum, with pentane as eluent. After evaporation of pentane *in vacuo*, the resulting liquid was subjected to bulb-to-bulb distillation at reduced pressure, yielding 4.9 g (76%) of liquid with $n^{27.5}$D 1.5217. *Anal.* Calcd for $C_{12}H_{18}S$: C, 74.14; H, 9.34. Found:[26] C, 74.24; H, 9.09.

2-Hexyl Phenyl Sulfone. A solution of 3.0 g of 2-hexyl phenyl sulfide in 10 ml of glacial acetic acid was treated with 7.0 ml of 30% hydrogen peroxide (*Caution:* severe heating) and heated on a steam bath for 1.3 hr. Following addition of water and extraction with benzene, the benzene solution was dried and concentrated on a steam bath. The residual liquid was purified by bulb-to-bulb distillation at reduced pressure yielding 1.6 g (47%) of clear, colorless liquid with $n^{27.5}$D 1.5155 which had characteristic strong infrared absorptions at 1300 and 1140 cm^{-1} (S=O stretch). *Anal.* Calcd for $C_{12}H_{18}O_2S$: C, 63.66; H, 8.02. Found:[26] (1) C, 63.56; H, 8.06. (2) C, 63.33; H, 7.85.

2-Hexyl phenyl selenide was prepared in 42% yield from the reaction of 2-hexyl *p*-toluenesulfonate with sodium benzeneselenate[30] in methanol in the same manner as 2-hexyl phenyl sulfide. The clear, pale-yellow liquid had $n^{27.5}$D 1.5427. *Anal.* Calcd for $C_{12}H_{18}Se$: C, 59.73; H, 7.53. Found:[26] (1) C, 59.89; H, 7.59. (2) C, 59.68; H, 7.63.

2-Hexyl 2,4,6-Trimethylbenzoate. Mesitoic acid[31] (5.0 g) was

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[24] *Cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1953, p 132.

[25] Inasmuch as isomerization of 1-hexene forms *cis*- in excess of *trans*-2-hexene (Table III), the possibility that *trans/cis* ratios of less than unity stem from this secondary reaction must be considered. This possibility is dismissed for two reasons: (a) direct measurement of isomerization rates (Table III) shows that isomerization was negligible under the reaction conditions concerned, and (b) other substrates under the same conditions gave *trans/cis* ratios greater than unity.

[26] All analyses by Triangle Chemical Laboratories, Chapel Hill, N. C.

[27] A. V. Bogdanov, M. F. Shostakovskii, and G. K. Krasil'nikova, *Izvest. Akad. Nauk SSSR*, 345 (1957); *Chem. Abstr.*, **51**, 14653 (1957); M. F. Shostakovskii and M. R. Kulibekov, *Zh. Obshch. Khim.*, **28**, 951 (1958); *Chem. Abstr.*, **52**, 17153 (1958).

[28] A 0.25 in. × 5 ft column of 20% SF-96 on Firebrick operated at 160° in an Aerograph Model 90P gas chromatograph separated 1-, 2-, and 3-hexyl phenyl ether.

[29] A. I. Vogel, *J. Chem. Soc.*, 616 (1948).

[30] D. G. Foster, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 771.

[31] D. M. Bowen, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 553

treated with 4 ml of thionyl chloride. After standing overnight at room temperature, the liquid was heated on a steam bath for 0.5 hr and then cooled. A solution formed by reaction of 0.80 g of sodium with 10.2 g of 2-hexanol was added slowly and the resulting mixture was heated for 2 hr on the steam bath. After addition of water and extraction with pentane, the pentane solution was dried and concentrated *in vacuo*. The residual liquid was chromatographed on alumina, using pentane as eluent. Evaporation of pentane *in vacuo* left 1.1 g (15%) of liquid which was homogeneous on a 0.25 in. × 2 ft gas chromatographic column of 10% Carbowax 20M on Chromosorb P operated at 170° and had $n^{27.5}\mathrm{D}$ 1.4888 and strong infrared absorptions at 1725 (C=O stretch) and 1270 cm^{-1} (C—O stretch). *Anal.* Calcd for $C_{16}H_{24}O_2$: C, 77.36; H, 9.75. Found:[26] C, 77.90; H, 9.60.

Diphenyl 2-Hexyl Phosphate.[32] A solution of 10.2 g of 2-hexanol in 50 ml of pyridine was cooled in an ice bath. Diphenyl phosphorochloridate (35.6 g) was added and the mixture was allowed to stand overnight at room temperature. Water was added and the mixture was extracted with chloroform. After drying and evaporation of chloroform *in vacuo*, the residual liquid was chromatographed on alumina, with benzene as eluent. Evaporation of benzene *in vacuo* left 30.0 g (90%) of colorless liquid with $n^{27.5}\mathrm{D}$ 1.5110 and infrared absorptions at 1290 (P=O stretch), 1198 (P—O—aryl stretch), and 1020 cm^{-1} (P—O—alkyl stretch). *Anal.* Calcd for $C_{18}H_{23}O_4P$: C, 64.66; H, 6.93. Found:[26] (1) C, 64.46; H, 7.04. (2) C, 64.45; H, 7.34.

Base-Solvent Solutions. Solutions of sodium methoxide in methanol were prepared as before.[11] *t*-Butyl alcohol was refluxed over and distilled from calcium hydride. Solutions were prepared by reaction, under nitrogen, of freshly cut potassium metal with the purified alcohol.

Elimination Products from Reactions of 2-Substituted Hexanes with Sodium Methoxide in Methanol and Potassium *t*-Butoxide in *t*-Butyl Alcohol. A volumetric flask was filled nearly to the mark with the desired base-solvent solution. The 2-substituted hexane and some *n*-hexane (internal standard) were weighed into the flask. Aliquots were sealed in ampoules and placed in appropriate thermostats for recorded times. The ampoules were removed, cooled in ice water or Dry Ice-isopropyl alcohol, and kept cold until analysis. A 1-μl portion of the contents of an ampoule was injected directly into the injection port[33] of an Aerograph Model 204 flame ionization gas chromatograph using 0.125 in. × 30 ft columns of 25% UCON 50HB100 on Chromosorb P operated at ambient temperatures.

Many of the determinations recorded in Tables I and II were repeated one or more times. Mean values are recorded; average deviations from the mean were in most cases substantially less than 1.0%, and in no case greater than 2.0%. Full details are given in the Dissertation of R. A. Bartsch.[1]

No effort was made to determine nonolefinic products, but the total yield of hexenes formed could be judged against the *n*-hexane internal standard. Substantially the same technique was used in investigating isomerization of 1-hexene. By studies of similar type, it was shown that 2-hexanol did not form any detectable amount of hexenes on reaction with 1.0 *M* t-BuO$^-$K$^+$–t-BuOH for 4 days at 99°.

In the experiments summarized in Table I, the $NaOCH_3$ concentration was 0.66 *M* except in the last three experiments (at 164.4°), where it was 2.0 *M*; the substrate concentration was 0.14 or 0.21 *M* except in the 164.4° experiments where it was 0.45 or 0.85 *M*. In the experiments summarized in Table II, the substrate concentration was mostly 0.05 to 0.55 *M*, but it was 1.45 *M* in the 2-hexyl phenyl ether experiment and 0.64 *M* in the 2-hexyl phenyl sulfone experiments. All concentrations of substrates and bases are uncorrected for thermal expansion between room temperature and reaction temperature.

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[32] *Cf.* P. Bringl and H. Muller, *Ber.*, 72, 2121 (1939).

[33] Glass inserts filled with glass wool were placed in the injection ports to prevent contamination of columns by the base.

Orientation of Olefin-Forming Elimination in Reactions of 2-Substituted Hexanes with Potassium *t*-Butoxide in Dimethyl Sulfoxide[1,2]

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Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island. *Received August 2, 1968*

Abstract: Compositions of the olefin product mixtures from the action of t-BuO$^-$K$^+$–dimethyl sulfoxide on 13 2-substituted hexanes are reported. Reactions were carried out under continuous flushing with nitrogen gas, and product isomerization was negligible. In most cases, the fractional yield of 1-hexene is lower in this system than in t-BuO$^-$K$^+$–t-BuOH. 2-Hexene *trans/cis* ratios vary dramatically. The very high *trans/cis* ratios of about 5.0 from 2-hexyl chloride, bromide, and iodide suggest that *syn* elimination occurs, while the very low ratios of about 0.4 from 2-hexyl fluoride and 2-hexyl phenyl ether suggest exceptional solvation of transition states when the leaving groups detach as highly basic ions of low polarizability. In a general way, positional orientation seems to correlate with the ease or difficulty of detaching the leaving group, and therefore with the relative degrees of breaking of the C_β–H and C_α–X bonds in the transition state.

In reactions of 2-substituted hexanes with sodium methoxide in methanol or potassium *t*-butoxide in *t*-butyl alcohol, both positional and geometrical orientation of elimination are for the most part in accord with expectations from the theory of the variable E2 transition state.[5,6] This theory is briefly outlined in the accompanying paper,[6] and is presented at greater length elsewhere.[7] Some orientation effects appear also to be affected or in a few cases largely determined by steric factors.

Orientation of elimination in the potassium *t*-bu-

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[1] Based on the Ph.D. Dissertation of R. A. Bartsch, June 1967; *Diss. Abstr.*, **28**, 3212-B (1968).

[2] Supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

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[5] R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968).

[6] R. A. Bartsch and J. F. Bunnett, *ibid.*, **91**, 1376 (1969).

[7] J. F. Bunnett, *Angew. Chem. Int. Ed. Engl.*, **1**, 225 (1962); *Angew. Chem.*, 74, 731 (1962); *Surv. Progr. Chem.*, in press.