The E2C Mechanism in Elimination Reactions. V.[1] Elimination from Five- and Six-Membered Alicyclics

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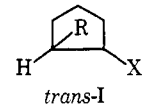
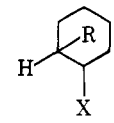
Abstract: The effects of changes in solvent, in base, in leaving group, in temperature, and in the nature and geometry of substituents, on rates and products of E2C-like dehydrohalogenations and dehydrotosylations of cyclopentyl and cyclohexyl derivatives have been studied. Rates are independent of the basicity and ionizing power of the solvent. 2,6-Lutidine prevents readdition of acid to olefin, but has no effect on rates in acetone. The E2C-like transition state appears to be loose, because rates in acetone are only a little faster than in *tert*-butyl alcohol. Rates of E2C-like reactions depend on the C nucleophilicity, rather than on the H basicity of the base, but for more E2H-like reactions the Brønsted correlation of rate with H basicity is satisfactory. Tosylate leaves more readily than bromide, in both E2C-like and SN2 reactions. It is essential that leaving group and β-hydrogen be capable of achieving anti geometry in the E2C-like transition state, but "anti-diaxial" eliminations are only *ca.* 20 times faster than "anti-diequatorial" E2C-like eliminations. The requirement of anti geometry is progressively relaxed as conditions become more E2H-like, *i.e.*, increasing proportions of syn elimination products are observed. The polar effect of substituents has little influence on rates of E2C-like reactions, but E2H-like reactions are strongly affected. Some bulky polarizable electron-withdrawing β substituents (*e.g.*, tosylate, aryl sulfones, bromine) slow E2C-like reactions, apparently because of dispersion force stabilization between substituent and potential leaving group. E2C-like reactions do not have unusual entropies of activation. Products of E2C-like reactions are often very different from those of E2H-like reactions. A careful choice of E2C-like or of E2H-like base and of solvent is recommended for specific synthetic tasks. The observations reported here all support the concept of an E2H–E2C spectrum of transition states.

This paper deals with some of the classical questions[3-7] of the mechanism of bimolecular β eliminations, in so far as they concern the E2C- and E2H-like reactions of five- and six-membered alicyclics. The answers to the questions are different, according to whether the reactions are E2C- or E2H-like. It is our hope that organic chemists who read this series will appreciate that much of the "folklore" surrounding bimolecular β eliminations has evolved from a study of E2H-like reactions in hydroxylic solvents (*e.g.*, of NaOEt–EtOH or KO-*tert*-Bu–*tert*-BuOH). A choice of E2C-like conditions may lead to products which would surprise a chemist who was familiar only with the products of E2H-like reactions.

One question is whether β eliminations require a syn or an anti arrangement of β-hydrogen and an α-leaving group.[3-11] Activated syn eliminations of HX from cyclopentyl derivatives, I, and to a lesser extent from II, are now well established under E2H-like conditions (*e.g.*, KO-*tert*-Bu–*tert*-BuOH as base, acidic β-hydrogen, poor leaving group) if the configuration of the acidic hydrogen and leaving group is geometrically prohibitive to anti elimination.[9-12]



trans-I



trans-II

The differences in the dihedral angle between β-hydrogen and leaving group in the most stable conformation of *the ground state* of reactants I and II were noted by DePuy.[10] He used them to explain the much greater tendency for syn E2H-like dehydrotosylation of *trans*-2-R-cyclopentyl than of *trans*-2-R-cyclohexyl tosylates. We have noted that many E2C-like reactions have a very strong preference for the anti geometry of β-hydrogen and leaving group *in the E2C-like transition* state,[1,13,14] so it is of interest to examine the products of E2C-like eliminations from I and II for traces of syn elimination.

The question of the effect on E2 rates of anti-diequatorial *vs.* anti-diaxial configurations of β-hydrogen and leaving group, in conformationally controlled substrates, has received some attention.[3,5,14-17] We dealt

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with it when discussing the E2C-like reactions of menthyl and neomenthyl tosylates and noted that the difference in rate between anti-aa and anti-ee E2C-like eliminations was much smaller than the corresponding difference for E2H-like reactions.[14] We now apply this question to the E2C-like dehydrotosylation of *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates, reactions first studied by Winstein, Darwish, and Holness.[17]

Substituent effects on rate are an important guide to mechanism.[5,6,13] In part II[13] we highlighted the enormous differences between the effects of α and β substituents on rates of E2C-like *vs.* E2H-like eliminations from acyclic systems. The related question of Hofmann or Saytzeff products from eliminations[3-7] was also examined. The result of competition between substitution and elimination in acyclic systems was very dependent on the nature of the α substituents and, for the same substituents, varied according to whether E2C-like or E2H-like conditions were used.[13] We now examine these substituent effects on rates and products of SN2, E2C-like, and E2H-like reactions of five- and six-membered alicyclics.

The reactions of cyclohexyl derivatives with strong carbon nucleophiles but weak hydrogen bases are particularly well suited for comparing the effect of solvent, of leaving group, and of nucleophile on rates of SN2 and E2C-like reactions. This is because both reactions are significant, *i.e.*, between 20 and 80% is elimination, with the remainder substitution. Preliminary reports have shown that rates of a few SN2 and E2C-like reactions respond in much the same way to change of solvent,[18] of leaving group,[19] and of base,[20,21] whereas rates of E2H-like reactions respond very differently to these variables. We now examine these questions in more detail.

Results

Rate Constants. Rate data are in Table I for the reaction of 0.02–0.05 *M* salts. There has been no allowance for the effect of ion association on rate.[21] In most cases fractions of elimination (F_E) were measured by titration of acid produced, and then of base remaining.[13,14] As noted, yields of elimination and substitution product were occasionally checked by vpc and proportions agreed with F_E by titration. Rate constants were calculated as described in parts I–IV,[1,13,14,21] with due allowance for nonreactive homoconjugates (HB_2^-) and heteroconjugates in acetone as solvent[21] as well as competition between substitution and elimination. Most reactions were performed in the presence of excess (0.04–0.08 *M*) 2,6-lutidine.

Solvolysis competed with some bimolecular reactions, in particular those of *trans*-4-*tert*-butylcyclohexyl tosylate in *tert*-butyl alcohol. Rates of solvolysis are recorded in Table I as instantaneous initial second-order rate constants for the reaction of a hypothetical 0.03 *M* base. This allows direct comparison of the rates of solvolysis with the rate of bimolecular elimination and substitution. The rates of SN2 and E2 reactions of RX, recorded as k^S and k^E in Table I, have been corrected approximately for solvolysis, k_1, through eq 1. The E2H-like dehydrotosylation of

$$\text{rate}/[RX] = k_1 + k^E[B^-] + k^S[B^-] \qquad (1)$$

trans-4-*tert*-butylcyclohexyl tosylate by KO-*tert*-Bu in *tert*-butyl alcohol is seriously complicated by solvolysis; the rate recorded is a maximum value for k^E.

Products of reactions of *trans*-1,2-dibromocyclohexane with bases are recorded in Table II and are discussed below.

The E2C-like reactions generate 2 mol of bromide ion and effectively consume 2 mol of base per mole of dehydrobromination, because consecutive substitution of the Hofmann product, 3-bromocyclohexene, by base is faster than the preceding dehydrobromination. This was shown in a separate experiment. Thus, the observed rate of bromide ion production and base consumption was twice the rate of initial dehydrobromination. This was allowed for in recording k^E. Iodide ion and *p*-nitrothiophenoxide in acetone *debrominated trans*-1,2-dibromocyclohexane; no *dehydro*bromination was observed. The kinetics were calculated on the basis of consumption of 3 mol of iodide ion or of 2 mol of *p*-nitrothiophenoxide, and production of 2 mol of bromide ion, per mole of substrate debrominated. Cyanide ion debrominates (78%) and dehydrobrominates (22%) *trans*-1,2-dibromocyclohexane, but both processes consume 2 mol of kinetically active cyanide ion in acetone, so the kinetics are not complex, if cyanide ion is followed.

The rate of dehydrochlorination of cyclohexyl chloride by chloride ion was followed by titration of acid and the rate of the SN2 reaction was followed by ^{35}Cl exchange.

A variety of products result from reaction of *cis*-2-bromocyclohexyl tosylate and of *cis*-1,2-ditosylatocyclohexane with bases (*vide infra*). The rate constants recorded in Table I for these reactions are sufficiently precise for our purposes, but are less reliable than other values in the table.

Tetrabutylammonium acetate slowly decomposes, presumably to butyl acetate, tributylamine, acetic acid, and 1-butene, in acetone at 50°. The rate constant is 8.5×10^{-6} M^{-1} sec^{-1}. Decomposition of NBu_4Cl in acetone has a rate constant of 8.5×10^{-7} M^{-1} sec^{-1} at 75°. These decompositions interfere only with the slow reaction of NBu_4OAc with *trans*-2-phenylcyclohexyl brosylate in acetone. Here the rate constants were recorded over the first 20% of reaction and calculated, rather than observed, infinities were used to determine $k^E + k^S$.

The E2C-like reaction of *trans*-2-*tert*-butylcyclohexyl tosylate with chloride ion is complicated by dehydrochlorination from the inverted substitution product. Thus, F_E increases as reaction proceeds. Initial rates are recorded, but the split into k^E and k^S is less precise than with some of the other values in Table I.

Product Analysis. Cyclohexene and substituted cyclohexanes, from reactions of cyclohexyl tosylate, bromide, chloride, and iodide, were checked by vpc and their proportions agreed with titrimetric F_E to within 10%. Some of the reactions deserve more detailed comment. The E2C-like reactions of *trans*-2-phenyl-

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Table I. Rates of β Elimination (k^E) and of Substitution (k^S) in Cyclohexyl and Cyclopentyl Derivatives at 75° in Acetone[a]

Substrate[b]	Base[b]	Log k^E	Log k^S	$10^2 F_E$[o]
$C_6H_{11}OTs$	Lut	−5.3[c]	(−5.3)[c]	
	$LiClO_4$	−5[c]	(−5)[c]	
	NBu_4ClO_4	−5[c]	(−5)[c]	
	LiCl	−3.73	−4.16	73
	NBu_4Cl[d]	−2.27	−2.69	72.3[g]
	NBu_4Cl[e]	−2.27	−2.69	73.0
	NEt_4Cl–DMF[f]	−2.48	−2.85	70[g]
	LiBr	−3.14	−3.43	66.4
	NBu_4Br	−2.97	−3.17	61.6
	NBu_4I	−4.2[c]	(−4.2)[c]	
	NBu_4SCN	−4.5[c]	(−4.5)[c]	
	NBu_4N_3	−2.68	−1.70	9.6
	NBu_4N_3[f]	−2.68	−1.70	9.6
	NBu_4OAc[f]	−1.86	−2.15	66
	NBu_4OAr	−3.37	−3.37	50
	NBu_4SAr	−2.90	−3.01	56
	NBu_4SAr–MeOH	−2.54[h]	−2.71[h]	60[h]
	NaSAr–EtOH,[f] 55°	−3.53[i]	−3.41[i]	43.5[i]
	NBu_4OPh	−2.29	−2.70	71
	NBu_4SPh	−1.38	−1.30	45[g]
	NBu_4SPh, 25°	−3.00	−2.92	45
	NaOEt–EtOH[f,i]	−2.96	3.85	82
	NaSPh–EtOH,[f] 55°	−2.81[i]	2.79[i]	49[i]
	Lut–*tert*-BuOH	−4.4[c]	(−4.4)[c]	*c*
	NBu_4Br–*tert*-BuOH	−3.29	−3.68	72
	NBu_4Cl–*tert*-BuOH	−3.04	−3.52	76
	KO-*tert*-Bu–*tert*-BuOH[f]	−3.23	<−5	>99[g]
$C_6H_{11}Br$	NBu_4ClO_4–DMF	−5[c]	(−5)[c]	*c*
	NEt_4Cl–DMF[f]	−3.12	−3.21	55
	NBu_4Cl	−3.24	−3.47	63
	NBu_4N_3	−2.81	−2.18	18
	NEt_4N_3–DMF[f,h]	−2.66	−1.96	17
	NEt_4N_3–MeOH[f,h]	−4.80	−4.30	25
	NBu_4Br	−4.4		
	NBu_4OAc, 51°	−3.00	−3.90	88[g]
	NBu_4OAr	−3.11	−3.90	86[g]
	NBu_4SAr	−3.31	−3.00	42[g]
	NaSAr–EtOH, 55°[i]	−4.47	−4.47	50
	NBu_4CN	−2.47	−3.5	92[g]
	NBu_4HCO_2	−2.51	−3.04	77[g]
	NaSPh–DMF, 25°[h]	−2.22	−2.40	60[g]
	NaSPh–EtOH, 55°[f,i]	−3.50	−3.59	55
	NaSPh–EtOH[h]	−2.52	−2.70	60[g]
	NaOEt–EtOH[f]	−2.98	−5.14	99.4[g]
	KO-*tert*-Bu–*tert*-BuOH[f]	−3.62		>99[g]
	NBu_4OAc	−1.98	−2.85	88[g]
$C_6H_{11}I$	NBu_4OAc, 51.5°[f]	−1.49	−2.46	92[g]
	NEt_4Cl–DMF[f]	−1.61	−1.94	66[g]
	NEt_4N_3–DMF, 25°[f]	−3.3	−2.6	20[g]
	NaN_3–MeOH[f]	−4.04	−3.85	40
	NaOEt–EtOH[f]	−2.04	−4.85	99.85[g]
	KO-*tert*-Bu–*tert*-BuOH[f]	−2.62		>99.9[g]
$C_6H_{11}Cl$	NEt_4Cl–DMF[f]	−5.4	−5.4[k]	50[g]
	NaOEt–EtOH[f]	−5.0	−6.92	98.9[g]
	NaSPh–EtOH,[f] 55°[f]	−5.66	−5.52	43
C_6H_{11}-$\overset{+}{S}Me_2I^-$	NEt_4Cl–DMF[f,l]	−3.56	−3.91	69[g]
	NaOEt–EtOH[f,m]	−2.38	<−4.7	>99.5[g]
	KO-*tert*-Bu–*tert*-BuOH[f,n]	−1.12		>99.5[g]
trans-4-*tert*-$BuC_6H_{10}OTs$	Lut	−5.2[c]	(−5.2)[c]	*c*
	$LiClO_4$	−4.6[c,f]	(−4.6)[c,f]	*c,f*
	$LiClO_4$	−4.6[c,d]	(−4.6)[c,d]	*c,d*
	NBu_4Cl–DMF	−3.08	−2.70	30.3
	$-CH_3CN$	−3.80[c]	(−3.80)[c]	
	NBu_4Cl–CH_3CN	−3.09[i]	−2.74[i]	34.7
	$-CH_3NO_2$	−4.44[c]	(−4.44)[c]	*c*
	NBu_4Cl–CH_3NO_2	−3.49[i]	−3.21[i]	34.8
	NBu_4ClO_4–CH_3NO_2	−4.43[c]	(−4.43)[c]	*c*
	NBu_4ClO_4–*tert*-BuOH	−4.28[c]	(−4.28)[c]	*c*
	NBu_4Cl–*tert*-BuOH	−3.70[i]	−3.70[i]	50
	NBu_4OAc	−2.54	−2.23	33
	NBu_4Br	−3.68	−3.19	24.1
	Lut–*tert*-BuOH	−4.31[c]	(−4.31)[c]	*c*
	NBu_4ClO_4–*tert*-BuOH	−4.15[c]	(−4.15)[c]	*c*
	NBu_4Cl–*tert*-BuOH	3.69[i]	3.62[i]	49
	KO-*tert*-Bu–*tert*-BuOH[f]	<−5[i]		
	NaOEt–EtOH[f]	<−4[i]		
cis-4-*tert*-$BuC_6H_{10}OTs$	Lut	−4.92[c]	(−4.92)[c]	*c*
	NBu_4ClO_4	−4.80	(−4.80)[c]	*c*
	NBu_4Br	−2.55	−2.81	64.8
	NBu_4Cl	−1.64	−2.17	77.2
	Lut–*tert*-BuOH	−3.92[c]	(−3.92)[c]	*c*
	NBu_4Cl–*tert*-BuOH	−2.69	−3.17	75.0
	KO-*tert*-Bu–*tert*-BuOH[f]	−3.54		100[g]
	NaOEt–EtOH[f]	−2.15		100[g]
trans-2-*tert*-$BuC_6H_{10}OTs$	NBu_4ClO_4	−2.85[c]	(−2.85)[c]	
	NBu_4Cl	−1.55[q]	−2.62	92
cis-2-*tert*-$BuC_6H_{10}OTs$	Lut	−3.13[c]	(−3.13)[c]	
	NBu_4Cl, 25°	−2.19[r]		100

Table I (*Continued*)

Substrate[b]	Base[b]	Log k^E	Log k^S	10^2F_E[c]
trans-2-MeC_6H_{10}-OTs	NBu_4Cl	−3.25[q]	−2.74	24.0
cis-2-MeC_6H_{10}-OTs	NBu_4Cl, 50°	−2.22[r]	3.35	93.5[q]
	NBu_4OAc, 51.0°	−2.51[r]	3.51	89[q]
	NBu_4OAr	−2.41[r]	−2.89	74[q]
	NBu_4SAr	−1.7[r]	−2.2	75[q]
	NBu_4OPh	−1.83[r]	−2.20	70[q]
	NBu_4SPh, 0.0°	−3.05[r]	−3.35	66[q]
	NBu_4SPh, 25.0°	−2.27[r]	−2.57	66[q]
trans-2-PhC_6H_{10}-OTs	NBu_4Cl	−3.81[q]	−3.44	30
cis-2-PhC_6H_{10} OBs	NBu_4ClO_4, 50.0°	−5.22[c]	(−5.22)[c]	*c*
	NBu_4Cl, 20.0°	−2.72[r,t]	−4.40	96
	NBu_4Cl, 35.0°	−1.95[r,t]		99.4
	NBu_4OAc, 25.0°	−1.08[r,t]		100
cis-2-Ph-$C_6H_{10}Cl$	NBu_4Cl, 50.0°	−4.85[r]		
trans-2-Ts-$C_6H_{10}OTs$	NBu_4Cl	−4.05[q]	−4.60	75
cis-2-Ts-$C_6H_{10}OTs$	NBu_4Cl	−1.03[r]		100
trans-2-Ph-$C_6H_{10}OBs$	Lut	−5.30[c]	(−5.30)[c]	*c*
	NBu_4Cl, 50.0°	−4.32[q,t]	−3.77	21.7
	NBu_4N_3, 50.0°	−4.22[q,t]	−3.80	35
	NBu_4N_3	−3.00[q,t]	−2.70	35
	NBu_4OAc, 50.0°	−3.82[p,q,t]	−3.72[p]	44.5[p]
	NBu_4OAc	−2.72[q,t]	−2.92	60
Δ^3-C_6H_9-OTs	NBu_4Cl	−2.15[s]	−2.75	20
4,4-Me_2-C_6H_9OTs	Lut	−5.11[c]	(−5.11)[c]	*c*
	NBu_4Cl	−2.43[s]	−2.15	34
	NBu_4Br	−3.35[s]	−2.74	20
3-β-Cholestanyl OTs	NBu_4Cl	−3.66[s]	−2.42	5.6
C_5H_9OTs	NBu_4Cl	−2.17	−0.70	3.3
trans-2-MeC_5H_6-OBs	Lut, 50.0°	−4.21[c]	(−4.21)[c]	*c*
	NBu_4Cl, 50.0°	−2.57[q]	−1.83	15.5
	KO-*tert*-Bu-*tert*-BuOH, 50.0°	<−4.4[i]	−1.83	15.5
trans-2-PhC_5H_8-OBs	Lut, 50.0°	−4.51[c]	(−4.51)[c]	*c*
	NBu_4Cl, 50.0°	−2.65[q,t]	−2.74	55.2
trans-2-PhC_5H_6-OBs	NBu_4OAc, 50.0°	−1.93[q,t]	−1.98	52.7
	tert-BuOH, 50.0°	−4.07[c]	(−4.07)[c]	
	NBu_4OAc-*tert*-BuOH, 50.0°	−3.30[i,t]		100
	KOPh-*tert*-BuOH, 50.0°	*Ca.* −4.1[i,t]		
cis-2-PhC_5H_8-OBs	NBu_4ClO_4, 50.0°	−4.20[c]	(−4.20)[c]	*c*
	NBu_4Cl, 30.0°,	−1.87[r,t]	−2.51	81.4
	NBu_4Cl, 15.0°	−2.64[r,t]	−3.25	80.6
	NBu_4OAc, 25.0°	−0.60[r,t]	<−2.60	>99
cis-2-PhC_5H_6Cl	NBu_4Cl, 50.0°	−4.34[r]		
Δ^3-C_5H_5-OTS	NBu_4Cl	−2.54[s]	−1.11	3.6
trans-2-BrC_6H_{10}-Br[u]	NBu_4Cl	−3.23[v]		100[v]
	NBu_4I, 100°	<−5.0[r]		100[v]
	NBu_4I, 100°	−3.03[w]		100[w]
	NBu_4CN	−2.98[v]		100[v]
	NBu_4CN	−2.43[w]		100[v]
	NBu_4SAr	−2.41[w]		100[w]
	NBu_4N_3	−2.25[v]		100[v]
	NBu_4OAc	−1.85[v]		100[v]
	NBu_4OAc[f]	−1.85[v]		100[v]
cis-2-Br-$C_6H_{10}Br$	NBu_4ClO_4	<−4[c]	(<4)[c]	*c*
	NBu_4Cl	−2.81[r,v]		>95[q]
	NBu_4CN, 25.0°	−1.64[r,v]		100[q]
	NBu_4N_3, 50.0°	−2.25[r,v]	−3.20	90[q]
	NBu_4HCO_2, 25.0°	−2.17[r,v]	−3.08	89[q]
	NBu_4OAc, 0.0°	−2.43[r,v]		100[q]
	NBu_4OAc, 25.0°	−1.42[r,v]		100[q]
	NBu_4OAc, 50.0°	−0.60[r,v]		100[q]
	NBu_4OAr, 25.0°	−2.71[r,v]		100[q]
	NBu_4OAr, 50.0°	−1.79[r,v]		100[q]
	NBu_4SAr	−2.20[r,v]		>90[q]
	NBu_4SPh, 25.0°	−1.34[r,v]		>90
	NBu_4OPh, 25.0°	−1.43[r,v]		100[q]
	NaOEt-EtOH, 50°[f]	−1.80[r,v]		>98[q]
cis-2-Br-$C_6H_{10}OTs$	NBu_4Cl	−3.6[z]		
	NBu_4OAc	−1.7[z]		
	NaOEt-EtOH[f]	−2.5[z]		>90
cis-2-OTs-$C_6H_{10}Br$	NBu_4Cl	<−4.3[v]		
	NBu_4OAc	<−2.5[v]		
	NaOEt-EtOH	−3.0[v]		>90
cis-2-OTs-$C_6H_{10}OTs$	NBu_4Cl	−4.1[z]	−4.0	45
	NBu_4OAc	−2.1[z]	−1.6	30

[a] Solvent is acetone containing 0.03–0.06 *M* 2,6-lutidine, temperature 75.0°, and base at 0.03–0.06 *M*, unless stated otherwise. Rate-constants in M^{-1} sec^{-1}. [b] Abbreviations are: OTs, *p*-toluenesulfonate; Lut, 2,6-lutidine; Ar, 4-nitrophenyl; OAc, acetate; DMF, dimethylformamide; OBs, *p*-bromobenzene sulfonate; Ts, *p*-toluenesulfonyl. [c] These reactions are mainly solvolyses; the rate of acid production is almost independent of base concentration. Rate constants are recorded as instantaneous initial second-order rate constants for a hypothetical acid-producing reaction, induced by 0.03 *M* base. The products were not analyzed so that the rate constant recorded

Footnotes to Table I (*Continued*)

is for "solvolysis" rather than for substitution or elimination. [d] 2,6-Lutidine at 0.034 *M*. [e] 2,6-Lutidine at 0.063 *M*. [f] No 2,6-lutidine. [g] F_E confirmed by vpc analysis. [h] E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90**, 6447 (1968). [i] D. J. McLennan, *J. Chem. Soc. B*, 705 (1966). [j] k^E and k^S have been corrected for the effect of competing solvolysis (*cf.* eq 1). [k] Measured by the rate of ^{36}Cl exchange. [l] Reaction is 98.9% SN2 attack at methyl carbon to give methylcyclohexyl sulfide. [m] Reaction is 81% SN2 at methyl carbon. [n] Reaction is 84% SN2 at methyl carbon. [o] F_E is the fraction of total bimolecular reaction which is elimination. [p] Corrected for decomposition of NBu_4OAc (see text). [q] Hofmann olefin is produced because of the requirement for anti geometry in the E2C-like transition state (see text). [r] Product of anti elimination is the Saytzeff olefin (see text). [s] The olefin was not identified. [t] Products given in Tables III and IV. [u] Products are in Table II. [v] Dehydrobromination. [w] Debromination. [z] Dehydrotosylation. [y] Substitution products were not detected by vpc.

Table II. Products[a] of Dehydrobromination and Debromination of *trans*-1,2-Dibromocyclohexane, in Acetone[c,b] at 75°

Base Y in NBu_4Y	1,3-Cyclohexadiene	3-Y-Cyclohexene	1-Y-Cyclohexene	1-Bromocyclohexene	Cyclohexene
I	*c*	*c*	*c*	*c*	100
$SC_6H_4NO_2$-4	*c*	*c*	*c*	*c*	100
CN	*c*	22	*c*	*c*	78
Cl	1	99	*c*	*c*	*c*
N_3	*c*	100	*c*	*c*	*c*
OAc	8	92	*c*	*c*	*c*

[a] *Cf.* eq 2. Products from 0.04 *M* reaction mixtures are expressed as a percentage of all products detected by vpc after 10 half-lives. Calibration with authentic samples confirmed that the sum of these products accounted for >95% of the initial *trans*-1,2-dibromocyclohexane. [b] Acetone contains excess 2,6-lutidine. [c] This product could not be detected; detection limit 0.5% of total products.

Table III. Products of SN2 and E2C-Like Reactions of *trans*-2-Phenylcycloalkyl Brosylates with NBu_4Cl[a,b]

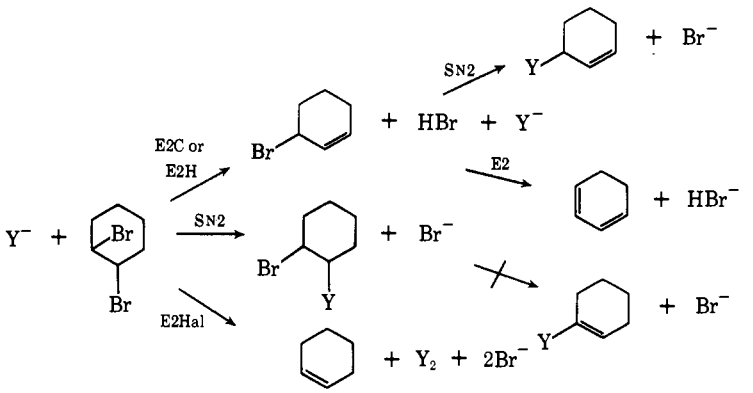
Substrate[d]	% 3-phenylcycloalkene	% 1-phenylcycloalkene	% *cis*-2-phenylcycloalkyl chloride	Half-lives[c]
trans-2-PhC_5H_8OBs	40.2	8.0	52.0	10
	54.1	11.7	34.2	34
	57.4	12.6	30.0	40
	57.0	14.0	29.0	49
	56.3	27.4	16.3	170
	52.9	42.6	4.5	560
trans-2-$PhC_6H_{10}OBs$	20.9	30.9	48.2	20
	20.5	48.3	31.2	42

[a] In acetone containing excess 2,6-lutidine at 50°. [b] Percentage of total peak areas, by vpc analysis. [c] The half-life was calculated from rates in Table I; the reaction mixture was left for this period prior to analysis. [d] OBs is *p*-bromobenzene sulfonate.

cyclohexyl and *trans*-2-phenylcyclopentyl sulfonate esters with chloride ion are complicated by slower consecutive dehydrochlorinations of the inverted substitution products. These consecutive reactions give 1-phenylcyclohexene[22] or 1-phenylcyclopentene, respectively, so that the proportion of *Saytzeff* product increases, as reaction proceeds. This is shown in Table III.

alkene which is produced by consecutive elimination from a substitution product can be made.

The *cis*-2-phenylcycloalkyl acetates do not dehydroacetylate in the presence of acetate ion, so that consecutive elimination is not a problem, when NBu_4OAc is a base. Thus, the proportions of 3-phenylcycloalkene to 1-phenylcycloalkene for reaction of NBu_4OAc in Table IV are more representative of kinetic products



(2)

The initial kinetic products recorded in parentheses in Table IV were estimated by extrapolation to zero time of the proportions in Table III of 1-phenyl- and 3-phenylcycloalkenes at various multiples of the half-life. The dehydrochlorinations of *cis*-2-phenylcyclohexyl chloride and of *cis*-2-phenylcyclopentyl chloride by NBu_4Cl in acetone at 50° have rate constants of 1.4×10^{-5} M^{-1} sec^{-1} and 4.6×10^{-5} M^{-1} sec^{-1}, respectively, so that this side reaction is insignificant in the very early stages of reaction. Thus, from the F_E for the reaction of NBu_4Cl with the *trans*-2-phenylcyclohexyl brosylates during the early stages of reaction, a reasonable estimate of the proportion of 1-phenylcyclo-

than are the ratios from reaction of NBu_4Cl. However, the former are more E2H-like reactions. The 3-phenylcycloalkenes were shown not to isomerize to the more stable 1-phenylcycloalkenes, under any of the reaction conditions.

The potential bimolecular reactions of *trans*-1,2-dibromocyclohexane with base, Y, are concurrent substitution (SN2), dehydrobromination (E2C or E2H), and debromination (E2Hal). Consecutive reactions then consume base and generate both acid and bromide ion. The possible reaction pathways are shown in eq 2, but in practice, elimination from the substitution product (SN2) to give 1-substituted cyclohexene was not observed by vpc. These reactions were monitored by vpc

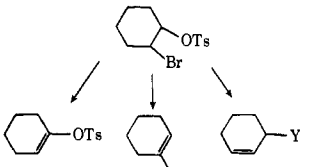
(22) L. S. McNamara and C. C. Price, *J. Org. Chem.*, 27, 1230 (1962).

Table IV. Cycloalkenes from Isomeric 2-Phenylcycloalkyl Brosylates. E1, E2C-Like, and E2H-Like Reactions in the Presence of 2,6-Lutidine

Substrate R in ROBs	Solvent	Base Y in NBu_4Y	T, °C	3-Phenylcycloalkene[a]	Half-life[e]	Substn product[b]	Mechanism[d]
trans-2-PhC_5H_8	Me_2CO	ClO_4	75	6.7	10		E1
	Me_2CO	Cl	50	(91)[c]	0[c]	(55)[c]	E2C
	Me_2CO	Cl	50	82.5	6		E2C
	Me_2CO	OAc	50	99.2	10,20	51.5	E2C
	tert-BuOH		50	14.4	10		E1
	tert-BuOH	OAc	50	84.7	10,30		E2C
	tert-BuOH	KOC_6H_5	50	34.4	10,30		E2C–E2H
	tert-BuOH	KO-*tert*-Bu	50	15.1	10,30		E2H
cis-2-PhC_5H_8	Me_2CO	ClO_4	75	9.5	15		E1
	Me_2CO	Cl	50	0.3	20		E2C
	Me_2CO	OAc	25	0.3	44		E2C–E2H
trans-2-PhC_6H_{10}	Me_2CO	Cl	50	(92)[c]	0[c]	(78.3)[c]	E2C
	Me_2CO	OAc	50	96.2	10,20	46.3	E2C
cis-2-PhC_6H_{10}	Me_2CO	Cl	20	0.5	20	1.7	E2C
	Me_2CO	OAc	25	1.5	44,75	1.3	E2C–E2H

[a] As a percentage of the total cycloalkenes, *i.e.*, of 3-phenyl- plus 1-phenylcycloalkene by vpc of 0.04 *M* reaction mixtures. [b] As a percentage of total cycloalkenes, plus substitution product. [c] Extrapolated to zero time for reasons described in text. Data from Table III. [d] Expected mechanism for elimination; E2C here denotes E2C-like, E2H denotes E2H-like, and E2C–E2H denotes "central" in the spectrum of transition states. E1 denotes a solvolysis reaction. [e] Reaction was left for this period, using half-lives estimated from Table I, prior to analysis.

Table V. Proportions of Products from Reactions of *cis*-2-Bromocyclohexyl Tosylate with Bases[a]

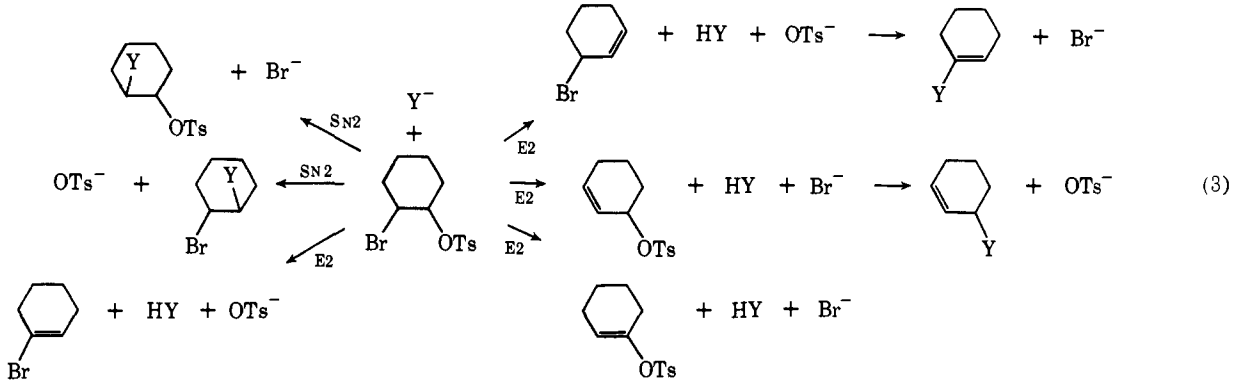


Base Y	T, °C				% Y^- consumed[h]	% Br^- produced[h]
NaOEt–EtOH[c]	50	26[g]	66[a]	8[a]	108	35
NBu_4OAc–Me_2CO[b,d]	50	<15[e]	85[a]	*f*	23	58
NBu_4Cl–Me_2CO[b,d]	100	<19[e]	81[a]	*f*	30	28

[a] By vpc analysis of 0.05 *M* reaction mixtures after 10 half-lives, using authentic materials as standards. [b] Containing excess 2,6-lutidine. [c] Expressed as a percentage of the total organic products by vpc. [d] Expressed as a percentage of the acid produced; there are also substitution products, *cf.* eq 3. [e] Calculated by assuming that this is the only source of acid, in addition to that produced from formation of 1-bromocyclohexene and of 3-Y-cyclohexene (*cf.* eq 3). [f] A dash indicates that this compound was not detected, *i.e.*, <1%. [g] Calculated by assuming that this is the only other source of bromide ion and noting the absence of any other products, *e.g.*, *cis*-1,2-diethoxycyclohexane, by vpc. [h] By titration.

at all stages and details are in Table II; analysis for bromide ion, acid, and for base, Y^-, agreed with the vpc results and reaction scheme 2. 3-Y-Cyclohexene and cyclohexene were the major products in all reactions of *trans*-1,2-dibromocyclohexane with bases; *cis*-1-Y-2-bromocyclohexane and its by-products, together with 1,3-cyclohexadiene, accounted for less than 8% of the total reaction products by vpc.

Multiple bimolecular eliminations of *cis*-2-bromocyclohexyl tosylate and of *cis*-1,2-ditosylatocyclohexane with bases are possible (*cf.* eq 3 and 4). They were analyzed by vpc and by titration of acid, of bromide ion, and of base. Product analyses are in Table V.

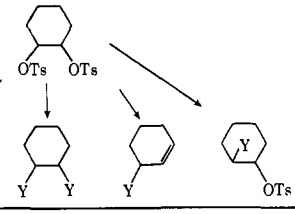


(3)

Substitution of *cis*-2-bromocyclohexyl tosylate by Y^- accounted for up to 30% of the total reaction, and the substitution component was even greater (up to 70%) in reactions of *cis*-1,2-ditosylatocyclohexane with bases. Product analyses are in Table VI.

Dimethylcyclohexylsulfonium iodide gave mainly cyclohexyl methyl sulfide and methyl Y by vpc in its

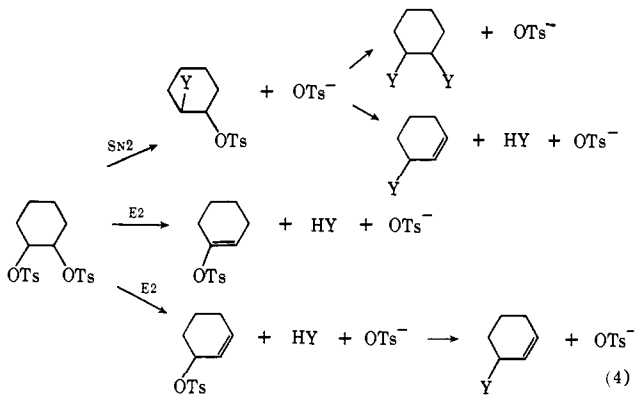
Table VI. Proportions of Products from Reactions of *cis*-1,2-Ditosylatocyclohexane with Bases in Acetone[a]



Base Y	T, °C	% Y⁻ consumed	% H⁺ produced
NBu_4Cl	100	58[c]	54[c]
NBu_4OAc	75	78[c]	55[c]

[a] Containing excess 2,6-lutidine. [b] By vpc analysis of 0.05 *M* reaction mixtures after 1 half-life. Starting material does not decompose to detectable products during vpc analysis. [c] By titration. Recorded as a percentage of the total products. [d] Calculated from *b* and *c* by assuming that these are the only other organic products; *cf.* eq 4. They cannot be analyzed by vpc.

reactions with bases Y. The proportions of this SN2 reaction at methyl carbon were 98.9% with NEt_4Cl in DMF, 81% with NaOEt in ethanol, and 84% with KO-*tert*-Bu in *tert*-butyl alcohol. However, it was a



simple matter to detect by vpc the small proportion of substitution to cyclohexyl Y and elimination to cyclohexene, and thus calculate the rates recorded in Table I.

cis-1,2-Dibromocyclohexane gave >95% of 1-bromocyclohexene and no cyclohexene or 3-substituted cyclohexene in its reactions with bases. The only detectable reaction is "Saytzeff" dehydrobromination. Especially interesting is the clean dehydrobromination of *cis*-1,2-dibromocyclohexane by *p*-nitrothiophenoxide in acetone, whereas *trans*-1,2-dibromocyclohexane gives only the debromination product, cyclohexene, with this base. Anti geometry of the two leaving groups is essential for both debromination and dehydrobromination by the *p*-nitrothiophenoxide ion.

cis-2-Methylcyclohexyl tosylate gave 1-methylcyclohexene and a little substitution product, in its reactions with E2C-like bases. No 3-methylcyclohexene (<0.2%) was formed over the first 30% of reaction with chloride ion, but a little appeared at longer reaction times. Presumably this was due to dehydrochlorination from the substitution product, *trans*-2-methylcyclohexyl chloride. By contrast, Froemsdorf and McCain[23] obtained 41% 3-methylcyclohexene in the very E2H-like reaction with KO-*tert*-Bu in DMSO.

The products from reaction of these three cis isomers confirm[13] the very pronounced tendency for Saytzeff, rather than Hofmann, elimination in E2C-like reactions.

(23) D. H. Froemsdorf and M. E. McCain, *J. Amer. Chem. Soc.*, **87**, 3983 (1965).

Experimental Section

Rates were measured as described in parts I–IV.[1,13,14,21] Products were extracted into pentane and analyzed by vpc, where noted, using authentic samples as standards and flame ionization detectors in a variety of instruments. Electrolytes and solvents were prepared and purified as described previously.[14,21]

Reactions of potassium *tert*-butoxide and of mercaptides were performed under nitrogen. Acetate ion was estimated by quenching a 5-ml sample in 10 ml of glacial acetic acid, containing as indicator 12 drops of saturated Bromphenol Blue in acetic acid. An excess of standardized perchloric acid in acetic acid was added and the solution was back titrated with sodium acetate in glacial acetic acid. Acetic acid generated in reactions was estimated by quenching with 30% ethanol–acetone; the solution was titrated with sodium methoxide to the blue end point of Bromthymol Blue, under a nitrogen atmosphere.

1-Methylcyclopentene, pure by vpc, was prepared from cyclopentanone and methyl iodide by a Grignard reaction, followed by dehydration of the resulting alcohol with phthalic anhydride or preferably iodine. The olefin was hydroborated[24] and the *trans*-2-methylcyclopentanol, bp 156°, $n^{25}D$ 1.4472 (lit.[25] bp 152–153°, $n^{20}D$ 1.4488) was separated by preparative vpc. The *p*-bromobenzenesulfonate was prepared with brosyl chloride in pyridine, but it would only solidify from petroleum ether at −80° and remelted at room temperature. Acetolysis gave the theoretically expected quantity of acid.

The following were prepared *via* the alcohols which were themselves prepared by standard procedures: *trans*-2-*tert*-butylcyclohexyl *p*-toluenesulfonate (tosylate), mp 67.8–68.8° (lit.[25] 66.5–66.8°); the cis isomer, mp 71.2–71.4° dec (lit.[25] 69–70° dec); *cis*-2-bromocyclohexyl tosylate, mp 78–79° (lit.[25] 79–80°); *cis*-1,2-ditosylatocyclohexane, mp 128–129° (lit.[26] 129°); *trans*-2-methylcyclohexyl tosylate,[27,28] mp 26.5–27.5°; *cis*-2-methylcyclohexyl tosylate,[27,29] mp 53.2–54.6°; 4,4-dimethylcyclohexyl tosylate,[27,30] mp 34.5–35.5°. *trans*-2-Phenylcyclohexyl *p*-bromobenzenesulfonate, mp 130–132° dec, and its cis isomer, mp 103.5–105° dec, and *trans*-2-phenylcyclohexyl tosylate, mp 125° dec, were prepared from the alcohols provided by Mr. R. F. Heck using the appropriate sulfonyl chloride in pyridine. *cis*- and *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonates[31] were obtained from Holness. *cis*- and *trans*-2-*p*-toluenesulfinylcyclohexyl tosylates[11] were obtained from R. Johnson. *cis*- and *trans*-2-phenylcyclopentyl *p*-bromobenzenesulfonates were obtained from E. Friedrich. The syntheses of *cis*- and *trans*-2-arylcyclopentanols and the 1- and 3-arylcyclopentenes have been discussed elsewhere.[10] Samples of 1- and 3-phenylcyclopentene and of 1- and 3-phenylcyclohexene for vpc calibration were provided by R. F. Heck; cyclohexyl

(24) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).
(25) H. L. Goering, R. L. Reeves, and H. H. Espy, *ibid.*, **78**, 4926 (1956).
(26) S. J. Angyal and R. J. Young, *Aust. J. Chem.*, **14**, 8 (1961).
(27) The alcohol was prepared as described in the reference and then converted to the sulfonate ester, using the sulfonyl chloride in dry pyridine.
(28) W. Hückel and A. Hubele, *Justus Liebigs Ann. Chem.*, **613**, 27 (1958).
(29) R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).
(30) E. L. Eliel and C. A. LuKach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).
(31) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

tosylate, mp 45–46°, was prepared by tosylating commercial cyclohexanol; cyclohexyl bromide, bp 163–164°, cyclohexyl chloride, and cyclohexyl iodide were available commercially; 4-cyclohexenyl tosylate was supplied by M. Battiste; 4-cyclopentenyl tosylate, mp 52.5–53°, and cyclopentyl *p*-toluenesulfonate, mp 27.1–27.9°, were obtained from J. Sonnenberg. All these sulfonate esters gave "infinities" corresponding to 98–100% of the expected consumption of base in their reactions with excess base.

The following were prepared by standard methods and their identity and purity established by vpc analysis and nmr: *trans*-1,2-dibromocyclohexane, bp 72° (2.5 mm), by brominating cyclohexene in carbon tetrachloride; *cis*-1,2-diacetoxycyclohexane, bp 110° (11 mm), by acetylation with acetic anhydride of cyclohexane-*cis*-1,2-diol; *cis*-1,2-dibromocyclohexane, bp 52° (0.2 mm) (lit.[32] 50–51° (0.1 mm)), by photolytic addition of hydrogen bromide to 1-bromocyclohexene;[32] *cis*-1,2-dichlorocyclohexane, bp 85° (18 mm) (lit.[33] 85° (18 mm)) by substitution of *trans*-2-chlorocyclohexanol with thionyl chloride in pyridine;[33] 3-acetoxycyclohexene, bp 67–68° (11 mm), by acetylation of 3-hydroxycyclohexene with acetic anhydride; dimethylcyclohexylsulfonium iodide, mp 106° (lit.[34] 105–106°), from the SN2 reaction of cyclohexylmethyl sulfide[35] with methyl iodide;[34] 3-bromocyclohexene, bp 78° (30 mm), by bromination of cyclohexene with *N*-bromosuccinimide in carbon tetrachloride;[36] 3-chlorocyclohexene, bp 49.5° (12 mm), by chlorination of cyclohexene with *tert*-butyl hypochlorite;[37] and 1-bromocyclohexene, bp 54–56° (20 mm), from reaction of 2,3-dibromocyclohexene with lithium aluminum hydride;[36] 3-ethoxycyclohexene, bp 60° (20 mm), from *trans*-1,2-dibromocyclohexane with sodium ethoxide.

Acid and halide ions were analyzed titrimetrically and the halides identified by the end point in a silver nitrate titration. The products recorded in Tables II–VI were analyzed by vpc. The values in Tables III and IV were calculated from relative peak areas of the isomers, but other analyses have been corrected for differences in molar response. Published retention times for 1-phenyl- and 3-phenylcyclohexene[22] under similar vpc conditions were used for identification. Authentic samples of the following were prepared for vpc calibration: 1-phenyl- and 3-phenylcyclopentene, cyclohexene, 1-bromocyclohexene, 3-ethoxycyclohexene, 3-acetoxycyclohexene, 1,3-cyclohexadiene, 3-bromocyclohexene, 3-chlorocyclohexene, 1-methylcyclohexene, cyclohexyl *tert*-butyl ether, cyclohexyl ethyl ether, *cis*-1,2-diacetoxycyclohexane, *cis*-1,2-dichlorocyclohexane, and cyclohexyl methyl sulfide. Cyclohexenyl tosylate could not be purified and decomposed on vpc columns.

Discussion

Kinetics (Table I). The reactions of Table I are bimolecular and exhibit the usual kinetic features[21] of bimolecular reactions in acetone. Rates of reaction of any one substrate with different bases vary over at least 10^4 according to the nature and concentration of the base. The bimolecular reactions are usually much faster than solvolyses in the presence of lutidine and nonbasic salts, like $LiClO_4$ and NBu_4ClO_4. Lithium chloride is less reactive than LiBr, but NBu_4Cl is more reactive than NBu_4Br, at the same concentrations in acetone. LiCl is much less reactive than NBu_4Cl in acetone. These effects are mainly a function of the extensive ion pairing of LiCl in acetone.[21] 2,6-Lutidine is not present in the E2C-like transition state, its presence or absence does not influence the overall rate of loss of substrate, but it was added to prevent addition of acids to product olefins, a process which interferes with the split of total rate into k^E and k^S.[21] Thiophenol had a marked tendency to add to cyclohexenes in acetone and even in DMF, unless 2,6-lutidine was present.

Anti Diaxial *vs.* Anti Diequatorial Elimination (Table VII). The 4-*tert*-butyl group is assumed to exert conformational control as an equatorial substituent in both *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates. Thus, the tosylate group is almost entirely axial in the cis isomer and equatorial in the trans isomer.[31]

Table VII. Anti Diaxial and Anti Diequatorial Eliminations

Substrate	k^{aa}/k^{ee} (NBu_4Cl)[a]	k^{aa}/k^{ee} (NaOEt)[c]	log k^s (NBu_4Cl)[e]
cis-4-*tert*-$BuC_6H_{10}OTs$ (aa)			−2.17
	30	>70[a]	
trans-4-*tert*-$BuC_6H_{10}OTs$ (ee)			−2.70
Neomenthyl OTs (aa)			>−2.63
	13[b]	50[d]	
Menthyl OTs (ee)			−2.96

[a] Ratio of k^E (Table I) for dehydrotosylation induced by NBu_4Cl in acetone at 75° from tosylates with anti diaxial (k^{aa}) and anti diequatorial (k^{ee}) geometry of H and OTs in the most stable conformation. [b] From ref 14, rates of elimination to form 2-menthene. [c] The base is sodium ethoxide in ethanol at 75°. [d] The substrates are menthyl and neomenthyl chloride, not tosylate; data from ref 5, p 470. [e] Rates of substitution by NBu_4Cl in acetone at 75° are from Table I.

Substitution (SN2) of an axial tosylate by NBu_4Cl in acetone is three times faster than substitution of an equatorial tosylate from the isomeric 4-*tert*-butylcyclohexyl tosylates.

The anti diaxial, E2C-like dehydrotosylation of *cis*-4-*tert*-butylcyclohexyl tosylate by NBu_4Cl is 30 times faster than the anti diequatorial, E2C-like dehydrotosylation of *trans*-4-*tert*-butylcyclohexyl tosylate. Similarly, anti diaxial dehydrotosylation of neomenthyl tosylate to 2-menthene by NBu_4Cl in acetone is only 13 times faster than anti diequatorial dehydrotosylation of menthyl tosylate to 2-menthene. It seems to be a feature of E2C-like reactions that anti diequatorial are only a little slower than anti diaxial eliminations.[14]

In contrast, many E2H-like reactions, *e.g.*, with alkoxides in alcohols as bases, are very much faster if the elimination is from substrates with anti diaxial rather than anti diequatorial arrangements of hydrogen and leaving group.[3,39,40] Thus, dehydrochlorination (anti aa) of neomenthyl chloride to 2-menthene is at least 50 times faster than dehydrochlorination (anti ee) of menthyl chloride by sodium ethoxide in ethanol and "anti diaxial" dehydrobromination of *cis*-4-*tert*-butylcyclohexyl bromide is 500 times faster than "anti diequatorial" dehydrobromination of the trans isomer by potassium *tert*-butoxide in *tert*-butyl alcohol.[39] We can only estimate a lower limit of 70 for k^{aa}/k^{ee}, *i.e.*, k^{ee} is estimated as a maximum possible value, because E1 ethanolysis swamps the E2H-like reactions, of NaOEt with *trans*-4-*tert*-butylcyclohexyl tosylate in ethanol (Table VII). All these reactions of sodium ethoxide in ethanol are more E2H-like than the corresponding reactions of NBu_4Cl in acetone, and reactions of KO-*tert*-Bu are even more E2H-like.

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Table VIII. Rates of Solvolysis and of NBu_4Cl-Promoted Bimolecular Substitution and Elimination of *trans*-4-*tert*-Butylcyclohexyl Tosylate at 75° [a]

Solvent	Log "k_2"[c] solvolysis	Log k^S	Log k^E	$10^2 F_E$[d]
Acetone	−5.3	−2.70	−3.08	30.3
DMF	−3.8	−2.74	−3.09	34.7
CH_3CN	−4.5	−3.21	−3.49	34.8
CH_3NO_2	−4.5	−3.70	−3.70	46.0
CH_3NO_2	−4.3[b]			
DMSO	−2.9			
tert-BuOH	−4.4	−3.62	−3.69	49
tert-BuOH	−4.3[b]			

[a] Solvents contained 0.04 *M* 2,6-lutidine and 0.03 *M* NBu_4Cl. [b] Solvent contained 0.03 *M* NBu_4ClO_4. [c] Rate of solvolysis is recorded as an initial instantaneous second-order rate constant (k_2, M^{-1} sec^{-1}) induced by 0.03 *M* base, for comparison with k^S and k^E. [d] F_E is the fraction of the total reaction which is elimination. [e] k^S and k^E in M^{-1} sec^{-1} from Table I.

hybridized carbons joined by a well-developed double bond.[13] The E2H-like transition state is tighter, with less change from sp^3 to sp^2 hybridization at C_α. This difference explains the k^{aa}/k^{ee} ratios in Table VII, just as it explains solvent effects,[18] isotope effects, leaving group tendencies,[19] and substituent effects[13] on rates of E2C-like and E2H-like reactions.

Solvent Effects[18] (Tables VIII and IX). The dehydrotosylations of *trans*-4-*tert*-butylcyclohexyl tosylate highlight an important advantage of acetone as a solvent for bimolecular reactions. The E2C-like reactions of this tosylate are about 100 times faster than its solvolysis in acetone containing 2,6-lutidine. However, its solvolysis competes more effectively with its E2 reactions when the solvent is *tert*-butyl alcohol, dimethylformamide, acetonitrile, nitromethane, or ethanol. A disadvantage of using acetone as solvent for bimolecular

Table IX. Solvent Effects on Rates of E2C-Like (Log k^E) and SN2 (Log k^S) Reactions

Substrate[c]	Base[c,d]	T, °C		Solvent: Me_2CO	DMF	MeOH	*tert*-BuOH
CH_3I[a]	OAc^-	25	Log k^E				
			Log k^S		+1.3	−5.6	
CH_3OTs[a]	Cl^-	25	Log k^E				
			Log k^S		−1.3	−5.1	
	ArS^-	25	Log k^E				
			Log k^S	−0.1	−0.2	−1.8	
CH_3Br[a]	N_3^-	25	Log k^E				
			Log k^S		−0.4	−4.3	
$C_6H_{11}OTs$[b]	Cl^-	75	Log k^E	−2.27	−2.48		−3.04
			Log k^S	−2.69	−2.85		−3.52
	ArS^-	75	Log k^E	−2.90		−2.54	
			Log k^S	−3.01		−2.71	
trans-4-*tert*-$BuC_6H_{10}OTs$[b]	Cl^-	75	Log k^E	−3.08	−3.09		−3.69
			Log k^S	−2.70	−2.74		−3.62
$C_6H_{11}Br$[b]	N_3^-	25	Log k^E		−4.8	−7.7	
			Log k^S		−4.0	−6.8	
trans-2-PhC_5H_6OBs[b]	OAc^-	50	Log k^E	−1.90			−3.30
			Log k^S				

[a] From ref 18. [b] From Table I. [c] OTs is *p*-toluenesulfonate, Ar is 4-nitrophenyl, OBs is *p*-bromobenzenesulfonate. [d] As NBu_4^+ salt.

We can allot a free-energy difference of *ca.* 1.7 kcal/mol at 75° between higher energy *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylate.[31] Thus, on ground-state considerations alone, the cis isomer would react about 20 times faster than the trans isomer. As noted, the observed k^{aa}/k^{ee} ratio is 30 for E2C-like reactions with NBu_4Cl. It follows that the molar free energies of "anti diaxial" and "anti diequatorial" E2C-like transition states are within 1 kcal of each other. It was likewise concluded that there is a very small difference in the E2C-like transition states which lead to 2-menthene from menthyl and neomenthyl tosylates.[14]

If rates of elimination depend only on the free-energy difference between isomeric reactants, then our claim[13] that E2C-like transition states are olefin-like (product-like) is strongly supported. The same olefin is obtained whether it be anti diaxial elimination from one isomer or anti diequatorial elimination from the other, so that the similar free energies, observed within each pair of E2C-like transition states, could mean that the transition states were very olefin-like. The inverted positions of base and leaving group in the isomeric transition states make little difference because the E2C-like transition state is seen as very loose, with base, β-hydrogen, and leaving group incorporated in the p orbitals of sp^2-reactions is that tetraalkylammonium salts, rather than alkali metal salts, should be used as base. This allows enhanced solubility and minimizes the effects of ion association on rate.[21] There is some evidence that tetrabutylammonium salts are as kinetically active in very nonionizing solvents (*e.g.*, dichloroethane, benzene)[21] as in acetone.

Rates of solvolysis of *trans*-4-*tert*-butylcyclohexyl tosylate (Table VIII) range over a factor of 25 at 75° in the solvents studied, whereas the chloride-induced, E2C-like dehydrotosylations of *trans*-4-*tert*-butylcyclohexyl tosylate proceed at much the same rate in acetone, *tert*-butyl alcohol, dimethylformamide, acetonitrile, and nitromethane, at 75°. These solvents have very different basicities toward hydrogen, they have different nucleophilicities toward carbon, and they have different ionizing power. Our conclusion from Table VIII is that the E2C-like transition state does not have a specific acid–base interaction with the solvent, nor is the reaction an ionization in the same sense as an SN1 or E1 reaction. Only the base interacts specifically with hydrogen and or carbon in the E2C-like transition state.

The effect of solvent transfer on rates of E2C-like reactions (log k^E) is much the same as that on the rates

Table X. Proportions of Anti to Syn Elimination Products from *trans*-2-R-Cyclopentyl- and -Cyclohexyl-X

R	X[h]	Base	Solvent	[3-RC_5H_7] / [1-RC_5H_7]	[3-RC_6H_9] / [1-RC_6H_9]	Mech[g]
C_6H_5	OBs	Lut	Me_2CO	0.08[a]		E1
C_6H_5	OBs	Lut	*tert*-BuOH	0.08[a]		E1
C_6H_5	OBs	KO-*tert*-Bu	*tert*-BuOH	0.18[a]		E2H
C_6H_5	OBs	KOC_6H_5	*tert*-BuOH	0.5[a]		E2H
C_6H_5	OBs	NBu_4OAc	*tert*-BuOH	5[a]		E2C–E2H
C_6H_5	OBs	NBu_4Cl	Me_2CO	>10[a]	>11[a]	E2C
C_6H_5	OBs	NBu_4OAc	Me_2CO	110[a]	32[a]	E2C
4-$CH_3C_6H_4SO_2$	OTs	KOH	Dioxane–H_2O	<0.1[b]		E2H
CH_3	OTs	C_5H_5N	C_5H_5N	0.11[c]		E1
CH_3	OTs	NaOEt	EtOH	6.2[d]		E2H
CH_3	OTs	KO-*tert*-Bu	*tert*-BuOH	99[d]		E2H[f]
Br	Br	NBu_4Cl	Me_2CO		>100[e]	E2C
Br	Br	NBu_4OAc	Me_2CO		>100[e]	E2C

[a] From Table IV. [b] Reference 11. [c] H. L. Goering and H. H. Espy, *J. Amer. Chem. Soc.*, **78**, 1454 (1956). [d] Reference 41. [e] Table II. [f] But this is more E2C-like than reaction of *trans*-2-phenylcyclopentyl brosylate with KO-*tert*-Bu (see text). [g] E1 is a solvolysis reaction, E2H means E2H-like, E2C means E2C-like, E2C–E2H means transition state is not close to either extreme structure. [h] OBs is *p*-bromobenzenesulfonate, OTs is *p*-toluenesulfonate.

of the concurrent SN2 reactions (log k^S, Table IX). This testifies to the similarity of charge distribution in SN2 and E2C-like transition states[18] from the same reactants. Of particular interest are the SN2 reactions and E2C-like dehydrotosylations induced by NBu_4OAc and NBu_4Cl. These are only about 10–50 times faster in acetone than in *tert*-butyl alcohol, which is an extremely small rate enhancement for transfer of a bimolecular reaction of chloride or acetate ion from a protic to a dipolar aprotic solvent of much the same dielectric constant.[18]

Such a small acceleration requires that the E2C-like and SN2 transition states be very loose, with chloride or acetate behaving in the transition state much as they do in the reactants and the leaving group as it does in the products, *i.e.*, as solvated anions. In tight SN2 or E2 transition states, such as those for SN2 reactions of methyl halides or methyl tosylate with chloride or acetate, we see a rate enhancement of between 10^3 and 10^6 on transfer from a protic to a dipolar aprotic solvent.[18]

Syn and Anti Eliminations (Tables II, IV, and X).[3-12] E2C-like reactions have a strong tendency to give the more substituted (Saytzeff) olefin, if given the choice of anti elimination to Saytzeff or Hofmann product.[13] The anti geometry of hydrogen and leaving group is an essential requirement however.[14] Thus, dehydrobrosylation of *cis*-2-phenylcyclopentyl brosylate with NBu_4Cl and NBu_4OAc gives at least 300 times more 1-phenylcyclopentene than the less stable 3-phenylcyclopentene. Solvolysis of *cis*-2-phenylcyclopentyl brosylate in acetone containing NBu_4ClO_4 and lutidine gives more 3-phenylcyclopentene than do the E2C-like reactions of this substrate. The proportion of olefins from solvolysis of the cis isomer is comparable to that from solvolysis of *trans*-2-phenylcyclopentyl brosylate. This suggests that the E1 reaction is elimination from very similar carbonium ion–brosylate anion intermediates from the two isomers. The enormous difference between product distribution from E1 solvolysis and that from E2C-like reactions argues against a carbonium ion-like (E1-like) intermediate for E2C-like reactions.[4] The stereochemical requirements of E2C-like reactions are more rigorous than those of E1 or E2H reactions. Although 41% 3-methylcyclohexene is obtained in E2H-like reactions of KO-*tert*-Bu in DMSO[23] with *cis*-2-methylcyclohexyl tosylate the Saytzeff product (1-R-cyclohexene) predominates (>98%) in the olefin mixture from the less E2H-like reaction of KO-*tert*-Bu in *tert*-butyl alcohol as solvent.[41] With E2C-like bases, the 1-R-cyclohexene is the major (>98%) product in dehydrotosylation of *cis*-2-methylcyclohexyl tosylate, dehydrobrosylation of *cis*-2-phenylcyclohexyl brosylate, and dehydrobromination of *cis*-1,2-dibromocyclohexene, provided that the reaction is sampled during the first half-life. The proportion of 3-R-cycloalkene from these cis isomers sometimes rises slightly as reaction proceeds, because of elimination from trans substitution products (*cf.* Tables V and VI).

The products from E1, E2C-like, and E2H-like reactions of trans 2-substituted cycloalkyl sulfonate esters and bromides are summarized in Table X. The E1 solvolysis and the E2H-like reactions of *trans*-2-phenylcyclopentyl brosylate give much more than 50% of the product of syn elimination, *i.e.*, 1-phenylcyclopentene. This is the most stable isomer of the phenylcyclopentenes. The E2C-like bases, however, have more difficulty with syn elimination and give very high proportions of the less stable product of anti elimination, 3-phenylcyclopentene.

The increase in the proportion of 3-phenylcyclopentene, which is the only possible product of anti elimination from *trans*-2-phenylcyclopentyl brosylate, as the base changes from KO-*tert*-Bu in *tert*-butyl alcohol through potassium phenoxide in *tert*-butyl alcohol to NBu_4OAc in *tert*-butyl alcohol, is surely evidence for the need of a spectrum of E2 transition states! Equally compelling is the increase in the proportion of anti product on changing from the reaction of *trans*-2-phenylcyclopentyl brosylate with KO-tert-Bu–*tert*-butyl alcohol to the reaction of *trans*-2-methylcyclopentyl tosylate[41] with the same base. Here a decrease in the acidifying effect of 2 substituent, from acidifying phenyl to methyl, introduces more E2C character in the reactions and hence a stronger requirement for anti elimination.

The products of elimination from the other *trans*-2-R-cycloalkyl derivatives in Table X confirm the conclusions discussed in detail for *trans*-2-phenylcyclo-

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Table XI. Substituent Effects on SN2 (Log k^S) and E2C-Like (Log k^E) Reactions of 2R-Cyclohexyl Tosylates[a]

R	NBu_4Cl, Me_2CO, 75° — Cis 2R: Log k^E	Cis 2R: Log k^S	Trans 2R: Log k^E	Trans 2R: Log k^S	NBu_4OAc, Me_2CO, 50°, cis 2R: Log k^E
H	−2.57[c]	−2.69	−2.57[c]	−2.69	−3.2[c]
Me	−1.2	−2.4	−3.25	−2.74	−2.5
i-Pr	−0.6[f]		−3.3[g]	−2.9[g]	
tert-Bu	−0.2[b]	<−4	−1.55[b]	−2.62	
Ph	−0.7[e]	<−3	−3.81	−3.44	−0.6[e]
Br	−3.64 (<−5)[h]				−1.7
4-$CH_3C_6H_4SO_2$	−1.03[b]	<−3	−4.05[b]	−4.60	
4-$CH_3C_6H_4SO_3$	−4.4[d] (<−5)[h]	−4.3[d]			−3.4[d] (<−5)[h]

[a] Rate constants in M^{-1} sec^{-1} are from Table I unless stated otherwise. Dehydrotosylation forms 1-R-cyclohexene from the cis isomers and 3-R-cyclohexene from the trans isomers, but see footnote *b*. In some cases rate constants have been extrapolated from lower temperatures, using activation energies for this, or related reactions. [b] The olefinic product was not analyzed by vpc, but is assumed to be always that of anti elimination and of anti Saytszeff elimination where possible. [c] These rate constants have been adjusted to allow for two equivalent anti hydrogens. [d] These rate constant have been adjusted to allow for two equivalent leaving groups. [e] Rate constants were measured for dehydrobrosylation and have been converted to those for dehydrotosylation by subtracting 0.6. [f] Estimated from k^E for reaction of neomenthyl tosylate (ref 14) by assuming that the 4-methyl substituent has negligible effect on rate (*cf.* Table XII). [g] Estimated from rates of reaction of menthyl tosylate (ref 14) by assuming that the 4-methyl group has negligible effect on rate (*cf.* Table XII). [h] Rate of Hofmann elimination to give 3-R-cyclohexene is shown in parentheses.

Table XII. Reactions of Alkyl and Cycloalkyl Tosylates with NBu_4Cl in Acetone Containing 2,6-Lutidine at 75°

R in ROTS	Log k^{S}[a]	Log k^E/n[a,b]	10^2F_E
C_5H_9	−0.7	−2.47	3.3
C_6H_{11}	−2.69	−2.57	72.3
$CH_3CH_2CHCH_3$[e]	−0.6	−2.6	3
cis-2-PhC_5H_6[c,d]	−1.6	−1.0	82.5
cis-2-PhC_6H_{10}[d]		−0.8	100
$CH_3CH(Ph)CHCH_3$[e]	−2.0	−1.7	64
Δ^3-C_5H_7[f]	−1.11	−2.84	3.6
Δ^3-C_6H_9[f]	−2.75	−2.15	20
cis-2-MeC_6H_{10}[c,d]	−2.3	−1.2	93.5
$CH_3CH(CH_3)CHCH_3$[e]	−1.83	−1.86	48.3
trans-2-PhC_5H_6[c,d]	−2.7	−2.6	55.2
trans-2-PhC_6H_{10}[c]	−3.4	−3.8	30
trans-2-MeC_5H_8[c,d]	−1.8	−2.6	15.5
trans-2-MeC_6H_{10}	−2.74	−3.25	24.0

[a] Rate constants for substitution (k^S) and elimination (k^E) are in M^{-1} sec^{-1} and from Table I unless stated otherwise. [b] Adjusted to allow for n equivalent anti hydrogens, *e.g.*, in cyclohexyl tosylate, $n = 2$. [c] Estimated by subtracting 0.6 from log k for reaction of the brosylate. [d] Extrapolated from measurements at another temperature, using activation energies of this or related reactions. [e] Reference 13. [f] Olefin not identified by vpc; F_E based on acid produced.

pentyl brosylate. Under E1 conditions, or if R is acidifying and the base is very E2H-like, activated syn eliminations predominate,[4,9,12] but under E2C-like conditions, anti elimination is strongly favored, even if it produces an olefin which is thermodynamically the much less stable isomer. The applications of this observation to synthetic work need hardly be stressed; either of two olefins can be obtained, depending on whether E2C-like or E2H-like conditions are chosen. The E2C-like Hofmann product is not readily available from equilibration to isomeric olefins.

The >99% anti debromination to cyclohexene of *trans*-1,2-dibromocyclohexane (Table II) and >99% anti dehydrobromination to 1-bromocyclohexene of *cis*-1,2-dibromocyclohexane by the same reagent, *p*-nitrothiophenoxide in acetone, provide an interesting illustration of the stereochemical requirements of β elimination reactions. The two reactions proceed at virtually the same rate, but clearly the requirement of anti geometry of leaving groups at C_α and C_β is just as great in the debromination (E2Hal) transition state as in the dehydrobromination (E2C-like) transition state. It is interesting to search for such similarities between E2C-like and E2Hal transition states and work is proceeding.

Two transition states, one E2C-like, the other E2Hal, of comparable energy are available to the reactants, *trans*-1,2-dibromocyclohexane and NBu_4CN in acetone (Table II). Both cyclohexene (78%) and 3-cyanocyclohexene (22%) (*cf.* eq 2) are observed. The E2Hal transition state is usually "tighter" than corresponding E2C-like transition states,[18] so that the proportion of cyclohexene should decrease upon transfer to a protic solvent, but this has not been tested.

Substituent Effects (Tables XI, XII, and XIII). The effects of substituents on rates of E2C and E2H-like eliminations from cycloalkyl derivatives can be predicted in part from those for elimination from acyclic systems.[3,4,5,13] In the acyclic compounds, changes in rate of elimination with change of substituent under E2C-like conditions are different from those under E2H-like conditions.[13] For example, E2C-like reactions are insensitive to electron withdrawal (acidification) by β substituents, whereas E2H-like eliminations are strongly accelerated by such substituents. An important factor in determining rates of E2C-like reactions was thought to be the size of the β substituent, because the change, from reactants to transition state, of sp^3 to sp^2 hybridization at C_β allows steric acceleration by bulky groups, as bond angles change from tetrahedral to trigonal. As reaction conditions become more E2H-like, *e.g.*, by change of base from chloride to acetate, rehybridization of C_β in the transition state is less advanced, and so steric acceleration diminishes; however, C_β becomes more negative and so rates of elimination respond more readily to electron withdrawal by β substituents. The result is that in acyclic systems, when the base is changed from chloride to acetate, β-phenyl and β-bromine become increasingly more activating, relative to β-methyl.[13]

All these substituent effects on rate are observed in the anti dehydrotosylations of cis 2-substituted cyclohexyl compounds by chloride ion to the Saytzeff product, 1-substituted cyclohexene (Table XI).[42] We have

(42) Reactions of cis and trans 2-substituted cycloalkyl tosylates, especially solvolysis reactions, have received much attention, some of

Table XIII. Rates of Anti Unactivated Elimination and Substitution of Cyclohexyl Tosylates. Effect of 2, 3, and 4 Substituents on Reaction with NBu_4Cl in Acetone at 75°[a]

R in ROTs[f]	Log k^S	Log k^E/n^h	10^2F_E	Comment[g]
cis-4-*tert*-BuC_6H_{10}	−2.17	−1.94	77.2	Axial OTs
4-Me-2-*i*-PrC_6H_9[b,c,i]		−2.15	100	Axial OTs
C_6H_{11}	−2.69	−2.57	72.3	Eq OTs
4,4-$Me_2C_6H_9$[d]	−2.15	−2.73	34	
trans-4-*tert*-BuC_6H_{10}	−2.70	−3.38	30.3	
all-trans-2,6-Me_2-4-*tert*-BuC_6H_8[b]	−2.1		0	
4-Me-2-*i*-PrC_6H_9[b,c,j]	−2.96	−3.27	33.4	
3-β-Cholestanyl[d]	−2.42	−3.96	5.6	
trans-2-MeC_6H_{10}	−2.74	−3.25	24.0	
trans-2-PhC_6H_{10}[e]	−3.4	−3.8	30	
trans-2-*tert*-BuC_6H_{10}[d]	−2.62	−1.55	92	
trans-2-TsC_6H_{10}[d]	−4.60	−4.05	75	

[a] Rate constants for substitution (k^S) and elimination (k^E) are in M^{-1} sec^{-1} and from Table I unless stated otherwise. [b] Reference 14. [c] The product is 2-menthene. [d] Olefin not identified. [e] Estimated by subtracting 0.6 from log k for reaction of the brosylate. [f] Ts is 4-$CH_3C_6H_4SO_2$. [g] We record the likely geometry of the tosylate in the most stable conformation of ROTs. [h] Corrected for number n of hydrogens available for anti elimination. [i] Neomenthyl tosylate. [j] Menthyl tosylate.

assumed Saytzeff dehydrotosylation of *cis*-2-*tert*-butylcyclohexyl tosylate or *cis*-2-*p*-toluenesulfinylcyclohexyl tosylate on the basis of related reactions, but lack an olefin analysis. The bulkiest alkyl group is *tert*-butyl and this is the most effective cis-2 substituent for increasing rate of elimination. It slows bimolecular substitution markedly, perhaps because of a "neopentyl-like" steric effect. β-Phenyl exerts similar effect on the E2C-like rates as does β-methyl, but β-phenyl slows the SN2 reaction more than does β-methyl. A change to more E2H-like conditions, by a change from chloride to acetate as base, allows phenyl and bromine substituents to exert their acidifying polar effect, relative to methyl, and so the former two substituents become activating, relative to methyl, just as in acyclic systems.[13]

The retarding effect of acidifying bromine, and *cis*-*p*-toluenesulfonyl β substituents and the negligible effects of *cis*-*p*-toluenesulfinyl relative to methyl on the rates of E2C-like dehydrotosylation by chloride ion cannot be explained by invoking only polar effects[8] and the steric acceleration accompanying the change from sp^3 to sp^2 hybridization at C_β. Certainly the absence of rate enhancement, by the very strongly acidifying sulfone and bromine relative to methyl, argues against there being much negative charge at C_β in the E2C-like transition state. The effect on E2C-like reactions contrasts dramatically with strong acceleration by these acidifying groups in E2H-like reactions.[8] However, it is difficult to explain rate retardation of E2C-like reactions by bulky bromine and *p*-toluenesulfonyl relative to hydrogen or methyl, in terms of the two effects considered above. We note that Hofmann elimination to give 3-R-cyclohexene from *cis*-2-R-cycloalkyl tosylates is not observed, *e.g.*, Hofmann E2C-like dehydrotosylation by chloride ion is more than 100 times slower from *cis*-2-bromocyclohexyl tosylate and from *cis*-1,2-ditosylatocyclohexane than from cyclohexyl tosylate. Substitution by chloride ion is also slowed by bulky substituents relative to substitution in cyclohexyl tosylate. Both elimination and substitution by chloride ion in *trans*-2-phenyl- and *trans*-2-*p*-toluenesulfinylcyclohexyl tosylate are slowed by these bulky substituents, relative to β-methyl or β-hydrogen. We are aware of the dangers of allocating a particular interaction mechanism to explain an "effect" on rate[43] and know how easy it is for the physical organic chemist to "balance up" a series of interactions to explain almost any observed effect. Nevertheless, we are tempted to put forward two interactions which help to explain the rate retarding effects, noted in Table XI, for substrates incapable of free rotation about C–C bonds. Firstly, they may be partly due to a "neopentyl like" unfavorable steric interaction of the 2 substituent with either the base or leaving tosylate, which are loosely bound to C_α in either the SN2 or the E2C-like transition state. Such retardation was sought, but not found by Bunnett and Eck.[44] An alternative is that reactions are slowed because the reactant tosylate is stabilized by dispersion force interactions between tosylate (the potential leaving group) and adjacent polarizable groups like bromine, phenyl, *p*-toluenesulfinyl, or *p*-toluenesulfonyl.[4,45] This is true, be they cis or trans diequatorial to each other, but the effect may be greater in the cis isomer.[42] This stabilization is lost in the E2C and SN1 transition states because the bond to the leaving group is very well broken. We note the greater stability of *cis- vs. trans*-1,2-dibromoethene[46] and the stability of the gauche conformation of 1-bromopropane in support of the postulate for stabilizing interactions between polarizable groups on adjacent carbon atoms. The appropriate combination of destabilizing or stabilizing interactions between leaving group and substituent, which are lost as the leaving group departs in the transition state, can of course "explain" the rate enhancing effect of 2-alkyl substituted tosylates, and the rate retarding effect of more polarizable substituents. The destabilizing effect of polarizable groups is seen in both cis and trans isomers, *i.e.*, for elimination toward or away from the 2 substituent.

In summary, the substituent effects in Table XI are in part a combination of polar effects, which enhance E2H- but not E2C-like reactions, of conjugation and hyperconjugation with a developing double bond, which enhances E2C-like reactions, of steric accelera-

which is summarized by M. Pankova, J. Sicher, M. Tichý, and M. C. Whiting, *J. Chem. Soc. B*, 365 (1968).

(43) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.
(44) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).
(45) E. L. Eliel and R. J. L. Martin, *ibid.*, 90, 689 (1968).
(46) W. K. Kwok and S. I. Miller, *Can. J. Chem.*, **45**, 1161 (1967).

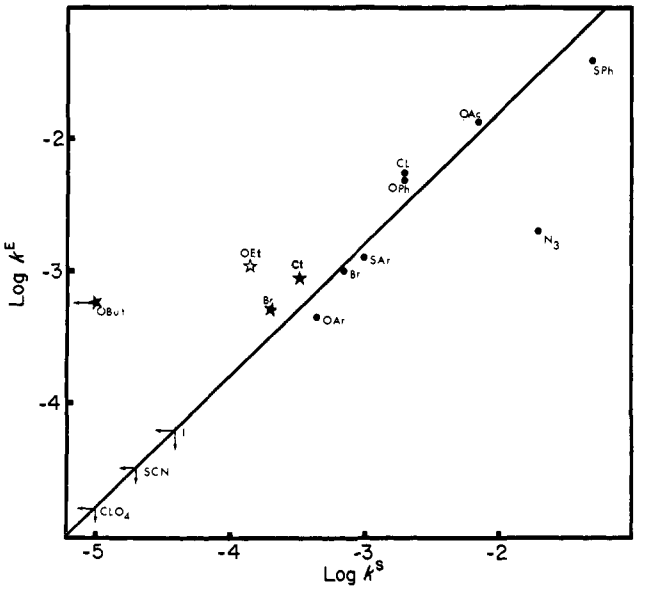

Figure 1. Swain–Scott plot of eq 5 with η fixed at 1.00, for rates of substitution (log k^S) and elimination (log k^E) at 75° of cyclohexyl tosylate with various bases in acetone containing 2,6-lutidine (NBu_4Y), in ethanol (NaOEt), and in *tert*-butyl alcohol (KO-*tert*-Bu and NBu_4Hal). Data are from Table I. The points for NBu_4I, NBu_4SCN, and NBu_4ClO_4 in acetone containing 2,6-lutidine represent maximum possible values of log k^E and log k^S, because solvolysis or attack by lutidine competes. Ar is 4-nitrophenyl.

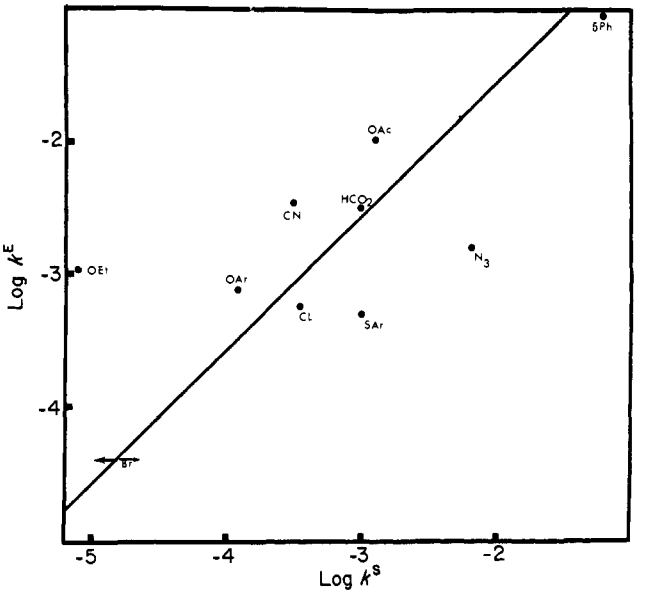

Figure 2. Swain–Scott plot of eq 5 with η fixed at 1.00, at 75°, for substitution and elimination reactions of cyclohexyl bromide with NBu_4Y in acetone containing 2,6-lutidine. The point, OEt, is for NaOEt in ethanol. The rate of substitution by bromide ion was not measured so that the point, Br, could be anywhere along the axis as shown. Ar is 4-nitrophenyl and data are from Table I.

tion, associated with a change from sp^3 to sp^2 hybridization at C_α and C_β, and of steric retardation which could arise from stabilizing dispersion interactions, which disappear in the transition state, between polarizable substituents and polarizable leaving group in the ground state of the reactant. Steric retardation could also result from destabilizing interactions of bulky substituents at C_β with base or leaving group at C_α in the transition state.[44,47]

The main point of interest for the organic chemist is that E2C-like eliminations respond to a change of substituent very differently from E2H-like reactions of alicyclics. The applications for synthetic problems are obvious; different bases do different jobs, according to the type of substrate.

In Table XII we compare rates of substitution and of E2C-like elimination in cyclopentyl, cyclohexyl, and related secondary acyclic tosylates. Substitution is much slower in cyclohexyl than in cyclopentyl or acyclic tosylates, for reasons which are well understood.[5,6] Dehydrotosylation proceeds at much the same rate from cyclopentyl, cyclohexyl, and 2-butyl tosylates and from their cis 2-substituted derivatives, but eliminations from trans 2-substituted cyclopentyl tosylates are a little faster than eliminations from the corresponding cyclohexyl tosylates. Fractions of elimination are usually greatest from cyclohexyl than from cyclopentyl or related acyclic tosylates. These tendencies are also observed in reactions with E2H-like bases.[39]

E2C-like dehydrotosylation of 4-cyclopentenyl tosylate is slower and of 4-cyclohexenyl tosylate is only slightly faster than dehydrotosylation of cyclopentyl tosylate and cyclohexyl tosylate, respectively. Although elimination from the "ene tosylates" could produce a conjugated diene, this process apparently is not favored in cyclic systems. On reason might be the ring strain which would be introduced in a diene-like, E2C-like transition state. Substitution of these two ene tosylates proceeds at virtually the same rate as substitution of the corresponding saturated tosylates.

Some miscellaneous rate data for substitution and dehydrotosylation of various substituted cyclohexyl tosylates, induced by chloride ion in acetone, are in Table XIII. In all cases, elimination is of a β-hydrogen attached to carbon carrying another hydrogen, *i.e.*, there is no direct β substituent effect. Substitution rates are little influenced by the substituents shown, except for slowing by bulky, polarizable phenyl or *p*-toluenesulfinyl. Dispersion force stabilization between substituent and leaving group may explain the retardation of SN2 rates as noted above for E2 rates.

Elimination rates in Table XIII differ by a factor of up to 300. Dehydrotosylation is fastest if the tosylate group is axial in the most stable conformation of the reactant, is slower if the tosylate is equatorial, and is slowest if an adjacent β substituent (*e.g.*, *p*-toluenesulfinyl) is bulky and capable of dispersion force stabilization with the tosylate leaving group. The fast dehydrotosylation of *trans*-2-*tert*-butylcyclohexyl tosylate, as noted for the cis isomer, may be a function of the distorted geometry of this reactant and its ability to return to a more stable geometry[42] in the olefin-like transition state.

We have not studied the effect of α substituents on rates of E2C-like reactions of alicyclic systems, but note McLennan's observation[48] that the E2C-like dehydrobrominations of 1-bromocyclohexane and 1,1-dibromocyclohexane by thiophenoxide in ethanol proceed at virtually the same rate; *i.e.*, an α-bromine substituent has very little effect on rates of these E2C-like reactions. It thus seems unlikely that positive

(47) D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969).

(48) D. J. McLennan, *J. Chem. Soc. B*, 705, 709 (1966).

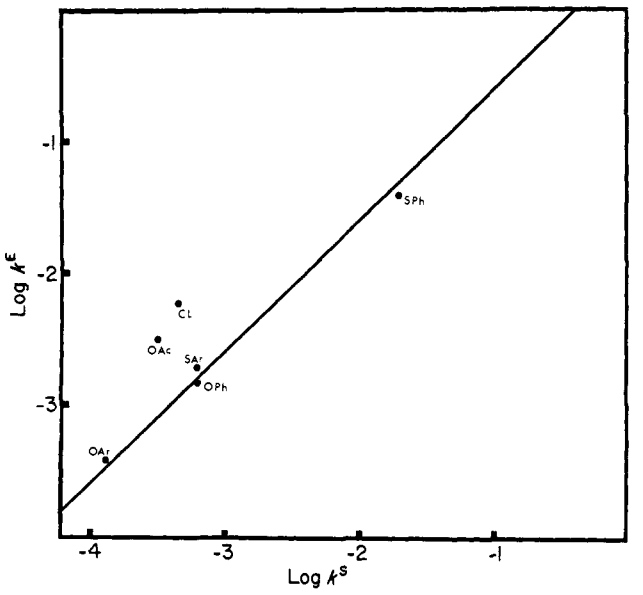

Figure 3. Swain–Scott plot of eq 5 with η fixed at 1.00 for substitution and Saytzeff elimination reactions of *cis*-2-methylcyclohexyl tosylate with NBu_4Y in acetone containing 2,6-lutidine at 50°. Ar is 4-nitrophenyl and data are from Table I.

charge is at C_α in a paenecarbonium E2 transition state because electronegative α-bromine slows formation of carbonium ions.[43] A similar conclusion was reached from α-substituent effects on E2C-like reactions of acyclic compounds.[13,49]

Nucleophilic Tendencies.[20,50,51] In this series of papers we have defined a new class of bimolecular elimination reaction induced by bases which are weak toward hydrogen. An important question is how the base is interacting with the organic reactant in the E2C-like transition state. The second-order kinetics tell us that the base is present in the E2C-like transition state, but the organic reactant has two acidic centers, β-hydrogen and α-carbon, with which the base can interact.

A useful probe into the site of attack is the difference in reactivity of bases toward acidic hydrogen and carbon, *i.e.*, the H nucleophilicity and C nucleophilicity of bases. Thus, C nucleophilicity is $RS^- > RO^-$ and $OAc^- \simeq Cl^-$,[18] whereas H nucleophilicity is $RO^- > RS^-$ and $OAc^- \gg Cl^-$ in dipolar aprotic solvents. One test for interaction of base with α-carbon, in the E2C transition state, is therefore to seek a correlation of rates of elimination, $k_{Y^-}{}^E$, induced by different bases, Y^-, with the C nucleophilicity of those bases.[20,21] The Swain–Scott[6,50] type of eq 5, where η is a correla-

$$\log k_{Y^-}{}^E = \eta \log k_{Y^-}{}^S + \text{constant} \qquad (5)$$

tion coefficient and $k_{Y^-}{}^S$ is the rate constant for substitution by the base Y^-, preferably from the same substrate under the same conditions, might be followed. The concurrent E2 and SN2 reactions of cyclohexyl sulfonate esters and halides are particularly suitable for eq 5, because significant proportions of both substitution and elimination are observed.[20] Plots of eq 5 for reactions of cyclohexyl tosylate, cyclohexyl bromide, and *cis*-2-methylcyclohexyl tosylate are in Figures 1, 2, and 3, respectively. They are drawn so

(49) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5029 (1970).
(50) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).
(51) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

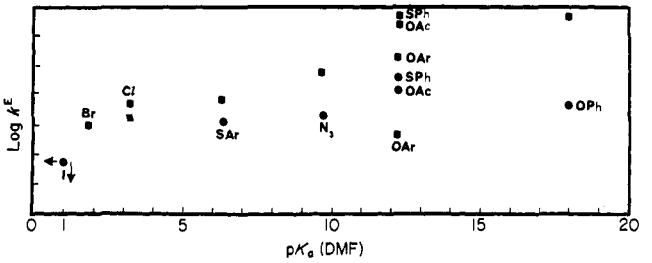

Figure 4. Brønsted plot of eq 6, *i.e.*, log k^E from Table I, for elimination induced by NBu_4Y with cyclohexyl tosylate at 75° (filled circles) and with *cis*-1,2-dibromocyclohexane at 50° (filled squares) in acetone containing 2,6-lutidine *vs.* pK_a of HY in dimethylformamide at 25° from ref 54 and 55. Both pK_a and log k^E for Y = iodide are maximum values, as shown; Ar is 4-nitrophenyl.

that η is unity, which is an extra restriction on the Swain–Scott equation, but a convincing one, and certainly suggest that some E2 reactions proceed by interaction of base with the organic substrate in a way which is modeled by the base–substrate interaction in the concurrent SN2 transition state. We conclude that the base is interacting with C_α in the E2C-like transition state.

We have proposed[20] a spectrum of E2 transition states, between E2C and E2H, so that deviations from eq 5 would be expected, as conditions became more E2H-like. Thus in Figures 1–3, alkoxides in alcohols, especially *tert*-butoxide in *tert*-butyl alcohol, have $k_{OR^-}{}^E$ greater than expected from $k_{OR^-}{}^S$. On the basis of greater scatter of strong H bases, cyclohexyl bromide (Figure 2) is apparently a more "E2H-like substrate" than is cyclohexyl tosylate (Figure 1). This is not surprising, in view of the tendency of tosylates to react through much looser transition states than do the corresponding bromides.[18] Azide ion in Figure 1 is a much more effective base in SN2 than in E2C-like reactions. We regard this as important and note the effectiveness of this base toward sp^2 carbon and carbonium ions, but we have no convincing explanation. A valid test of whether a base is interacting with hydrogen in an associative transition state is to see whether rates of elimination, $k_{Y^-}{}^E$, correlate with the H nucleophilicity of different bases Y^-. The Brønsted equation (6) is thought to test if such a correlation exists.[4,52,53] It uses H basicity as a model for H nucleophilicity. In eq 6, the pK_a of the acid HY should be

$$\log k_{Y^-}{}^E = \beta pK_a[HY] + \text{constant} \qquad (6)$$

that in the same solvent as used for the elimination reactions.[20] Plots of eq 6 for rates of elimination in acetone from cyclohexyl tosylate[20] (filled circles) and from *cis*-1,2-dibromocyclohexane (filled squares) are in Figure 4. We have values of the pK_a of HY in dimethylformamide[54] but not in acetone, but have noted[54,55] that pK_a values are linearly related in a variety of dipolar aprotic solvents, so the plots are a valid test of eq 6. We also note that $k_{Y^-}{}^E$ in acetone is linearly related to $k_{Y^-}{}^E$ in dimethylformamide.

(52) J. F. Bunnett, "Investigation of Rates and Mechanisms of Reactions," S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Wiley, New York, N. Y., 1961, p 177.
(53) R. F. Hudson, *Chimia*, **16**, 173 (1962).
(54) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

Table XIV. Nucleophilic Tendencies of Hand C Nucleophiles in Elimination Reactions in Acetone at 75° [c]

Substrate	Log k_{Cl}^{-E}/k_{OAc}^{-E}	Log $k_{PhS}^{-E}/k_{PhO}^{-E}$	Log $k_{ArS}^{-E}/k_{ArO}^{-E}$
E2C (Δ log k_Y^{-S})[d]	+0.3 to −0.8	0.8–1.4	+0.4–0.9
$C_6H_{11}OTs$	−0.41	+0.91	+0.47
trans-4-*tert*-$BuC_6H_{10}OTs$	−0.54		+0.47
$C_6H_{11}Br$	−1.26		−0.20
cis-2-PhC_5H_8OBs	−1.4[b]		
cis-2-$PhC_6H_{10}OBs$	−1.5[b]		
cis-2-$BrC_6H_{10}OTs$	−1.9		
cis-2-$BrC_6H_{10}Br$	−3.0	+0.1[b]	−1.4
erythro-$CH_3CHBrCHBrCO_2Me$[f]	−6.5[a]		
E2H (ΔpK_a)[b,e]	−8.7[b]	*Ca.* −6[b]	−5.7[b]

[a] At 50.0°. [b] At 25°. [c] Rate constants k^E in M^{-1} sec^{-1} from Table I unless stated otherwise. Products are those of anti elimination to give Saytzeff olefin if possible. [d] This is the range of rate ratios expected for a pure E2C reaction if η in eq 5 was unity, *i.e.*, if there was an exact parallel with nucleophilic tendencies toward secondary sulfonate esters in SN2 reactions. [e] This is the difference in pK_a of the corresponding acids in DMF at 25° from ref 54 and 55 and is the ratio of rate constants roughly expected for an extreme E2H reaction in acetone at 75°, assuming an exact Brønsted correlation in eq 6. [f] Reference 56.

The points for cyclohexyl tosylate form a scatter diagram; there is absolutely no correlation between log k_Y^{-E} and pK_a for reactions of cyclohexyl tosylate with different bases in acetone. The more E2H-like dehydrobrominations of the more acidic *cis*-1,2-dibromocyclohexane tend toward a Brønsted correlation, with $\beta = 0.3$. Figure 4 is important because it shows that Brønsted correlations might be successful, if reactions were strongly E2H-like.

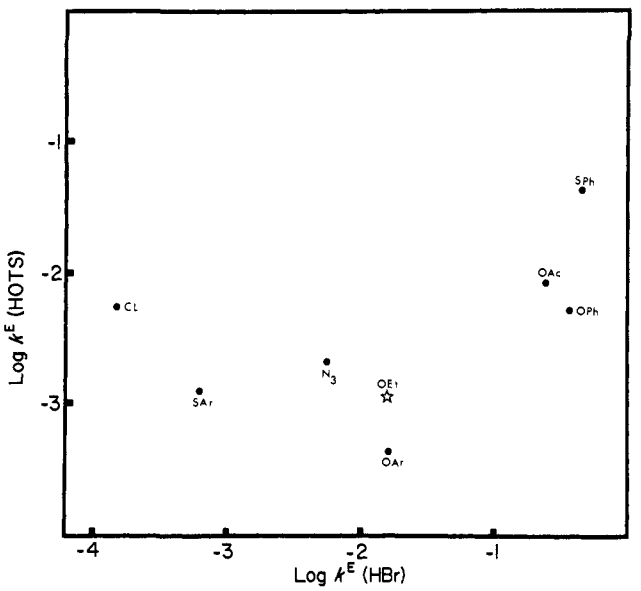

Figure 5. Response of rate to change of base in NBu_4Y of dehydrotosylation of cyclohexyl tosylate (log k^E(HOTs)) at 75° and dehydrobromination of *cis*-1,2-dibromocyclohexane (log k^E(HBr)) at 50° in acetone containing 2,6-lutidine. A point for NaOEt in ethanol is included. Data are from Table I; Ar is 4-nitrophenyl.

To summarize, we find that under E2C-like conditions, log k_Y^{-E} correlates with C nucleophilicity but not with H nucleophilicity; under more E2H-like conditions, log k_Y^{-E} correlates with H nucleophilicity but not with C nucleophilicity. Figure 5 emphasizes the very different response of log k_Y^{-E} to change of base between E2C-like reactions of cyclohexyl tosylate and the more E2H-like reactions of *cis*-1,2-dibromocyclohexane. Surely Figure 5 is evidence of the need for a spectrum of E2 transition states.

A further test of H nucleophilicity (eq 6) or C nucleophilicity (eq 5) as a factor in determining k_Y^{-E} is applied in Table XIV. Rough rate ratios in dipolar aprotic solvents are log k_{Cl}^{-S}/k_{OAc}^{-S} = +0.3 to −0.8, log $k_{PhS}^{-S}/k_{PhO}^{-S}$ = 0.8–1.4 and log $k_{ArS}^{-S}/k_{ArO}^{-S}$ = 0.4–0.9[18] (Ar is 4-nitrophenyl), for substitution at 75° in cyclohexyl and cyclopentyl sulfonate esters and bromides (*cf.* Table I). The corresponding relative acidities at 25° in DMF[54,55] are: $-\log K_a(HCl)/K_a(HOAc) \simeq -8.7$; $-\log K_a(PhSH)/K_a(PhOH) = <-6$; and $-\log K_a(ArSH)/K_a(ArOH) = -5.7$. Thus, if η in eq 5 and β in eq 6 are unity, log k_{Cl}^{E}/k_{OAc}^{E} will range between 0.3 (E2C reactions) and −8.7 (E2H reactions), log $k_{PhS}^{-E}/k_{PhO}^{-E}$ between 1 (E2C reactions) and <−6 (E2H reactions), and log $k_{ArS}^{-E}/k_{ArO}^{-E}$ between 0.5 and −5.7. These ratios involve rate differences of over 10^6, so they provide a sensitive probe into the nature of E2 transition states. Steric factors also influence these ratios (*cf.* log k_{Cl}^{-S}/k_{OAc}^{-S} = +0.2 for *cis*-2-methylcyclohexyl tosylate and −0.5, for cyclohexyl tosylate) but their influence is small relative to the total range of H and C basicity effects.

The presentation as in Table XIV suggests that there is a shift toward more E2C-like reactions (at least of the RO^- base of the pairs in the table) in the series of substrates: *cis*-1,2-$C_6H_{10}Br_2$, *cis*-2-$BrC_6H_{10}OTs$, *cis*-2-$PhC_6H_{10}OBs$, *cis*-2-PhC_5H_8OBs, $C_6H_{11}Br$, alkyl-substituted cyclohexyl tosylate. This is an order which mixes decreasing acidification by β substituents[56] and increasing leaving group tendencies[4] (*i.e.*, from Br to OTs) and we believe that these two factors are important in determining whether a reaction is E2C-like or E2H-like.

Table XV. Reactivity of Bases in Elimination Reactions in *tert*-Butyl Alcohol at 75° [a]

Substrate	Log k^{E}[a] NBu_4Br	NBu_4Cl	KO-*tert*-Bu	Lut[b]
$C_6H_{11}OTs$	−3.29	−3.04	−3.23	−4.4
trans-4-*tert*-$BuC_6H_{10}OTs$		−3.69	−5	−4.2
cis-4-*tert*-$BuC_6H_{10}OTs$		−2.69	−3.54	−3.9

[a] Rate constants k^E are in M^{-1} sec^{-1} and are taken from Table I. [b] These are solvolysis rates, expressed as second-order rate constants for reaction of a hypothetical 0.03 *M* base in the presence of 2,6-lutidine.

(55) A. J. Parker, unpublished work.
(56) D. Cook, A. J. Parker, and M. Ruane, *Tetrahedron Lett.*, 5715 (1968).

Table XVI. Leaving Group Tendencies of Tosylate and Bromide in E2 Reactions in Acetone at 75°

	Log k_{OTs}^{E} − log k_{Br}^{Eb} — Base						
Substrate[a]	NBu_4Br	NBu_4Cl	NBu_4SAr^c	NBu_4N_3	NBu_4OAc	NBu_4OAr^c	KO-*tert*-Bu[d]
$C_6H_{11}X$	1.4	1.0	0.41	0.13	0.12	−0.2	+0.38
cis-2-$BrC_6H_{10}X$		−0.5			−1.6		

[a] X is *p*-toluenesulfonate or bromine. [b] Rate constant k_{OTs}^{E} is for dehydrotosylation, k_{Br}^{E} is for dehydrobromination; data from Table I. [c] Ar is 4-nitrophenyl. [d] In *tert*-butyl alcohol.

Table XVII. Arrhenius Activation Energies and Log *B* Terms for E2C Reactions in Acetone

Reaction	E_a, kcal mol^{-1}	Log *B*
$C_6H_{11}Br$ + NBu_4OAc	20.7	11.0
trans-2-$PhC_6H_{10}OBs$ + NBu_4N_3	25.1	12.8
cis-2-$BrC_6H_{10}Br$ + NBu_4OAc	14.8	9.4

The concept of an E2C–E2H spectrum for β eliminations explains the data in Table XIV in a way that no current mechanistic proposal for E2 reactions can. Any mechanism for E2 reactions must explain why 4-nitrothiophenoxide ion is five times *more* effective than 4-nitrophenoxide ion in the dehydrotosylation of *cis*-2-methylcyclohexyl tosylate but is 25 times *less* effective than 4-nitrophenoxide, in dehydrobromination of *cis*-1,2-dibromocyclohexane. All the reactions are in acetone, a dipolar aprotic solvent, but the same type of effect is observed in protic solvents, so differences in H bonding solvation of these anions are not a factor.

Any mechanism for E2 reactions must also explain the data in Table XV. NBu_4Cl in *tert*-butyl alcohol is nearly twice as effective in the dehydrotosylation of cyclohexyl tosylate as is potassium *tert*-butoxide in *tert*-butyl alcohol. The reactions are in the same solvent. Solvolysis introduces some uncertainty, but NBu_4Cl in *tert*-butyl alcohol is at least 10 times more effective than KO-*tert*-Bu in *tert*-butyl alcohol, in the dehydrotosylation of *cis*- and *trans*-4-*tert*-butylclylohexyl tosylate. The E2C–E2H spectrum can explain this, because NBu_4Cl in *tert*-butyl alcohol is more effective than KO-*tert*-Bu in *tert*-butyl alcohol at attacking carbon in SN2 reactions. It is more difficult to explain if we require attack only at hydrogen by both bases, because we think that NBu_4Cl is more than 10^{15} times *less basic* toward hydrogen than is KO-*tert*-Bu in hydroxylic solvents.

Leaving Group Tendencies. We have commented on the similarity of leaving group tendencies between very E2C-like reactions and SN2 reactions of cyclohexyl X with chloride ion in acetone.[19] Our conclusion from the excellent linear plot of log k_X^E *vs.* log k_X^S (Figure 6) for five leaving groups, X, is that changes occurring at C_α from reactants to SN2 or E2C-like transition state are similar, *i.e.*, that the base is attacking C_α in each transition state.

Leaving group tendencies of tosylate relative to bromide provide an informative probe into the nature of transition states.[57,58] Positive values of log k_{OTs}/k_{Br} generally indicate loose transition states and negative values indicate tight transition states, but extremely tight transition states may also have positive values,[58] as shown for the reaction of KO-*tert*-Bu with cyclohexyl X. In Table XVI we show changes in tosylate–bromide leaving group tendencies as conditions change from E2C-like to more E2H-like. Values of log k_{OTs}^{E}/k_{Br}^{E} become more negative as the base becomes stronger toward hydrogen (the base strength of the anions increases from left to right in Table XVI).[54,55] They also become more negative for reaction of the same base, as the substrate becomes more acidic, *i.e.*, from cyclohexyl-X to *cis*-2-bromocyclohexyl-X. The changes in leaving group tendencies agree with the conclusion which we reached from solvation of transition states,[18] that E2H-like transition states are tighter than the corresponding E2C-like transition states.

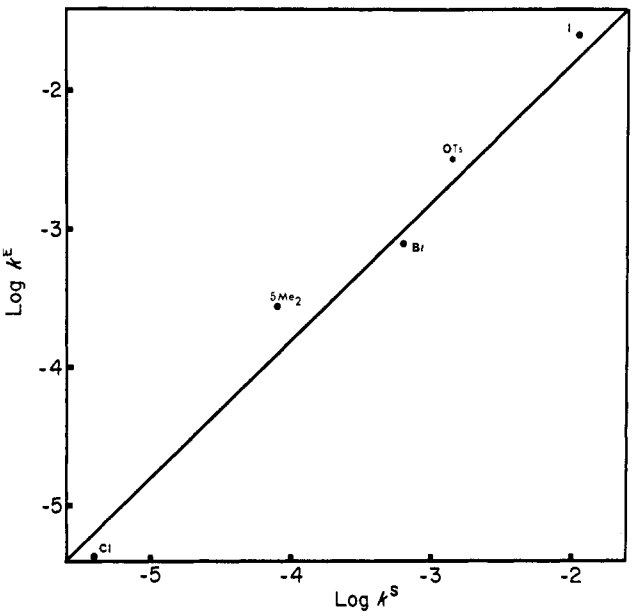

Figure 6. Response of rates of elimination of HX (log k^E) and substitution (log k^S) of cyclohexyl X, induced by NBu_4Cl in acetone containing lutidine at 75°, to change of leaving group X.

Enthalpies and Entropies of Activation. Concurrent E2C and SN2 reactions have very similar activation energies, *i.e.*, F_E changes very little with temperature (Table I). Values of log *B* in the Arrhenius equation are between 9 and 13 for E2C-like reactions (Table XVII), *i.e.*, the "4-centered" geometry which we suggest for the very loose E2C-like transition state is not reflected in abnormal entropies of activation. Values of log *B* for anion–molecule SN2 reactions in acetone are usually between 9 and 13.[18,55]

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(58) A. F. Cockerill, *Tetrahedron Lett.*, 4913 (1969).