the contribution to the rate (if any) due to the hydroxide ion. This was subtracted from were the pseudo-first-order rates; the second-order rate constants obtained by dividing the corrected first-order constants by the concentration of amine used. This method was used for determining the trimethylamine promoted rates of elimination of *cis*- and *trans*-2-(*p*-tolylsulfonyl)cyclohexyl arylsulfonates.

Acknowledgment. We would like to thank Professor Jack Hine for helpful comments, particularly with regard to the possible importance of internal return. This work was supported in part by the American Petroleum Institute (Project 48B).

The E2C Mechanism in Elimination Reactions. II.[1] Substituent Effects on Rates of Elimination from Acyclic Systems

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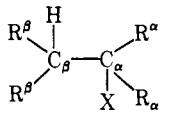
Received May 25, 1970

Abstract: The effects of alkyl, aryl, benzyl, bromine, and carbomethoxy substituents on rates of bimolecular β-eliminations are reported. A spectrum of transition states, ranging from E2H-like to E2C-like, is utilized and the response of the various transition states to substituent effects is very different. The E2C-like transition state is very product-like. E2C-like reactions give high yields of the most stable isomer (*e.g.*, Saytzeff or *trans*-olefin) provided that the requirement of anti geometry of β-hydrogen and leaving group is not violated. Tetrabutylammonium acetate in acetone is an excellent base system for promoting fast clean β-elimination from secondary or tertiary acyclic systems.

The effect of α-substituents, R^{α}, and β-substituents, R^{β}, on the reactivity of compounds I in bimolecular substitution (SN2) and elimination (E2) reactions is now a classical problem of physical organic chemistry.[5-8]



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The questions commonly asked about β-elimination reactions are whether the products are predominantly Hofmann or Saytzeff, or, more generally, whether the kinetic products are predominantly the least or most stable olefin.[6-12] A related question is whether the products are predominantly *trans*- or *cis*-olefins.[6,7,12-14] A question asked more frequently now is whether the products are those of anti or of syn elimination.[15-18]

The answers to these questions are currently interpreted by most chemists in terms of a spectrum of E2 transition states extending between the extremes of paene-carbanion (C_{β} negative) and paene-carbonium (C_{α} positive).[7,19] In this series of papers we hope to establish a different spectrum of E2 transition states (III), extending between the extremes of tight paene-carbanion (II) and loose[20] paene-olefin (III) or, as we prefer, between E2H and E2C.[21] It therefore is of interest to seek answers to the above questions for reactions of halide ions in acetone with alkyl halides or tosylates,[18] reactions which we classify as E2C-like. Most of the existing information about E2 reactions

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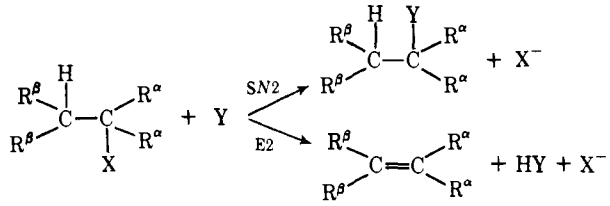
Table I. Substituent Effects on Rates of Bimolecular Elimination and Substitution[a]



(1)

No.[b]	R^β	R^β	R^α	R^α	T, °C	Log k^{s}[c]	Log k^{E}[c]	10^2F_E[d]
(a) X = Br, Y = NBu_4Cl in acetone[e] + 2,6-lutidine[e]								
1[f]	H	H	H	H	25.0	−1.93		0.0
1[f]	H	H	H	H	50.0	−0.70		0.0
1[f,g,h]	H	H	H	H	25.0	−1.87		0.0
2[f]	H	H	Me	H	50.0	−2.44		0.0
2[i]	H	H	Me	H	100.0	−1.0		0.0
3	H	H	*i*-Pr	H	50.0	−3.19	−6	0.1[m,n]
4[i]	H	H	*tert*-Bu	H	100.0	−3.4	−4.1	17.6
5[j,l]	H	H	Me	Me	50.0	−4.3	−3.05	96
5[k,l]	H	H	Me	Me	69.9		−2.26	
6[l]	H	H	Me	Et	50.0	−4.0	−3.03	90[m,n]
7[k]	H	H	Me	*tert*-Bu	69.9		−2.07	
8[m]	H	H	Me	CMe_2Br	75.0		−3.00	100
9[n]	H	H	Me	$PhCH_2$	59.5		−2.75	
10[j]	Et	H	H	H	25.0	−2.27		0.0
11	Ph	H	H	H	50.0	−2.0		0.0
3	Me	Me	Me	H	50.0	−3.19	−3.19	51.4
13[p]	Br	CO_2Me	Me	H	39.8		−3.02	100
13[p]	Br	CO_2Me	Me	H	25.0		−3.68	100
13[p]	Br	CO_2Me	Me	H	52.8		−2.50	100
14[p]	Br	Me	Me	H	76.4	−3.68	−3.59	55
6[q]	Me	H	Me	Me	75.0		−4.9[q]	98
6	Me	H	Me	Me	50.0	−4.0	−2.03	99.2
9[n]	Ph	H	Me	Me	59.5		−1.90	
15[q,p]	Ph	H	Ph	H	50.8	−1.89	−2.55	17
16[q,p]	Me	H	Ph	H	25.0	−2.18	−4.2	1
17[q,p]	Me	H	Ar[t]	H	25.0	−1.75	<−4	<0.4
18[q,h,i]	Me	Me	H	H	25.0	−3.35		0.0
19[q,h,i]	Me	H	H	H	25.0	−2.03		0.0
31[p]	Br	Me	Me	H	75.0	−3.14	−3.43	33
(b) X = Cl, Y = NaSPh in ethanol								
6	Me	H	Me	Me	50.0		−3.68	94 ± 5[s]
30	Me	Me	Me	Me	50.0		−3.26	95 ± 6[s]
6	H	H	Me	Et	50.0		−4.05	94 ± 5[s]
5[l,r]	H	H	Me	Me	50.0	−5.3	−4.08	96[s]
(c) X = OTs,[t] Y = NBu_4Cl in acetone + 2,6-lutidine								
2[f]	H	H	Me	H	50.0	−2.19		0.0
3	H	H	*i*-Pr	H	50.0	−2.98	−5.0	1[m,n]
11	Ph	H	H	H	50.0	−1.35		0.0
12[p,f]	Ph	H	Me	H	75.0	−1.56[u]	−2.59[u]	8.7
3[f]	Me	Me	Me	H	50.0	−2.95[u]	−2.98[u]	47.1
3	Me	Me	Me	H	50.0	−2.98	−3.00	48.7
3[f]	Me	Me	Me	H	75.0	−1.83[u]	−1.86[u]	48.3
(d) X = OBs,[t] Y = NBu_4Cl in acetone + 2,6-lutidine								
20[p,v]	An[t]	Me	Me	H	50.0	−2.66	−2.03	81.0
21[p,v]	An[t]	Me	Me	H	50.0	−2.60	−1.82	86.0
4[l]	H	H	*tert*-Bu	H	75.0	−2.98	−2.97	50.4
(e) X = OTs,[t] Y = NBu_4Br in acetone[f,w]								
2	H	H	Me	H	50.0	−2.80		0.0
2	H	H	Me	H	75.0	−1.71		0.0
3	H	H	*i*-Pr	H	75.0	−2.35	−5	0.5[m,n]
4	H	H	*tert*-Bu	H	75.0	−4.4	−4.7	34 ± 6
11[x]	Ph	H	H	H	50.0	−2.00		0.0
12[p]	Ph	H	Me	H	75.0	−2.2	−3.5	4.1
22	Ph	Me	H	H	75.0	−2.23	−4.5	0.5
23[p]	Me	H	Me	H	75.0	−1.63	−3.28	2.2
24[p]	An[e]	H	Me	H	75.0	−2.18	−3.51	4.5
25	Me	Me	H	H	75.0	−1.68		0.0
3	Me	Me	Me	H	75.0	−2.35	−2.51	44.6
20[v,p]	An[t]	Me	Me	H	75.0	−2.96	−2.71	64.0
(f) X = OBs,[t] Y = NBu_4Br in acetone[f,w]								
26[p]	Ph	Ph	Me	H	50.0	−3.72	−2.67	92.1
26[p]	Ph	Ph	Me	H	75.0	−2.80	−1.76	91.5
10[y]	Et	H	H	H	25.0	−2.04		0.0
20[p]	An[t]	Me	Me	H	50.0	−3.15	−2.94	62.8
4[l,x]	H	H	*tert*-Bu	H	75.0	−3.47	−3.66	38.4

Table I (*Continued*)

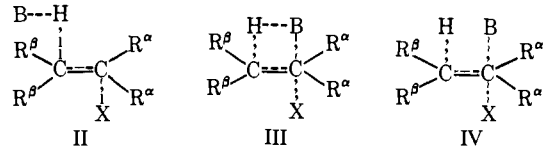
No.[b]	R^{β}	R^{β}	R^{α}	R^{α}	T, °C	Log k^{s} [c]	Log k^{E} [c]	$10^2 F_E$ [d]
(g) X = Br, Y = NBu_4N_3 in acetone[f]								
1[g,h]	H	H	H	H	25.0	−1.8		0.0
1[g,h]	H	H	H	H	75.0	+0.6		0.0
5[h]	H	H	Me	Me	75.0	−2.77	−2.17	80
7[i,l]	H	H	Me	*tert*-Bu	75.0	−3.18	−1.76	96.5
13[p]	Br	CO_2Me	Me	H	0.0		−1.02	100
11[z]	Ph	H	H	H	50.0	−1.23[s]		0
2[g,h]	H	H	Me	H	25.0	−2.39		0
25[g,h]	Me	Me	H	H	25.0	−2.90		0
(h) X = Br, Y = NBu_4OAc in acetone[f,u]								
1[h,g,aa]	H	H	H	H	25.0	−2.53		0.0
2[g,h,aa]	H	H	Me	H	25.0	−3.97		0.0
5[j]	H	H	Me	Me	50.0		−2.15	100
8[m]	H	H	Me	Me_2CBr	75.0		−2.44	100
14[p]	Br	Me	Me	H	0.2		−2.32	100
14[p]	Br	Me	Me	H	76.4		−0.66	100
14[p]	Br	Me	Me	H	25.0		−1.55	100
3[p]	Me	Me	Me	H	25.0	−4.03	−3.12	89
3[p]	Me	Me	Me	H	50.0	−2.91	−2.05	89
13[p]	Br	CO_2Me	Me	H	−72		−2.23	100
13[p]	Br	CO_2Me	Me	H	−54		−0.72	100
13[p]	Br	CO_2Me	Me	H	−47		−0.47	100
16[p,q]	Me	H	Ph	H	25.0	−0.95	−2.0	8
15[p,q]	Ph	H	Ph	H	0.8	−2.79	−2.22[p]	81
15[kk]	Ph	H	Ph	H	0.8		−4.64	81
11[z]	Ph	H	H	H	50.0	−0.74[s]		0.0
(i) X = Br, Y = NBu_4Br in acetone + 2,6-lutidine[bb]								
2	H	H	Me	H	75.0		−6.3	
9[n]	H	H	Me	$PhCH_2$	59.5		−3.56	
12	H	H	$PhCH_2$	H	75.0		−6.70	
16[p]	Me	H	Ph	H	75.0		−3.36	
16[kk]	Me	H	Ph	H	75.0		−5.36[kk]	
17[p]	Me	H	Ar[t]	H	75.0		−3.59	
17[kk]	Me	H	Ar[t]	H	75.0		−5.50[kk]	
15[q,f]	Ph	H	Ph	H	75.0		−2.8[w]	
15[kk]	Ph	H	Ph	H	75.0		−4.86[kk]	
15[p]	Ph	H	Ph	H	75.0		−3.16	
9[n]	Ph	H	Me	Me	59.5		−3.05	
12[p]	Ph	H	Me	H	75.0		−4.40	
12[kk]	Ph	H	Me	H	75.0		−5.57[kk]	
5[j]	H	H	Me	Me	75.0		−2.90	
23[p]	Me	H	Me	H	75.0		−4.80	
23[kk]	Me	H	Me	H	75.0		−5.5[kk]	
23	H	H	Et	H	75.0		−6.1	
19	Me	H	H	H	75.0		−5.94	
(j) X = Br, Y = NaOEt in ethanol[f]								
1[dd]	H	H	H	H	25.0	−4.19		0
1[cc]	H	H	H	H	55.0	−2.71	−4.80	1.0
2[cc]	H	H	Me	H	55.0	−4.68	−4.12	75
2[ee]	H	H	Me	H	25.0	−5.98	−5.76	79
29[cc]	H	H	Ph	H	25.0		−5.10	
5[cc]	H	H	Me	Me	25.0		−4.5[cc]	100
6[cc]	H	H	Me	Et	25.0		−4.77	100
6[cc]	Me	H	Me	Me	25.0		−4.38	100
23[p,cc]	Me	H	Me	H	25.0	−5.85	−5.55	66
11[ff]	Ph	H	H	H	50.0	−3.50	−2.26	94.6[s]
11[gg]	Ph	H	H	H	30.1		−3.38	99.6
27[gg]	An[t]	H	H	H	30.1		−3.79	99.9
28[gg]	Ar[t]	H	H	H	30.1		−0.13	99.2
18[cc]	Me	Me	H	H	55.0	−4.24	−4.07	62[s]
19[dd]	Me	H	H	H	55.0	−3.26	−4.28	8.8
19[dd]	Me	H	H	H	25.0	−4.67	−6.08	8.8
(k) X = OTs,[t] Y = NaOEt in ethanol[f,hh]								
1[dd]	H	H	H	H	55.0	−2.25	−5.2	0.1
2[dd]	H	H	Me	H	55.0	−3.23	−3.86	19
4	H	H	*tert*-Bu	H	50.0		−5.30	100
11[ii]	Ph	H	H	H	30.1	−4.59	−4.89	38.6
27[gg,ii]	An[t]	H	H	H	30.1	−4.87	−5.47	20
3	Me	Me	Me	H	50.0	−4.50	−4.05	82[s]
3	H	H	*i*-Pr	H	50.0	−4.50	−4.70	40[mm]
19[dd]	Me	H	H	H	55.0	−2.69	−5.39	0.2
18[dd]	Me	Me	H	H	55.0	−3.74	−5.22	3.3

Table I (*Continued*)

No.[b]	R^β	R^β	R^α	R^α	T, °C	Log k^{s} [c]	Log k^{E} [c]	$10^2 F_E$ [d]
(l) X = Br, Y = KO-*tert*-Bu in *tert*-butyl alcohol[f]								
1[dd]	H	H	H	H	40.0	−4.14	−5.09	10
2[ll]	H	H	Me	H	25.0		−5.64	100
19[dd]	Me	H	H	H	40.0	−4.80	−4.82	48
11[ii]	Ph	H	H	H	50.0		−1.43	100
11[ii]	Ph	H	H	H	30.0		−2.04	100
27[ii]	An[t]	H	H	H	30.0		−2.60	100
28[dd]	Ar[t]	H	H	H	33.0		+0.95	100
16[p]	Me	H	Ph	H	75.1	−3.87	−2.89	92
16[kk]	Me	H	Ph	H	75.1	−3.87	−4.71[kk]	92
15[p]	Ph	H	Ph	H	25.0		−2.16	100
15[kk]	Ph	H	Ph	H	25.0		−5.01[kk]	100
5[ll]	H	H	Me	Me	25.0		−5.25	100
23[p,ll]	Me	H	Me	H	25.0		−6.18	100
23[kk]	Me	H	Me	H	25.0		−6.4[kk]	100
18[dd]	Me	Me	H	H	55.0	−5.51	−4.45	92
6[dd,ll]	Me	H	Me	Me	25.0		−6.04	100
6[ll]	H	H	Me	Et	25.0		−5.62	100
29[ll]	H	H	H	Ph	25.0		−4.81	100
12[p]	Ph	H	Me	H	75.0		−1.67	100
12[kk]	Ph	H	Me	H	75.0		−3.39[kk]	100
12	H	H	$PhCH_2$	H	75.0		−4.96	100
(m) X = OTs,[t] Y = NaSPh in ethanol[f]								
3	H	H	*i*-Pr	H	50.0	−2.66	−4.15	3[mm]
3	Me	Me	Me	H	50.0	−2.66	−2.86	37[s]
4	H	H	*tert*-Bu	H	50.0		−4.1	

[a] This work unless stated otherwise; the concentrations of reactants (usually 0.02–0.06 *M*, but NBu_4Br = 0.10 *M*), additives (0.04–0.08 *M*), and rate expressions noted are for this work, but values taken from the literature are thought to be directly comparable. Solvolysis rates are at least 100 times slower than rates of total bimolecular reactions, unless noted otherwise. [b] The numbers correspond to the following compounds, with X as leaving group, as noted in the table: 1, 1-X-ethane; 2, 2-X-propane; 3,3-methyl-2-X-butane; 4, 3,3-dimethyl-2-X-butane; 5, 2-methyl-2-X-propane; 6, 2-methyl-2-X-butane; 7, 2,3,3-trimethyl-2-X-butane; 8, 2,3-dimethyl-2-bromo-3-X-butane; 9, 1-phenyl-2-methyl-2-X-propane; 10, 1-X-butane; 11, 2-phenyl-1-X-ethane; 12, 1-phenyl-2-X-propane; 13, *erythro*-methyl 2-bromo-3-X-butanoate; 14, *rac*-2-bromo-3-X-butane; 15, 1,2-diphenyl-1-X-ethane; 16, 1-phenyl-1-X-propane; 17, 1-(*p*-nitrophenyl)-1-X-propane; 18, 2-methyl-1-X-propane; 19, 1-X-propane; 20, *erythro*-3-*p*-anisyl-2-X-butane; 21, *threo*-3-*p*-anisyl-2-X-butane; 22, 2-phenyl-1-X-propane; 23, 2-X-butane; 24, 1-(*p*-anisyl)-2-X-propane; 25, 2-methyl-1-X-propane; 26, 1,1-diphenyl-2-X-propane; 27, 2-(*p*-anisyl)-1-X-ethane; 28, 2-(*p*-nitrophenyl)-1-X-ethane; 29, 1-phenyl-1-X-ethane; 30, 2,3-dimethyl-2-X-butane: 31, *meso*-2,3-dibromobutane. [c] Rate constant M^{-1} sec^{-1} for bimolecular substitution, k^s, and for bimolecular elimination, k^E, as estimated from total rate and F_E. Unless noted otherwise, rate constants were calculated from the usual second-order rate expression. [d] F_E is the fraction of total elimination and is not necessarily that of the isomer shown, unless noted. F_E is the ratio of acid produced to X^- generated, or to Y^- consumed + acid generated. Elimination could be confidently detected down to 1%. [e] Unless stated otherwise; *cf.* footnote *g*. [f] No 2,6-lutidine. [g] Solvent is dimethylformamide. [h] D. Cook and A. J. Parker, *J. Chem. Soc. B*, 142 (1968). [i] D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969). [j] A. J. Parker and M. Ruane, unpublished work. [k] D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969). [l] Solvolysis was only *ca.* ten times slower than the total rate. [m] M. Ruane, unpublished work; competing solvolysis creates some uncertainty. [n] J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **35**, 76 (1970). [o] Estimated from reaction of NBu_4Br by assuming that NBu_4Cl reacts ten times faster; *cf.* other data in this table. [p] Rates are for the kinetic product of anti elimination and, if anti elimination can give a *cis*- or *trans*-olefin (*cf.* Table X), are for the thermodynamically most stable (usually *trans*) olefin. [q] X is Cl. [r] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956). [s] F_E determined bromometrically. [t] Ar is 4-nitrophenyl, OTs is *p*-toluenesulfonate, OBs is 4-bromobenzenesulfonate, An is 4-methoxyphenyl. [u] Rate constants calculated from rate expression 2. [v] Reference 1. [w] Rate constants calculated from expression 3. [x] Contains 0.04 *M* 2,6-lutidine. [y] S. Winstein, L. G. Savedoff, S. G. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, 24 (1960). [z] X is OTs. [aa] LiOAc is the base; it reacts *ca.* ten times slower than NBu_4OAc in DMF. [bb] The usual first-order rate expression was used to estimate k_1 sec^{-1}, which was then divided by the initial concentration of NBu_4Br to obtain k_2 in M^{-1} sec^{-1}. [cc] Reference 5; *cf. dd*. [dd] G. M. Fraser and H. M. R. Hoffman, *J. Chem. Soc. B*, 265 (1967); *ibid.*, 425 (1967). [ee] V. J. Shiner, *J. Amer. Chem. Soc.*, **74**, 5285 (1952). [ff] M. L. Dhar, E. D. Hughes, C. K. Ingold, and S. Masterson, *J. Chem. Soc.*, 2055 (1948). [gg] C. H. De Puy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, **79**, 3710 (1957). [hh] NaOEt at *ca.* 0.6 *M*. [ii] W. H. Saunders and D. H. Edison, *J. Amer. Chem. Soc.*, **82**, 138 (1960). [jj] C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2532 (1960). [kk] Rate constant is for formation of the *cis*-olefin; *cf.* footnote *p*. [ll] H. C. Brown, I. Moritani, and Y. Okamoto, *J. Amer. Chem. Soc.*, **78**, 2193 (1956). [mm] F_E for formation of this isomer; *cf.* footnote *d*.

is for reactions of alkoxides with alkyl halides or tosylates, reations which we would classify as E2H-like. The present work on E2C-like reactions supplements existing data on E2H-like reactions, to give a much broader view of the whole spectrum of E2 reactions.



II E2H III IV E2C

The major conclusion from this paper is that by an intelligent choice of base and solvent, one can utilize a particular region of an E2 spectrum and thus obtain the desired proportions of isomeric olefins in the shortest possible time.

Results

Kinetics. The rates of elimination (log k^E) and substitution (log k^s) reactions of a variety of compounds, I, are recorded in Table I. They were calculated from the total rate constant for concurrent substitution plus elimination, using the fraction of elimination or substitution.[1,18] Acid produced by elimination and base consumed by substitution were estimated by titration. Halide ions consumed as base by substitution, or generated as leaving group by substitution plus

elimination, were estimated by potentiometric titration with silver nitrate. Solvolysis of secondary tosylates or bromides in acetone in the presence of 2,6-lutidine or NBu_4ClO_4 was at least 100 times slower, and of the tertiary bromides was at least ten times slower than the major bimolecular reactions with bases. We cannot be certain that some of the minor concurrent reactions (*e.g.*, 0.1% of total reaction) are E2 or SN2 reactions, but we treat them as such and they do provide upper limits for rates of these minor reactions.

Bimolecular reactions of bases in the presence of 2,6-lutidine, as well as reactions with sodium ethoxide and with sodium thiophenoxide, followed the normal second-order kinetic expression.[1] The products and rates were independent of the concentration of 2,6-lutidine. For reactions of alkyl bromides or tosylates with NBu_4Cl or NBu_4OAc in acetone which did not contain 2,6-lutidine or equivalent base, the formation of unreactive HCl_2^- or $H(OAc)_2^-$ was allowed for, *i.e.*, rate expression 2 was used. HCl and HOAc are weaker acids than HBr or HOTs in acetone. It was

$$k_2 = \frac{2.303}{[b - (I + F_E)a]\Delta t} \Delta \log \frac{[b - (I + F_E)x]}{[a - x]} \quad (2)$$

$$k_2 = \frac{2.303}{[b - (I - F_E)a]\Delta t} \Delta \log \frac{[b - (I - F_E)x]}{[a - x]} \quad (3)$$

found that rate expression 3 best fitted the observed rates of reactions of alkyl bromides or tosylates with NBu_4Br in the presence or absence of 2,6-lutidine in acetone. This was no doubt because product bromide or tosylate ion consumed the acid generated in elimination, so that bromide ion was only consumed by the substitution of tosylate by bromide. In (2) and (3), k_2 is the combined rate constant for elimination and substitution, b is the initial stoichiometric concentration of base, F_E is the fraction of total reaction which gives acid, a is the initial concentration of I, and x is the concentration of I which has been consumed at time t.[1] Rate expression 3 was also used for reactions of NBu_4Cl in dimethylformamide. Equation 4 was used for reactions of NBu_4Br in DMF with alkyl bromides.

$$k_2 = \frac{2.303}{(b + a)\Delta t} \Delta \log \frac{(b + x)}{(a - x)} \quad (4)$$

Oxidation of sodium thiophenoxide produces base, which thus lowers F_E. The oxidation is not sufficiently serious to influence the rate constant, but the values of F_E used to split k_2 for thiophenoxide reactions in Table I may be a little low. For reasons to be given in a later paper in this series, no allowance in the recorded rate constant is made for incomplete dissociation of 0.03–0.10 *M* tetrabutylammonium salts in acetone.

Reaction Products. Acid production, base consumption, and halide ion production indicated the extent of substitution and elimination. Bromometric analysis established the extent of elimination in reactions of sodium ethoxide. These were the only forms of analysis for the products of many of the reactions recorded in Table I in which only one olefin was expected. However, when isomeric olefins were expected, more detailed analyses were usually carried out. Results are in Table II.

The substrates for data in Table II were analytically pure by nmr and elemental analysis, except for 1-phenyl-2-bromopropane, which contained up to 10% *trans*-1-phenyl-1-propene. The 1,2-diphenyl-1-bromoethane contained <0.01% *cis*- or *trans*-stilbene.

The olefinic products were identified and estimated by vpc comparison with authentic samples of actual products and likely products, or by preparative vpc of reaction mixtures, which were than analyzed by nmr. Measurements were recorded at 10 and 20 half-lives, *i.e.*, at completion of reaction. Products did not change, except as noted in Table II. At earlier stages of reaction, decomposition of substrates on the vpc columns was often a serious complication. In a few cases substitution products also decomposed and so were separated before analysis. Mass spectral analysis of a vpc fraction from the reaction of 1-phenyl-1-bromopropane with potassium *tert*-butoxide showed a molecular ion of $C_{13}H_{20}O$, which identified it as a substitution product.

Control experiments established that the olefins did not isomerize under the reaction conditions, or during analysis, except for the slow isomerization of 3,3-dimethyl-1-butene and methyl 2-bromo-*cis*-but-2-enoate. Analysis by vpc confirmed the F_E values as calculated from titration, for the reactions recorded in Table II. The reactions of NBu_4Cl and NBu_4OAc with *erythro*-methyl 2,3-dibromobutanoate in acetone were monitored at all stages by vpc. The proportion of methyl 2-bromo-*trans*-crotonate increased with time, due to consecutive isomerization of the cis isomer. This was especially noticeable with NBu_4Cl as base, because of the higher reaction temperature. The proportion of trans isomer was extrapolated back to zero time to give the maximum yield of kinetic product, as recorded in Table II.

The reaction of racemic 2,3-dibromobutane with NBu_4OAc in acetone gave 100% 2-bromo-*trans*-2-butene by vpc, but the reaction with NBu_4Cl gave only 0.55 mol of 2-bromo-*trans*-2-butene, 1.45 mol of bromide ion, and 0.65 mol of acid per mole of racemic 2,3-dibromobutane after 20 half-lives. A 0.08-mol sample of chloride ion was consumed. The remaining 0.45 mol of organic reaction products probably were racemic 2,3-dichlorobutane and 2-chloro-*cis*-2-butene.

The reactions of 1-phenyl-2-bromopropane were carried out on an impure substrate containing 10% *trans*-1-phenyl-1-propene, but since this known impurity was also a reaction product it was allowed for in both the kinetics and product analysis.

Only one olefin, 3,3-dimethyl-1-butene, is possible from E2 reactions of 3,3-dimethyl-2-butyl brosylate, so the other products in Table II must come from a route other than E2. Isomerization of 3,3-dimethyl-1-butene could only account for 2% rearranged products, because after 86 hr at 75° (60 half-lives for the slower elimination) a mixture of 0.0076 *M* *p*-toluenesulfonic acid, 0.0275 *M* NBu_4Br, 0.0300 *M* 2,6-lutidine, and 0.0228 *M* olefins had changed from 42.6% to 35.6% 3,3-dimethyl-1-butene, from 10.2% to 15.6% 2,3-dimethyl-1-butene, and from 47.2% to 48.8% 2,3-dimethyl-2-butene. The rearranged olefins, in the reactions of 3,3-dimethyl-2-butyl brosylate with halide ions in acetone, probably arise from unimolecular ionization, with methyl participation. This competing

Table II. Olefinic Products of Elimination[a]

Substrate[b] R in RX	X[b]	Salt	T, °C	% olefins[c]		
				2-Me-2-butene	2-Me-1-butene	3-Me-1-butene
3-Me-2-butyl	OTs	NBu_4Cl	50.0	99.1	0.1	0.8
3-Me-2-butyl	OTs	NBu_4Cl	75.0	98.6		1.4
3-Me-2-butyl	OTs	NBu_4Br	75.0	99.3	0.4	0.3
3-Me-2-butyl	OTs	NaOEt[d]	50.0	81.3	0.7	18.0
3-Me-2-butyl	OTs	NaSPh[d]	50.0	95.5	0.7	3.8
3-Me-2-butyl	Br	*e*	50.0	97.8	2.2	
3-Me-2-butyl	Br	NBu_4Cl	50.0	99.9		0.1
2-Me-2-butyl	Br	*e*	50.0	50.0	50.0	
2-Me-2-butyl	Br	NBu_4Cl	50.0	91.0	9.0	
2-Me-2-butyl	Cl	NaSPh[d,f]	50.0	70.5	29.5	
				1-Butene	*cis*-2-Butene	*trans*-2-Butene
		KO-*tert*-Bu[g-i]	55.0	9	27	64
2-Butyl[k]	Br	NBu_4Br	75.0	4	14	82
				3,3-Me_2-1-butene	2,3-Me_2-2-butene	2,3-Me_2-1-butene
3,3-Me_2-2-Bu	OBs		75.0	11.7	45.9	42.3
3,3-Me_2-2-Bu	OBs	NBu_4Cl	75.0	93.3	3.5	3.2
3,3-Me_2-2-Bu	OBs	NBu_4Br	75.0	68.0	14.0	18.0
				2-Br-*cis*-2-butene	2-Br-*trans*-2-butene	
rac-2-Br-3-Bu	Br	NBu_4OAc	25.0		100	
rac-2-Br-3-Bu	Br	NBu_4Cl	75.0		100	
				Me-2-Br-*cis*-butenoate	Me-2-Br-*trans*-butenoate	
erythro-Me-2-Br-3-butanoate	Br	NBu_4OAc	−70	99.0	1.0	
	Br	NBu_4Cl	50	98.0[l]	2.0[l,m]	
				cis-Stilbene	*trans*-Stilbene	
		n, *h*	37	0.05	99.95	
1,2-Ph_2-ethyl	Br	NBu_4Br	75	2	98	
1,2-Ph_2-ethyl	Br	NBu_4OAc[n]	25	0.4	99.6	
1,2-Ph_2-ethyl	Br	NaOMe[o]	25	0.6	99.4	
1,2-Ph_2-ethyl	Br	KO-*tert*-Bu[j]	25	0.7	99.3	
				trans-1-Aryl-1-propene[b]	*cis*-1-Aryl-1-propene[b]	3-Aryl-1-propene[b]
1-Ar-1-propyl	Br	NBu_4Br	75	98.8	1.2	
1-Ph-1-propyl	Br	NBu_4Br	75	99	1.0	
1-Ph-1-propyl	Br	KO-*tert*-Bu[j,p]	75	98.5	1.5	
1-Ph-2-propyl	Br	NBu_4Br	75	92.7	6.8	0.5
1-Ph-2-propyl	Br	KO-*tert*-Bu[j]	75	98.1	1.9	0.05
1-Ph-2-propyl		KO-*tert*-Bu[g,h]	55	98.4	1.6	0.03

[a] The reaction mixtures were in acetone containing 0.04–0.08 *M* 2,6-lutidine, with substrates at 0.03–0.06 *M* and base at 0.04–0.12 *M*, unless stated otherwise. [b] OTs is *p*-toluenesulfonate, Ar is 4-nitrophenyl, aryl is 4-nitrophenyl or phenyl, OBs is 4-bromobenzenesulfonate. [c] Percentage of the total olefins. A dash indicates that this olefin could not be detected; the detection limit is 0.1%. [d] Solvent is ethanol. [e] This is an E1 reaction in acetone containing 2,6-lutidine, accompanied by a bromide ion induced E2C-reaction, because Br^- is the leaving group. [f] 3-Methyl 2-butylphenyl sulfide, bp 91°, was obtained in 55% yield. [g] Solvent is dimethyl sulfoxide. [h] For equilibration of the olefins see text. [i] T. J. Wallace, J. E. Hofmann, and A. Schriesheim [*J. Amer. Chem. Soc.*, **85**, 2739 (1963)] also report these proportions in DMSO at 55°. [j] Solvent is *tert*-butyl alcohol. [k] Products from E2 reactions with other bases are given in ref 11 and R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970). [l] The cis isomer was 25% isomerized to trans isomer after 48 hr at room temperature. [m] The trans isomer is very much more stable and the trans/cis ratio increases with time; this value was estimated by extrapolation to zero reaction time. [n] Solvent is dimethylformamide. [o] Solvent is 80% v/v DMSO–MeOH. [p] We detected 8% substitution product by vpc and this was identified as $C_{13}H_{20}O$ by mass spectral analysis.

ionization is significant with bromide ion as base, but with the more reactive chloride ion, it is minor.

Equilibration of Olefins. Results are in Table II. Neat methyl 2-bromo-*cis*-but-2-enoate isomerized to >99.9% trans isomer, by nmr and vpc, on standing in sunlight for 3 days. *cis*- and *trans*-stilbene were equilibrated in DMF with irradiated iodine as catalyst.[22] The equilibrium ratio of [*trans*-stilbene]/[*cis*-stilbene] was 2200 in DMF at 37° by vpc analysis, no matter whether equilibrium was approached from *cis*- or from *trans*-stilbene, both of which were >99.9% pure by vpc. *trans*-1-Phenyl-1-propene and 3-phenyl-1-propene were separately equilibrated to the same proportions of phenylpropenes with potassium *tert*-butoxide in dimethyl sulfoxide at 55°.[23]

Experimental Section

Titration Procedures. These were as described in part I.[1] Sodium thiophenoxide and sodium ethoxide were titrated as bases in dry ethanol with *p*-toluenesulfonic acid in methanol to the bromophenol blue end point. The concentration of thiophenol in a duplicate sample was determined by addition of 1 ml of water and titration with sodium methoxide to the phenolphthalein end point. Olefins from reactions of sodium ethoxide were determined bromometrically.

(22) G. Fischer, K. A. Musykat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).

(23) A. Schriesheim and C. A. Rowe, *J. Amer. Chem. Soc.*, **84**, 3160 (1962).

With azide or acetate as base, the sample was titrated with sodium methoxide to the thymol blue end point, under nitrogen. This gave the concentration of acid produced by elimination.[1] The sample was then titrated with hydrochloric acid in 90% acetone–water to the bromophenol blue end point. This gave the fraction of substitution. Control experiments established the validity of these procedures.[1]

Reactants. Tetra-*N*-butylammonium salts were prepared by standard procedures.[1] Sodium thiophenoxide in ethanol was prepared by addition of sodium ethoxide to an excess of freshly distilled thiophenol in ethanol under nitrogen. Solutions were used without delay. Potassium *tert*-butoxide was prepared by dissolving potassium in *tert*-butyl alcohol under nitrogen. 2-Bromobutane was a redistilled commercial sample, giving one peak by vpc.

The following substrates were prepared by methods described in the literature: 1-phenyl-1-bromopropane, bp 92–94° (3 mm) (lit.[24] 94–95° (5 mm), pure by nmr; 1,2-diphenyl-1-bromoethane,[13] pure by nmr, uv and bromide analysis, after charcoal filtration; 1,1-diphenyl-2-propyl *p*-bromobenzenesulfonate, mp 94–95° (lit.[25] 94–95°); 2-phenylethyl *p*-toluenesulfonate, mp 38.0–39.2° (lit.[26] 35.5–36.6°); 1-phenyl-2-propyl *p*-toluenesulfonate, mp 90.8–91.6° (lit.[27] 93.7–94.0°); 1-(4-methoxyphenyl)-2-propyl *p*-toluenesulfonate, mp 79.0–80.1° (lit.[27] 80.0°); 3,3-dimethyl-2-butyl *p*-bromobenzenesulfonate, mp 52.5–53.2° (lit.[28] mp 53.2–53.5°); 2-methyl-2-chlorobutane, bp 84°, n^{25}D 1.4030 (lit.[29] bp 56.4° (300 mm), n^{25}D 1.4023); 2-methyl-2-bromobutane, bp 104–106°, n^{23}D 1.4400 (lit.[30] bp 49.8° (100 mm, n^{25}D 1.4392); 2-bromopropane, bp 57–58°, n^{25}D 1.4223 (lit.[31] n^{25}D 1.4228); 3,3-dimethyl-2-butyl *p*-toluenesulfonate,[28] solvolysis 96%; 2-phenyl-1-propyl *p*-toluenesulfonate, mp 50.6–51.4°; 2-propyl *p*-toluenesulfonate, 2-methyl-1-propyl *p*-toluenesulfonate, and 2-butyl *p*-toluenesulfonate were prepared from the purified alcohols using the procedure described below for tosylation of 3-methyl-2-butanol. Infinity samples from reaction with excess base established that these substrates were between 96 and 100% of the expected molecular weight.

erythro-Methyl 2,3-dibromobutanoate was prepared by converting crotonic acid to the methyl ester, bp 119.0–119.5° (lit.[32] 121°), which was pure by vpc and nmr analysis, with methanol and sulfuric acid. The ester was brominated in carbon tetrachloride at 0° over a period of 6 hr. The product was twice distilled; the fraction with bp 83.0° (10 mm) was collected and used without delay. The elemental analysis was for $C_5H_8O_2Br_2$ and the nmr was as expected. Analysis by vpc on a UCON column at 120° established that it was a single isomer. Anti debromination by *p*-nitrothiophenoxide in acetone gave 100% methyl crotonate, which confirmed that it was the erythro isomer. The compound slowly isomerized to 5% threo isomer over 6 weeks at 0°.

d,l- and *meso*-2,3-dibromobutane were prepared by brominating *cis*-2-butene and *trans*-2-butene, respectively (>99% pure by vpc), at −15°.[33] The dibromides were fractionated twice. The elemental analysis was for $C_4H_8Br_2$ and the difference in nmr chemical shift of the methyl and methine multiplets identified the two isomers.[34]

3-Methyl-2-butanol was prepared in two ways, first from isopropyl bromide and acetaldehyde.[35] Acetaldehyde was added to the Grignard at −10° which is a revision of the literature method. In the second method it was prepared from 3-methyl-2-butanone by reduction with lithium aluminum hydride.[36] Nmr analysis confirmed the purity and identity of the alcohol. The alcohol was converted to the tosylate using a 10% mole excess of *p*-toluenesulfonyl chloride in pyridine.[37] The mixture was left overnight at 0°. It was poured onto ice and stirred until it crystallized. If crystals did not form the oil was dissolved in ether; the ether extract was washed with ice cold 6% hydrochloric acid, then with cold water, sodium bicarbonate, and more water. The ether was dried and removed at <25° on a rotary evaporator. In both cases, the impure tosylate was recrystallized from pentane at −20°. It was stored under pentane at −15° until required. The melting point was variable, 11–22°,[38] but elemental and nmr analysis were satisfactory.

3-Methyl-2-bromobutane was prepared from the tosylate. The 3-methyl-2-butyl tosylate was heated with excess NBu_4Br in acetone, containing an equimolar proportion of 2,6-lutidine, for 2 hr at 75° in a sealed tube. The reaction gives *ca.* 60% substitution and 40% elimination, but is superior to other procedures involving conversion of the alcohol to the bromide. The reaction mixture was poured into cold water, extracted with pentane, washed with dilute HCl, then water, and dried, and the pentane removed at <20°. The product (bp 114–115°) was isolated by preparative vpc on a 12 ft, 15% UCON column at 30°. The nmr spectrum was consistent with the structure of 3-methyl-2-bromobutane and the product was pure by vpc. The elemental analysis was satisfactory.

1-Phenyl-2-bromopropane was prepared as described in the literature.[39] The compound could not be distilled without decomposition, so it was filtered through activated charcoal. Bromide analysis, nmr, and vpc confirmed that 90% 1-phenyl-2-bromopropane, contaminated with 10% *trans*-1-phenyl-1-propene, was present. Since the impurity is a reaction product, the sample was used as such, with due allowance for the *trans*-1-phenyl-1-propene.

1-(4-Nitrophenyl)-1-bromopropane was prepared from 1 g of 1-(4-nitrophenyl)-1-propanol[40] by refluxing with aqueous hydrogen bromide (6 g, *d* 1.49) for 10 min. Ether was added and the extract was washed with sodium bicarbonate and water. The ether was dried over magnesium sulfate and removed. The oil was dissolved in hexane, filtered through activated charcoal, and cooled to −70°. The resulting crystals had mp 60–61° and the expected nmr spectrum. *Anal.* Calcd for $C_9H_{10}BrNO_2$: C, 44.28; H, 41.3; N, 5.74. Found: C, 44.03; H, 3.96; N, 5.74.

Reaction Products. Isomeric Butenes. The *cis*- and *trans*-2-butenes were available commercially and were used as vpc standards. The isomeric butenes were not completely resolved on our 20 ft 5% squalane on Chromosorb W column at 25°, but separation was adequate for our purposes.

Isomeric Pentenes. 2-Methyl-2-butene was obtained from the National Bureau of Standards and was used to establish vpc retention times. Dehydration of *tert*-amyl alcohol with hot 1:2 aqueous sulfuric acid gave[41] a 9:1 mixture of 2-methyl-2-butene and 2-methyl-1-butene by vpc. Dehydroiodination of 1-iodo-3-methylbutane with hot ethanolic KOH gave a mixture of olefins, bp 23–38°, containing[42] 3-methyl-1-butene and 2-methyl-1-butene in a ratio of 2:1 by vpc. A 2-m, 25% dodecyl phthalate on 40–60 mesh firebrick column at 50° was used for analysis.

Isomeric Hexenes. 3,3-Dimethyl-1-butene, bp 41.0 (756 mm) (lit.[43] 41.0 (760 mm), and a mixture of 2,3-dimethyl-1- and -2-butenes, bp 55–65° (lit.[44] 55–65°), were prepared by methods described in the literature. Vpc analysis was on a 1-m 30% 3-methyl-3-nitropimelonitrile on 40–60 mesh firebrick column at 50°.

The following products had their structures confirmed by nmr and their purity was checked by a single peak on vpc analysis. The methyl 2-bromo-*cis*- and *trans*-crotonates were separated by preparative vpc on a 15% HYPROSE column at 80° from the products of reaction of NBu_4OAc with *erythro*-methyl 2,3-dibromobutanoate in acetone at 25°. The major olefin was assigned the cis configuration on the basis of expected anti elimination and its nmr spec-

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trum.[45-47] The vinylic proton in the trans-olefin (τ 2.74, quartet, J = 6.8 cps) is cis to the carbonyl group and is deshielded 0.61 ppm relative to the corresponding absorption (τ 3.35, quartet, J = 6.8 cps) in methyl 2-bromo-*cis*-crotonate. Similar deshielding (0.63 ppm) was observed in *trans*-crotonic acid, relative to *cis*-crotonic acid.[47] Methyl 2-bromo-*cis*-crotonate isomerized to 100% trans isomer on standing in the pure state at room temperature for 3 days. It is more stable in acetone solution. The analytical vpc was on a 10-ft 5% UCON Polar on 50 HB 2000 N.A.W. Chromosorb W at 100°, or on a 3-ft PORAPAK Q column at 100°.

2-Bromo-*trans*-2-butene was isolated from a large scale reaction of *d,l*-2,3-dibromobutane with NBu_4OAc in acetone by pouring into water and extracting with pentane. The colorless liquid was fractionated, bp 86.0–86.5°, $n^{20}D$ 1.4572 (lit.[48] bp 85.5°, $n^{20}D$ 1.4579). The cis isomer has bp 93–94°, $n^{20}D$ 1.4620.[48] The nmr spectrum does not distinguish between the isomers, the vinylic proton absorbs at τ 4.36, and calculations by the method of Simon[46] give chemical shifts close to this value for both isomers. An anti elimination is expected[1,18] and the physical constants confirm the trans isomer. Analytical vpc was at 35° on the 5% UCON column described above.

The commercial *trans*-stilbene was purified, mp 124°, by preparative vpc on a SE30 column at 210°. *cis*-Stilbene in hexane was purified by chromatography on basic alumina. Both isomers contained <0.02% of the other by analytical vpc on a 10% Apiezon L on Chrom W column at 180°. The pure samples were stored in the dark at 0° and used without delay.

3-Phenyl-1-propene, bp 156° (lit.[49] bp 156°), and *trans*-1-phenyl-1-propene, bp 175–177° (lit.[50] bp 176–177°), were prepared as described in the literature. They were analyzed by vpc on the Apiezon L column at 100–110°. A third peak with a retention time slightly less than the trans isomer appeared in reaction products and in isomerization of either of these olefins. It was assumed to be *cis*-1-phenyl-1-propene.

trans-1-(4-Nitrophenyl)-1-propene, mp 92–93 (lit.[51] 93–94°), was a reaction product from dehydrobromination of 1-(4-nitrophenyl)-1-bromopropane with NBu_4Br in acetone. It was identified by nmr and its purity confirmed by a single peak upon vpc analysis on the Apiezon L column at 180°.

Equilibration. Pure *cis*-stilbene and *trans*-stilbene were each equilibrated over 3 days in the presence of iodine in dimethylformamide at 37° by irradiation with a Hanovia uv lamp using a cupric chloride–calcium chloride solution as filter.[22] The mixture was analyzed by vpc until a constant proportion was reached. Pure *trans*-1-phenyl-1-propene and 3-phenyl-1-propene were each equilibrated with KO-*tert*-Bu in dimethyl sulfoxide under nitrogen at 55° for 2 hr.[23] The mixture was analyzed by vpc until a constant proportion was reached. *trans*-2-Butene and *cis*-2-butene were each equilibrated with KO-*tert*-Bu in dimethyl sulfoxide[23,52] under nitrogen at 55° for 2 days. The mixture was monitored by vpc during this period. There was some loss of olefin during and after equilibration but equilibrium proportions remained constant once equilibrium was reached.

Product Analyses. Olefins were identified by vpc analysis on the columns and at the temperatures noted above. Most of the measurements were made on Perkin-Elmer 800 or Perkin-Elmer 900 gas chromatographs, equipped with flame ionization detectors. Techniques varied during the 14 years covered by this work, but random checks, using procedures current in 1969, agreed with the earlier analyses.

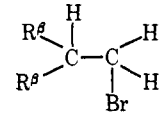
The most common and current procedure was to recover olefins from reaction mixtures plus an internal standard (*e.g.*, cyclohexane) by thorough extraction (five times) with pentane. The pentane extract was washed with water, dilute acid, and sodium bicarbonate and dried over potassium carbonate Occasionally reactants and substitution products decomposed to olefins during analysis. If the volatility was sufficiently different, as it is with tosylates and brosylates, the pentane extract was flash distilled at 1 mm into a cold trap. In early work with ethanol as solvent, volatile olefins were separated by bubbling nitrogen through reaction mixtures, through a sintered disk, a 1-ft Vigreux column, a sodium hydroxide solution, over solid potassium carbonate, and finally trapping in a cold trap. The trapped olefins were then dissolved in pentane.

Extraction "blanks" showed a loss of from 5 to 10% olefins with the current procedure. Olefins did not isomerize under the analysis conditions, and, except where noted, did not change between 10 and 20 half-lives of the reaction.

Discussion

The kinetic data of Table I are grouped in a way appropriate to this discussion in Tables III–IX. We

Table III. Effect of β-Substituents on Rates of SN2 (Log k^s) and E2 (Log k^E) Reactions at Primary Carbon[a]



No.[g]	R	R	NBu_4Cl, Me_2CO log k_s[a,b] 25°	KO-*tert*-Bu–*tert*-BuOH, 40° Log k^s	Log k_nE[f]	NaOEt, EtOH, 30° Log k^s	Log k_nE[f]
1	H	H	−1.93	−4.14	−5.57	−4.0	−6.3
19	Me	H	−2.1[c]	−4.80	−5.12	−4.4	−6.2
11	Ph	H	−3.0[d]	*e*	−2.03	−4.6	−3.68
28	Ar[g]	H		*e*	+0.9[d]	*e*	−0.43
27	An[g]	H		*e*	−2.6[d]		−4.09
18	Me	Me	−3.5[c]	−6.0	−4.9[d]	−5.3[d]	−5.1[d]

[a] Data from Table I. [b] These reactions were >99% SN2, so that log k^E is at least two units more negative than log k^s. [c] This value for acetone as solvent was estimated from rate in dimethylformamide. [d] Extrapolated from rates measured at a temperature within 25° of this by assuming an activation energy of 16–19 kcal mol^{-1}. [e] These reactions were >99% E2 so that log k^s is at least two units more negative than log k^E. [f] Values are corrected for the number of hydrogens available for this dehydrobromination, *i.e.*, log k^E(obsd) − log n where n is 1, 2, or 3. [g] Ar is 4-nitrophenyl, An is 4-methoxyphenyl, numbers refer to compounds as in footnote *b* to Table I.

note that many E2 reactions of NBu_4Cl and NBu_4OAc in acetone are faster than E2 reactions of "classical" bases, *e.g.*, KO-*tert*-Bu in alcohols. Due allowance has been made in Tables II–IX for statistical factors, such as the number of equivalent hydrogens or number of equivalent branches available for elimination.[5] Some of the rate constants have been extrapolated, from rate constants as recorded in Table I for other temperatures, by assuming the same activation energies as for related reactions. There are uncertainties introduced by this procedure, but they are not of a magnitude which would influence our discussion. Values extrapolated in this way are marked in Tables II–IX. We also record maximum values for rate constants in situations where none of a competing reaction is observed, by setting a detection limit of 1%.

The following principles for the E2C–E2H-like spectrum[1,21,53,54] are assumed throughout this discussion. (a) Other things being equal, eliminations from any one substrate will proceed through a more E2C-like transition state in the order of bases, NBu_4Br > NBu_4-

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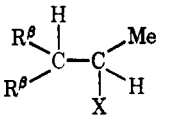
(54) See Table VII, footnote *g*.

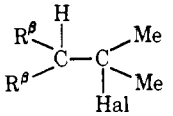
Table IV. Effects of β-Substituents on Rates of SN2 (Log k^s) and E2 (Log k^E) Reactions at Secondary Carbon[a]



No.[b]	R	R^β	NBu_4Br, OTs[c,d] Me_2CO, 75.0° Log k^s	NBu_4Br, OTs[c,d] Me_2CO, 75.0° Log k_n^E [e]	NBu_4Cl, OTs[c,d] Me_2CO, 50.0° Log k^s	NBu_4Cl, OTs[c,d] Me_2CO, 50.0° Log k_n^E [e]	NBu_4Cl, Br[c] Me_2CO, 50.0° Log k^s	NBu_4Cl, Br[c] Me_2CO, 50.0° Log k_n^E [e]	Me_2CO, Br[c] Log k_n^E [e] NBu_4OAc 25°	Me_2CO, Br[c] Log k_n^E [e] NBu_4Br 75°	Br,[c] 50.0° Log k_n^E [e] NaOEt[k]	Br,[c] 50.0° Log k_n^E [e] KO-*tert*-Bu[k]
2	H	H	−1.71	*Ca.* −6[l]	−2.19	<−6.0[l]	−2.44	−7[i]	<−7	−7.1	−4.9[f]	−4.6[f]
23	Me	H	−1.63	−3.7						−5.1	−4.8[f]	−5.2[f]
12	Ph	H		−3.6[f,i]	−2.6[f]	−3.9[f]				−4.7		−2.7[f]
24	An[d]	H	−2.18	−3.81								
3	Me	Me*	−2.35	−2.51	−2.98	−3.00	−3.19	−3.19	−3.12		−4.3[h]	
14	Br	Me*					−4.9[f,i]	−4.9[f,i]	−1.85[i]			
31	Br	Me*					−4.5[f,i]	−4.7[f,i]				
20	An[d]	Me	−2.96	−2.71	−3.6[g]	−3.0[g]						
21	An[d]	Me*			−3.6[g]	−2.8[g]						
13	Br	CO_2Me*					<−4.6	−2.60	+3.04			
26	Ph	Ph*	−3.7[g]	−2.7[g]								

[a] Data from Table I; compounds marked with an asterisk have a nonbonding interaction between cis-destined groups in the E2 transition state. [b] Numbers refer to compounds in footnote *b* to Table I. [c] This is the X group. [d] OTs is *p*-toluenesulfonate, An is 4-methoxyphenyl. [e] The observed value of log k^E in Table I has been adjusted to allow for the number of hydrogens (*n*) available for elimination, *i.e.*, value recorded here is log k_n^E = log k^E (Table I) − log *n*. [f] The rate was extrapolated from an observed rate at a temperature within 25° of this by assuming an activation energy of 16–19 kcal mol^{-1}. [g] Extrapolated from data for X = *p*-bromobenzenesulfonate; *cf.* other data in Table I. [h] Extrapolated from data for X = *p*-toluenesulfonate; *cf.* other data in Table I. [i] The two equivalent bromines have been allowed for. [j] Estimated from the usual difference of *ca.* 10 in reactivity between NBu_4Cl and NBu_4Br in E2C-like reactions; *cf.* data in Table I. [k] Base is in its conjugate acid as solvent. [l] Estimated from leaving group tendencies of tosylate *vs.* bromide in E2C-like reactions.

Table V. Effect of β-Substituents on Rates of E2 Dehydrohalogenations at a Tertiary Carbon[a]



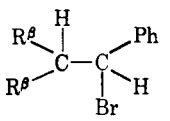
No.	R	R^β	Log k_n^E [b] NBu_4Br, Br[d] Me_2CO, 75.0°	Log k_n^E [b] NBu_4Cl, Br[d] Me_2CO, 50.0°	Log k_n^E [b] NaSPh, Cl[d] EtOH, 50.0°	Log k_n^E [b] NaOEt, Br[d] EtOH, 25°	Log k_n^E [b] KO-*tert*-Bu, Br[d] *tert*-BuOH, 25°
5	H	H	−3.9	−4.00	−5.03	−5.4	−6.2
6	Me	H*		−2.33	−3.98	−4.68	−6.3
9	Ph	H*	−2.8[c]	−2.6[c]			
30	Me	Me*			−3.26		

[a] Data from Table I; all but compound 5 have nonbonding interactions between cis-destined groups in the E2 transition state and are marked with an asterisk. [b] The observed log k^E in Table I has been adjusted to allow for the number, *n*, of hydrogens available for elimination, *i.e.*, log k_n^E = log k^E (Table I) − log *n*. [c] Extrapolated from measurement at 59.5°. [d] This is the halogen leaving group.

has a strong tendency to utilize E2H-like transition states with most substrates. (c) Acidifying, *e.g.*, electron withdrawing, substituents at C_β increase the tendency of any moderately basic anion (*e.g.*, acetate) to utilize more E2H-like transition states.[53] (d) Alkyl bromides eliminate through more E2H-like transition states than do the corresponding alkyl tosylates, under the same conditions.[54] (e) There is a strict stereochemical requirement that hydrogen and leaving group be anti in the E2C-like transition state.[1] Syn eliminations are sometimes observed in E2H-like reactions, *e.g.*, in reactions induced by potassium *tert*-butoxide in *tert*-butyl alcohol,[14–16] indicating relaxation of the anti requirement for E2H-like reactions.

SN2 Reactions. Bimolecular nucleophilic substitution reactions are retarded by bulky alkyl groups at C_α or C_β,[5,6,55] the "neopentyl effect" being an outstanding example.[55] Additional examples are in Tables I, III, IV, VII–IX. The retardation is moderate for β-substituents, even for very bulky alkyl or aryl groups, R^β in I, but as shown, particularly in Table VII, there is

Table VI. Effect of β-Substituents on SN2 and E2 Rates[a] in Benzylic Systems[a,b]



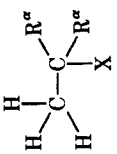
No.	R^β	R^β	NBu_4Br, Me_2CO, 75° Log k^E	NBu_4Cl, DMF, 25° Log k^s	NBu_4Cl, DMF, 25° Log k^E	NBu_4OAc, DMF, 25° Log k^s	NBu_4OAc, DMF, 25° Log k^E	KO-*tert*-Bu, *tert*-BuOH, 75° Log k^s	KO-*tert*-Bu, *tert*-BuOH, 75° Log k^E
16	Me	H	−3.38	−2.18	−4.2	−0.94	−2.0	−3.9	−2.89[c]
15	Ph	H	−3.16	−2.9	−3.7[c]	−1.8[c]	−1.2[c]	<−2[d]	*Ca.* 0[d]

[a] From Table I, numbers refer to footnote *b*, Table I. [b] No statistical correction has been made for available hydrogens. [c] The rate was extrapolated from an observed rate at a temperature within 25° of this. [d] Extrapolated from 25°, approximate value. [e] For formation of *trans*-olefin.

Cl > NBu_4N_3 > NBu_3OAc in acetone, > NaOEt > KO-*tert*-Bu in alcohols.[21] (b) Potassium *tert*-butoxide a very substantial retardation of SN2 rates (10^5 in *k*)

(55) See Table I, footnote *h*.

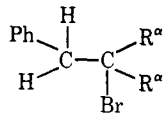
Table VII. Effect of α-Substituents on Rates of E2 and SN2 Reactions[b]



No.	R^α	R^α	NBu_4Br, Me_2CO, 75° Log k^s, X = OTs	Log k^E, X = Br	NBu_4Cl, Br, Me_2CO, 50° Log k^s	Log k^E	NBu_4N_3, Br, Me_2CO, 75° Log k^s	Log k^E	NBu_4OAc, Br, Me_2CO, 75° Log k^E	NaOEt, Br, EtOH, 25° Log k^s	Log k^E	NaOEt, OTs, EtOH, 25° Log k^E	KO-*tert*-Bu, Br, *tert*-BuOH, 40° Log k^E
1	H	H	*Ca.* 0[f]		−0.70		+0.6[f]			−4.19	<−6.0[c]	−5.4[e]	−5.09
2	Me	H	−1.71	−6.6[a]	−2.44	<−6[a]	0[f]		<−5[c]	−5.98		−4.36[a,e]	−5.3[a,e]
23	Et	H								−5.85			−5.4
3	*i*-Pr	H	−2.35	*Ca.* −6[a]	−3.19	−6						−4.70	
4	*tert*-Bu	H	−4.4	*Ca.* −6[a]	−5[d]	−6[d]						−5.30	
12	$PhCH_2$	H		−6.7									−6[f]
5	Me	Me		−3.3[a]	−4.3	−3.53[a]	−2.77	−2.65[a]	−2.63[a]			−5.0[a]	−5.2[a,e]
6	Me	Et			−4.0	−3.33[a]						−5.07[a]	−5.4[a,e]
7	Me	*tert*-Bu				−3.3[a,e]	−3.18	−2.06[a]					
8	Me	CMe_2Br			<−5	−4.6[a,e]			−4.04[a,e]				
9	Me	$PhCH_2$		−3.3[a,e]		−3.3[a,e]							
29	Ph	H									−5.10		−4.2[c]

[a] Allowance has been made for methyl groups, *e.g.*, compound no. 8 has four equivalent ways of eliminating HBr, so the log k^E recorded here is log k^E (Table I) − log 4. [b] Data from Table I; numbers refer to footnote *b* of Table I. [c] Elimination was not observed, so that log k^E is at least two units more negative than log k^s. [d] Extrapolated from rate at 100° by assuming an activation energy of 20–24 kcal mol^{-1}; this is an approximate value. [e] Extrapolated from rate at a temperature within 25° of this value. [f] Extrapolated over a temperature range >25°, a very approximate value. [g] Estimated from relative leaving group tendencies of bromine and tosylate in very E2C-like reactions (*cf.* D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968)) and from relative reactivity of Cl^- and Br^- as bases; *cf.* other data in Table I.

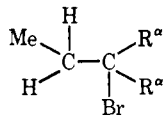
Table VIII. Effect of α-Substituents on Rates of E2 and SN2 Reactions[a]



No.	R^α	R^α	NBu_4Br, Me_2CO, 75°, log k^E	NBu_4Cl, Me_2CO, 50° Log k^s	Log k^E	KO-*tert*-Bu, *tert*-BuOH 30°, log k^E
11	H	H	<−5[e]	−2.0	<−4	−2.04
12	Me	H	−4.40[b]			−3.7[b,c]
9	Me	Me*	−2.5	<−4	−2.2	
15	Ph	H	−3.16[b]	−2.2[d]	−2.9[b,d]	−1.9[b]

[a] Data from Table I; compound marked with an asterisk has nonbonding interactions between cis-destined groups in the E2 transition state. [b] Product is *trans*-olefin. [c] Extrapolated from rate measured at 75° assuming an activation energy of 18–20 kcal mol^{-1}. Very approximate. [d] Estimated from value for chloride ion as base; E2C-like reactions of bromide ion are *ca.* ten times slower; *cf.* other data in Table I.

Table IX. Effect of α-Substituents on Rates of E2 and SN2 Reactions[a]



No.	R^α	R^α	NBu_4Br, Me_2CO 75°, log k^E	NBu_4Cl, DMF, 25° Log k^s	Log k^E	KO-*tert*-Bu, *tert*-BuOH 40°, log k^E
19	H	H	−5.94	−2.03		−4.82
23	Me	H	−4.80[c]			−5.6[c,d]
16	Ph	H	−3.38[c]	−2.18[e]	−4.2[c]	−4.5[c,d]
17	Ar[b]	H	−3.59[c]	−1.75		
6	Me	Me*	−2.0[f]	−5[d,e]	−3.0[d,e]	−5.4[d]

[a] See footnote *a*, Table VIII. [b] Ar is 4-nitrophenyl. [c] For formation of *trans*-olefin. [d] Extrapolated from data measured within 25° of this temperature by assuming an activation energy of 16–19 kcal mol^{-1}. [e] Rate constant estimated for DMF from data measured in acetone as solvent. [f] Estimated from rate of reaction with NBu_4Cl as base; *cf.* data in Table I.

by bulky alkyl groups, R^α in I. The substituent effect of R^α as phenyl on the rate of SN2 reactions is small. One possibility is that the steric effect opposes the electronic effect of a phenyl substituent. The SN2 transition state is much looser when R^α is phenyl rather than hydrogen[20] The concept of tight and loose transition states[20] explains why SN2 reactions of substituted benzyl halides are rather insensitive to the change in R^α from 4-methoxyphenyl, through phenyl to 4-nitrophenyl, despite the very different electronic effect of these substituents. Another example of a negligible effect of α-aryl substituents is provided in Table IX by the SN2 reactions of the 1-aryl-1-bromopropanes.

Concurrent SN2 and E2 reactions.[6,7] An advantage of E2C-like dehydrobrominations by bromide ion in acetone, which we have utilized, is that the SN2 exchange is of no consequence, unless the multiple Walden inversions destroy some desirable stereochemical configuration. Thus we have observed the E2C-like reaction of bromide ion with isopropyl bromide, even though the SN2 symmetrical exchange[5,7] is *ca.* 10^4 times faster than the elimination.

The F_E values in Table I reveal that elimination competes effectively with substitution, even in reactions of primary alkyl halides and tosylates, provided that the bases are strongly E2H-like, but are poor carbon nucleophiles (*e.g.*, KO-*tert*-Bu). In contrast, elimination has not yet been observed in the reactions of strongly E2C-like bases (*e.g.*, NBu_4Br) with primary alkyl halides or tosylates. Elimination reactions of secondary alkyl halides or tosylates with E2H-like bases[5] compete strongly with substitution (*i.e.*, F_E in Table I is high), but with E2C-like bases competition with the substitution reactions is usually negligible. Only if both groups R^β in I are bulky, or if the one group R^α is very bulky, do the E2C-like reactions of secondary substrates compete with substitution. Dehydrohalogenation of *tert*-alkyl halides,[55] rather than substitution, is the predominant bimolecular reaction with both E2C-like and E2H-like bases. One of the few occasions in which substitution is a significant competitor is that in which the base is azide ion.[55]

The qualitative principle behind these generalizations as to F_E is that bulky alkyl groups, R^β and R^α, *retard* the rate of the SN2 reaction,[5] they have a negligible effect on the E2H-like reaction,[5] and they *accelerate* the E2C-like reaction.

Substituent Effects on E2 Reactions.[6,7] It is important to note that if an E2 transition state contains bulky cis-destined substituents, especially if it is an E2C-like transition state, then a strong steric retardation may be observed (*cf.* Table X). This is superimposed on the usual electronic, hyperconjugative, conjugative, and R^α–R^α or R^β–R^β nonbonding interactions and is peculiar to the cis configuration. We have tried to avoid situations of this type and to concentrate on trans-destined substituents in our generalizations. Data for cis-destined substituents are marked by an asterisk in Tables III–IX.

Table X. Stereoselectivity in E2 Reactions[a]

Substrate	Base	Solvent	*T*, °C	[Trans]/[cis]
$PhCH_2CHBrPh$	Pyrol[c]	Vap[c]	180	24
	Equil[d]	DMF	37	2200
	Equil	Toluene	27	500[e]
	NBu_4Br	Me_2CO	75	49
	NBu_4OAc	DMF	25	220
	NaOMe	DMSO–MeOH[f]	25	160
	KO-*tert*-Bu	*tert*-BuOH	25	140
$CH_3CH_2CHBrPh$	Equil[d]	DMSO	50	62
	Equil	Vapor	25	3.7[g]
	NBu_4Br	Me_2CO	75	100
	KO-*tert*-Bu	*tert*-BuOH	75	70
$PhCH_2CHBrCH_3$	Equil[d]	DMSO	50	62
	NBu_4Br	Me_2CO	75	14
	KO-*tert*-Bu	*tert*-BuOH	75	52
	Equil	Vapor	25	3.7[g]
$CH_3CH_2CHBrAr$[b]	NBu_4Br	Me_2CO	75	80
$CH_3CH_2CHBrCH_3$	NBu_4Br	Me_2CO	75	5.7
	KO-*tert*-Bu	*tert*-BuOH	50	1.5[h,i]
	KOEt	EtOH	70	3.1[i,j]
	KO-*tert*-Bu	DMSO	55	3.65[i,j]
	NBu_4F	DMF	25	3.45[j]
	Equil[d]	DMSO	55	2.4
	Equil	Vapor	25	2.4[g]

[a] Data from Table II. [b] Ar is 4-nitrophenyl. [c] Pyrolysis of 1,2-diphenyl-1-bromoethane in the injector block of P. E. 900 gas chromatograph at 180°. [d] Each isomer was equilibrated by methods described in the text. [e] Reference 22. [f] 80% v/v DMSO. [g] *Cf.* footnote *g*, Table XI. [h] *Cf.* ref 11. [i] D. H. Froemsdorf, M. E. McCain, and W. W. Wikison, *J. Amer. Chem. Soc.*, **87**, 3984 (1965). [j] See Table II, footnote *k*.

β-Methyl Substituents (Tables I, III–VI). E2C-like reactions are accelerated up to 100 times by a change of R^β from hydrogen to methyl, but rates of E2H-like reaction are little influenced by this change.

Methyl groups are bulkier than hydrogen, they decrease acidity at C_β, and they hyperconjugate with well developed double bonds. The observation noted suggests that E2C-like transition states have well-developed double bonds between C_α and C_β, with no charge at C_β and a poorly developed double bond.

β-Aryl Substituents (Tables I, III–VI). E2H-like reactions are accelerated by up to one million times by change of R^β from methyl to an aryl group, but rates of E2C-like reactions are only very slightly increased by this change. In E2H-like reactions, there are substantial differences between the effect of β-4-nitrophenyl, phenyl, and 4-methoxyphenyl, but phenyl and 4-methoxyphenyl *have the same effect* on rates of E2C-like reactions. Despite nonbonding cis effects, two β substituents R^β as Ph, Ph; Me, Me; or Me, anisyl, are more effective than one, *i.e.*, R^β as Ph, H; or Me, H which are more effective than none, *i.e.*, R^β as H, H in E2C-like reactions. However it makes virtually no difference to the rate of E2C-like reactions whether the β substituents are methyl, phenyl, *p*-anisyl, or a combination of these.

Aryl substituents are bulky, they conjugate with double bonds, provided that they can achieve coplanarity, and they increase acidity at C_β.[5,7] Steric effects and conjugative effects might not change much through a series of para-substituted aryl groups. The large para substituent effect noted for E2H-like reactions is thus best explained by negative charge at C_β in the E2H transition state. The small para substituent effect (H to OMe) noted for E2C-like reactions indicates no negative charge at C_β in the E2C transition state. The overall enhancement by all aryl groups relative to hydrogen indicates a well-developed double bond, *i.e.*, an E2C transition state like products. The negligible effect of aryl relative to methyl is not consistent with a well-developed double bond in the E2C-like transition state.[5,7] It may be that β-aryl groups have not achieved coplanarity in the E2C-like transition state, but the effect of β-aryl substituents on E2C-like reactions needs further study. McLennan[56] has observed that dehydrochlorination of compounds $(RC_6H_4)_2CHCCl_3$ by chloride ion in acetone is accelerated by electron withdrawing para substituents R. Such compounds are quite acidic and chloride is a poor leaving group, so that in this case even E2 reactions of chloride ion have had their transition states moved toward the E2H side of the spectrum, *i.e.*, they respond to electron withdrawal at C_β. Dipole–dipole interactions between two β-aryl groups at sp^3 to sp^2 carbon may also be important.

β-Bromine or Carbomethoxy (Table IV). Dehydrobrominations by acetate ion of the more acidic dibromides (numbered 13, 31, and 14 in Table IV), despite a nonbonding cis effect, are up to one million times faster than dehydrobromination of the much less acidic monobromides numbered 2 and 3. This suggests that acetate ion is utilizing an E2 transition state,

(56) D. J. McLennan and R. J. Wong, *Tetrahedron Lett.*, 881 (1970).

with some negative charge at C_β, in reactions of compounds in which R^β are acidifying substituents, such as Br and CO_2Me. This transition state, which responds so strongly to acidifying substituents, must be more E2H-like than that utilized by chloride ion in acetone, because rates of the chloride ion reactions are much the same, whether R^β are Me, Me; or Br, CO_2Me and are slower if R^β is Me, Br in either a meso or d,l isomer, leading to *cis*- or *trans*-2-bromobutene, respectively. The similarity of rates for these meso and d,l isomers suggests that the cis nonbonding effect is not large in this case.

Acetate ion is a much stronger hydrogen base than chloride ion in dipolar aprotic solvents ($pK_{HOAc} \simeq 12$, $pK_{HCl} \simeq 3$ in DMF)[57] so it is not surprising that it should utilize a more E2H-like transition state, given the opportunity provided by acidifying β-substituents.

The dehydrobrominations of compounds 2, 3, 13, 14, and 31 induced by chloride ion are all strongly E2C-like. The substituent effects suggest that the double bond is well developed and there is little negative charge at C_β. Thus there is the usual substantial rate increase when R^β is changed from small hydrogens to two bulkier groups but it makes little difference whether the bulky groups are methyl, bromine, or carbomethoxy. This enhancement is associated with a change to sp^2 hybridization at C_β, in the formation of the transition state.

The very different responses of E2 reactions of acetate ion and of chloride ion to acidifying β-substituents clearly demand at least two different transition states, with very different charge distribution at C_β. The E2C–E2H spectrum (II–IV) satisfies this requirement. The relative rate constants, $\log k^E(OAc^-) - \log k^E(Cl^-)$ for elimination from various substrates, provide a useful guide to the tendency of those substrates to react through E2H-like or E2C-like transition states.[5,3] The greater the difference, the more "E2H-like" the substrate. Some eliminations induced by acetate ion, *e.g.*, dehydrotosylation of cyclohexyl tosylate,[21] are strongly E2C-like reactions, in which rates of elimination induced by acetate are only 10–20 times faster than those induced by chloride ion. However, we might anticipate rate differences of up to 10^9, *i.e.*, the difference in acid dissociation constants of HOAc and HCl in DMF,[57] for eliminations from extremely E2H-like substrates.

α-Alkyl Groups (Tables VII–IX). As expected for an associative reaction,[5,55] SN2 reactions of azide ion in Table VII are substantially retarded, E2H-like reactions, especially those with potassium *tert*-butoxide as base, are slowed, and E2C-like reactions are accelerated, by increasingly bulky groups, R^α.

The E2H-like reactions are slowed only slightly by alkyl groups at C_α because most of the changes are at C_β in the E2H-like transition state. The main effects of R^α are in their nonbonding interactions, both with R^β and the H-bound base, in the preferred conformation for the E2H-like transition state.

In the E2C-like reactions at both secondary and tertiary C_α, the rate enhancing effect of alkyl groups is little influenced by whether the R^α alkyl groups are methyl, ethyl, isopropyl, *tert*-butyl, or benzyl, but despite cis nonbonding effects, two bulky substituents are much more effective at rate enhancement than one, *i.e.*, tertiary alkyl halides eliminate more rapidly by the E2C-like mechanism than do secondary alkyl halides. Nonbonding interactions of bulky R^α groups, both with each other and with the leaving groups, are relieved by the change from sp^3 to sp^2 hybridization of C_α in the E2C-like transition state. This, together with hyperconjugative interactions with the well-developed double bond,[5] accounts for the rate acceleration of E2C-like reactions by α-alkyl groups.

Eck and Bunnett[58] have also noted that bulky groups as R^α slow SN2 reactions, but accelerate E2C-like reactions. They presented some arguments[59] which they regarded as conclusive evidence against any association between base, B, and C_α in the E2C-like transition state. We only regard the response to α-substituents as further evidence, if any is required,[1] that SN2 and E2C-like reactions do not have the same transition state. Some of the differences are that the C_α–B bond is tighter in the SN2 than in the E2C-like transition state, the hybridization at C_β is changing from sp^3 to sp^2 in the E2C-like but not in the SN2 transition state, and finally, alkyl groups at C_α can interact with a well-developed double bond in the E2C-like but not in the SN2 transition state. Nonbonding interactions, of the type which retard SN2 reactions, fall off with distance,[5,6] so that the difference between the SN2 and E2C-like transition states, as noted above, could be sufficient to account for the rate decrease in SN2 reactions and for the absence of retardation of E2C-like reactions.[59] The rate enhancement of E2C-like reactions, by bulky groups as R^α, is comparable to and occurs for much the same reason as the rate enhancement observed in SN1 reactions[5,6] of the same compounds. The hybridization at C_α changes from sp^3 to sp^2 from reactants to both transition states. In this respect, E2C-like transition states are SN1-like; the difference is that there is negligible positive charge at C_α in the E2C transition state.

α-Aryl Groups (Tables VII–IX). E2H-like reactions are accelerated very slightly by α-phenyl substituents, but an α-phenyl substituent is more than ten times more effective than α-methyl. A single α-phenyl leads to a faster E2H-like reaction than do two α-methyl groups, but the effect on E2H-like reactions of phenyl substitution at C_α is much less than at C_β. This is expected, if most of the changes are at C_β in the E2H-like transition state.

Two α-methyl substituents are more effective than a single α-phenyl substituent in accelerating E2C-like reactions. This is in contrast to E2H-like reactions, but is in agreement with our picture of much more advanced sp^2 hybridization of C_α in the E2C-like transition state.

A phenyl and a 4-nitrophenyl α-substituent have much the same effect on the rate of E2C-like reactions. The steric requirements and ability to conjugate with a double bond are comparable for the two aryl substituents, but the 4-nitrophenyl group is much more strongly electron withdrawing than phenyl. If there were positive charge at C_α in the E2C-like transition state, a phenyl substituent would lead to a faster reaction than would 4-nitrophenyl. We have only to recall a reaction in which positive charge *is* developed at C_α

(57) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

(58) See Table I, footnote *k*.

(59) See Table I, footnote *i*.

to appreciate this point. Thus the SN1 reactions of benzyl bromide are much faster than those of nitrobenzyl bromide.[5,6] The similar effects of a α-phenyl and α-4-nitrophenyl groups on rates of E2C-like reactions are strong evidence against a *paene*-carbonium transition state,[7d] for E2C-like reactions. We conclude that there is virtually no positive charge at C_α in the E2C-like transition state. This is also shown by the effects of α-phenyl and α-methyl groups on rates of E2C-like reactions. A phenyl group is much more effective than methyl at stabilizing positive charge at C_α as shown by the SN1 reactions of benzyl bromide which are more than 500 times faster than those of ethyl bromide.[5,6] However α-methyl and α-phenyl substituents have similar effects on rates of E2C-like reactions, so there cannot be positive charge at C_α in the E2C-like transition state.

The effect of α-aryl groups on rates of E2C-like reactions is as expected for a transition state with little charge at C_α, but, as with β-aryl substituents, we would have expected, but did not find, rate enhancement by conjugation with a well-developed double bond. Our conclusion is that the α-aryl group is not completely coplanar with the developing double bond, but as noted, more work on the effect of α and β phenyl groups is needed.

1-Phenyl-1-bromopropane and 1-phenyl-2-bromopropane with NBu_4Br in acetone of course gives the same major product, *trans*-1-phenylprop-1-ene and hydrogen bromide. If the respective E2C-like transition states are very like this same product, then the rate difference will be directly proportional to the free energy difference between the reactants, *i.e.*, the isomeric phenylbromopropanes.

1-Phenyl-1-bromopropane dehydrobrominates ten times more rapidly than 1-phenyl-2-bromopropane at 75° in acetone, suggesting that if the transition states are of similar energy, then the latter bromide is *ca.* 1.3 kcal/mol more stable than 1-phenyl-1-bromopropane. We do not know if this is so, but we are attempting to equilibrate the phenylbromopropanes.

Reaction Products (Tables X–XII). The kinetic products from E2C-like and E2H-like reactions are in most cases as expected from the preceding discussion of substituent effects. The products can be predicted from the generalization that E2C-like transition states are very product-like, whereas E2H-like transition states are carbanion-like. They illustrate the main theme of this paper, namely that *quite different, but predictable, proportions of isomeric olefins usually result from E2C-like reactions than from the "classical" E2H-like reactions.* The synthetic applications of this observation should be obvious.

Reaction times vary, but as shown in Tables IV–IX chloride or bromide ion in acetone induces a much more rapid elimination from very weakly acidic substrates than do the conventional bases, sodium ethoxide in ethanol or potassium *tert*-butoxide in *tert*-butyl alcohol. However, the alkoxides in alcohols cause more rapid elimination than halide ions in acetone from more acidic substrates, such as those with β-phenyl or β-halogen substituents. Tetrabutylammonium acetate in dipolar aprotic solvents is a particularly effective base for promoting E2 reactions of all types.

Hofmann–Saytzeff Tendencies (Table XI).[6,4,12] E2C-like eliminations from alkyl halides or tosylates give higher yields of Saytzeff olefin than do E2H-like reactions. Some of the highest yields of Saytzeff olefin ever recorded as kinetic products from E2 eliminations of these substrates are in Table XI. The proportion of Hofmann products is close to the equilibrium value in a solvent like acetone;[60] indeed in some cases it is lower than the equilibrium proportion; *cf.* footnote *d*, Table XI. The reason is that α- or β-alkyl substituents strongly accelerate E2C-like reactions but slow or have little effect both on E2H-like reactions and on the E1 decomposition of carbonium ions. The dehydrotosylation of 3-methyl-2-butyl tosylate by sodium ethoxide is more E2C-like (or less E2H-like than dehydrotosylation by potassium *tert*-butoxide; this follows because reaction with the former base gives a higher yield of 2-methyl-2-butene, the Saytzeff olefin. Potassium *tert*-butoxide usually gives higher proportions of Hofmann olefin than does sodium ethoxide, in accord with the more E2C-like character of sodium ethoxide. NBu_4Cl in turn is more E2C-like than sodium ethoxide, as shown by the yields of Hofmann olefin in Table XI. The E1 decomposition of 2-bromo-2-methylbutane gives 50% of 2-methyl-1-butene. This is very different from the 9% of 2-methyl-1-butene from the E2C-like reaction. In this respect the E2C-like reaction is not E1-like.

A β-phenyl substituent is less effective in E2C-like than in E2H-like reactions, so a higher yield of the unconjugated olefin, 3-phenyl-1-propene, results from the E2C-like than from the E2H-like reaction of 1-phenyl-2-bromopropane. In this case it is the E2H-like reaction which gives close to the equilibrium proportion of Hofmann olefin, emphasizing the special role of β-phenyl in E2C-like reactions.

Anti Eliminations (Table XII).[6,7,12,14,15–18,61] The most stringent stereochemical requirement of E2C-like reactions is that they give the products of anti elimination of H and X.[1,18] This requirement persists only part of the way into the E2H region, but in the E2C region it is reminiscent of the universal requirements of the Walden inversion.[5,6] In our opinion, the two requirements arise from much the same source, interaction of the base and leaving group with a p orbital of an sp^2 hybridized carbon atom. This opinion was arrived at independently by Sicher and Závada.[16] Thus in E2C-like reactions the base is anti to the leaving group and since the most effective hydrogen-bonding interaction is when the base and β-hydrogen are as close as possible, a trans–anti parallel geometry of β-hydrogen and leaving group in the E2C-like transition state III (not necessarily in reactant) is a rigorous stereochemical requirement. The first three reactions in Table XI give the least stable of the possible cis or trans isomers but there is no sign of the products of syn elimination. Clearly the requirement for anti geometry is far more stringent than any tendency of E2C-like reactions to give the most stable olefin.

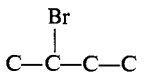
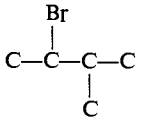
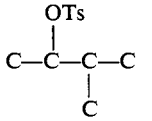
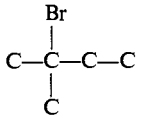
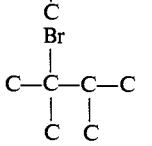
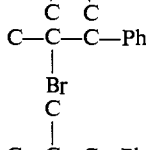
Stereoselectivity (Table XII).[6,7,12,13,14,15,62] The kinetic products from anti elimination, where the α-carbon is

(60) Schriesheim and Rowe, ref 23, have shown that many olefin proportions at equilibrium in DMSO are close to those calculated for the gas phase, and in concentrated sulfuric acid.

(61) See Table II, footnote *k*.

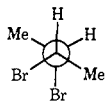
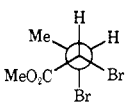
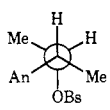
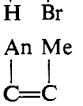
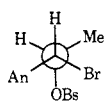
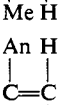
(62) (a) K. Mislow and M. Raban, "Topics in Stereochemistry," Vol. I, Interscience, New York, N. Y., 1967, Chapter 1; (b) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

Table XI. Hofmann–Saytzeff Tendencies in E2C-Like and E2H-Like Reactions[a]

Substrate	Base: NBu_4Br, Me_2CO, 75°	NBu_4Cl, Me_2CO, 50°	NaOEt, EtOH, 50°	KO-*tert*-Bu, *tert*-BuOH, 50°	Lut,[c] Me_2CO, 50°	Equil[d]
			% 1-Olefin[b]			
	4		19[i]	54[e,n]		9[f]
		0.1			<0.1	0.2[g]
	0.3	0.8	18	76.9[h]	1[h]	0.2[g]
		9[i]	37.4[e,k]	73[e,k,l]	50	8.2[g]
			21[e]	73[e]		18[g]
	0.5			0.05		0.03[f]
	22[m]	14[m]				7

[a] Data from Table II unless stated otherwise. [b] The percentage of total olefins which is 1-olefin; the other products are the Saytzeff 2-olefins (cis and trans). [c] Solvolysis in the presence of 2,6-lutidine, influenced by an E2C reaction of the product bromide ion. [d] Proportion of 1-olefin in equilibrium mixture. [e] Reference 11. [f] At 55° in dimethyl sulfoxide after equilibration with KO-*tert*-Bu; see footnote *g*. [g] In gas phase at 25° from "Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953, p 475. Equilibration of related olefins in DMSO[23] and on activated alumina: H. Pines and L. A. Schaap, "Advances in Catalysis," Vol. XII, Academic Press, New York, N. Y., 1960; gives olefin proportions corresponding to the gas phase values. It is possible that equilibration in acetone and *tert*-butyl alcohol would give distributions close to those in the gas phase and in solvents like dimethyl sulfoxide. [h] Reference 12b. Solvolysis in 1-butanol gives 1% 1-olefin. [i] Sodium thiophenoxide in refluxing ethanol gives 25.7% 1-olefin. [j] Solvolysis in ethanol gives 18% 1-olefin; see Table II, footnote *k*. [k] W. H. Saunders, S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965). [l] Solvolysis in *tert*-butyl alcohol gives 28% 1-olefin; ref 11. [m] See Table I, footnote *n*. [n] In DMSO the percentage of 1-olefin is 30; *cf.* Table II, footnote *k*.

Table XII. Anti Eliminations in E2C-Like Reactions in Acetone[a]

Substrate[b]	Base	*T*, °C	Major product	% olefin[c,e]
	NBu_4OAc	25.0		>99.9
	NBu_4Cl	75.0		>99.9
	NBu_4OAc	−70.0		99.0
	NBu_4Cl	50.0		>98
	NBu_4Cl	50.0		>99.9
	NBu_4Cl	50.0		>99.9[d]

[a] Data from Table II. [b] An is 4-methoxyphenyl, OBs is 4-bromobenzenesulfonate. [c] Percentage of major olefin, relative to all olefins produced. [d] Data from ref 1. [e] No 1-olefin could be detected with a detection limit of 0.1%, in the products from any of these eliminations.

an asymmetric center and the β-carbon atom carried two diastereotopic hydrogens, can be either *cis*- or *trans*-olefins. This provides a useful, but not definitive,[62] indicator of whether the E2 transition state is reactant-like or product-like. An anti elimination is certain for the E2C-like reactions[1,18] but this is less certain for all the E2H-like reactions in Table XII. A very product-like E2 transition state (*e.g.*, E2C) should give olefins in proportions close to their equilibrium values, but an anti or syn transition state which is very reactant-like, or paene-carbonium, or paene-carbanion (*e.g.*, E2H), leads to a variety of proportions.

The E2C-like dehydrobromination of 1,2-diphenyl-1-bromoethane by bromide ion gives a high yield of *trans*-stilbene, but the trans/cis ratio is *ca.* 20 times lower than the equilibrium proportion. The value recorded for the E2C-like products would be *ca.* 100, had it been measured at 25°. The *trans-cis*-stilbene ratio is much the same through the E2C-E2H spectrum, *i.e.*, for E2H-like bases which are either small (OMe^-), or bulky (O-*tert*-Bu), for intermediate bases (OAc^-), and for strongly E2C-like bases, (Br^-). The Hammett–Curtin principle[7,13,62] is of little value here in determining the timing of these transition states. It should be remembered that substituent effects on rate suggest that an α- or β-phenyl substituent is not well conjugated with the developing double bond in the E2C-like transition state.

The E2C-like dehydrobrominations of 1-phenyl-1-bromopropane and of 1-phenyl-2-bromopropane both give *trans*- and *cis*-1-phenyl-1-propene. We have concluded that E2C-like reactions have transition states which are product-like, so that dehydrobromination of these isomers by bromide ion should give trans/cis proportions of product which are similar and close to the equilibrium proportion. Both the E2C-like and the E2H-like reactions of these isomeric phenylbromopropanes give trans/cis ratios which are reasonably close to the equilibrium proportion, but it is the E2C-like reactions which show the greatest deviations. We tentatively suggest that, in line with our conclusions from substituent effects on rate, phenyl substituents, especially when at C_β, are not strongly conjugated with the developing double bond in the E2C-like transition state.

The much higher than equilibrium proportions of 3-phenyl-1-propene from E2C-like reactions of 1-phenyl-2-bromopropane (Table XI) are in accord with this suggestion. The E2H-like reactions of potassium *tert*-butoxide with the phenyl bromopropanes give *as kinetic products* close to the equilibrium proportions of 3-phenyl-1-propene (Table XI) and *trans*- and *cis*-phenyl-1-propene (Table X). Competing syn and anti eliminations, and/or a transition state, like products are suggested.

The ratio of *trans*- to *cis*-2-butene is very much higher in E2C-like than in E2H-like reactions of 2-bromobutane. This ratio has been studied recently by a number of investigators,[11,12,61] using bases from the E2H region of the spectrum. Our value is the highest recorded for an E2 reaction. We suggest that the higher the ratio, the more E2C-like the reaction, provided that they are anti eliminations.[61] On this basis, sodium ethoxide is more E2C-like (less E2H-like) than potassium *tert*-butoxide and NBu_4Br is more E2C-like than sodium ethoxide. The ratio from the E2C-like reaction with NBu_4Br in acetone is significantly higher than the equilibrium proportion in a similar solvent, DMSO, in the gas phase, and in concentrated sulfuric acid.[60] The differences could be due to weak conformational interactions, involving the bulky, but loosely bound, entering and leaving bromide ions. These interactions would be superimposed on the "product-like" cis effect of E2C-like reactions.

In all of the cases studied, E2C-like reactions give high proportions of *trans*-olefins. E2H-like reactions of acidic substrates also give high proportions of *trans*-olefins, but E2H-like reactions of weakly acidic substrates, *e.g.*, 2-butyl bromide and especially 2-butyl tosylate, give low proportions of *trans*-olefin.[11,12]

In summary then, the E2C-like and E2H-like reactions are very different in their response to substituent effects on rate and in their stereoselectivity. Like Bunnett and Baciocchi,[63] we think that the E2C-like transition state appears to be very like products, but we also think that there is some loose interaction of E2C-like bases with α-carbon. One reason for this opinion is the stringent requirement for antiparallel geometry of β-hydrogen and leaving group in E2C-like transition states[18] and the relaxation of this requirement in E2H-like transition states. This stereochemical requirement, just as much as the response of the rate of E2C-like reactions to changes in the carbon and hydrogen basicity of the base,[21] are best explained in terms of transition state III, in which the base interacts with both β-hydrogen and α-carbon. The influence of aryl substituents on E2C-like reactions is not entirely as expected from our picture of the E2C-like transition state.

Excess tetrabutylammonium acetate in acetone is an excellent base system for promoting fast clean β-elimination of HX from compounds I. E2C-like reactions give high yields of Saytzeff olefins and of *trans*-olefins, but the requirements of anti geometry of leaving group and β-hydrogen cannot be violated.

Acknowledgments. We are grateful to the National Science Foundation and the Australian Research Grants Committee, who supported part of this work.

(63) See Table I, footnote *n*.