Positional and Geometrical Orientation in Eliminations from 2-Bromoalkanes Induced by Sodium Methoxide–Methanol, Potassium *t*-Butoxide–*t*-Butyl Alcohol, and Potassium *t*-Butoxide–Dimethyl Sulfoxide[1,2]

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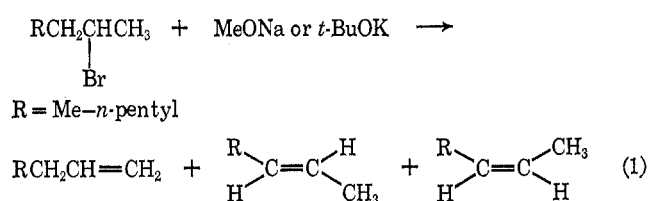
Olefinic products from reactions of a series of 2-bromoalkanes (C$_4$–C$_8$) with MeONa–MeOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–DMSO are reported. Compositions of the olefin mixtures are determined over ranges of temperatures under conditions of negligible product isomerization. In all three base–solvent systems, the percentage of 1-alkene increases in an attenuated fashion as the alkyl group of the substrate is varied from 2-butyl through 2-octyl. With MeONa–MeOH and *t*-BuOK–DMSO, the *trans-/cis*-2-alkene ratio is dependent upon the alkyl group of the 2-bromoalkane, increasing in the order 2-butyl < 2-octyl < 2-heptyl < 2-hexyl < 2-pentyl, whereas with *t*-BuOK–*t*-BuOH the order is 2-octyl < 2-heptyl < 2-hexyl < 2-butyl < 2-pentyl. The effects of the nature of the alkyl group upon positional and geometrical orientation are discussed.

Recent investigations of base-catalyzed eliminations of 2-substituted alkanes[4] have demonstrated that positional and geometrical orientation[5] may vary widely with changes in the leaving group, the base, and the solvent. The influence of the nature of the alkyl group of the 2-substituted alkane upon orientation has remained relatively unexplored.

Orientation in eliminations from 2-alkyl bromides (C$_4$–C$_6$) and 2-alkyl arenesulfonate esters (C$_4$–C$_6$, C$_8$) has been reported.[4] However, results determined under a variety of conditions in several laboratories must be compared.

Results

Using gas–liquid partition chromatography (glpc), the relative proportions of the three isomeric olefins formed in dehydrohalogenations from a series of 2-bromoalkanes (C$_4$–C$_8$) induced by MeONa–MeOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–DMSO (eq 1) have been measured.

$$\text{RCH}_2\text{CHCH}_3 \ + \ \text{MeONa or } t\text{-BuOK} \ \longrightarrow$$
$$\underset{\text{Br}}{|}$$

R = Me–*n*-pentyl

$$\text{RCH}_2\text{CH}=\text{CH}_2 \ + \ \underset{H}{\overset{R}{>}}C=C\underset{CH_3}{\overset{H}{<}} \ + \ \underset{H}{\overset{R}{>}}C=C\underset{H}{\overset{CH_3}{<}} \quad (1)$$

Reactions with Sodium Methoxide–Methanol.—The

relative amounts of the isomeric olefins formed in reac-

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(2) Portions of this work were described at the 24th Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 1969.

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(4) (a) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968); (b) **91**, 1376 (1969); (c) **91**, 1382 (1969); (d) H. C. Brown and R. L. Klimisch, *ibid.*, **87**, 5517 (1965); (e) **88**, 1425 (1966); (f) A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962); (g) D. H. Froemsdorf and M. E. McCain, *ibid.*, **87**, 3983 (1965); (h) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965); (i) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966); (j) D. H. Froemsdorf and M. D. Robbins, *ibid.*, **89**, 1737 (1967); (k) D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem. Commun.*, 90 (1968); (l) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965); (m) C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **30**, 673 (1965).

(5) Positional orientation refers to the relative proportions of 1- and 2-alkenes formed, whereas geometrical orientation compares the relative amounts of *trans*- and *cis*-2-alkene produced.

tions of the 2-bromoalkanes with MeONa–MeOH were determined at four temperatures from 30–90°. The results are listed in Table I. Previous investigations have demonstrated kinetically controlled formation of products under the reaction conditions.[4a]

At a given temperature, the percentage of terminal olefin shows an attenuated increase as the series is traversed from 2-bromobutane to 2-bromoheptane. The relative olefinic proportions are the same for 2-bromoheptane and 2-bromooctane. The *trans-/cis*-2-alkene ratio is lowest for 2-bromobutane, maximal for 2-bromopentane, and intermediate for the other series members.

Reactions with Potassium *t*-Butoxide–*t*-Butyl Alcohol.—The olefins resulting from reactions of the 2-bromoalkanes with *t*-BuOK–*t*-BuOH at four temperatures in the range 30–90° are reported in Table II. Under the employed reaction conditions, isomerization of the product olefins is negligible.[4b]

Hofmann orientation predominates and an attenuated increase is again noted in passing from 2-bromobutane to the higher homologs. The *trans-/cis*-2-alkene ratio increases as the 2-alkyl group is varied: 2-octyl < 2-heptyl < 2-hexyl < 2-butyl < 2-pentyl.

Reactions with Potassium *t*-Butoxide–Dimethyl Sulfoxide.—Although special experimental techniques were utilized, the propensity of *t*-BuOK–DMSO for isomerization of olefins[6] limited observation of reactions of 2-bromoalkanes with this base–solvent system to 30 and 50°. Higher temperatures resulted in isomerized olefinic products. Results are given in Table III.

Differences between the present results and reported values[4c] for 2-bromohexane are due to improvements in experimental procedure. Reaction with *t*-BuOK–DMSO is so rapid that essentially complete reaction occurs upon mixing. In the earlier study, mixing (and reaction) took place at room temperature. In agreement, the present results at 30° are the same as those reported at 50°.

The reaction of 2-bromohexane with *t*-BuOK–DMSO at 50° yields 90 ± 2% hexenes.

Again the percentage of terminal olefin increases markedly between 2-bromobutane and 2-bromopentane

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

TABLE I

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BROMOALKANES WITH 0.55 M SODIUM METHOXIDE–METHANOL

| R of RBr[a] | Temp, °C | Total alkenes, % | | | 2-Alkene/ 1-alkene | trans-2-Alkene/ cis-2-alkene |
		1-Alkene	trans-2-Alkene	cis-2-Alkene		
2-Butyl	30.0[b]	12.7 ± 0.4[c]	68.7 ± 0.5	18.6 ± 0.6	6.9	3.7
	49.8[d]	14.6 ± 0.3	65.8 ± 0.7	19.6 ± 0.7	5.8	3.4
	69.6	16.6 ± 0.3	62.7 ± 0.3	20.7 ± 0.1	5.0	3.0
	89.6	18.3 ± 0.4	60.6 ± 0.4	21.1 ± 0.4	4.5	2.9
2-Pentyl	30.0[b]	16.1 ± 0.3	69.1 ± 0.1	14.8 ± 0.4	5.2	4.7
	49.8[b]	18.4 ± 0.1	66.2 ± 0.2	15.4 ± 0.2	4.4	4.3
	69.6	21.0 ± 0.3	63.0 ± 0.2	16.0 ± 0.2	3.8	3.9
	89.6	23.0 ± 0.3	60.3 ± 0.3	16.7 ± 0.3	3.4	3.6
2-Hexyl[e]	30.0	18.3 ± 0.4	65.8 ± 0.7	15.9 ± 0.3	4.5	4.1
	49.8[f]	20.7 ± 0.5	62.5 ± 0.5	16.8 ± 0.3	3.8	3.7
	69.6	23.2 ± 0.2	59.8 ± 0.2	17.0 ± 0.1	3.3	3.5
	89.6	26.1 ± 0.3	57.0 ± 0.2	16.9 ± 0.1	2.8	3.4
2-Heptyl	30.0	19.7[g]	64.4	15.9	4.1	4.0
	49.8[f]	22.0 ± 0.1	61.2 ± 0.1	16.8 ± 0.1	3.6	3.6
	69.6	25.0[g]	57.8	17.2	3.0	3.4
	89.6	26.9[g]	55.8	17.3	2.7	3.2
2-Octyl	30.0	20.5 ± 0.2	62.5 ± 0.1	17.0 ± 0.1	3.9	3.7
	49.8	21.9 ± 0.3	61.3 ± 0.4	16.8 ± 0.2	3.6	3.6
	69.6	24.2 ± 0.2	58.3 ± 0.4	17.5 ± 0.1	3.1	3.3
	89.6	27.2 ± 0.4	55.6 ± 0.2	17.2 ± 0.5	2.7	3.2

[a] [RBr] = 0.14–0.66 M. [b] Two runs. [c] Deviations are standard deviations of the set. [d] Four runs. [e] These results are in accord with extensive studies of products from reactions of 2-bromohexane with MeONa–MeOH reported in ref 4a, except that trans-2-hexene and 1-hexene were consistently 1.0% higher and lower, respectively, in this work. [f] Three runs. [g] Single sample.

TABLE II

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BROMOALKANES WITH 1.0 M POTASSIUM t-BUTOXIDE–t-BUTYL ALCOHOL

| R of RBr[a] | Temp, °C | Total alkenes, % | | | 2-Alkene/ 1-alkene | trans-2-Alkene/ cis-2-alkene |
		1-Alkene	trans-2-Alkene	cis-2-Alkene		
2-Butyl[b]	30.0	50.8 ± 0.5[c]	29.8 ± 0.2	19.4 ± 0.3	0.97	1.54
	49.8	50.0 ± 0.3	30.1 ± 0.1	19.9 ± 0.3	1.00	1.51
	69.6	48.8 ± 0.6	30.7 ± 0.2	20.5 ± 0.1	1.05	1.50
	89.6	49.0 ± 0.2	30.5 ± 0.4	20.5 ± 0.4	1.04	1.48
2-Pentyl	30.0	83.6 ± 0.4	10.4 ± 0.2	6.0 ± 0.2	0.20	1.73
	49.8	81.2 ± 0.3	12.0 ± 0.3	6.8 ± 0.2	0.23	1.76
	69.6	79.4 ± 0.1	12.8 ± 0.1	7.8 ± 0.1	0.26	1.64
	89.6	77.7 ± 0.1	13.9 ± 0.1	8.4 ± 0.2	0.29	1.65
2-Hexyl[d]	30.0	86.6 ± 0.1	7.7 ± 0.1	5.7 ± 0.1	0.15	1.35
	49.8	83.6 ± 0.3	9.7 ± 0.1	6.7 ± 0.2	0.20	1.45
	69.6	81.9 ± 0.4	10.5 ± 0.3	7.6 ± 0.2	0.22	1.38
	89.6	80.0 ± 0.4	11.7 ± 0.3	8.3 ± 0.1	0.25	1.41
2-Heptyl	30.0	87.5 ± 0.3	7.2 ± 0.2	5.3 ± 0.1	0.14	1.36
	49.8	84.6 ± 0.4	8.8 ± 0.2	6.6 ± 0.2	0.18	1.33
	69.6	82.9[e]	10.0	7.1	0.20	1.40
	89.6	81.4 ± 0.2	10.6 ± 0.1	8.0 ± 0.2	0.23	1.32
2-Octyl	30.0	86.2 ± 0.1	7.8 ± 0.1	6.0 ± 0.1	0.16	1.29
	49.8	85.5[e]	8.1	6.4	0.17	1.26
	69.6	82.8 ± 0.6	9.6 ± 0.3	7.6 ± 0.3	0.21	1.26
	89.6	81.7 ± 0.7	10.2 ± 0.3	8.1 ± 0.4	0.22	1.26

[a] [RBr] = 0.17–0.46 M. [b] Reference 4e reports 54% 1-butene and trans-/cis-2-butene = 1.47 under the same conditions, while ref 4h records 53% 1-butene and trans-/cis-2-buten = 1.64 at 55°. [c] Deviations are standard deviations of the set. [d] Reference 4b reports the following data (% 1-hexene, trans-/cis-2-hexene, temp, °C): 89.2, 1.34, 29.7; 86.6, 1.22, 50.8; 83.6, 1.30, 75.8; 80.2, 1.39, 99.0. [e] Single sample.

and exhibits progressively smaller increases for the higher series members. The very large trans-/cis-2-alkene ratios are noteworthy. The ratio is minimal for 2-bromobutane, maximal for 2-bromopentane, and intermediate for the others.

For comparison, the olefinic products from the reaction of 2-bromobutane with t-BuOK–DMF were measured. The results, which are included in Table III, show that changing the solvent from DMSO to DMF only slightly affects the relative olefinic proportions. This provides strong evidence that t-bu-

toxide ion and not the anion of DMSO is the effective base in t-BuOK–DMSO.[4m]

Differences in Enthalpies and Entropies of Activation between Two Isomeric Olefins.—The relative proportions of the isomeric olefins from the series of 2-bromoalkanes were measured at several temperatures. Therefore, the differences in the enthalpies and entropies of activation, $\Delta\Delta H^{\ddagger}_{A-B}$ and $\Delta\Delta S^{\ddagger}_{A-B}$, respectively, between isomeric alkenes A and B could be calculated from the slopes and intercepts of linear plots of log (per cent olefin A/per cent olefin B) vs.

TABLE III

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BROMOALKANES WITH 0.8 M POTASSIUM t-BUTOXIDE–DIMETHYL SULFOXIDE

R of RBr[a]	Temp, °C	Total alkenes, %			2-Alkene/	trans-2-Alkene/
		1-Alkene	trans-2-Alkene	cis-2-Alkene	1-alkene	cis-2-alkene
2-Butyl[b]	30.0[c]	29.5 ± 0.4[d]	55.0 ± 0.6	15.5 ± 0.3	2.39	3.6
	49.8[c]	30.4 ± 0.5	53.8 ± 0.5	15.8 ± 0.4	2.29	3.4
	49.8[e]	30.5 ± 0.2	55.1 ± 0.2	14.4 ± 0.2	2.28	3.8
2-Pentyl	30.0[c]	43.2 ± 0.2	48.4 ± 0.1	8.4 ± 0.2	1.31	5.8
	49.8	43.5 ± 0.1	46.8 ± 0.2	9.7 ± 0.2	1.30	4.8
2-Hexyl[f]	30.0	46.9 ± 0.1	44.3 ± 0.1	8.8 ± 0.2	1.13	5.0
	49.8[c]	46.8 ± 0.1	43.3 ± 0.2	9.9 ± 0.2	1.14	4.4
2-Heptyl	30.0	49.0 ± 0.1	42.3 ± 0.1	8.7 ± 0.1	1.04	4.9
	49.8	49.2 ± 0.1	41.1 ± 0.2	9.7 ± 0.1	1.03	4.2
2-Octyl	30.0[g]	50.4 ± 0.1	41.7 ± 0.1	7.9 ± 0.1	0.98	5.3

[a] [RBr] = 0.08–0.62 *M*. [b] Reference 4h reports 31% 1-butene and *trans-/cis-*2-butene = 3.65 at 55°, and ref 4k records 31.5% 1-butene and *trans-/cis-*2-butene = 3.76 at 25°. [c] Two runs. [d] Deviations are standard deviations of the set. [e] In dimethylformamide. [f] Reference 4c lists 47.0 ± 0.4% 1-hexene and *trans-/cis-*2-hexene = 4.86 ± 0.02 at 51°. [g] Olefinic products from reaction at 50° could not be determined without apparent isomerization.
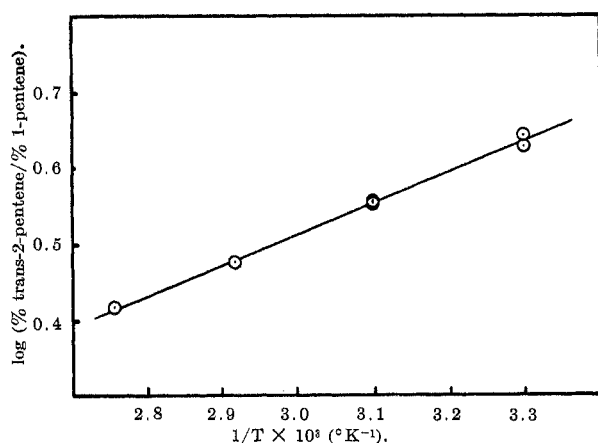

Figure 1.—Arrhenius plot of relative amounts of *trans*-2-pentene and 1-pentene from reaction of 2-bromopentane with MeONa–MeOH.

$1/T$. An Arrhenius plot from the reaction of 2-bromopentane with MeONa/MeOH is shown in Figure 1.

The computed values[7] are displayed in Tables IV–VI for reactions with MeONa–MeOH, t-BuOK–t-BuOH, and t-BuOK–DMSO, respectively. Uncertainties in differences in enthalpies of activation are estimated to be 0.3 kcal/mol, and those in entropies, 1 cal/deg mol. For the reaction of 2-bromohexane with MeONa–MeOH, the calculated differences in enthalpies and entropies of activation are within experimental error of those determined by kinetic studies.[4a]

Discussion

Effect of Base–Solvent System upon Orientation.— For a given 2-bromoalkane, the influence of the base–solvent systems upon positional and geometrical orientation observed in this investigation is in agreement with earlier studies of eliminations from 2-bromobutane and 2-bromohexane.[4b,c,h] In these previous investigations, the percentage of 1-alkene and the *trans-/cis-*2-alkene ratio were interpreted as indicating, respectively, the ratio of C–H to C–Br stretching in the elimination transition states and the degree of double-bond character in the internal olefin transition states. For

TABLE IV

$\Delta\Delta H^{\ddagger}$ AND $\Delta\Delta S^{\ddagger}$ VALUES FOR FORMATION OF PAIRS OF OLEFINS IN REACTIONS OF 2-BROMOALKANES WITH SODIUM METHOXIDE–METHANOL

R of RBr	trans-2-Alkene vs. 1-alkene		cis-2-Alkene vs. 1-alkene		trans-2-Alkene vs. cis-2-alkene	
	$\Delta\Delta H^{\ddagger}$ [a]	$\Delta\Delta S^{\ddagger}$ [b]	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$
2-Butyl	−1830	−0.4	−860	+0.1	−970	−0.5
2-Pentyl	−1850	−0.9	−940	−1.1	−910	+0.1
2-Hexyl	−1840	−1.3	−1110	−1.6	−730	+0.4
2-Heptyl	−1730	−1.1	−890	−1.1	−830	0
2-Octyl	−1510	−0.4	−960	−1.3	−550	+0.8

[a] In cal/mol. [b] In cal/deg mol.

TABLE V

$\Delta\Delta H^{\ddagger}$ AND $\Delta\Delta S^{\ddagger}$ VALUES FOR FORMATION OF PAIRS OF OLEFINS IN REACTIONS OF 2-BROMOALKANES WITH POTASSIUM t-BUTOXIDE–t-BUTYL ALCOHOL

R of RBr	trans-2-Alkene vs. 1-alkene		cis-2-Alkene vs. 1-alkene		trans-2-Alkene vs. cis-2-alkene	
	$\Delta\Delta H^{\ddagger}$ [a]	$\Delta\Delta S^{\ddagger}$ [b]	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$
2-Butyl	250	+2.0	370	+1.5	−120	+0.5
2-Pentyl	1300	+2.4	1530	+2.0	−230	+0.4
2-Hexyl	1770	+3.3	1670	+2.3	100	+1.0
2-Heptyl	1700	+2.9	1710	+2.3	−20	+0.6
2-Octyl	1280	+1.6	1390	+1.4	−110	+0.1

[a] In calories/mole. [b] In calories/degree mole.

TABLE VI

$\Delta\Delta H^{\ddagger}$ AND $\Delta\Delta S^{\ddagger}$ VALUES FOR FORMATION OF PAIRS OF OLEFINS IN REACTIONS OF 2-BROMOALKANES WITH POTASSIUM t-BUTOXIDE–DIMETHYL SULFOXIDE

R of RBr	trans-2-Alkene vs. 1-alkene		cis-2-Alkene vs. 1-alkene		trans-2-Alkene vs. cis-2-alkene	
	$\Delta\Delta H^{\ddagger}$ [a]	$\Delta\Delta S^{\ddagger}$ [b]	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	$\Delta H A^{\ddagger}$	$\Delta\Delta S^{\ddagger}$
2-Butyl	−510	+1.7	−140	+0.5	−370	+1.3
2-Pentyl	−370	+1.2	+1350	+3.4	−1740	−2.3
2-Hexyl	−210	+1.4	+1170	+2.7	−1380	−1.3
2-Heptyl	−280	+1.0	+1090	+2.2	−1320	−1.3

[a] In calories/mole. [b] In calories/deg mole.

eliminations from 2-bromoalkanes induced by MeONa–MeOH and t-BuOK–DMSO, the transition states were suggested to have similar amounts of heterolysis of the C–H and C–Br bonds and a high degree of double-bond character, whereas, for eliminations promoted by t-BuOK–t-BuOH, more advanced C–H bond rupture than C–Br bond cleavage and an only slightly developed carbon–carbon double bond were postulated. At present, the factors responsible for the changes in

orientation produced by variation of the base–solvent system are not fully understood.[4b,c,8]

For transition states with a high degree of double-bond character (productlike), correlation between *trans-* and *cis-2-*alkene isomer composition and the relative stabilities of the *trans-* and *cis-2-*alkenes might be anticipated. The relative stabilities of the geometrical 2-butene, 2-pentene, and 2-heptene isomers in the gas phase have been determined by iodine-catalyzed equilibration.[9] Figure 2 is a comparison of *trans-* and *cis-2-*alkene composition from reactions of 2-bromoalkanes with MeONa–MeOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–DMSO and *trans-* and *cis-2-*alkene isomer stabilities expressed as free-energy differences. Although these plots are only qualitative owing to limited ranges of free energies and numbers of points, there appears to be a crude correlation with MeONa–MeOH and *t*-BuOK–DMSO, but a complete lack of correlation with *t*-BuOK–DMSO. These results are in accord with the transition-state characters given above.

Effect of 2-Alkyl Groups upon Positional Orientation. —Transition states for formation of 1-alkene, *trans-2-* alkene, and *cis-2-*alkene by base-catalyzed elimination from a 2-bromoalkane, $RCH_2CHBrCH_3$, are represented by structures **1**, **2**, and **3**, respectively. In all three
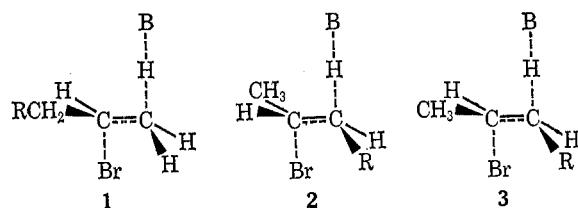
base–solvent systems, the relative proportion of 1-alkene increased in an attenuated fashion as R was varied from methyl through *n*-pentyl. Larger increases were noted when potassium *t*-butoxide was the base than with sodium methoxide.

An attractive explanation for both observations is destabilization of transition states **2** and **3** owing to steric interactions between the base and R. It would be anticipated that variation of R would have little effect upon transition state **1**. The data presented in Table VII indicate a relatively small effect upon the rate of formation of 1-alkene for replacement of a methyl R group with ethyl in two base–solvent systems. However, this change produces an overriding decrease in rate of formation of the internal olefins.

Two types of steric interactions between the base and R are possible.[10] Restrictions on the rotational freedom of R (for R > Me), producing a rate-retarding decrease in entropy, might arise if transition states **2** and **3** were obliged to assume certain strain-free conformations to avoid direct compressions of the base

(8) I. N. Feit and W. H. Saunders, Jr., *Chem. Commun.*, 610 (1967); W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).

(9) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964); K. W. Egger and S. W. Benson, *ibid.*, **88**, 236 (1966); K. W. Egger, *ibid.*, **89**, 504 (1967).

(10) The following discussion is a refinement of the steric theory of orientation presented previously by Brown, *et al.* (Table VII, footnote *a*) and in ref 11.

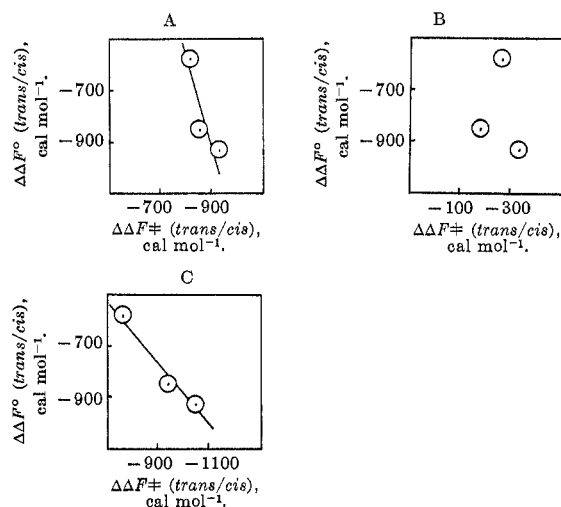(11) H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **75**, 4112 (1953).

Figure 2.—Plots of $\Delta\Delta F°$, the free energy corresponding to the *trans-2-*alkene–*cis-2-*alkene equilibria (at 237°), *vs.* $\Delta\Delta F^{\ddagger}$ (*trans–cis*), the difference in the free energy of activation for *trans-* and *cis-2-*alkene formation from reactions of 2-bromoalkanes at 30° with (A) MeONa–MeOH, (B) *t*-BuOK-*t*-BuOH, and (C) *t*-BuOK–DMSO.

TABLE VII

RATE CONSTANTS[a] FOR FORMATION OF ISOMERIC OLEFINS
IN REACTIONS OF 2-BUTYL AND 2-PENTYL BROMIDE WITH
1.0 M SODIUM ETHOXIDE–ETHANOL AND POTASSIUM
t-BUTOXIDE-*t*-BUTYL ALCOHOL AT 25°

		$-k_2{}^b \times 10^6$ for formation of——		
			trans-	*cis-*
R of RBr	Base–solvent	1-Alkene	2-Alkene	2-Alkene
2-Butyl	EtOK–EtOH	0.55	2.30	0.63
2-Pentyl	EtOK–EtOH	0.63	1.73	0.40
2-Butyl	*t*-BuOK-*t*-BuOH	0.71	0.42	0.27
2-Pentyl	*t*-BuOK-*t*-BuOH	0.66	0.080	0.045

a Rate constants for overall reaction and olefin yields from M. L. Dhar, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948); H. C. Brown, I. Moritani, and Y. Okamoto, *J. Amer. Chem. Soc.*, **78**, 2193 (1956). Relative proportions of isomeric olefins determined as follows (base–solvent, alkyl bromide, % 1-alkene, % *trans-2-*alkene, % *cis-2-*alkene): KOEt–EtOH, 2-butyl bromide, 15.9, 66.5, 18.6; KOEt–EtOH, 2-pentyl bromide, 22.7, 62.7, 14.6; *t*-BuOK-*t*-BuOH, 2-butyl bromide, 50.9, 29.8, 19.3; *t*-BuOK-*t*-BuOH, 2-pentyl bromide, 84.0, 10.2, 5.8. *b* In l./sec mol.

against R.[12] Alternatively, unavoidable crowding of the base against R with concomitant restricted rotation of R (for R > Me) would increase the enthalpy and decrease the entropy of transition states **2** and **3**. Both the restricted-rotation and direct-compression steric proposals predict decreases in the transition-state entropy of **2** and **3** as R is increased.

Since formation of 1-alkene from $RCH_2CHBrCH_3$ is relatively insensitive to the nature of R, differences in $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ for *trans-2-*alkene *vs.* 1-alkene and *cis-2-*alkene *vs.* 1-alkene for the series of 2-bromoalkanes (Tables IV–VI) represent primarily changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for formation of *trans-* and *cis-2-*alkene wrought by variation of R. If the destabilization of transition states **2** and **3** is indeed due to the proposed steric effects, decreases in $\Delta\Delta S^{\ddagger}$ for *trans-2-*alkene

(12) A well-documented case of entropy decrease caused by restricted rotation in Finkelstein reactions of ethyl and *n*-propyl halides is discussed in ref 13.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 410.

vs. 1-alkene and *cis*-2-alkene *vs.* 1-alkene are expected as R is made larger.

Examination of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ for eliminations from the series of 2-bromoalkanes induced by MeONa–MeOH (Table IV), *t*-BuOK–*t*-BuOH (Table V), and *t*-BuOK–DMSO (Table VI) reveals none of the anticipated decreases in $\Delta\Delta S^{\ddagger}$ as R is changed from methyl to higher homologs. Failure to observe detectable steric effects with MeONa–MeOH might be attributed to the limited steric requirements of the base. However, even with the bulky base potassium *t*-butoxide, steric interactions between the base and R are apparently unimportant.

Another conceivable explanation[14] of the destabilization of 2 and 3 as R is increased is an unfavorable electronic interaction of R. Transition states for elimination from 2-bromoalkanes promoted by *t*-BuOK–*t*-BuOH are proposed to have a high degree of C–H bond cleavage, but an only slightly ruptured C–Br bond.[4h] Such timing would result in partial negative charges on the β-carbon atoms and a high sensitivity to destabilizing, electron-donating properties[15] of R in the transition states leading to internal olefin. Both the magnitude and rapid attenuation of the increases in transition-state enthalpy for formation of *trans*- and *cis*-2-alkene relative to 1-alkene as R is increased in *t*-BuOK–*t*-BuOH (Table V) are consistent with this explanation. However, this proposal is seemingly inapplicable to eliminations induced by MeONa–MeOH and *t*-BuOK–DMSO, in which the transition states are postulated to have similar amounts of heterolysis of the C–H and C–Br bonds.

Experimental Section

2-Bromoalkanes.—2-Bromobutane (Eastman) was distilled, yielding only one fraction. Other 2-bromoalkanes were prepared by reaction of secondary alcohols[16] with triphenylphosphine and bromine in dimethylformamide.[4a,17] Homogeneity of the 2-bromoalkanes was demonstrated by glpc using a 20 ft × 0.25 in. column of 15% Carbowax 20M on Chromosorb P. Physical properties for the 2-bromoalkanes corresponded to literature values.

Base–solvent solutions were prepared as before.[4a–c]

Reactions of 2-bromoalkanes with sodium methoxide in methanol and potassium *t*-butoxide in *t*-butyl alcohol were conducted and elimination products were analyzed as before.[4b]

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(14) We thank a referee for pointing out that external effects, such as steric hindrance of R to solvation or to ionic aggregation, could play an important role.

(15) As judged from Taft σ* values: R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 591.

(16) Commercially available alcohols were distilled and shown to be homogeneous by glpc.

(17) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

Reactions of 2-Bromoalkanes with Potassium *t*-Butoxide in Dimethyl Sulfoxide.—The base–solvent solution (5.0 ml) was pipetted into an apparatus designed to sweep olefinic products from the reaction solution with nitrogen and carry them to a receiving trap. A sweep of dry nitrogen was started (200–400 ml/min) and the reaction vessel and attached trap were lowered into a thermostat and a liquid nitrogen filled dewar flask, respectively. The neat 2-bromoalkane (0.4–2.3 mmol) was injected through a rubber septum into the base–solvent solution with a syringe. After 5–15 min, the nitrogen sweep was halted. The reaction vessel and trap were removed and the trap was separated. *n*-Hexane (2 ml) (for 2-heptyl and 2-octyl bromide reactions) or methanol (for reactions of other 2-bromoalkanes) was added to the trap. Resulting solutions were cooled with Dry Ice–isopropyl alcohol (solutions of heptenes and octenes were kept at room temperature) and were analyzed by direct injection of a 0.1–0.3-μl portion into the gas chromatograph.

In one run at 50°, a mixture of weighed amounts of 2-bromohexane and *n*-hexane (internal standard) was subjected to the reaction procedure. From comparison of hexene and hexane peak areas, an olefin yield of 90 ± 2% was calculated.

Glpc analysis of olefinic reaction products was accomplished with a Varian Aerograph Model 204 flame-ionization gas chromatograph. Separation of isomeric olefins from each other, solvent, and unreacted 2-bromoalkane was usually achieved with 30 ft × 0.125 in. columns of 20% UcON 50HB100 on Chromosorb P operated at ambient temperatures (for butenes, pentenes, and hexenes), at 70° (for heptenes), or at 90° (for octenes). Owing to similar retention times for heptenes and methanol on these columns, 20 ft × 0.125 in. columns of 20% XF-1150 on Chromosorb P operated at 0° were used to analyze elimination products from reactions of 2-bromoheptane with MeONa–MeOH. Relative areas of the cleanly separated peaks for the isomeric olefins were determined with a disk integrator.

Stability of Olefinic Products to Reaction Conditions.—To test for isomerization of olefinic products in eliminations induced by *t*-BuOK–DMSO, a synthetic mixture of 55.6 ± 0.5% 1-hexene, 3.4 ± 0.2% *trans*-2-hexene, and 41.0 ± 0.5% *cis*-2-hexene was subjected to the reaction procedure. The trapped hexene mixture analyzed as follows: (A) from reaction at 50°, 54.6 ± 0.5% 1-hexene, 3.6 ± 0.2% *trans*-2-hexene, and 41.8 ± 0.5% *cis*-2-hexene; and (B) from reaction at 70°, 47.3 ± 0.5% 1-hexene, 4.2 ± 0.3% *trans*-2-hexene, and 48.5 ± 0.5% *cis*-2-hexene.

Calculations.—For eliminations of each 2-bromoalkane in the three base–solvent systems, plots of log (per cent *trans*-2-alkene/per cent 1-alkene), log (per cent *cis*-2-alkene/per cent 1-alkene), and log (per cent *trans*-2-alkene/per cent *cis*-2-alkene) *vs.* 1/*T* were prepared and the data were analyzed by a computer programmed for linear regression least squares analysis. The intercepts were equal to $\Delta\Delta S^{\ddagger}/2.303R$, while the slopes were equal to $-\Delta\Delta H^{\ddagger}/2.303R$. A statistical factor correcting for the number of β hydrogens available was applied to entropy of activation calculations involving formation of 1-alkenes.[4b] Uncertainties in $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ were estimated from the standard deviations of the slopes and intercepts, respectively.