Figure 4. $\Delta H^{\pm}$ and $\Delta H_\alpha^{\pm}$ for solvolysis of *tert*-butyl chloride in ethanol–water mixtures at 25° ($Z_1 > 0.75$) and 37.5° ($Z_1 < 0.75$).

increase of ln k with Z_1 by an essentially electrostatic theory in which the charge separation in the transition state is promoted by the change to a more polar solvent medium. However, analysis of Henry's law constants[36] and heats of solution[37] of *tert*-butyl chloride showed that this is only a partial explanation. In water-rich mixtures ($Z_1 > 0.7$) the characteristic medium effects on $\Delta G^{\pm}$ and $\Delta H^{\pm}$ are due largely to medium effects in the $(CH_3)_3CCl$ ground state, rather than in the transition state.[36,37a] On the other hand, in alcohol-rich mixtures ($Z_1 < 0.2$), the characteristic medium effects on $\Delta G^{\pm}$ and $\Delta H^{\pm}$ are due largely to medium effects in the transition state,[36,37c] and it has even been suggested that there is a change in reaction mechanism.[37c]

Our thesis in this paper is that quantities measured at

(37) (a) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Amer. Chem. Soc.*, **85**, 1350 (1963); (b) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965); (c) E. M. Arnett, W. G. Bentrude, and P. M. Duggleby, *ibid.*, **87**, 2048 (1965).

constant Z_1, such as $\delta_M\Delta G^{\pm}$ and $\Delta H^{\pm}$, are inherently complex because they include changes in the relative partial molal functions of the solvent components, and that their variation with Z_1 gives accordingly a distorted picture of the underlying solvent effects. The distortion is removed by transforming the functions to endostatic conditions.

Returning to the solvolysis of *tert*-butyl chloride, the plot of $\delta_M\Delta G^{\pm}$ *vs.* Z_1 (Figure 3) is an approximately straight line which gives no obvious indication of the changeover in the medium effect, from being dominated by the ground state to being dominated by the transition state. On the other hand, $\delta_M\Delta G_\alpha^{\pm}$ is a sigmoid function which shows marked changes in both water-rich and alcohol-rich mixtures and only minor changes in between. The plot of $\Delta H^{\pm}$ *vs.* Z_1 (Figure 4) is quite complicated, with a marked hump near $Z_1 \approx 0.87$; the plot of $\Delta H_\alpha^{\pm}$ *vs.* Z_1 is simpler, with the hump being transformed into a broader minimum.

Data for $\Delta C_p^{\pm}$ are available only for water-rich mixtures and are a complex function of Z_1. Transformation to $\Delta C_{p,\alpha}^{\pm}$ (Table VI) does not lead to any obvious reduction in complexity.

Concluding Remarks

It is clear from the preceding examples that transformation to endostatic conditions causes some functions of Z_1 to become simpler, while others (such as $\delta_M\Delta G^{\pm}$ in Figure 3) become more complicated. However, in each case the transformed relationship should be easier to interpret, because of the exact analogy of endostatic functions to corresponding functions in one-component solvents. With more experience, and with the availability of more accurate data for the required transformations, one may hope that the analysis of endostatic relationships will give a sharper insight into solvation effects.

Orientation in Base-Promoted β-Elimination Reactions. Effects of Base Strength and Size

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Abstract: Orientation in β-eliminations from 2-iodobutane promoted by a wide variety of oxygen, nitrogen, and carbon bases in dimethyl sulfoxide has been determined. By the use of linear free energy relationships, a fundamental control of orientation by base strength and the level of base complexity necessary for the onset of steric effects are demonstrated. Sensitivity of orientation to base strength is dependent upon the first atom of the base, decreasing in the order, oxygen > nitrogen > carbon.

A long-standing controversy concerning the relative importance of base strength and size in determining orientation for olefin-forming elimination re-

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(2) National Science Foundation Undergraduate Research Participant, 1972.

actions has recently been resolved.[3,4] Fundamental

(3) R. A. Bartsch, G. M. Pruss, B. A. Bushaw, and K. E. Wiegers, *J. Amer. Chem. Soc.*, **95**, 3405 (1973).
(4) Froemsdorf and Robbins have earlier reported a qualitative relationship between orientation observed in eliminations from 2-butyl tosylate induced by six oxyanion bases in DMSO and the pK_a's of the oxyanion bases in *water* which suggested that orientation could be significantly affected by base strength alone: D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967).

control of positional orientation[5] in eliminations from 2-iodobutane promoted by oxyanion bases was demonstrated.[3] However, for the very hindered base 2,6-di-tert-butylphenoxide, steric effects became important. In order to probe the level of base complexity necessary for the onset of steric interactions, a wide variety of oxygen, nitrogen, and carbon bases have now been examined.

Results

The relative proportions of isomeric butenes which are produced from reactions of 2-iodobutane with alkali metal phenoxides, alkoxides, anilides, and methides in dimethyl sulfoxide (DMSO) are recorded in Tables I–IV. A nitrogen gas sweep procedure[6] was employed

Table I. Olefinic Products from Reactions[a] of 2-Iodobutane with Alkali Metal Phenoxides in DMSO at 50.0°

| | Total butenes, % | | |
Base	1-Butene	trans-2-Butene	cis-2-Butene
Sodium phenoxide	10.6 ± 0.9[b]	70.6 ± 0.9	18.8 ± 0.4
Sodium 2-tert-butylphenoxide	11.3 ± 0.1	68.7 ± 0.2	20.0 ± 0.1
Sodium 2,6-dimethyl-phenoxide	11.3 ± 0.3	63.6 ± 1.0	25.1 ± 0.3
Sodium 2-methyl-6-tert-butylphenoxide	13.1 ± 0.3	64.3 ± 0.4	22.6 ± 0.1
Sodium 2,6-di-isopropylphenoxide	12.8	63.7	23.5
Sodium 2,6-di-sec-butylphenoxide	13.7 ± 0.3	62.6 ± 0.1	23.7 ± 0.3
Potassium 2,6-di-tert-butylphenoxide[c]	19.2 ± 0.4	63.6 ± 0.7	17.2 ± 0.6
Sodium 2,6-di-tert-butyl-4-methoxy-methylphenoxide	18.6 ± 0.1	63.6 ± 0.3	17.8 ± 0.3

[a] [2-BuI] = 0.1 M, [ArONa] = 0.25 M or saturated solution. [b] Standard deviation from repetitive analysis of trapped butene mixture. [c] Reference 3.

Table II. Olefinic Products from Reactions[a] of 2-Iodobutane with Alkali Metal Alkoxides in DMSO at 50.0°

| | Total butenes, % | | |
Base	1-Butene	trans-2-Butene	cis-2-Butene
EtONa[b]	17.1	63.7	19.2
NaOCH₂CH₂ONa	17.6 ± 0.6[c]	62.4 ± 0.2	20.0 ± 0.5
Me₃COK[d]	20.7	59.5	19.8
Et₃CONa	20.9 ± 0.5	60.4 ± 0.5	18.7 ± 0.2
Ph₃CONa	17.7 ± 0.2	62.7 ± 0.3	19.6 ± 0.3

[a] [2-BuI] = 0.1 M, [RONa] = 0.25 M or saturated solution. [b] R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *Tetrahedron Lett.*, 3795 (1970). [c] Standard deviation from repetitive analysis of trapped butene mixture. [d] Reference 3.

to prevent isomerization of the olefinic products. Appropriate control experiments demonstrated negligible amounts of butenes were produced from solvolysis of 2-iodobutane under the reaction conditions. DMSO was chosen as the solvent in order to suppress the recently recognized, complicating effect of base association upon orientation in eliminations from secondary alkyl halides and arenesulfonates.[7,8]

Plots of free-energy differences between transition states for formation of terminal and internal olefins, $\Delta\Delta G^{\ddagger}$ (1-butene-trans-2-butene) and $\Delta\Delta G^{\ddagger}$ (1-butene-cis-2-butene) vs. pK_a values for the conjugate acids of the anilide and methide bases, are shown in Figures 1–4.

Discussion

The primary deuterium isotope effects,[9] exclusive anti-elimination stereochemistry,[9] and high trans-/cis-2-alkene ratios[6] which have been observed in base-promoted eliminations from 2-alkyl halides in DMSO evince a normal concerted E2 mechanism for the present olefin-forming reactions of 2-iodobutane.

Oxyanion Bases. Divergence from linear relationships between free-energy differences of transition states for formation of 1-butene and the 2-butenes vs. pK_a values for the conjugate acids of oxyanion bases was found in reactions of 2-iodobutane with 2,6-di-tert-butylphenoxide, but not with phenoxide, in DMSO.[3] The divergence was attributed to base steric effects.[3] It was therefore of interest to determine at what level of base complexity steric effects become important for phenoxide ion bases. The data in Table I show relatively small changes in orientation as 2 and 6 substituents of phenoxide ion bases are systematically varied from H to sec-Bu. However, marked changes are noted when results for 2,6-di-sec-butylphenoxide and 2,6-di-tert-butylphenoxide are compared. Such disproportionate changes would be anticipated at the threshold for steric interactions. The similarity of orientation for reactions employing 2,6-di-tert-butylphenoxide and 2,6-di-tert-butyl-4-methoxymethylphenoxide ion bases demonstrates that para ring sites[10] are not the effective basic centers for the very hindered bases.

Although not observed for tert-butoxide,[3] it was thought that steric effects might become important for oxyanion bases derived from even more hindered tertiary alcohols. The similarity of orientation for eliminations promoted by tert-butoxide, 3-ethyl-3-pentoxide, and 1,1,1-triphenylmethoxide ions (Table II) indicates that hindrance of the oxyanion centers of tertiary alkoxides is insufficient to produce noticeable steric effects.

Corey and Terashima[11] have recently reported a dramatic increase in the ratio of elimination to substitution products in reactions of a substituted cyclopentyl tosylate with carboxylate anions when oxalate was used in place of formate. A possible "bidentate" attack by oxalate upon hydrogen was proposed.[11] It seems reasonable to anticipate "bidentate" base attack would exhibit significantly different orientation than elimination induced by a monoanionic base. The essentially identical butene proportions observed for reactions of 2-iodobutane with ethoxide and the dianion of ethylene glycol (Table II) suggest that "bidentate" base attack is unimportant.

Anilide Bases. Linear relationships for free-energy differences between transition states for formation of terminal and the internal olefins and base strength exist

(5) Positional orientation refers to the relative amounts of 1-butene and 2-butenes which are formed.
(6) R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970).

(7) R. A. Bartsch, G. M. Pruss, R. L. Buswell, and B. A. Bushaw, *Tetrahedron Lett.*, 2621 (1972).
(8) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Amer. Chem. Soc.*, **95**, 6745 (1973).
(9) R. A. Bartsch, *J. Amer. Chem. Soc.*, **93**, 3683 (1971).
(10) T. Fujisawa and T. Kojima, *J. Org. Chem.*, **38**, 687 (1973).
(11) E. J. Corey and S. Terashima, *Tetrahedron Lett.*, 111 (1972).

Table III. Olefinic Products from Reactions[a] of 2-Iodobutane with 0.25 M Sodium Anilides in DMSO at 50.0°

| System | Conjugate acid of anilide | pK_a of conjugate acid in DMSO | Total butenes, % | | |
			1-Butene	trans-2-Butene	cis-2-Butene
1	4-Chloro-2-nitroaniline	18.0[b]	7.2 ± 0.2[c]	71.6 ± 0.6	21.2 ± 0.5
2	2-Methyl-4-nitroaniline	20.3[b]	8.5 ± 0.4	70.0 ± 0.5	21.5 ± 0.2
3	Diphenylamine	22.6[b]	11.4 ± 0.4	73.9 ± 0.6	14.7 ± 0.3
4	2,5-Dichloroaniline	24.6[d]	9.6 ± 0.4	71.1 ± 0.5	19.3 ± 0.4
5	4-Cyanoaniline	25.6[d]	9.8 ± 0.4	70.0 ± 0.3	20.2 ± 0.2
6	3-Chloroaniline	26.7[d]	11.8 ± 0.1	68.7 ± 0.6	19.5 ± 0.5

[a] [2-BvI] = 0.1 M. [b] E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolf, and R. P. Quirk, J. Amer. Chem. Soc., 95, 1492 (1973). [c] Standard deviation from repetitive analysis of trapped butene mixture. [d] J. Courtot-Coupez and M. Le Demezet, Bull. Soc. Chim. Fr., 1033 (1969).

Table IV. Olefinic Products from Reactions[a] of 2-Iodobutane with 0.25 M Sodium Methide Bases in DMSO at 50.0°

| System | Conjugate acid of methide | pK_a of conjugate acid in DMSO | Total butenes, % | | |
			1-Butene	trans-2-Butene	cis-2-Butene
7	2,4-Pentanedione	13.4[b]	7.6 ± 0.4[c]	71.1 ± 0.3	21.3 ± 0.5
8	Nitroethane	13.9[b]	7.5 ± 0.1	72.4 ± 0.6	20.1 ± 0.4
9	Nitromethane	15.9[b]	7.7 ± 0.3	72.4 ± 0.6	19.9 ± 0.3
10	1,3-Diphenyl-2-propanone	(16.1)[d]	9.9 ± 0.5	68.4 ± 0.8	21.7 ± 0.4
11	Dibenzyl sulfone	22[e]	15.0 ± 0.3	62.4 ± 0.4	23.6 ± 0.4
12	Dimethyl sulfone	28.5[e]	8.9 ± 0.1	68.5 ± 0.3	22.6 ± 0.3
13	Triphenylmethane	28.8[f]	21.2 ± 0.5	55.5 ± 0.3	23.3 ± 0.4
14	Diphenylmethane	30.2[f]	17.4 ± 0.3	63.9 ± 0.6	18.7 ± 0.5
15	Dimethyl sulfoxide	32.9[g]	9.5 ± 0.3	68.6 ± 0.5	21.9 ± 0.3

[a] [2-BuI] = 0.1 M. [b] C. D. Ritchie and R. E. Uschold, J. Amer. Chem. Soc., 90, 2821 (1968). [c] Standard deviations from repetitive analysis of trapped butene mixture. [d] The value cited is the pK_a of benzyl phenyl ketone in monoglyme: H. D. Zook, W. L. Kelly, and I. Y. Posey, J. Org. Chem., 33, 3477 (1968). [e] F. G. Bordwell, R. H. Imes, and E. C. Steiner, J. Amer. Chem. Soc., 89, 3905 (1967). [f] E. C. Steiner and J. M. Gilbert, J. Amer. Chem. Soc., 87, 382 (1965). [g] R. Stewart and J. R. Jones, J. Amer. Chem. Soc., 89, 5069 (1967).

for five of six anilide bases (Figures 1 and 2). These relationships demonstrate intrinsic control of positional orientation by base strength for nitrogen, as well as oxygen, bases. Deviation of points for the anion of diphenylamine (system 3) from these relationships is ascribed to base steric effects.

Methide Bases. Plots of free-energy differences between transition states for formation of 1-butene and the 2-butenes vs. pK_a values for conjugate acids of the carbon bases are shown in Figures 3 and 4. Omitting the points for the enolate anions (broken squares), linear relationships for four of the seven carbon bases are found. The anions derived from dibenzyl sulfone (system 11) and diphenylmethane (system 14), as well as triphenylmethane (system 13), deviate markedly from the lines in the direction anticipated for steric effects.[3] Thus, for carbon, as well as nitrogen bases, attachment of two large groups such as phenyl or sulfonyl to the anionic center produces elimination orientation which is consistent with the onset of basic steric effects.

The points for enolate anions produced from 2,4-pentanedione and 1,3-diphenyl-2-propanone (broken squares) appear to correlate better with the line reported for oxygen bases[3] (broken line) than that for carbon bases (Figures 3 and 4). This indicates proton abstraction by enolate oxygen and is consistent with the exhalation of O-alkylation of enolate anions which is noted in DMSO.[12]

Base Strength and Size. Fundamental control of positional orientation by base strength for eliminations from 2-iodobutane induced by dissociated anionic oxygen, nitrogen, and carbon bases in DMSO has been demonstrated. The slopes of the linear free energy relationships for oxygen,[3] nitrogen (Figures 1 and 2),

(12) H. D. Zook and J. A. Miller, J. Org. Chem., 36, 1112 (1971).

and carbon bases (Figures 3 and 4) are: for 1-butene–trans-2-butene, O = 0.042 ± 0.002, N = 0.032 ± 0.006, C = 0.009 ± 0.001; for 1-butene–cis-2-butene, O = 0.037 ± 0.002, N = 0.036 ± 0.005, C = 0.005 ± 0.001. Thus, sensitivity of positional orientation to base strength decreases in the order O > N > C. Orientation is most sensitive to base strength when the β hydrogen (hard acid[13]) is removed by an oxygen base (hard base).

Steric effects for dissociated bases are observed with anions derived from 2,6-di-tert-butylphenol, diphenylamine, diphenylmethane, dibenzyl sulfone, and triphenylmethane. Examination of Dreiding stereomodels reveals that for each of these bases, a plane passed through the basic atom is intersected by other atomic centers even when the remaining portion of the anion is arranged so as to relieve such contact. However, when the residual portion of the base can be oriented such that impingement upon this plane does not occur (e.g., for 2,6-di-sec-butylphenoxide), basic steric effects are unimportant. These findings will allow for the synthesis of new "super bases" which combine the orientation control of a sterically hindered base with the high reactivity of a dissociated base.[14]

Experimental Section

Base–Solvent Solutions. Into a 25-ml three-necked flask

(13) R. R. Pearson and J. Songstad, J. Amer. Chem. Soc., 89, 1827 (1967).

(14) Base steric effects and low reactivity (compared with dissociated bases) are observed for associated oxyanion bases.[7,8]

(15) We thank the Ethyl Corporation for generous gifts of alkylated phenols and MSA Corporation for a sample of potassium 2,6-di-tert-butylphenoxide.
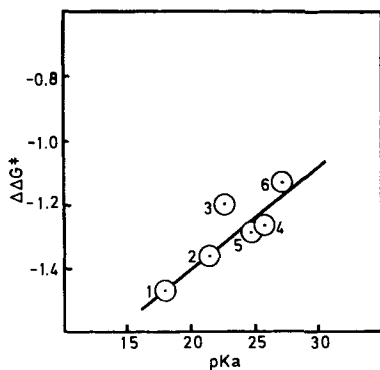
Figure 1. Plot of free-energy difference for formation of 1-butene and trans-2-butene in kcal/mol vs. the pK_a of the conjugate acid of anilide bases. System numbers refer to Table III.
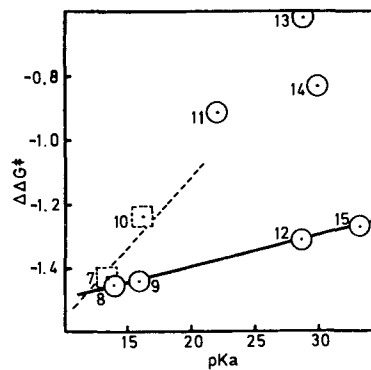

Figure 3. Plot of free-energy difference for formation of 1-butene and trans-2-butene in kcal/mol vs. the pK_a of the conjugate acid of methide bases. System numbers refer to Table IV.
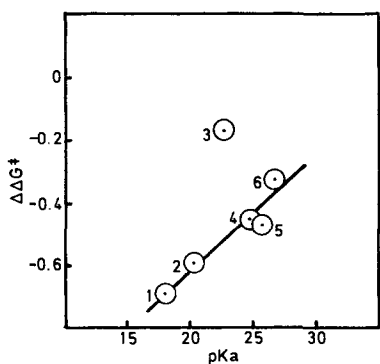

Figure 2. Plot of free-energy difference for formation of 1-butene and cis-2-butene in kcal/mol vs. the pK_a of the conjugate acid of anilide bases. System numbers refer to Table III.
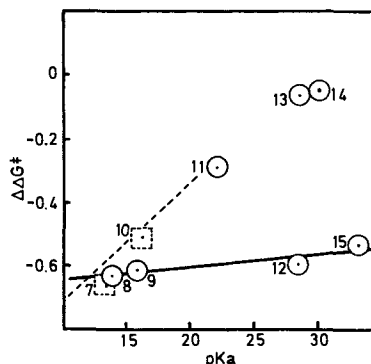

Figure 4. Plot of free-energy difference for formation of 1-butene and cis-2-butene in kcal/mol vs. the pK_a of the conjugate acid of methide bases. System numbers refer to Table IV.

equipped for inert atmosphere was weighed 0.24 g (0.0050 mol) of NaH (50% dispersion in mineral oil). The NaH was washed five times with pentane to remove the mineral oil. DMSO (20 ml) was added to the NaH followed by 0.0058 mol of the conjugate acid of the desired base. The mixture was stirred until a homogeneous solution was obtained. In some instances, heating of the mixture with a water bath was employed to facilitate the reaction.

Sodium 2,6-di-tert-butyl-4-methoxymethylphenoxide was produced by reaction of 0.96 g (0.020 mol) of NaH (50% dispersion in mineral oil, washed as above) and 2.37 g (0.010 mol) of 3,5-di-tert-butyl-4-hydroxybenzyl alcohol in 80 ml of DMSO. The mixture was stirred for 2.5 hr at room temperature yielding a white pre-

cipitate. Addition of 1.60 g of MeI (0.011 mol) and stirring for 2.5 hr at room temperature produced a clear, golden-colored solution which was used directly.

Procedure. The experimental procedure (10 min reaction period) and glpc analytical techniques reported by Bartsch[6] were employed. Using this experimental method, a general reproducibility of ±1% in percentages of isomeric olefins has been observed when a given elimination reaction has been run by a number of students over a period of several years.

Control Experiment. Negligible amounts of butenes resulted from reactions of 2-iodobutane with DMSO under the reaction conditions utilized for the base-promoted reactions.