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 $n^{27.5}\text{D}$ 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 $n^{27.5}\text{D}$ 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.

(3) Jesse M. Metcalf Fellow, 1964–1965; ICI (Organics) Fellow, 1965–1966.

(4) Address inquiries to this author at the University of California, Santa Cruz, Calif. 95060.

(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); *Ang w. Chem.*, 74, 731 (1962); *Surv. Progr. Chem.*, in press.

Table I. Olefinic Products from Reactions of 2-Substituted Hexanes with Potassium *t*-Butoxide in Dimethyl Sulfoxide at 50.8°

Leaving group, X	Leaving group no.	[*t*-BuOK], *M*	[Substrate], *M*	Time, min	Total Hexenes yield,[a] %	Per cent of total hexenes: 1-Hexene	Per cent of total hexenes: *trans*-2-Hexene	Per cent of total hexenes: *cis*-2-Hexene	**2:1**	*trans*:*cis*
I	1	0.6	0.33	25	63	35.0	54.6	10.4	1.86	5.2
Br	2	0.6	0.47	65	72	47.0	44.0	9.0	1.13	4.9
Cl	3	0.6	0.27	60	58	59.4	33.8	6.8	0.68	4.9
F	4	0.4	0.11	25	*b*	81.3	5.3	13.4	0.23	0.42
		0.6	0.12	70	*b*	81.8	5.6	12.6	0.22	0.42
		0.8	0.07	30	*b*	78.2	5.8	16.0	0.28	0.36
		0.6[c]	0.26	135[c]	*b*	89.9	4.1	6.0	0.11	0.67
OBs[d]	5	0.6	0.34	43	76	73.4	19.8	6.7	0.36	2.9
OSO_2Ph[e]		0.6	0.48	50	68	72.2	20.2	7.6	0.38	2.7
OTs[f]		0.4	0.26	30	61	72.8	20.2	7.0	0.38	2.9
OTMB[g]	6	0.6	0.39	170	*b*	84.6	11.4	3.9	0.18	2.9
OC_6H_5	7	0.5	0.74	540	*b*	88.7	3.8	7.6	0.12	0.49
SC_6H_5	8	0.5	0.44	655	*b*	74.1	15.9	10.0	0.35	1.6
SeC_6H_5	9	0.5	0.31	420	*b*	67.6	21.0	11.4	0.48	1.8
ODPP[h]	10	0.7	0.37	210	*b*	52.3	34.8	13.2	0.92	2.6
$SO_2C_6H_5$	11	0.5	0.33	40	14	94.6	1.2	4.2	0.06	0.30

[a] See Experimental Section. [b] Yield could not be determined; see Experimental Section. [c] Room temperature. [d] *p*-Bromobenzenesulfonoxy group. [e] Benzenesulfonoxy group. [f] *p*-Toluenesulfonoxy group. [g] 2,4,6-Trimethylbenzoyloxy group. [h] $OPO(OC_6H_5)_2$; see text regarding complications in this case.

toxide–dimethyl sulfoxide system has been less extensively studied. Wallace, Hofmann, and Schriesheim[8] showed that elimination could be effected, in this system, from several classes of compounds normally resistant to elimination. Snyder and Soto[9] studied eliminations from some alkyl arenesulfonates in this system and in $NaOCH_3$–dimethyl sulfoxide. Froemsdorf and coworkers[10] have studied several aspects of eliminations from *sec*-alkyl *p*-toluenesulfonates or 2-butyl bromide in $t\text{-BuO}^-K^+$–dimethyl sulfoxide and other base–solvent systems. Griffith, Meges, and Brown[11] described orientation in reactions of $t\text{-BuO}^-K^+$–dimethyl sulfoxide and $(C_2H_5)_3CO^-K^+$–dimethyl sulfoxide with 2-butyl chloride, bromide, and iodide.

Pánková, Sicher, and Závada[12] have presented evidence that, in reactions of diastereomeric *sec*-alkyltrimethylammonium ions in $t\text{-BuO}^-K^+$–dimethyl sulfoxide and other base–solvent systems, *trans* olefins are formed by *syn* elimination and *cis* olefins by *anti* elimination. A similar conclusion was drawn in respect to reactions of diastereomeric cycloalkyl *p*-toluenesulfonates with $t\text{-BuO}^-K^+$–dimethylformamide.[13] However, in reactions of the diastereomeric 3-deuterio-2-butyl *p*-toluenesulfonates with $t\text{-BuO}^-K^+$–dimethyl sulfoxide, *anti* elimination occurs predominantly with almost total exclusion of *syn* elimination.[10e]

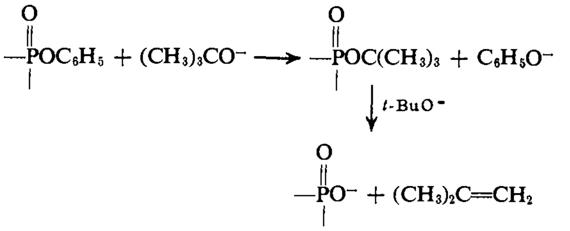
Results

Because olefins are readily isomerized in the highly basic $t\text{-BuO}^-K^+$–dimethyl sulfoxide system,[14] the ampoule technique employed in studying reactions with $NaOCH_3$–CH_3OH and $t\text{-BuO}^-K^+$–$t\text{-BuOH}$[5,6] could not be used in the present determinations. Instead, reactions were carried out, at 50.8°, in an apparatus continuously bubbled with nitrogen gas and volatile products were collected in a trap cooled by liquid nitrogen.[10a] Blank experiments showed no appreciable amount of olefin isomerization to occur under these conditions.

Positional and geometrical orientation of elimination were determined in reactions of 13 2-substituted hexanes with $t\text{-BuO}^-K^+$–dimethyl sulfoxide. Results are tabulated in Table I.

When 2-hexyl diphenyl phosphate was mixed with $t\text{-BuO}^-K^+$–dimethyl sulfoxide, heat was immediately evolved, but in contrast to other instances of immediate exothermic reaction (2-hexyl chloride, bromide, iodide, and the arenesulfonates) only small amounts of hexenes were generated in this initial reaction. However, another product, more volatile than the hexenes, was formed; its infrared spectrum was identical with that of 2-methylpropene.

2-Methylpropene was probably formed by a two-step sequence: displacement of phenoxide from phosphorus by *t*-butoxide, and β-elimination in the *t*-butyl group of the resulting ester.



$$\text{—}\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}\text{OC}_6\text{H}_5 + (\text{CH}_3)_3\text{CO}^- \longrightarrow \text{—}\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}\text{OC(CH}_3)_3 + \text{C}_6\text{H}_5\text{O}^- \xrightarrow{t\text{-BuO}^-} \text{—}\overset{\text{O}}{\overset{\|}{\underset{|}{\text{P}}}}\text{O}^- + (\text{CH}_3)_2\text{C}{=}\text{CH}_2$$

We do not know whether one or two such sequences occurred; the actual leaving group was therefore either $-OP(OC_6H_5)O_2^-$ or $-OPO_3^{2-}$.

Each datum in Table I was confirmed by at least one repeat experiment, and thus is reproducible. In those cases where other workers have investigated the action of $t\text{-BuO}^-K^+$–dimethyl sulfoxide on homologous substrates, our results resemble those previously reported. Thus, 2-pentyl *p*-toluenesulfonate was re-

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(8) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963); **86**, 1561 (1964); *Nature*, **199**, 1287 (1963).

(9) C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **30**, 673 (1965); *Tetrahedron Lett.*, 3261 (1965).

(10) (a) D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, **87**, 3983 (1965); (b) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965); (c) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966); (d) D. H. Froemsdorf and M. D. Robbins, *ibid.*, **89**, 1737 (1967); (e) D. H. Froemsdorf, W. Dowd, W. A. Gifford, and S. Meyerson, *Chem. Commun.*, 449 (1968).

(11) D. L. Griffith, D. L. Meges, and H. C. Brown, *ibid.*, 90 (1968).

(12) M. Pánková, J. Sicher, and J. Závada, *ibid.*, 394 (1967).

(13) J. Závada, M. Svoboda, and J. Sicher, *Tetrahedron Lett.*, 1627 (1966).

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

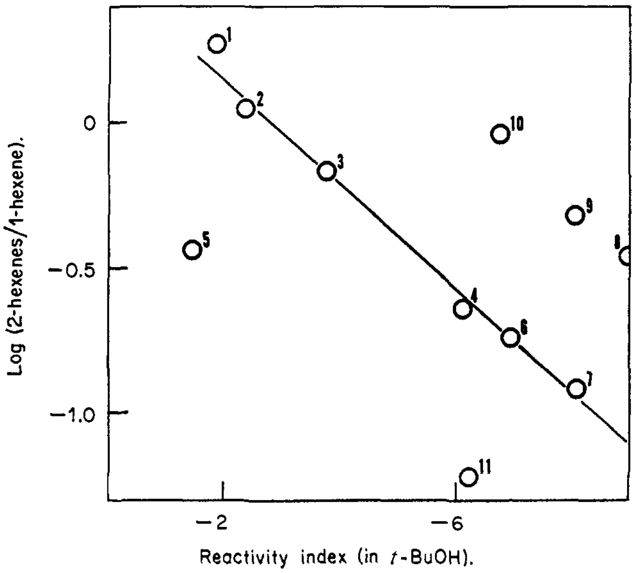


Figure 1. Relation of log (2-hexenes/1-hexene ratio), for reactions in *t*-BuO$^-$K$^+$–dimethyl sulfoxide, to reactivity index in *t*-BuOH. Leaving groups are identified by number; see Table I.

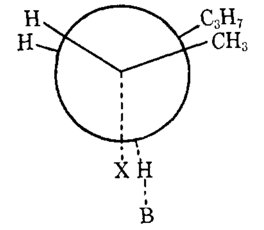
ported by Froemsdorf and McCain[10a] to form pentenes in *trans*/*cis* ratio of 3.3 and 2-enes/1-ene ratio of 0.39; the corresponding ratios in Table I are 2.9 and 0.38, respectively. The percentages of 1-butene obtained from 2-butyl chloride, bromide, and iodide by Griffith, *et al.*,[11] are lower than the corresponding percentages of 1-hexene in Table I by a nearly constant factor of 16–18%, while their *trans*/*cis* ratios of 3.5–4.1 compare with ours of 5.2–4.9.

There are remarkably few similarities between the reactions of Table I and reactions of the same substrates with *t*-BuO$^-$K$^+$–*t*-BuOH.[6] Whereas for the latter system a plot of log (2-hexenes/1-hexene ratio) against reactivity index is V-shaped, a similar plot (Figure 1) of the data of Table I (against reactivity index in *t*-BuOH[15]) has a suggestion of linearity though several points deviate. Moreover, in most cases the fractional yield of 1-hexene is substantially higher in *t*-BuOH than in dimethyl sulfoxide.

As to the *trans*/*cis* ratios, they show little correlation either with the reactivity index or with *trans*/*cis* ratios in *t*-BuOH. The changes in *trans*/*cis* ratio among the halides are noteworthy: the ratios of 1.1 to 2.0 in *t*-BuOH shift upward for the chloride, bromide, and iodide to the unusually high range of 4.9 to 5.2 in dimethyl sulfoxide, while that for the fluoride plunges to 0.4. For the arenesulfonates, the change of *trans*/*cis* ratio from about $^1/_3$ in *t*-butyl alcohol to nearly 3 in dimethyl sulfoxide is striking, and similar to effects reported for homologous substrates by other workers.[10a,c,16]

Discussion

Geometrical Orientation. The *trans*/*cis* ratios in Table I for 2-hexyl chloride, bromide, and iodide are very high (4.9–5.2), much higher than observed in the reactions of these halides with *t*-BuO$^-$K$^+$–BuOH or $NaOCH_3$–CH_3OH, and higher than observed with any other of our 13 substrates in any of the three base–solvent systems.[5,6] Indeed, we know of no other elimination from a straightforward 2-substituted *n*-alkane that has given such a high *trans*/*cis* ratio. However, the *trans*/*cis* ratio of 2.47 from pyrolysis of 2-hexyl acetate at *ca.* 450°[17] extrapolates to 7.5 at 50° on the assumption that the transition states preceding *trans*- and *cis*-2-hexene are of equal entropy. The acetate pyrolysis is a *syn* elimination. A high *trans*/*cis* ratio is expected from a *syn* elimination, the more so the more fully eclipsed is the transition state, because in the transition state preceding the *cis* olefin the juxtaposition of *cis*-destined alkyl groups causes severe crowding, as illustrated in Newman projection **1**. Crowding is worse than in *anti* elimination transition states preceding *cis* olefins, while no comparable adverse interactions between alkyl substituents occur in those preceding *trans* olefins.



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The high *trans*/*cis* ratios from 2-hexyl chloride, bromide, and iodide are thus suggestive of a *syn* elimination mechanism.

There is some precedent for a change in the stereochemical course of elimination from alkyl halides with change in the base–solvent system. In reactions of a series of cycloalkyl bromides with *t*-BuO$^-$K$^+$–*t*-BuOH, studied by Závada, Krupicka, and Sicher,[18] rate–ring size profiles suggest that *trans*-cycloalkenes are formed by *syn* elimination and *cis*-cycloalkenes by *anti* elimination, but the same substrates appear to react with $C_2H_5O^-K^+$–C_2H_5OH to form both *cis*- and *trans*-cycloalkenes largely if not exclusively by *anti* elimination.

If the reactions of 2-hexyl chloride, bromide, and iodide with *t*-BuO$^-$K$^+$–dimethyl sulfoxide are correctly judged to be *syn* eliminations, the question arises as to whether the mechanism is a variation of the E2 mechanism or a different one. This might seem a semantic question, but the corollary as to whether the theory of the variable E2 transition state applies to *syn* eliminations should be susceptible of experimental test. Within the set of three 2-hexyl halides, the dependence of 2-hexenes/1-hexene ratio on leaving group is qualitatively the same as in *anti* eliminations of the same halides.[5,6] Tentatively, it seems appropriate to consider these probable *syn* eliminations as variants of the E2 mechanism.

The *trans*/*cis* ratios for the arenesulfonates are about 2.8, significantly lower than for the chloride,

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(15) Reactivity indices evaluated in reactions with *t*-BuO$^-$K$^+$–*t*-BuOH are used because of the lack of even semiquantitative information about reaction rates in *t*-BuO$^-$K$^+$–dimethyl sulfoxide.

(16) H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **87**, 5517 (1965).

(17) C. H. DePuy, C. A. Bishop, and C. N. Goeders, *ibid.*, **83**, 2151 (1961).

(18) J. Závada, J. Krupicka, and J. Sicher, *Chem. Commun.*, 66 (1967).

bromide, and iodide, and in the range typical of *anti* elimination. The stereochemical course of elimination from 2-butyl *p*-toluenesulfonate in this system is known to be *anti*.[10e] The change from predominantly *cis* 2-alkene in *t*-BuO^-K^+–*t*-BuOH to predominantly *trans* in *t*-BuO^-K^+–dimethyl sulfoxide has been discussed elsewhere.[10c] Similar changes occur in the cases of 2-hexyl 2,4,6-trimethylbenzoate and 2-hexyl diphenyl phosphate (*cf.* Table II of the accompanying paper[6]), and a similarity of cause seems probable.

2-Hexyl fluoride and 2-hexyl phenyl ether share the characteristic of giving slightly more *trans*- than *cis*-2-hexene in *t*-BuO^-K^+–*t*-BuOH,[6] but decidedly more *cis* than *trans* in *t*-BuO^-K^+–dimethyl sulfoxide. These two leaving groups afford anions of high basicity and low polarizability, and it is conceivable that electrophilic solvation in the transition state is necessary in order to get them away from carbon. The few *t*-butyl alcohol molecules present might perform that function, but it is difficult to see why the steric consequences in dimethyl sulfoxide should be more serious than in *t*-butyl alcohol solvent. On the other hand, if electrophilic solvation by the sulfur of dimethyl sulfoxide were involved, a great deal of bulk would be introduced close to the first atom of the leaving group, and the consequence might be to favor formation of *cis* olefin.

In the case of 2-hexyl phenyl sulfone, the leaving group is bulky about its first atom regardless of the solvent, and it gives more *cis*- than *trans*-2-hexene in both *t*-BuOH[6] and dimethyl sulfoxide. It is to be noted that 2-pentyltrimethylammonium ion gives more *cis*- than *trans*-2-pentene in several alkoxide ion–alcohol systems;[19] in this case, too, the leaving group is unavoidably bulky about its first atom.

Positional Orientation. Let us focus attention on Figure 1. First, we must note that the positions of several points are affected by special factors. The point (no. 10) for 2-hexyl diphenyl phosphate, in which case the true leaving group is $-OPO_3^{2-}$ or $-OP(OC_6H_5)O_2^-$ (*vide supra*), should be shifted about three units to the left to correct for special entropy effects in reactions between anionic species,[20] and if so shifted it would lie close to the line drawn. In cases where unusual steric effects dominate *trans*/*cis* ratios, retardation of the formation of *trans*- or *cis*-2-hexene also alters the 2-hexenes/1-hexene ratio.

Nevertheless, there is a suggestion in Figure 1 of some correlation of positional orientation with the ease or difficulty of detaching the leaving group from carbon. Because of the considerable number of points which lie far away from the line drawn in Figure 1 and of uncertainties arising from use of a reactivity index evaluated in another base–solvent system, one cannot claim a linear relationship or even resolutely deny the existence of a V-shaped correlation as encountered with *t*-BuO^-K^+–*t*-BuOH. Nevertheless the data suggest, over-all, that the relative degrees of C_β–H and C_α–X breaking in the transition state have a good deal to do with determining positional orientation in this system, although special steric factors cause important perturbations.

It is remarkable, with respect to the theory of the variable E2 transition state, that Hofmann orientation (forming 1-hexene) is in most cases less pronounced in *t*-BuO^-K^+–dimethyl sulfoxide than in *t*-BuO^-K^+–*t*-BuOH. The alcohol has greater capacity for electrophilic solvation of leaving groups detaching as anions, and *t*-BuO^- is a weaker base in *t*-BuOH than in dimethyl sulfoxide; both factors would seem to call for less paenecarbanion character, and therefore a lesser predominance of Hofmann orientation, in *t*-BuOH. Perhaps there is some further influence of solvents on transition-state character that has not yet been taken adequately into account.

Experimental Section

Preparation of the several 2-substituted hexanes and our general methods of glpc analysis are described elsewhere.[1,5,6] Dimethyl sulfoxide was purified by fractional freezing. Solutions were prepared by adding dimethyl sulfoxide to weighed amounts of potassium *t*-butoxide (Alfa Inorganics, sublimed) in volumetric flasks. After thorough mixing, a small amount of undissolved material was allowed to settle, and the solution was decanted.

Elimination Products from Reactions of 2-Substituted Hexanes with Potassium *t*-Butoxide in Dimethyl Sulfoxide. The 2-substituted hexane was weighed into a volumetric flask and the flask was filled to the mark with the desired solution of potassium *t*-butoxide in dimethyl sulfoxide. An exothermic reaction was evident when the 2-hexyl arenesulfonates, diphenyl 2-hexyl phosphate, 2-iodohexane, 2-bromohexane, and 2-chlorohexane were mixed with the base–solvent solution. The contents of the flask were quickly mixed and transferred to an apparatus designed to sweep olefinic reaction products from the reaction solution with nitrogen and carry them to a receiver trap. Flushing with nitrogen was commenced, and the reaction vessel and attached receiver trap were lowered into a 50.8° thermostat and a liquid nitrogen-filled dewar, respectively. After a recorded time, the receiver was disconnected and its contents were removed, weighed, and analyzed immediately by injection of a 0.05–02-μl portion into the Aerograph Model 204 gas chromatograph. With the less reactive substrates the olefin yield could not be determined with this technique.

Reaction of Diphenyl 2-Hexyl Phosphate with Potassium *t*-Butoxide in Dimethyl Sulfoxide. A solution of 3.67 g of potassium *t*-butoxide in 25 ml of dimethyl sulfoxide was placed in a reaction vessel. Diphenyl 2-hexyl phosphate (1.0 g) was placed in a side arm of the reaction vessel which was tilted so that initially no mixing of the compound and the base–solvent system occurred. A receiver trap was attached to the reaction vessel and the apparatus was evacuated to 1 mm and sealed. When the reaction vessel was tilted so that the diphenyl 2-hexyl phosphate and base–solvent solution mixed, a vigorous evolution of gas was observed. The reaction vessel and receiver trap were lowered into a 50.8° thermostat and liquid nitrogen cooled dewar, respectively. Only slight gas evolution was noted after the initial reaction upon mixing. After 0.5 hr, the receiver trap was disconnected from the reaction vessel and attached to a 10-cm path length gas infrared cell. Removal of the dewar from the trap allowed the reaction product to thaw and transfer to the infrared cell. The infrared spectrum of the gas perfectly matched a recorded spectrum of 2-methylpropene (isobutylene).

Olefin Isomerization Studies. A synthetic mixture of 46.0 ± 1.8% 1-hexene, 4.6 ± 0.2% *trans*-2-hexene, and 49.5 ± 1.1% *cis*-2-hexene was prepared and subjected to the normal reaction procedure. The trapped hexene mixture analyzed as follows: 47.4 ± 2.2% 1-hexene; 4.5 ± 0.2% *trans*-2-hexene; and 48.2 ± 1.3% *cis*-2-hexene.

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(19) I. N. Feit and W. H. Saunders, Jr., *Chem. Commun.*, 610 (1967).

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