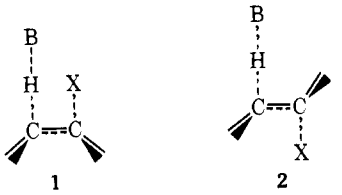
The Stereochemistry of Base-Catalyzed β Elimination from 2-Bromobutane[1,2]

Richard A. Bartsch

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received September 22, 1970*

Abstract: The stereochemistry of β elimination from *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutane (**3** and **4**, respectively) induced by a variety of base–solvent combinations has been determined. Both *cis*- and *trans*-2-butene are formed by exclusive anti elimination with EtOK–EtOH, *sec*-BuOK–*sec*-BuOH, *tert*-BuOK–*tert*-BuOH, *tert*-BuOK–DMSO, *tert*-BuOK–THF, and *n*-Bu_4NF–DMF. Within experimental error, equal primary deuterium isotope effects were observed for the formation of *trans*-2-butene from **3** and *cis*-2-butene from **4** in a given base–solvent system.

The role of syn- and anti-elimination transition states (**1** and **2**, respectively) in base-catalyzed β eliminations from simple acyclic compounds has recently received considerable attention[1,3–14] Stereochemical investigations of eliminations for secondary alkyl bromides,[1] *p*-toluenesulfonates,[6,8,11,12] trimethylammonium salts,[3–5,7,9–11,13,14] and dimethylsulfonium salts[13,14] indicate that syn-elimination stereochemistry is more common than previously imagined. Particularly intriguing is the effect of the reaction solvent upon the relative amounts of syn and anti elimination.[3–5,10–12]



1 2

On the basis of the very high *trans*-2-hexene:*cis*-2-hexene ratios observed in eliminations from 2-hexyl iodide, bromide, and chloride induced by potassium *tert*-butoxide in dimethyl sulfoxide, a syn-elimination mechanism was proposed.[15,16] The only stereochemical studies of dehydrohalogenation of acyclic secondary alkyl halides report anti elimination in reactions of *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutane with potassium ethoxide and potassium hydroxide in ethanol.[18,19] Therefore, an investigation of elimination stereochemistry in reactions of *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutane with a variety of base–solvent combinations was undertaken.

Results

Photochemically initiated free-radical addition of deuterium bromide to *trans*- and *cis*-2-butene[20] at −90° produced *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutane (**3** and **4**, respectively). Analysis by mass spectrometry of these diastereomeric compounds and the butenes resulting from their reactions with potassium *tert*-butoxide in dimethyl sulfoxide revealed a lower degree of stereospecificity in the free-radical addition than previously reported.[20] The *d,l-erythro*-3-deuterio-2-bromobutane was contaminated with 2 ± 1% of the threo isomer and 3 ± 1% of undeuterated material. The *d,l-threo*-3-deuterio-2-bromobutane contained 7 ± 1% of the erythro compound and 7 ± 1% of undeuterated 2-bromobutane.

Products from Base-Catalyzed β-Elimination Reactions of *d,l-erythro*- and *d,l,-threo*-3-Deuterio-2-bromobutane. Reactions of **3** and **4** with a variety of base–solvent combinations were conducted in an apparatus designed to sweep the evolved butenes from the reaction solution.[21] A methanolic solution of the trapped butenes was subjected to analytical gas–liquid partition chromatography (glpc) to determine the relative amounts of the olefinic products and to preparative glpc to separate and collect the *trans*-2-butene, *cis*-2-butene, and 1-butene. The relative olefinic proportions observed in reactions of *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutane and 2-bromobutane with a variety of base–solvent combinations are presented in Table I. The deuterium content of the three isomeric olefins was determined by mass spectrometry at low ionizing voltages. Tables II and III record the ob-

(1) For a preliminary communication of a portion of this work, see R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970).
(2) Presented at the 25th Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970.
(3) D. S. Bailey and W. H. Saunders, Jr., *Chem. Commun.*, 1599 (1968).
(4) D. S. Bailey, F. C. Montgomery, G. W. Chodak, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 6911 (1970).
(5) D. S. Bailey and W. H. Saunders, Jr., *ibid.*, **92**, 6904 (1970).
(6) D. H. Froemsdorf, W. Dowd, W. A. Gifford, and S. Meyerson, *Chem. Commun.*, 449 (1968).
(7) D. H. Froemsdorf, H. R. Pinnick, Jr., and S. Meyerson, *ibid.*, 1600 (1968).
(8) D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967).
(9) M. Pánková, J. Sicher, and J. Závada, *Chem. Commun.*, 394 (1967).
(10) M. Pánková, J. Závada, and J. Sicher, *ibid.*, 1142 (1968).
(11) J. Sicher, J. Závada, and M. Pánková, *ibid.*, 1147 (1968).
(12) J. Závada, M. Pánková, and J. Sicher, *ibid.*, 1145 (1968).
(13) J. Závada and J. Sicher, *Collect. Czech. Chem. Commun.*, **30**, 438 (1965).
(14) J. Závada and J. Sicher, *Proc. Chem. Soc.*, 96 (1963).
(15) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1382 (1969).
(16) A syn–anti elimination dichotomy, *i.e.*, formation of *trans*-olefin by syn elimination and *cis*-olefin by anti elimination, has been postulated in eliminations from cycloalkyl bromides promoted by potassium *tert*-butoxide in *tert*-butyl alcohol and in benzene.[17]
(17) J. Závada, J. Krupička, and J. Sicher, *Collect. Czech. Chem. Commun.*, **33**, 1393 (1968).
(18) G. H. Helmkamp and N. Schnautz, *J. Org. Chem.*, 24, 529 (1959).
(19) P. S. Skell, R. G. Allen, and G. H. Helmkamp, *J. Amer. Chem. Soc.*, **82**, 410 (1960).
(20) P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).
(21) Isomerization of olefinic products with strongly basic potassium *tert*-butoxide in dimethyl sulfoxide is negligible under these conditions.[15,22]
(22) R. A. Bartsch, *J. Org. Chem.*, **35**, 1334 (1970).

Table I. Relative Olefinic Proportions in Base-Catalyzed Elimination from 2-Bromobutane

Base–Solvent	Temp, °C	Isomer		Total butenes, % *trans*-2-Butene	*cis*-2-Butene	1-Butene
EtOK–EtOH	70	*d,l-erythro*	Obsd	30.6 ± 0.1[a]	34.2 ± 0.2	35.2 ± 0.1
			Corr[b]	28.8	35.3	35.9
		d,l-threo	Obsd	65.9 ± 0.6	9.2 ± 0.3	24.9 ± 0.4
			Corr[b]	69.0	6.5	24.5
		Undeuterated		58.6 ± 0.2	20.6 ± 0.1	20.8 ± 0.3
sec-BuOK–*sec*-BuOH	70	*d,l-erythro*	Obsd	19.9 ± 0.2	31.4 ± 0.1	48.7 ± 0.1
			Corr[b]	18.3	32.2	49.5
		d,l-threo	Obsd	52.4 ± 0.2	8.9 ± 0.2	38.6 ± 0.2
		Undeuterated		46.9 ± 0.3	21.4 ± 0.2	31.7 ± 0.2
tert-BuOK–*tert*-BuOH	70	*d,l-erythro*	Obsd	10.1 ± 0.2	25.9 ± 0.3	64.0 ± 0.2
			Corr[b]	7.6	27.3	65.1
		d,l-threo	Obsd	33.3 ± 0.3	8.7 ± 0.1	58.0 ± 0.3
			Corr[b]	35.1	6.4	58.5
		Undeuterated[c]		30.7	20.5	48.8
tert-BuOK–DMSO	30	*d,l-erythro*	Obsd	22.0 ± 0.2	26.0 ± 0.3	52.0 ± 0.3
			Corr[b]	20.2	26.8	53.0
		d,l-threo	Obsd	56.7 ± 0.1	6.4 ± 0.1	36.9 ± 0.2
			Corr[b]	59.3	3.9	36.8
		Undeuterated[c]		55.0	15.5	29.5
tert-BuOK–THF	25	*d,l-erythro*	Obsd	16.7 ± 0.2	23.1 ± 0.2	60.2 ± 0.4
			Corr[b]	14.8	23.8	61.4
		d,l-threo	Obsd	56.0 ± 0.3	4.0 ± 0.3	40.0 ± 0.1
		Undeuterated		51.8 ± 0.4	14.3 ± 0.2	33.7 ± 0.4
n-Bu_4NF–DMF	50	*d,l-erythro*	Obsd	34.4 ± 0.2	33.2 ± 0.4	32.4 ± 0.4
			Corr[b]	32.4	34.4	33.2
		d,l-threo	Obsd	69.9 ± 0.6	8.8 ± 0.2	21.3 ± 0.7
		Undeuterated[d]		64.5 ± 0.4	18.7 ± 0.5	16.7 ± 0.1

[a] Standard deviation. [b] Corrected for butenes from diastereomeric contaminant and unlabeled impurity. [c] Reference 22. [d] R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970).

Table II. Deuterium Content of Olefinic Products from Reactions of *d,l-erythro*-3-Deuterio-2-bromobutane with Several Base–Solvent Systems

Base–Solvent	Temp, °C		Total butenes, % *trans*-2-Butene d_0	*trans*-2-Butene d_1	*cis*-2-Butene d_0	*cis*-2-Butene d_1	1-Butene d_0	1-Butene d_1
EtOK–EtOH	70	Obsd	28.9	1.7	0.6	33.6	2.2	33.0
		Calcd[a,b]	28.9	1.7	0.8	33.4	0.6	34.6
sec-BuOK–*sec*-BuOH	70	Obsd	18.7	1.2	0.6	30.8	3.3	45.4
		Calcd[a,c]	18.7	1.2	0.8	30.6	0.9	47.8
tert-BuOK–*tert*-BuOH	70	Obsd	9.6	0.5	0.3	25.6	3.3	60.7
		Calcd[a,d]	9.6	0.5	0.7	25.2	1.4	62.6
tert-BuOK–DMSO	30	Obsd	20.8	1.2	0.5	24.5	1.9	50.1
		Calcd[a,e]	20.8	1.2	0.5	24.5	0.8	51.2
tert-BuOK–THF	25	Obsd	15.6	1.1	0.6	22.5	3.0	57.2
		Calcd[a,f]	15.6	1.1	0.5	22.6	1.0	59.2
n-Bu_4NF–DMF	50	Obsd	32.4	2.0	0.8	32.4	1.4	31.0
		Calcd[a,g]	32.4	2.0	0.8	32.4	0.5	31.9

[a] Calculated for contaminating 2.8% of 2-bromobutane and the threo isomer. [b] 2.5% threo isomer. [c] 2.2% threo isomer. [d] 1.5% threo isomer. [e] 2.0% threo isomer. [f] 2.0% threo isomer. [g] 2.8% threo isomer.

Table III. Deuterium Content of Olefinic Products from Reactions of *d,l-threo*-3-Deuterio-2-bromobutane with Several Base–Solvent Systems

Base–Solvent	Temp, °C		Total butenes, % *trans*-2-Butene d_0	*trans*-2-Butene d_1	*cis*-2-Butene d_0	*cis*-2-Butene d_1	1-Butene d_0	1-Butene d_1
EtOK–EtOH	70	Obsd	4.0	54.2	9.9	2.8	2.2	26.9
		Calcd[a,b]	6.5	51.7	9.9	2.8	1.5	27.6
tert-BuOK–*tert*-BuOH	70	Obsd	2.4	30.7	7.0	1.7	5.6	52.4
		Calcd[a,c]	3.2	30.2	7.0	1.7	3.5	54.5
tert-BuOK–DMSO	30	Obsd	2.5	51.0	4.9	2.1	1.7	35.3
		Calcd[a,d]	5.0	53.5	4.9	2.1	1.7	35.3

[a] Calculated for contaminating 7.1% of 2-bromobutane and the erythro isomer. [b] 8.0% erythro isomer. [c] 6.9% erythro isomer. [d] 7.3% erythro isomer.

served deuterium content of the three butene isomers for eliminations from **3** and **4**, respectively, as well as calculated values which include contributions from contaminating diastereomeric and unlabeled impurities.[23]

(23) Small differences of the present values from those previously reported[1] reflect improved analytical techniques.

Table IV. Deuterium Isotope Effects in Eliminations from *d,l-erythro-* and *d,l-threo*-3-Deuterio-2-bromobutane

Base-Solvent	Temp, °C	*erythro*-3-Deuterio-2-bromobutane k_H/k_D[a] (*trans*-2-butene)	*erythro*-3-Deuterio-2-bromobutane k_H/k_D[b] (*cis*-2-butene)	*threo*-3-Deuterio-2-bromobutane k_H/k_D[b] (*trans*-2-butene)	*threo*-3-Deuterio-2-bromobutane k_H/k_D[a] (*cis*-2-butene
EtOK–EtOH	70	3.5	1.01	1.00	3.8
sec-BuOK–*sec*-BuOH	70	4.0	1.04		
tert-BuOK–*tert*-BuOH	70	4.4	1.03	1.04	3.8
tert-BuOK–DMSO	30	4.9	1.08	1.11	5.0
tert-BuOK–THF	25	6.4	0.98		
n-Bu_4NF–DMF	50	4.0	1.08		

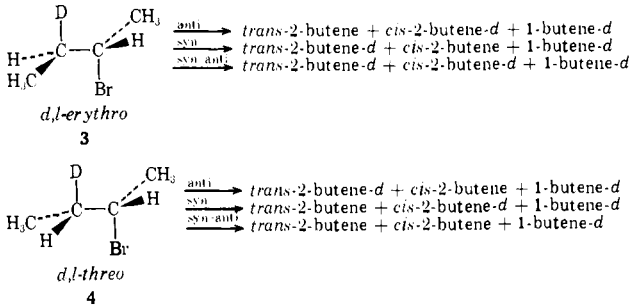
[a] Estimated uncertainty ±0.3. [b] Estimated uncertainty ±0.05.

Deuterium Isotope Effects. From the relative olefinic proportions recorded in Table I, deuterium isotope effects for the formation of the internal olefins from *d,l-erythro-* and *d,l-threo*-3-deuterio-2-bromobutane may be calculated.[24,25] The computed deuterium isotope effects are listed in Table IV.

Discussion

Stereochemistry of Elimination from 2-Bromobutane. Three extreme stereochemical possibilities for elimination from **3** and **4** may be envisioned: (1) all anti elimination; (2) all syn elimination; and (3) syn–anti elimination (*trans*-olefin *via* syn elimination and *cis*-olefin *via* anti elimination).[2] The consequences of these limiting alternatives upon the deuterium content of the three isomeric butenes formed from **3** and **4** are outlined in Chart I. For reaction of *d,l-erythro*-3-deuterio-2-bromobutane with a variety of base–solvent combinations, deuterated *cis*-2-butene and 1-butene, but undeuterated *trans*-2-butene, were observed (Table II). However, the olefins derived from *d,l-threo*-3-deuterio-2-bromobutane consisted of deuterated *trans*-2-butene and 1-butene and undeuterated *cis*-2-butene (Table III). These results clearly demonstrate a preferred anti-elimination stereochemistry in the formation of internal olefins from **3** and **4**. The relatively small amounts of *trans*-2-butene-*d*, and *cis*-2-butene from **3** and *trans*-2-butene and *cis*-2-butene-*d* from **4** arise from diastereomeric and unlabeled impurities in the starting materials. Incursion of a minor syn-elimination pathway producing these products seems unreasonable in view of the near constancy of their proportions in a wide variety of solvents (*vide infra*).

Chart I



The present results correlate in a most satisfactory manner with a developing pattern for stereochemistry in eliminations from acyclic and monocyclic (C_8–C_{16}) secondary alkyl *p*-toluenesulfonates and trimethylammonium salts, in which a dependence upon the nature of the alkyl group, solvent, and base has been noted. In eliminations from secondary *p*-toluenesulfonates promoted by alkoxide ions, variation of the alkyl group from 1,1,4,4-tetramethyl-8-cyclodecyl[26,27] to 5-decyl[12] to 2-butyl[6,8] entails a change from syn–anti elimination with the cyclic system to all anti for the 2-butyl compound. 5-Decyl *p*-toluenesulfonate was intermediate, with the portion of syn–anti elimination increasing as the solvent became less "dissociating," dimethylformamide < *tert*-butyl alcohol < benzene. Generally similar effects upon stereochemistry for change of alkyl group, solvent, and base have been reported in alkoxide ion induced eliminations from alkyl- and cycloalkyltrimethylammonium salts.[28]

For alkoxide ion induced dehydrohalogenation of cycloalkyl bromides (C_8–C_{16}), there is a change from syn–anti elimination in the "nondissociating" solvents *tert*-butyl alcohol and benzene, to anti in ethanol and dimethylformamide.[17] In the present investigation, strictly anti elimination from 2-butyl bromide occurs even under the conditions most favorable to syn–anti elimination, *i.e.* strong bases and solvents of low dielectric constant.[4,12,29] These results establish similar trends in the effects of the alkyl group upon elimination stereochemistry for secondary alkyl halides, *p*-toluenesulfonates, and trimethylammonium salts.

Although a change of alkyl group from 2-butyl to 2-hexyl could conceivably incur a minor amount of syn–anti elimination,[30] the current results appear to make untenable the proposal of all syn elimination in reactions of 2-hexyl halides with potassium *tert*-butoxide in dimethyl sulfoxide.[15] The high *trans*-2-alkene:*cis*-2-alkene ratios which were the basis for this proposal have been found to be characteristic for 2-alkyl halide eliminations promoted by a wide variety of bases in dipolar aprotic solvents.[31]

Previous studies of elimination stereochemistry for secondary alkyl halides, *p*-toluenesulfonates, and trimethylammonium salts have uniformly employed hydroxide or alkoxide ion bases. Therefore, the all anti stereochemistry observed in eliminations from **3** induced by a relatively unknown fluoride ion base[32] is of special interest.

(24) M. S. Silver, *J. Amer. Chem. Soc.*, **83**, 3487 (1961).
(25) M. Svoboda, J. Závada, and J. Sicher, *Collect. Czech. Chem. Commun.*, **30**, 438 (1965).
(26) J. Závada, M. Svoboda, and J. Sicher, *Tetrahedron Lett.*, 1626 (1966).
(27) M. Svoboda, J. Závada, and J. Sicher, *Collect. Czech. Chem. Commun.*, **33**, 1415 (1968).
(28) See ref 4 and 5 and papers cited therein.
(29) J. Sicher and J. Závada, *Collect. Czech. Chem. Commun.*, **33**, 1278 (1968).
(30) For eliminations from alkyltrimethylammonium salts, some syn–anti elimination is noted for the 2-hexyl derivative, even though the 2-butyl compound elimination seems to be all anti.[4,5]
(31) R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *J. Org. Chem.*, **36**, 662 (1971).
(32) R. A. Bartsch, *ibid.*, **35**, 1023 (1970).

Deuterium Isotope Effects for Formation of Internal Olefins. The k_H/k_D ratios presented in Table IV provide further confirmation of exclusive anti elimination for formation of the internal olefins from **3** and **4**. Thus, deuterium isotope effects of 3.5–6.4 are noted when rupture of a C–D bond precedes olefin formation. Conversely, if a C–D bond is not broken, only a small secondary deuterium isotope effect is anticipated and ratios of approximately unity are found.

In three base–solvent combinations (EtOK–EtOH, *tert*-BuOK–*tert*-BuOH, *tert*-BuOK–DMSO), the isotope effects for formation of *trans*-2-butene from **3** and *cis*-2-butene from **4** are the same, within experimental error. These results demonstrate, for the first time, similar amounts of C–H stretching in transition states leading to *trans*-2-alkene and *cis*-2-alkene in base-catalyzed β elimination from a 2-substituted alkane. This evidence seemingly contradicts the tentative suggestion by Sicher, Závadá, and Pánková[11] of intrinsic differences in reactivity of the two β-hydrogens.

The small increase in deuterium isotope effect for formation of *trans*-2-butene from **3** as the base–solvent solution is changed from EtOK–EtOH to *tert*-BuOK–*tert*-BuOH parallels that reported for eliminations from 2-phenylethyl bromide.[33,34] However, interpretation of such changes in magnitude of the isotope effect is complicated by the double-valued nature of the primary deuterium isotope effect.[35,36] In the absence of an additional mechanistic probe,[37] it is not possible to ascertain whether a change to a stronger base[40] gives rise to more or to less carbon–hydrogen bond stretching in the transition state, as predicted by theories of Bunnett[41] and Thornton,[42,43] respectively.

It should be noted that in the anti elimination[44,45] from 2-phenylethyl trimethylammonium salts, in which the proton is more than half transferred,[43] a large increase in primary deuterium isotope effect was observed as the base–solvent system was varied from EtOK–EtOH to *tert*-BuOK–*tert*-BuOH.[33,46] Thus, less carbon–hydrogen bond stretching in the transition state for the stronger base is suggested. However, differences in size, charge type, and reactivity of trimethylammonio and bromo leaving groups do not allow for extrapolation to the present system.

Experimental Section

Reagents. Purification of solvents and preparation of base–solvent solutions were performed as before.[31,32] Solutions of alkoxides in alcohols were 1.0 *M*, while *tert*-BuOK–DMSO and *n*-Bu_4NF–DMF were 0.8 *M*. The saturated solution of *tert*-BuOK in THF was prepared by addition of excess *tert*-BuOK to THF (Baker, reagent) from freshly opened bottles.

***d,l-erythro-* and *d,l-threo*-3-Deuterio-2-bromobutane** were synthesized by the procedure of Skell and Allen[20] with the modification of conducting the irradiation at −90°. Both **3** and **4** were homogeneous to glpc analysis on a 20 ft × 1/4 in. column of 15% Carbowax 20 M on Chromosorb P operated at 70°. The deuterium content of **3** and **4** was ascertained by mass spectrometry (70 eV) using the M_{58}/M_{57} peak ratios for the 2-butyl fragment (previous calibration with 2-butyl bromide). The concentration of diastereomeric impurities was measured by determining the per cent of *trans*-2-butene-*d* from **3** and the per cent of *cis*-2-butene-*d* from **4** in reactions with *tert*-BuOK–DMSO at 30°[47] using mass spectrometry (*vide infra*).

Elimination reactions of *d,l-erythro-* and *d,l-threo*-3-deuterio-2-bromobutane were conducted using the apparatus and procedure previously described for reactions of 2-bromoalkanes with *tert*-BuOK–DMSO.[22] Analytical glpc of the methanolic butene mixture was performed as before.[22] For the alkoxide–alcohol combinations, the relative olefinic proportions were determined from reactions employing an ampoule method.[48] Preparative glpc separation of the butene isomers was conducted on a Varian Aerograph A-90P gas chromatograph using a 20 ft × 1/4 in. column of 20% SF-96 on Chromosorb P operated at −15°. Mass spectrometric analysis of the separated butene isomers with a Varian M66 mass spectrometer was effected at minimal ionizing voltage, examining the M_{58}/M_{57} peak ratio (with previous calibration of the small M − 1 peak using Phillips research grade *cis*- or *trans*-2-butene).

Deuterium isotope effects were calculated from the relative olefinic proportions in reactions of **3**, **4**, and 2-bromobutnea with a given base–solvent combination.[24,25]

Acknowledgment. A portion of this work was supported by a National Science Foundation Faculty Summer Research Stipend awarded by the Research Committee of Washington State University. The mass spectrometer used in this study was purchased chiefly with NSF funds. Dr. K. D. McMichael is thanked for assistance with the mass spectrometric analysis.

(33) W. H. Saunders, Jr., and D. H. Edison, *J. Amer. Chem. Soc.*, **82**, 138 (1960).
(34) A. F. Cockerill, S. Rottschafer, and W. H. Saunders, Jr., *ibid.*, **89**, 901 (1967).
(35) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).
(36) Here it is assumed that a three-centered proton transfer approximates the relevant portion of the five-centered base-catalyzed β-elimination transition state.
(37) Hammet ρ values for eliminations from 2-arylethyl bromides induced by EtOK–EtOH[38] and *tert*-BuOK–*tert*-BuOH[34,39] are too similar to be useful. The ρ value in the *tert*-butoxide induced reactions appears to vary somewhat depending upon the choice of substituents.[34,39]
(38) C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, **79**, 3710 (1957).
(39) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960).
(40) Positional and geometrical orientations in phenoxide-promoted eliminations from 2-iodobutane in ethanol and *tert*-butyl alcohol are quite similar, indicating the change of solvent has a relatively small effect.[31]
(41) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962); *Surv. Progr. Chem.*, **5**, 53 (1969).
(42) E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967).
(43) L. J. Steffa and E. R. Thornton, *ibid.*, **89**, 6149 (1967).
(44) P. J. Smith and A. N. Bourns, *Can. J. Chem.*, **48**, 125 (1970).
(45) A. N. Bourns and A. C. Frost, *ibid.*, **48**, 133 (1970).
(46) W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).
(47) This reactive base–solvent system gives a nearly quantitative yield of elimination products from 2-bromoalkanes under the reaction conditions.[22]
(48) R. A. Bartsch and J. J. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1376 (1969).