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Orientation in Base-Catalyzed β Elimination from 2-Butyl Halides. A Dichotomy between Alcoholic and Dipolar Aprotic Solvents

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Olefinic products from reactions of 2-butyl halides with a variety of bases in alcoholic, dipolar aprotic, and mixed solvents are reported. Comparison of these results with those from the literature for other base-solvent systems reveals a striking dichotomy between orientation in base-catalyzed β elimination in alcoholic and in dipolar aprotic solvents. In alcoholic solvents, an inverse dependence of the *trans*-:*cis*-2-butene ratio and the per cent of 1-butene exists. However, in dipolar aprotic solvents, high *trans*-:*cis*-2-butene ratios of 3.0–4.0, which are independent of the per cent of 1-butene, are observed. Novel linear free-energy relationships between log (% *trans*-2-butene/% 1-butene) and log (% *cis*-2-butene/% 1-butene) for 52 base–solvent–leaving group combinations are discussed.

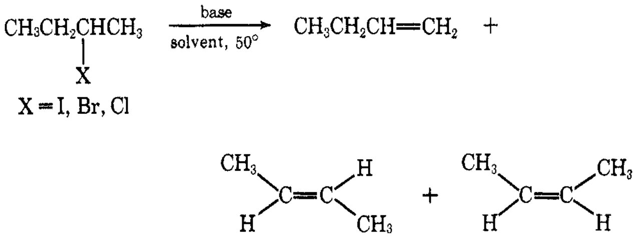
During the last decade, a number of investigations of the factors affecting positional and geometrical orientation[2] in base-catalyzed β eliminations from 2-alkyl halides have appeared.[3] The effects of the nature of the leaving group, the base, the solvent, and the 2-alkyl group have been examined.

The base–solvent systems employed in these studies have usually been alkoxide ions in the corresponding alcohols or in dipolar aprotic solvents. When compared to alcoholic solvents, unusually high *trans*-:*cis*-2-alkene ratios have been noted in eliminations from 2-alkyl halides (excluding 2-alkyl fluorides) induced by alkoxide ions in dipolar aprotic solvents.[3b,e] Recently the variety of base–solvent combinations was expanded by report of halide ion promoted dehydrohalogenation of 2-butyl halides in DMF and DMSO.[3a] In this investigation, unusual orientation was again observed: *trans*-:*cis*-2-butene ratios were uncommonly high and were essentially invariant with change in the per cent 1-butene. Thus it appeared that high *trans*-:*cis*-2-alkene ratios might be characteristic of base-catalyzed eliminations from 2-alkyl halides in dipolar aprotic solvents. In order to investigate this possibility, a study of eliminations from 2-butyl halides induced by several previously unexamined bases in dipolar aprotic solvents was undertaken. In addition, eliminations promoted by a number of alkoxide and phenoxide ions in alcohols and alkoxide ions in mixed solvent systems were examined to further delineate the differences between the effects of alcoholic and dipolar aprotic solvents.

Results

Using gas–liquid partition chromatography (glpc), the relative proportions of the three isomeric olefins formed in reactions of 2-butyl iodide, bromide, and chloride with a variety of base–solvent combinations have been determined (Scheme I). The reactions were all conducted at 50° for comparison with reported values from other systems.

SCHEME I



Reactions of 2-Butyl Iodide with Unusual Bases in DMF.—The relative amounts of isomeric olefins resulting from reactions of cyanide, acetate, benzoate, and phenoxide ions with 2-butyl iodide in DMF are presented in Table I (systems 1–5). In all cases, the 2-butenes, Saytzeff olefins, strongly predominate and high *trans*-:*cis*-2-butene ratios (3.3–3.8) obtain. Comparison of systems 1 and 2 indicates an insensitivity of orientation to the identity of the metal counterion. In previously reported fluoride ion promoted eliminations (Table I, systems 12, 13, 14, and 15; Table III, systems 34, 35, 36, and 37; Table IV, systems 52, 53, 54, and 55), an apparent dependence of orientation upon the cation has been attributed to small amounts of water in the solvent for reactions of the tetraalkylammonium fluoride hydrates.[3a]

Under the reaction there is a negligible contribution from E1 processes.[3a] Sodium nitrite, nitrate, and thiocyanate were of insufficient strength to produce clean E2 reactions. No attempt was made to measure the low butene yields.

Reactions of 2-Butyl Halides with Phenoxide and Alkoxides in Alcohols.—The relative proportions of isomeric butenes resulting from a number of previously unreported phenoxide and alkoxide ion induced eliminations from 2-butyl halides in alcoholic solvents are presented in Table II (systems 16, 17, 18, 19, and 21), Table III (systems 26, 27, 28), and Table IV (systems 46 and 47).

Control experiments demonstrated the absence of a significant unimolecular elimination pathway under the reactions conditions. That phenoxide ion is the effective base in the phenoxide–alcohol systems was demonstrated by the constancy of olefinic proportions in eliminations from 2-butyl bromide promoted by varying concentrations of phenoxide in ethanol containing an excess of phenol (see Experimental Section).

The effects upon butene composition of variation of the alcoholic solvent for a common base are shown in re-

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[1] National Science Foundation Undergraduate Research Participant.

[2] 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.

[3] (a) R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970); (b) *ibid.*, **35**, 1334 (1970); (c) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968); (d) *ibid.*, **91**, 1376 (1969); (e) *ibid.*, **91**, 1382 (1969); (f) H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966); (g) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *ibid.*, **87**, 3984 (1965); (h) D. L. Griffith, D. L. Meges, and H. C. Brown, *Chem. Commun.*, 90 (1968); (i) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965); (j) W. H. Saunders, Jr., S. R. Fahrenholtz, and J. P. Lowe, *Tetrahedron Lett.*, 1 (1960).

TABLE I

OLEFINIC PRODUCTS FROM REACTIONS OF 2-IODOBUTANE WITH VARIOUS BASES IN DIPOLAR APROTIC SOLVENTS AT 50°

System no.	Base	Solvent	Total butenes, %			*trans*-2-Butene: *cis*-2-butene
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
1	KCN[a,b]	DMF	3.3 ± 0.1[c]	74.4 ± 0.5	22.3 ± 0.5	3.34 ± 0.11
2	NaCN[a,b]	DMF	3.7 ± 0.2	73.8 ± 0.6	22.6 ± 0.7	3.27 ± 0.09
3	NaOAc[a,b]	DMF	6.7 ± 0.2	73.7 ± 0.3	19.6 ± 0.3	3.76 ± 0.06
4	NaOCOPh[a,b]	DMF	7.4 ± 0.1	72.8 ± 0.6	19.8 ± 0.6	3.68 ± 0.14
5	PhOK[b,d]	DMF	11.5 ± 0.1	69.5 ± 0.4	19.0 ± 0.5	3.66 ± 0.11
6	LiI[e]	DMF	1.5	76.8	21.6	3.55
7	LiI[e]	DMSO	2.2	75.2	22.6	3.33
8	LiBr[e]	DMF	2.1	77.6	20.3	3.83
9	LiBr[e]	DMSO	3.3	74.4	22.3	3.33
10	LiCl[e]	DMF	2.4	78.0	19.6	3.95
11	LiCl[e]	DMSO	2.6	75.8	21.7	3.50
12	LiF[e]	DMF	18.9	63.1	18.0	3.51
13	LiF[e]	DMSO	19.4	61.5	19.1	3.23
14	Me_4NF[e]	DMF	9.5	71.1	19.4	3.66
15	*n*-Bu_4NF[e]	DMF	10.6	69.6	19.7	3.53

[a] Saturated solution. [b] [2-BuI] = 0.4 *M*. [c] Standard deviation. [d] [PhOK] = 0.4 *M*. [e] Reference 3a.

TABLE II

OLEFINIC PRODUCTS FROM REACTIONS OF 2-IODOBUTANE WITH VARIOUS BASES IN ALCOHOLS AND TOLUENE AT 50°

System no.	Base	Solvent	Total butenes, %			*trans*-2-Butene: *cis*-2-butene
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
16	EtOK[a]	EtOH	11.7 ± 0.3[b]	67.6 ± 0.2	20.8 ± 0.2	3.25 ± 0.02
17	PhOK[c]	EtOH	7.9 ± 0.4	72.2 ± 0.2	19.9 ± 0.5	3.62 ± 0.11
18	*sec*-BuOK[a]	*sec*-BuOH	17.1 ± 0.3	61.0 ± 0.3	21.8 ± 0.2	2.79 ± 0.03
19	PhOK[c]	*sec*-BuOH	8.9 ± 0.4	70.8 ± 0.5	20.3 ± 0.4	3.48 ± 0.08
20	*tert*-BuOK[d]	*tert*-BuOH	33.5	44.5	22.0	2.02
21	PhOK[c]	*tert*-BuOH	10.6 ± 0.4	67.8 ± 0.6	21.5 ± 0.3	3.16 ± 0.06
22	Et_3COK[d]	Et_3COH	49.3	30	20	1.50
23	*tert*-BuOK[d]	Toluene	36.1	40	23	1.70
24	Et_3COK[d]	Toluene	46.8	34	19	1.75

[a] [2-BuI] and [base] = 0.1-0.2 *M*. [b] Standard deviation. [c] [2-BuI] = 0.15 *M*, [PhOK] = 0.1 *M*, [PhOH] = 1.0 *M*. [d] Reference 3h.

TABLE III

OLEFINIC PRODUCTS FROM REACTIONS OF 2-BROMOBUTANE WITH VARIOUS BASE–SOLVENT SYSTEMS AT 50°

System no.	Base	Solvent	Total butenes, %			*trans*-2-Butene: *cis*-2-butene
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
25	MeONa[a]	MeOH	14.6	65.8	19.6	3.36
26	EtOK[b]	EtOH	17.9 ± 0.2[c]	62.3 ± 0.2	19.8 ± 0.2	3.14 ± 0.03
27	PhOK[d]	EtOH	11.8 ± 0.1	67.8 ± 0.3	20.4 ± 0.4	3.32 ± 0.08
28	*sec*-BuOK[b]	*sec*-BuOH	26.3 ± 0.2	53.7 ± 0.2	20.0 ± 0.2	2.68 ± 0.04
29	*tert*-BuOK[e]	*tert*-BuOH	53.5	27.7	18.8	1.47
30	Et_3COK[e]	Et_3COH	71.3	16	13	1.26
31	*tert*-BuOK[e]	Toluene	52.2	28	20	1.38
32	Et_3COK[e]	Toluene	65.8	20	14	1.37
33	LiCl[f]	DMF	9.8	70.1	20.1	3.48
34	LiF[f]	DMF	29.3	55.0	15.7	3.50
35	LiF[f]	DMSO	29.5	54.2	16.3	3.32
36	Me_4NF[f]	DMF	15.5	66.5	18.0	3.68
37	*n*-Bu_4NF[f]	DMF	16.7	64.5	18.7	3.45
38	EtOK[g,h]	DMSO	27	57	16	3.35
39	*tert*-BuOK[a]	DMF	30.5	55.1	14.4	3.82
40	*tert*-BuOK[i,j]	DMAC	26.7 ± 0.1	57.0 ± 0.1	16.3 ± 0.2	3.50 ± 0.04
41	*tert*-BuOK[j,k]	Sulfolane	27.7 ± 0.3	54.1 ± 0.1	18.2 ± 0.2	2.97 ± 0.03
42	*tert*-BuOK[a]	DMSO	30.4	53.8	15.8	3.40
43	*tert*-BuOK[j]	50% *tert*-BuOH–50% DMSO	29.4 ± 0.2	53.1 ± 0.2	17.5 ± 0.2	3.03 ± 0.04
44	*tert*-BuOK[j]	75% *tert*-BuOH–25% DMSO	29.1 ± 0.2	52.4 ± 0.3	18.5 ± 0.2	2.84 ± 0.04
45	*tert*-BuOK[j]	90% *tert*-BuOH–10% DMSO	32.9 ± 0.1	48.7 ± 0.1	18.4 ± 0.1	2.65 ± 0.01

[a] Reference 3b. [b] [2-BuBr] = 0.1-0.6 *M*, [base] = 0.1-0.2 *M*. [c] Standard deviation. [d] [2-BuBr] = 0.17 *M*, [PhOK] = 0.1 *M*, [PhOH] = 1.0 *M*. [e] Reference 3h. [f] Reference 3a. [g] At 55°. [h] Reference 3g. [i] *N,N*-Dimethylacetamide. [j] [2-BuBr] = 0.2 *M*, [*tert*-BuOK] = 0.5 *M*. [k] Tetramethylene sulfone.

TABLE IV

OLEFINIC PRODUCTS FROM REACTIONS OF 2-CHLOROBUTANE WITH VARIOUS BASE–SOLVENT SYSTEMS AT 50°

System no.	Base	Solvent	Total butenes, %			*trans*-2-Butene: *cis*-2-butene
			1-Butene	*trans*-2-Butene	*cis*-2-Butene	
46	EtOK[a]	EtOH	22.3 ± 0.2[b]	58.9 ± 0.2	18.8 ± 0.3	3.13 ± 0.05
47	*sec*-BuOK[c]	*sec*-BuOH	33.7 ± 0.3	47.2 ± 0.3	19.1 ± 0.6	2.46 ± 0.09
48	*tert*-BuOK[d]	*tert*-BuOH	67	18.5	14.5	1.28
49	$\mathrm{Et_3COK}$[d]	$\mathrm{Et_3COH}$	80.1	11	9	1.14
50	*tert*-BuOK[d]	Toluene	66.8	17	16	1.03
51	$\mathrm{Et_3COK}$[d]	Toluene	77.0	13	10	1.29
52	LiF[e]	DMF	39.8	47.6	12.6	3.79
53	LiF[e]	DMSO	40.8	45.6	13.6	3.36
54	$\mathrm{Me_4NF}$[e]	DMF	22.1	61.3	16.6	3.72
55	*n*-$\mathrm{Bu_4NF}$[e]	DMF	22.5	61.1	16.4	3.76

[a] [RCl] = 0.4 *M*, [EtOK] = 0.1 *M*. [b] Standard deviation. [c] [RCl] = 0.15 *M*, [*sec*-BuOK] = 0.2 *M*. [d] Reference 3h. [e] Reference 3a.

actions of 2-butyl iodide with potassium phenoxide in ethanol, *sec*-butyl alcohol, and *tert*-butyl alcohol (Table II, systems 17, 19 and 21). The relatively small changes in butene proportions indicate that the much larger effects noted for variation of alkoxides in the respective alcohols (Table II systems 16, 18, and 20) are attributable primarily to differing base strengths and not to a solvent effect.

Reactions of 2-Butyl Bromide with Potassium *tert*-Butoxide in Dipolar Aprotic Solvents and in *tert*-Butyl Alcohol–DMSO Mixtures.—Previous investigations of base-catalyzed eliminations from 2-alkyl halides in dipolar aprotic solvents have been confined to DMF and DMSO. Orientation in elimination from 2-butyl bromide promoted by potassium *tert*-butoxide in *N*,*N*-dimethylacetamide and tetramethylene sulfone are reported in Table III (systems 40 and 41). The *trans*-:*cis*-2-butene ratios are high, in agreement with earlier studies in DMF and DMSO.[3a,b]

The results from a study of olefinic proportions from reactions of 2-butyl bromide with potassium *tert*-butoxide in the mixed solvent system of *tert*-butyl alcohol–DMSO are presented in Table III (systems 43, 44, and 45). As the proportion (by volume) of DMSO is increased from 0 to 10%, a pronounced effect upon both positional and geometrical orientation is observed (compare systems 29 and 45). Further increases in the proportion of DMSO to 25 and then 50% (systems 44 and 43, respectively) exhibit much smaller effects. Dramatic enhancement of the rate of elimination from 2-arylethyl bromides promoted by potassium *tert*-butoxide in *tert*-butyl alcohol upon addition of small amounts of DMSO has been reported by Saunders and coworkers.[4]

Discussion

In addition to the results of the present study, reported olefinic proportions from dehydrohalogenation of 2-butyl halides with other base–solvents systems at 50°[3a,b,f–h] are collected in Tables I–IV. In all, 55 base–solvent–leaving group combinations are included.

Reactions of 2-Butyl Halides with Bases in Dipolar Aprotic Solvents.—Orientation in eliminations from 2-butyl iodide, bromide, and chloride induced by a wide variety of bases in DMF and DMSO at 50° has now been observed (Table I; Table III, systems 33–39, 42; Table IV, systems 52–55). The first atoms of these bases range from oxygen (alkoxide, phenoxide, carboxylate ions) to carbon (cyanide ion) to halogen (halide ions). With this variety of bases, the proportion of 1-butene varies from 2 to 40%. However, the *trans*-:*cis*-2-butene ratios remain high and essentially constant in the range 3.3–4.0. It is apparent that the concomitant changes observed in the per cent of 1-butene and the *trans*-:*cis*-2-butene ratios for reactions of 2-alkyl halides with alkoxide ions in alcohols[3b–d,f–j] are not found when DMF and DMSO are the reaction solvents.

The geometrical orientation noted for eliminations induced by potassium *tert*-butoxide in *N*,*N*-dimethylacetamide and tetramethylene sulfone (Table III, systems 40 and 41) suggests that high *trans*-:*cis*-2-butene ratios are a general feature of base-catalyzed eliminations from 2-butyl halides in dipolar aprotic solvents.

In eliminations from 2-substituted alkanes, *trans*-:*cis*-2-alkene ratios have been interpreted as indicating the extent of double bond formation in the internal olefin transition states.[3b,d,g,i] The greater the degree of double bond character, the greater is the eclipsing of cis-destined alkyl groups, resulting in a higher *trans*-:*cis*-2-alkene ratio. According to this criterion, a high degree of double bond character exists in the internal olefin transition states for all base-catalyzed eliminations from 2-butyl halides in dipolar aprotic solvents.[5] The reason for this divergence of orientation for eliminations in dipolar aprotic solvents from that observed in alcoholic solvents is not evident at this time.

Effect of Base and Solvent upon Orientation in Elimination from 2-Butyl Halides.—The availability of data on such a large number of base–solvent–leaving group combinations encourages a search for novel relationships. In Figure 1, log (% *cis*-2-butene/% 1-butene) (*i.e.*, the relative rates of formation of *cis*-2-butene and 1-butene) is plotted against log (% *trans*-2-butene/% 1-butene) for eliminations in dipolar aprotic solvents. Figure 2 is a similar plot for reactions in which the solvents were alcohols and toluene. Both plots exhibit excellent linearity when the number of sources of data is considered. These linear free-energy relationships attest to regularities in the effects of base, solvent, and leaving group upon product compositions in base-catalyzed β eliminations from 2-butyl halides.

The plot for eliminations in dipolar aprotic solvents (Figure 1) has a slope of 1.00. Thus, the aforementioned insensitivity of the relative rates of formation of

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[4] A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **89**, 901 (1967).

[5] A high degree of double bond character exists in internal olefin transition states for reactions of 2-bromoalkanes with potassium *tert*-butoxide in DMSO.[3b]

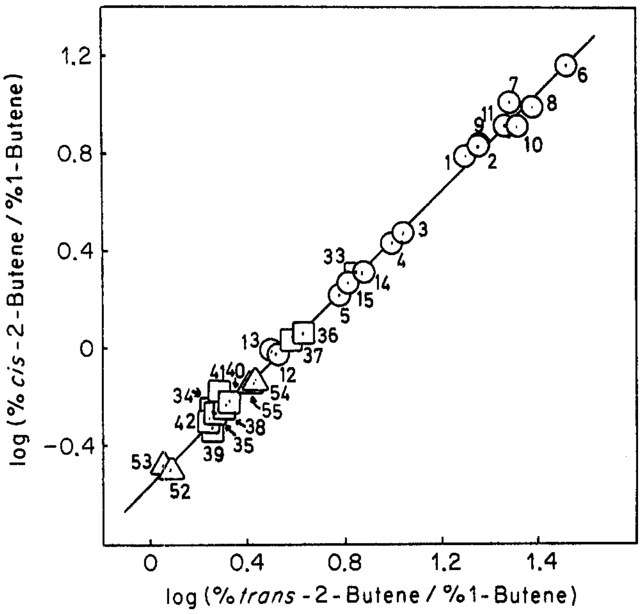

Figure 1.—Plot of log (% *cis*-2-butene/% 1-butene) *vs.* log (% *trans*-2-butene/% 1-butene) for base-catalyzed elimination from 2-butyl halides in dipolar aprotic solvents at 50°: ⊙ = 2-butyl iodide; ⊡ = 2-butyl bromide; △ = 2-butyl chloride.

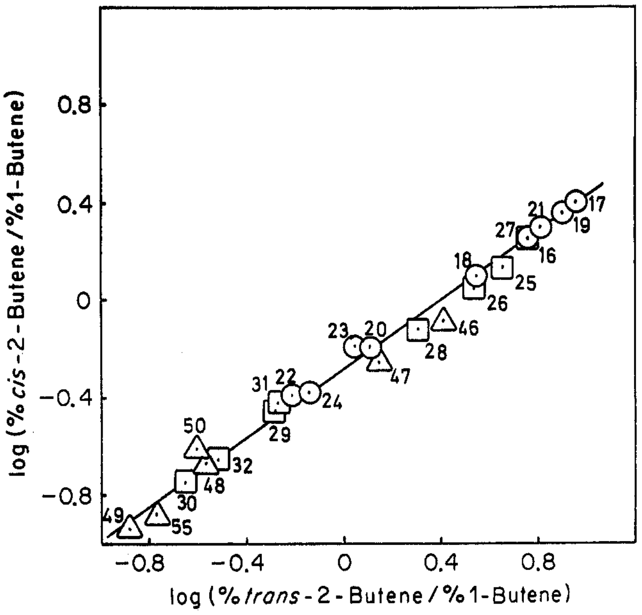

Figure 2.—Plot of log (% *cis*-2-butene/% 1-butene) *vs.* log (% *trans*-2-butene/% 1-butene) for base-catalyzed elimination from 2-butyl halides in alcohols and toluene at 50°: ⊙ = 2-butyl iodide; ⊡ = 2-butyl bromide; △ = 2-butyl chloride.

trans- and *cis*-2-butene (*i.e.*, the *trans*-:*cis*-2-butene ratio) to that for 1-butene is clearly demonstrated.

The slope in Figure 2 for the alcoholic solvents is 0.70. This means that as the per cent of 1-butene increases, the per cent of *trans*-2-butene suffers a proportionately greater decrease than the per cent of *cis*-2-butene. Thus, in alcoholic media, *trans*-:*cis*-2-butene ratios of 3.2–3.6 are observed when the per cent of 1-butene has a low value of 8–15% (systems 16, 17, 19, 21, 25, and 27). However, much lower *trans*-:*cis*-2-butene ratios of 1.1–1.5 are noted when the relative proportions of 1-butene is 49–80% (systems 22, 29, 30, 48, and 49). Rationalizations of this inverse relationship between the *trans*-:*cis*-2-alkene ratio and the per cent of 1-alkene have been offered.[3c,d,g] It is indeed interesting that the products of eliminations induced by alkoxide ions in toluene (systems 23, 24, 31, 32, 50, and 51) correlate with products from eliminations employing alkoxide ions in alcohols (Figure 2).

The linear free-energy relationships presented in Figures 1 and 2 allow certain inferences concerning base-catalyzed β eliminations from 2-butyl halides to be made. First, the linearity strongly suggests that the stereochemistry of elimination in dipolar aprotic solvents and in alcoholic media is invariant. A change from anti- to syn-elimination stereochemistry should produce significant irregularities in the relative rates of formation of *trans*- and *cis*-2-alkene because of the strong destabilization of the syn elimination *cis*-2-alkene transition state by eclipsing effects.[3e,6] An anti-elimination stereochemistry has been demonstrated in eliminations from *erythro*-3-deuterio-2-bromobutane in a variety of dipolar aprotic and alcoholic solvents.[7] It therefore appears that anti elimination occurs for the entire series of base–solvent–leaving group combinations.

Although the steric requirements of the base are varied widely, Figures 1 and 2 exhibit no discontinuities in the relative rates of formation of the internal olefins. A sudden onset of steric interactions with bulky bases,[8] such as potassium *tert*-butoxide, would be expected to strongly influence the relative rates of formation of *trans*- and *cis*-2-butene because of the different steric interactions in the two transition states. Similar conclusions concerning the unimportance of the steric proportions of the base upon orientation have been reached previously.[3b]

Orientation in eliminations from 2-butyl *p*-toluenesulfonate induced by 13 base–solvent combinations at 55° has been reported by Froemsdorf.[9] When points for these reactions were entered onto the plots for the 2-butyl halides, no correlation was found. This observation further reveals the significant differences between halide and *p*-toluenesulfonate leaving groups,[3c] which probably result from the asymmetry of the latter.

Experimental Section

Reagents.—Anhydrous dimethylformamide and dimethyl sulfoxide (Baker, reagent) were stored over molecular sieves. *N*,*N*-Dimethylacetamide and tetramethylene sulfone (Aldrich, reagent) and anhydrous ethanol were used directly. *sec*-Butyl and *tert*-butyl alcohol were distilled from calcium hydride. 2-Butyl halides were obtained as before.[3b] Potassium *tert*-butoxide (MSA) was used directly.

Base–Solvent Solutions.—Potassium *tert*-butoxide in *tert*-butyl alcohol was prepared as before.[3d] Potassium ethoxide in ethanol and *sec*-butoxide in *sec*-butyl alcohol were prepared in similar fashion. Solutions of 0.1 *N* potassium phenoxide and 1.0 *N* phenol in alcohols resulted from addition of 2.5 ml of 0.2 *N* potassium alkoxide in alcohol to 0.52 g of phenol in a 5-ml volumetric flask, addition of the 2-butyl halide, and dilution to 5 ml with the appropriate alcohol. Potassium *tert*-butoxide in *tert*-butyl alcohol–DMSO mixtures were prepared from potassium

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(6) D. S. Bailey and W. H. Saunders, Jr., *Chem. Commun.*, 1598 (1968).

(7) R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970); R. A. Bartsch, unpublished results.

(8) Evidence that orientation in elimination from 2-alkyl halides by alkoxide ions of moderate proportions is not controlled by steric factors has recently been obtained: R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *Tetrahedron Lett.*, 3795 (1970).

(9) D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967).

tert-butoxide and appropriate amounts (by volume) of *tert*-butyl alcohol and DMSO.

Reaction Procedure.—Reactions of 2-butyl halides with potassium phenoxide and alkoxides in alcohols,[3b] and with bases in dipolar aprotic solvents and *tert*-butyl alcohol–DMSO mixtures,[3a] were conducted and elimination products were analyzed as before.

Control Experiments.—Negligible amounts of butenes (determined by glpc) were formed in the reaction of 2-butyl iodide (starting material most prone to E1 reaction) with an equivalent amount of 2,6-lutidine (sterically hindered base, present to inhibit acid-catalyzed reaction) in *tert*-butyl alcohol at 50° for 24 hr.

Reaction of 2-butyl iodide with varying concentrations of potassium phenoxide in ethanol in the presence of excess phenol gave the following olefinic proportions ([PhOK], [PhOH], % 1-butene, % *trans*-2-butene % *cis*-2-butene): 0.05 *M*, 1.05 *M*, 7.8 ± 0.2, 72.3 ± 0.2, 19.9 ± 0.1; 0.10 *M*, 1.00 *M*, 7.9 ± 0.3, 72.1 ± 0.6, 20.0 ± 0.3; 0.15 *M*, 0.95 *M*, 8.0 ± 0.2, 71.6 ± 0.2, 20.4 ± 0.4. Within experimental error, the relative amounts of butenes are invariant, indicating the absence of significant ethoxide ion promoted elimination. Based upon the pK_a's of ethanol and phenol in ethanol,[10] less than 1% of ethoxide is calculated to be present in an ethanolic solution of 0.1 *M* phenoxide and 1.0 *M* phenol.

Registry No.—2-Iodobutane, 513-48-4; 2-bromobutane, 78-76-2; 2-chlorobutane, 78-86-4.

(10) B. D. England and D. A. House, *J. Chem. Soc.*, 4421 (1962).

A Discussion of Inductive, Conjugative, and Steric Strain Effects on Polarographic Reduction Potentials of a Series of Biphenyl- and Phenanthrene-Related Compounds[1]

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In this study are reported the polarographic half-wave reduction potentials in dimethylformamide of a series of alkyl-substituted phenanthrenes and biphenyls. The shifts in the half-wave potential *vis-à-vis* the unsubstituted parent compounds are discussed in terms of hyperconjugative, inductive, and steric strain effects. Using the inductive model for alkyl substitution and making suitable correction for the hyperconjugative effect, correlation of half-wave potential shifts with HMO coefficients is attempted. Deviations from the expected correlation are explained in terms of steric interactions, and a semiquantitative estimate of these interactions is presented.

There has been rather sustained interest in recent years in the effects that substituent alkyl groups have on the physical and chemical properties of fused and bridged aromatic hydrocarbons. Changes in electronic spectra,[3-7] polarographic half-wave potentials ($E_{1/2}$),[6-11] and ionization potentials[7,12] have been discussed. In certain cases, such as that of biphenyl, the steric requirements of substitution can result in a change in the planarity of one part of the conjugated system relative to the rest of the molecule. Such perturbations of the conjugative resonance interaction have been shown to result in shifts of the so-called ultraviolet conjugation band ($\sim$250 nm)[3-5,11,13] and in shifts of polarographic $E_{1/2}$ values.[10,11]

Where rigid conjugated systems, such as fluorenes and phenanthrenes, are involved, changes in planarity on substitution are not so significant. However, Streitwieser and Schwager[9] showed that, besides the normal inductive effect, hyperconjugative interaction of the added alkyl group with the π system of the aromatic parent compound constitutes an appreciable portion of the shift in $E_{1/2}$ when substitution is made at a site with a fairly large Hückel molecular orbital (HMO) coefficient (c). When a correction is made for the conjugative interaction, fairly successful correlation of $E_{1/2}$ shifts (with respect to the unsubstituted parent) with the HMO coefficients was obtained.[9] If the hyperconjugative interaction is neglected, the results are not so satisfactory.[8,9] Valenzuela and Bard have also shown hyperconjugation to be an important consideration.[14]

When the alkyl substituent takes the form of a bridge between two parts of a conjugated system (such as in fluorene and 9,10-dihydrophenanthrene) $\Delta E_{1/2}$ values are even more difficult to correlate with inductive effects alone.[8] Steric effects may be important in the $E_{1/2}$ shifts of these compounds, but in earlier studies they have either not been a major factor or they have not been considered where inconclusive results were obtained.[8]

In this investigation the reduction $E_{1/2}$ values of a series of biphenyl- and phenanthrene-related compounds (where the added substituent is an alkyl group) were obtained in dimethylformamide (DMF) media. All of the factors enumerated above have been considered, with particular attention paid to molecules possessing steric strain, and to those species where the alkyl substituent is a bridging group. For many molecules it was found that correlation of $E_{1/2}$ shifts (corrected for conjugation effects) with the inductive effect of the added alkyl group is far from successful. These deviations from the "normal" correlation behavior are equated to steric strain, and this strain is estimated semiquantitatively.

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