-1.94 ± 0.05, and correlation coefficient = 0.999) (see Figure 3). If the value for the intercept is accepted as a reliable estimate of the pK_{BH^+} of ethanol one is then able to calculate an acidity function for alcohols using eq 1. Since the protonation of ethanol spans a substantial range of acid concentrations it is possible to obtain H_{ROH} values from 33 to 94% H_2SO_4 using but a single indicator. Unfortunately the function is not defined for the very important region from the end of the pH scale to 33% H_2SO_4.

The values of H_{ROH} obtained by plotting $-(\log I + 1.94)$ against per cent H_2SO_4 and drawing a smooth curve through the experimental points are summarized in Table III and the function is compared with several other known acidity functions in Figure 4. As can be seen the alcohol acidity function increases much less rapidly with increasing acid concentration than for any other known acidity functions, thus suggesting that the protonation of alcohols (in analogy with most other oxygen bases) proceeds with a large demand for water of solvation.

Further work designed to bridge the low acid region and to correlate the rates of certain reactions of alcohols with this function are currently under way in our laboratories.

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Mechanisms of β-Elimination Reactions in Which the Proton Is Activated by an Electron-Withdrawing Group

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Abstract: Leaving group effects for both syn and anti base-initiated eliminations from cyclohexane systems wherein the β proton is activated by an $ArSO_2$ group have been found to be small. From arguments based on the similarity of leaving group effects, activation parameters, and ρ values, it is concluded that both syn and anti eliminations in such activated systems (acyclic as well as C_5 and C_6 cyclic) are occurring by the *same* mechanism. Retardation of proton abstraction due to chair deformation in cyclohexane systems bearing 1,2-diequatorial substituents is pointed out as a hitherto unrecognized factor retarding syn elimination and contributing to high anti:syn rate ratios. The small leaving group effects are interpreted in terms of a carbanion mechanism. The faster rate of elimination reactions relative to deuterium exchange reactions in analogous systems, as well as the high degree of stereoselectivity shown in eliminations from acyclic systems, can be accommodated by the carbanion mechanism if internal return is assumed to play an important role.

The favorable geometry provided by a diaxial coplanar arrangement of leaving groups in base-initiated 1,2-elimination reactions was first pointed out by Hückel, Tappe, and Legutke in their dehydrochlorinations of menthyl and neomenthyl chlorides.[2] The importance of the geometric factor was emphasized by the 10^3–10^4 rate ratios for anti:syn eliminations in the benzene hexachloride system.[3] Cristol suggested a duality of mechanism to explain these results, a concerted mechanism for anti eliminations and a carbanion mechanism for syn eliminations.[3] A carbanion mechanism was also used to account for syn eliminations in systems where the favored anti coplanarity could not be readily attained.[4] A duality of mechanism, concerted anti for the erythro isomer and carbanion anti for the threo isomer, was also suggested for lyate ion initiated eliminations in ethanolic sodium hydroxide with 2-*p*-toluenesulfonyl-1,2-diphenylchloroethanes, which are stereoconvergent.[5]

When a β-hydrogen is activated by the strongly electron-withdrawing $ArSO_2$ group the geometric preference is overcome by an electronic factor, and activated syn elimination occurs to the exclusion of nonactivated anti elimination in the cyclohexane system.[6] Even the mildly electron-withdrawing phenyl group is able to activate the β-proton sufficiently to make activated syn elimination preferred to nonactivated anti elimination for the Hofmann degradation in the cyclohexane system.[7]

Reversible carbanion formation for $ArSO_2$-activated syn eliminations in the cyclohexane and cyclopentane series was ruled out by the observation of general base rather than specific hydroxide catalysis.[8] (This result has been augmented by more recent studies showing the absence of deuterium exchange in systems of this type.[9]) Rate-limiting "irreversible" carbanion formation[10] was

(1) Abstracted in part from the Ph.D. Dissertation of Thomas F. Sullivan, Northwestern University, June 1958.

(2) W. Hückel, W. Tappe, and G. Legutke, *Justus Liebigs Ann. Chem.*, **543**, 191 (1940).

(3) S. J. Cristol, *J. Amer. Chem. Soc.*, **69**, 338 (1947); S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951).

(4) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952); S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957); S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).

(5) S. J. Cristol and P. Pappas, *J. Org. Chem.*, **28**, 2066 (1963).

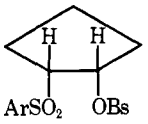
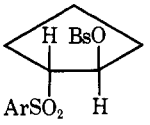
(6) F. G. Bordwell and R. J. Kern, *J. Amer. Chem. Soc.*, 77, 1141 (1955).

(7) (a) J. Weinstock and F. G. Bordwell, *ibid.*, 77, 6706 (1955); (b) S. J. Cristol and F. R. Stermitz, *ibid.*, **82**, 4692 (1960); (c) A. C. Cope, G. A. Berchtold, and D. L. Ross, *ibid.*, **83**, 3859 (1961); (d) G. Ayrey, E. Buncel, and A. N. Bournes, *Proc. Chem. Soc. London*, 458 (1961); (e) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, 27, 293 (1962).

(8) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Amer. Chem. Soc.*, **78**, 3473 (1956).

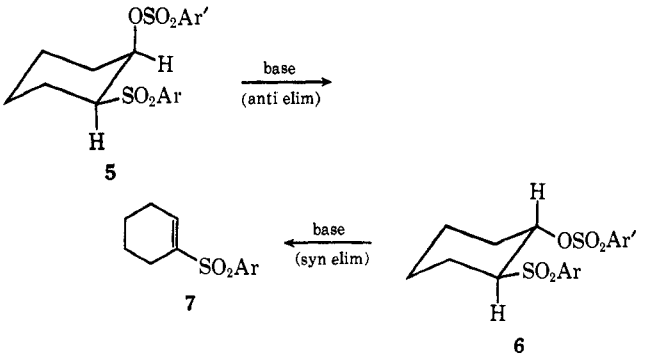
(9) W. M. Jones, T. G. Squires, and M. Lynn, *ibid.*, **89**, 318 (1967).

not ruled out, but a concerted mechanism was preferred for the syn as well as the anti eliminations, because the anti:syn ratio with hydroxide ion was much lower than in the benzene hexachloride system (425 for the cyclohexane system and 20 in the cyclopentane system).[8] Furthermore, the anti:syn rate ratio became still smaller with trimethylamine as the base (25 in the cyclohexane system and 1.8 in the cyclopentane system).[8] This point of view was strengthened further by the comparison of rates and activation parameters for trimethylamine-initiated eliminations in acyclic and cyclopentane systems summarized below.[11] (Numbers in parentheses are relative rates in 50% (v/v) aqueous dioxane at 25°.)

$ArSO_2(Me)CH(OBs)Me$	$ArSO_2(Me)CH(Me)OBs$
1 (*threo*)	2 (*erythro*)
anti elim (1.0), $E_a = 14.5$; $\Delta S^{\ddagger} = -24$	anti elim (2.3), $E_a = 13$; $\Delta S^{\ddagger} = -28$
	
3	4
anti elim (9.7), $E_a = 12$; $\Delta S^{\ddagger} = -27$	syn elim (7.0), $E_a = 12$; $\Delta S^{\ddagger} = -26$

The similarity in rates and activation parameters for the eliminations of **1–4** strongly suggested that these reactions were all occurring by the *same* mechanism. There appeared to be good reason to believe that the anti eliminations were concerted.[12] It followed that the syn elimination of **4** must also be concerted.[11] Since anti eliminations from the cyclohexane analog (**5**) have been generally accepted as being concerted,[13,14] the fact that trimethylamine-initiated anti elimination from **5** is 4.5 times *slower* than the syn elimination from **4** can also be construed as evidence for concerted syn elimination in the cyclopentane series.[8] (We recognized that orbital overlap was as favorable for syn elimination as for anti elimination, but that this path was rendered less likely by eclipsing effects—see the Discussion and footnote 11 in ref 11.) These views regarding the cyclopentane system appear to have been tacitly accepted since the conclusion has been reached that a syn elimination in a cyclopentane system analogous to **4**, but with Ar instead of $ArSO_2$ as the activating group, is concerted and it was suggested that syn elimination becomes favored as the dihedral angle approachs zero.[15]

On the other hand, our conclusion that the much slower syn elimination from the cyclohexyl analog, **6**, is concerted has been challenged.[13,14] For syn eliminations of analogs of **6** with lyate ion in 80% (v/v) EtOH–H_2O, $k_{OTs}:k_{Cl}$ was found to be *ca.* 1:1, whereas for the parent cyclohexyl system it was *ca.* 100:1.[13] This argues against a concerted syn elimination.[13] More recently Jones, Squires, and Lynn have observed a small $k_{OTs}:k_{OMs}$ ratio in systems comparable to **6**, and have presented this and other arguments against the syn concerted mechanism.[9] In this paper we report leaving group effects for systems **5** and **6**, determined by comparing the effect of meta and para substituents in the OSO_2Ar' grouping on the rates of reaction and leaving group effects for **6** with Br or Cl in place of OSO_2Ar'.



Results

The rates of anti and syn eliminations initiated from *cis*- and *trans*-(2-*p*-tolysulfonyl)cyclohexyl arenesulfonates (**5** and **6**, respectively) by hydroxide ion and by trimethylamine in 50% (v/v) water–dioxane were measured at several temperatures [Ar = $SO_2C_7H_7$; Ar' = (a) *p*-$NO_2C_6H_4$, (b) *p*-BrC_6H_4, (c) C_6H_5, and (d) *p*-CH_3]. For hydroxide ion initiated (syn) eliminations of **6a–6d** the rates were determined conductometrically at 25, 37.8, and 50° (Table I).

Table I. Kinetic Data for the Reactions of *trans*-2-(*p*-Tolylsulfonyl)cyclohexyl Arenesulfonates with Hydroxide Ion in 50% (v/v) Aqueous Dioxane

Arenesulfonate	*T*, °C	10^3k, M^{-1} sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate at 0°
p-Nitrobenzene	0.0	9.18[a]	17	−7	3.8
	25.0	140			
	37.8	487			
	50.0	1300			
p-Bromobenzene	0.0	6.0[a]	16	−13	2.5
	25.0	69.5			
	37.8	217			
	50.0	550			
Benzene	0.0	4.21[a]	17	−9	1.75
	25.0	56.4			
	37.8	172			
	50.0	500			
p-Toluene	0.0	2.41[a]	17.5	−8	1.0
	25.0	36.0			
	37.8	133			
	50.0	369			

[a] Extrapolated.

The corresponding cis compounds (**5a–5d**) underwent (anti) elimination too rapidly to be measured by the same technique. The rates at 0° were obtained, however, by measuring pH as a function of time under pseudo-first-order conditions with the sulfone in excess. By use of sufficiently dilute reactants at least ten readings were obtained (change of 0.45 pH unit, or more) before any deviation from linearity in a plot of

(10) For classifications of carbanion eliminations, see (a) Z. Rappoport, *Tetrahedron Lett.*, 3601 (1968); (b) J. F. Bunnett, *Survey Progr. Chem.*, **5**, 53 (1969); (c) F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5950 (1970).

(11) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(12) See, *e.g.*, the arguments presented by P. S. Skell and J. H. McNamara, *ibid.*, **79**, 85 (1957), for the anti eliminations observed with **1** and **2** (iodides instead of brosylates) initiated by pyridine in benzene.

(13) H. L. Goering, D. L. Relyea, and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(14) J. Hine and O. B. Ramsay, *ibid.*, **84**, 973 (1962).

(15) C. H. DePuy, G. F. Morris, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

Table II. Rates of Reaction of *cis*-2-(*p*-Tolylsulfonyl)cyclohexyl Arenesulfonates with Hydroxide Ion in 50% (v/v) Aqueous Dioxane at 0°

Arenesulfonate	k, M^{-1} sec^{-1}	Relative rates
p-Nitrobenzene	8.3	2.6
p-Bromobenzene	6.15	1.9
Benzene	4.16	1.3
p-Toluene	3.25	1.0

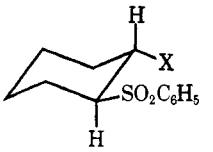
Table III. Kinetic Data for the Reaction of 2-(*p*-Tolylsulfonylcyclohexyl) Arenesulfonates with Trimethylamine in 50% Dioxane

Arenesulfonate	T, °C	10^4k, M^{-1} sec^{-1}	E_a, kcal/mol	$\Delta S^{\neq}$, eu	Rel rate at 25° [b]
A. Trans series (syn elimination)					
p-Nitrobenzene	25.0	2.47			2.2
p-Bromo-	0.0	0.095[a]			1.4
benzene	25.0	1.60	18	−16	
	38.4	5.96			
	50.1	17.1			
Benzene	25.0	1.49			1.3
p-Toluene	25.0	1.13			1.0
B. Cis series (anti elimination)					
p-Nitrobenzene	25.0	94.6			3.0
p-Bromo-	0.0	6.43[a]			2.1
benzene	25.0	66.1	15	−20	
	30.0	104			
	38.4	202			
Benzene	25.0	39.4			1.25
p-Toluene	25.0	31.9			1.0

[a] Extrapolated. [b] Calculated separately for each stereochemical series.

rates at 25° for the cis and trans series are given in Table III. Hammett ρ values for these elimination reactions are summarized in Table IV.

The study was extended to an examination of hydroxide-initiated syn eliminations from *trans*-(2-benzenesulfonyl)cyclohexyl chloride (**8a**), bromide (**8b**), and tosylate (**8c**) using the conductometric method (Table V).



8a, X = Cl
b, X = Br
c, X = $OSO_2C_7H_7$

Discussion

Syn and Anti Eliminations Occur by the Same Mechanism: A Conformational Effect Retards C_6 Syn Eliminations. The results given in Tables I–V confirm the conclusions of Goering, Relyea, and Howe[13] and of Jones, Squires, and Lynn[9] that leaving group effects for syn eliminations in C_6 systems wherein the β proton is activated by an $ArSO_2$ group are small. Note in particular the small size of the $k_{Br}:k_{Cl}$ and $k_{OTs}:k_{Cl}$ ratios (4.2:1.0 and 1.3:1.0, respectively). Values of a comparable size (7.0:1.0 and 4.1:1.0) have been observed recently for amine-initiated eliminations (presumably *anti*) with $PhSO_2CH_2CH_2X$ in acetonitrile.[17]

Table IV. Hammett ρ Values for Elimination Reactions in 50% (v/v) Aqueous Dioxane

Type of compound	Type of elimination	Base	T, °C	ρ	r
trans-2-(*p*-Tolylsulfonyl)cyclohexyl	Syn	Hydroxide ion	0	+0.56	0.945
arenesulfonates	Syn	Hydroxide ion	25	+0.59	0.987
	Syn	Trimethylamine	25	+0.33	0.982
cis-2-(*p*-Tolylsulfonyl)cyclohexyl	Anti	Hydroxide ion	0	+0.42	0.962
arenesulfonates	Anti	Trimethylamine	25	+0.50	0.964

pH *vs.* time occurred. From the initial pH, obtained by extrapolation to zero time, calculations showed that the measurements were made between 15 and 50% completion of the reaction. The accuracy of the method was verified by determining the rate of hydrolysis of ethyl acetate in water and the rate of elimination of *trans*-2-(*p*-tolylsulfonyl)cyclopentyl *p*-toluenesulfonate in 50% (v/v) aqueous dioxane. The results, which agreed well with the literature values, are shown in Table VIII in the Experimental Section. The rates of elimination of **5a–5d** at 0° and the relative rates are given in Table II.

The rates of elimination of **6a–6d** and **5a–5d** initiated by trimethylamine were determined by the conductometric method using buffer solutions.[8] General base catalysis was again observed in every case. The rates of elimination of **5b** and **6b** were determined at several temperatures and the apparent energies and entropies of activation calculated.[16] These data and the relative

Table V. Kinetic Data for Reaction of *trans*-2-Phenylsulfonylcyclohexyl Halides and *p*-Toluenesulfonate with Hydroxide Ion in 50% (v/v) Aqueous Dioxane

Group eliminated	T, °C	10^3k, M^{-1} sec^{-1}	E_a, kcal/mol	$\Delta S^{\neq}$, eu	Rel rate at 0°
Chloride (**8a**)	0.0	4.42[a]	16	−11	1
	19.6	34.0			
	30.1	93.3			
	40.4	221			
Bromide (**8b**)	0.0	18.6[a]	16	−9	4.2
	19.6	139			
	25.0	227			
	30.8	398			
p-Toluene-	0.0	5.70[a]	16	−10	1.3
sulfonate (**8c**)	19.6	44.2			
	30.1	116			
	40.4	339			
	50.0	598			

[a] Extrapolated.

It is significant that the leaving group effects for anti C_6 eliminations in **5** as well as syn C_6 eliminations in **6** are

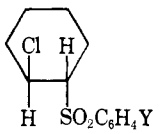
(16) No correction was made for any variation of amine concentration with temperature due to shifts of equilibrium. However, this will be the same for **5b** and **6b**.

(17) Y. Yano and S. Oae, *Tetrahedron*, **26**, 27 (1970).

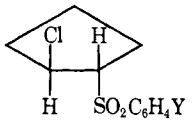
Table VI. Comparison of the Relative Rates of anti and syn Eliminations in Cyclopentane and Cyclohexane Systems Activated by $ArSO_2$ or Ar Groups

No.	System	Base	Medium	T, °C	Anti:syn	Anti C_5: anti C_6	Syn C_5: syn C_6	Ref
1	2-*p*-Tolylsulfonylcycloalkyl tosylates	HO^-	50% (v/v) H_2O–dioxane	25	20 (C_5) 435 (C_6)	2.9	63	8
2	2-*p*-Tolylsulfonylcycloalkyl tosylates	Me_3N	50% (v/v) H_2O–dioxane	25	1.2 (C_5) 25 (C_6)	5.4	115	8
3	2-*p*-Tolylsulfonylcycloalkyl tosylates	Et_3N	50% (v/v) H_2O–dioxane	25	6.5 (C_5) 116 (C_6)	7.3	129	8
4	2-Phenylsulfonylcycloalkyl chlorides	HO^- EtO^-	80% (v/v) EtOH–H_2O	0	39 (C_5) 490 (C_6)	2.4	31	13
5	2-Phenylcycloalkyl tosylates	*tert*-BuO^-	*tert*-BuOH	50	9.1 (C_5) $>10^4$ (C_6)	14	Large	15
6	2-Phenylcycloalkyltrimethylammonium salts	HO^-	H_2O		133 (C_6)			7
7	2-*p*-Toluenesulfonylcycloalkyl tosylates	Piperidine	DMF	30	32 (C_6)			9
8	2-*p*-Toluenesulfonylcycloalkyl mesylates	Piperidine	DMF	30	18.6 (C_6)			9

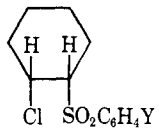
small (see Tables I–III). This is further evidence that activated syn and anti eliminations are proceeding by the same mechanism.[11] Reexamination of the data of Goering, Relyea, and Howe[13] for systems **9–12** by estimating ρ values provides further support for this view.



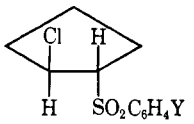
9, $\rho \cong +1.5$ ($r = 0.9997$)
syn elimination[18]



10, $\rho \cong +1.5$ (0.998)
syn elimination[18]



11, $\rho \cong +1.9$ ($r = 0.993$)
syn elimination[18]



12, $\rho \cong +1.8$ (0.998)
anti elimination[18]

The similarity of the ρ values for syn and anti eliminations in systems **9–12**, as well as for **5** and **6** (Table IV), strongly suggests that all of these reactions are occurring by the same mechanism. [The ρ values obtained by Yano and Oae for an analogous acyclic system, $ArSO_2CH_2CH_2Cl$, reacting with amine bases are also of a comparable order of magnitude to those of **9–12** (+1.6 to +1.8).[17]]

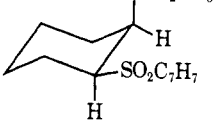
The principal basis for the postulate of a duality of mechanism is the large anti:syn rate ratio observed in some cyclohexane systems, most notably the benzene hexachloride system.[3] A comparison is made in Table VI of anti:syn rate ratios for a variety of eliminations in cyclohexane and cyclopentane series activated by $ArSO_2$ and by phenyl groups.

Examination of Table VI shows that with $ArSO_2$ or Ph groups activating the β-proton high anti:syn rate ratios are observed in cyclohexane systems. Table VI also reveals an appreciable, but smaller, preference for anti elimination in cyclopentane systems as compared to anti eliminations in cyclohexane systems.

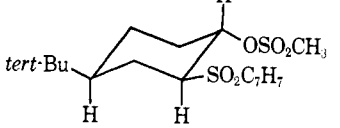
(18) Eliminations initiated by base in 80% (v/v) EtOH–H_2O at 0°.[13] Rate data were available for *p*-CH_3, H, *p*-Cl, and *p*-NO_2 substituents for **9** and **10**, and for *p*-CH_3, H, and *p*-Cl substituents for **11** and **12**. The ρ values were computed by W. J. Boyle, Jr.

Since eliminations in cyclopentane systems are relatively fast, and since anti:syn ratios in the cyclopentane systems are sometimes relatively small (Table VI), it turns out that in three of the systems (no. 2, 3, and 5) syn C_5 eliminations are actually faster than anti C_6 eliminations (by factors of 5.4:1.2, 7.3:6.5, and 14.9:1, respectively). It is clear from this latter comparison and the high syn C_5:syn C_6 ratios (Table VI) that the high anti C_6:syn C_6 rate ratios are *not due* to anti C_6 *eliminations being particularly favored*, but rather to syn C_6 *eliminations being unusually slow*. This point is brought out further by a comparison of the relative rates for system 2 and its acyclic analogs, **1** and **2**. With brosylate as the leaving group the relative elimination rates at 25° are **1** (anti acyclic, 1.0); **2** (anti acyclic, 2.3); **3** (anti C_5, 9.7); **4** (syn C_5, 7.0); **5** (anti C_6, 2.0); **6** (syn C_6, 0.05).

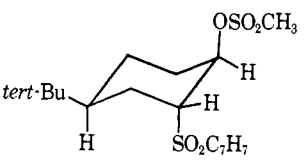
Additional information on geometric preferences is provided by the observation that the piperidine-initiated anti:syn ratio for **13**:**14** is 42:1.0 and for **13**:**15** is 3.3:1.0.[9]



13



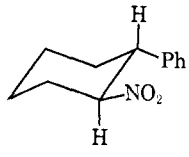
14



15

It is clear from the results reported in Table VI and those with **14** and **15** that the high anti:syn rate ratios usually associated with activated eliminations in cyclohexane systems are *not* dictated solely by the preference for an anti coplanar transition state. The ratio depends on the nature of the base and solvent as well as on conformational effects. Furthermore, conformational effects may well cause a high ratio as much by retarding the syn elimination as by accelerating the anti elimination. The evidence for this statement comes from the

comparisons made above and from the recent observation that methoxide-initiated abstraction of the proton from **16** (analogous to **6** and **14**) is 350 times slower than that from **17**.[19]



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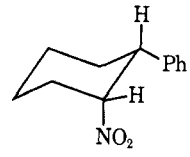
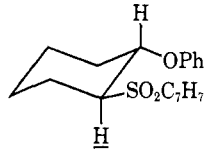


17

The difference in reactivities of **16** and **17** was traced to a retardation for **16** caused by deformation of the cyclohexane ring.[19b] There is evidence in the literature to indicate that retardation of abstraction of an α-axial proton in cyclohexane systems containing 1,2-diequatorial substituents (like **6**) relative to abstraction of an α-axial proton in comparable systems containing 1,2-axial–equatorial substituents (like **5**) *may be a general phenomenon.* For example, Redman and Stirling have found that syn elimination from *trans*-2-phenoxycyclohexyl *p*-tolyl sulfone (**18**) (by a carbanion mechanism) is six times slower than from *cis*-2-phenoxycyclohexyl *p*-tolyl sulfone (**19**),[20] and House and Richey observed that proton abstraction of the axial proton α to the carbonyl group in *trans*-2-methylcyclohexyl chloromethyl ketone (**20a**) was about 100 times slower than abstraction of the proton in the cis isomer **20b**.[21]



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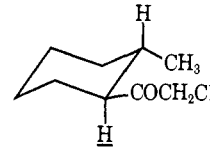
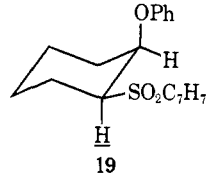


20a

relatively slow proton abstractions[20,21]



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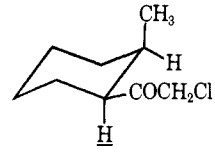


20b

relatively rapid proton abstractions[20,21]

This retardation effect appears to be large enough to account for a substantial fraction of the preference for anti over syn eliminations in activated 1,2-disubstituted cyclohexane systems.[22] Thus, the slow syn elimination for **6** relative to the rapid anti elimination for **5** must in part be due to this effect. It is noteworthy in this respect that a high anti:syn rate ratio is not observed for **13**:**15** (3.3:1.0) where this retardation effect should be absent. Here, however, another factor, namely, the relatively high ground state energy of **15**, must also contribute to the low ratio.

Eliminations Are Rapid Relative to Deuterium Exchange in Analogous Systems. Another point that needs to be reexamined with respect to these elimination reactions is the conclusion that they are too rapid to be accounted for by a carbanion mechanism,[23] and the rebuttal of that conclusion.[14] The rate of hydroxide ion catalyzed dedeuteration of *p*-tolyl cyclohexyl sulfone-*1*-d_1 (**22**) was shown by Weinstock, Bernardi, and Pearson to be almost 10^5 times slower than the rate of syn elimination from its analog, **6**.[23] [Since the k_H/k_D isotope effect in such reactions is known to be small,[14,24] the rate of carbanion formation from the protium species corresponding to **22** should be only slightly faster.] They estimated that the inductive effect of the tosyloxy group in **6** could account for no more than 10^2 of the almost 10^5 rate difference. Later Hine and Ramsay found that the methoxy analog of **19** underwent deuterium exchange at a rate 500 times that reported for **22**, and concluded from this, together with an estimate of $\sigma^*_{TsOCH_2}$, that the inductive effect of the tosyloxymethyl group might be large enough to accommodate the carbanion mechanism for **6**.[14] Their estimate of 500, based on deuterium exchange with the methoxy analog of **19**, does not take into account, however, the conformational retarding effect of the equatorial tosyloxy group in **6** (compare **16**). Furthermore, the ρ^* value of 5.2, based on the H and CH_3O points, appears unrealistically large when compared with values for other deprotonation reactions. For example, $\rho^* = 1.59$ for the acetate ion catalyzed bromination of ketones,[25] and $\rho^* = 1.78$ for the methoxide catalyzed deuterium exchange of the α hydrogen atoms in RCH_2CO_2-Me esters.[26] Note, in addition, that these values should be divided by *ca.* 2.8, the methylene transmission coefficient, for comparison with the 5.2 value, since the latter is for abstraction of a β, rather than an α, proton. Therefore, it does not seem possible to account for more than *ca.* 10^3 acceleration, on the basis of an inductive effect.[27]

Accommodation of the Data to a Carbanion Mechanism. From the point of view of mechanism the one conclusion that comparison of the rate data, activation parameters, and ρ values seems to demand is that eliminations activated by a sulfone group in acyclic, C_5 cyclic, and C_6 cyclic systems (as exemplified by **1**–**6** or **8**–**12**) are all proceeding by the same mechanism. The data do not allow a clear-cut choice between an irreversible carbanion mechanism[10] and a concerted mechanism, however, without further analysis. Recently we have come to doubt the efficacy of concerted mechanisms for nucleophilic bimolecular reactions which require the simultaneous formation and breaking of as many as four bonds.[28] With respect to 1,2 eliminations activated by a nitro group the evidence supports an irreversible carbanion mechanism rather than a concerted mechanism.[10c] We have extrapolated this result to 1,2 eliminations activated by other elec-

(19) (a) F. G. Bordwell and M. M. Vestling, *J. Amer. Chem. Soc.*, **89**, 3906 (1967); (b) F. G. Bordwell and K. C. Yee, *ibid.*, **92**, 5933 (1970).

(20) R. P. Redman and C. J. M. Stirling, unpublished results. We wish to thank Professor Stirling for this information.

(21) H. O. House and F. A. Richey, Jr., *J. Org. Chem.*, **32**, 2151 (1967).

(22) The retardation effect appears to be due to a combination of a lowering of the ground state energy and steric screening of the axial proton by the equatorial group.[19b] The presence of a second axial substituent, as in 1,1,2-trisubstituted cyclohexanes, prevents ring formation.[10c]

(23) J. Weinstock, J. L. Bernardi, and R. G. Pearson, *J. Amer. Chem. Soc.*, **80**, 4961 (1958).

(24) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).

(25) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 608.

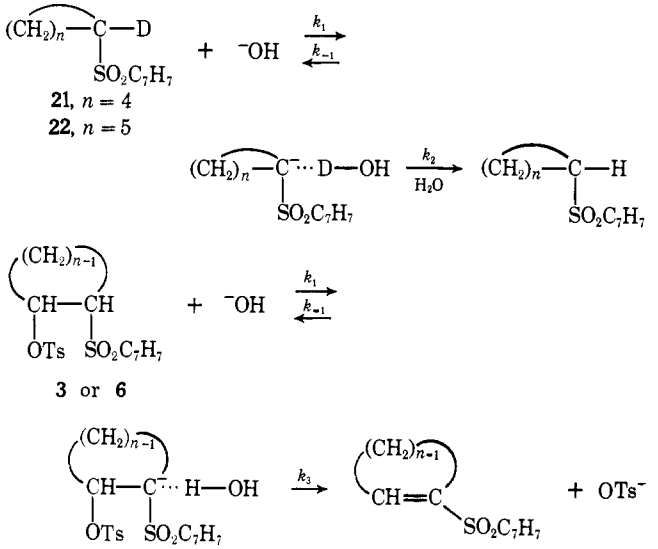
(26) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).

(27) This estimate was obtained by assuming $\rho^* = 2.3$ for removal of a proton α to a sulfonyl group and using $\sigma^*_{TsOCH_2} = 1.31$.[14]

(28) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

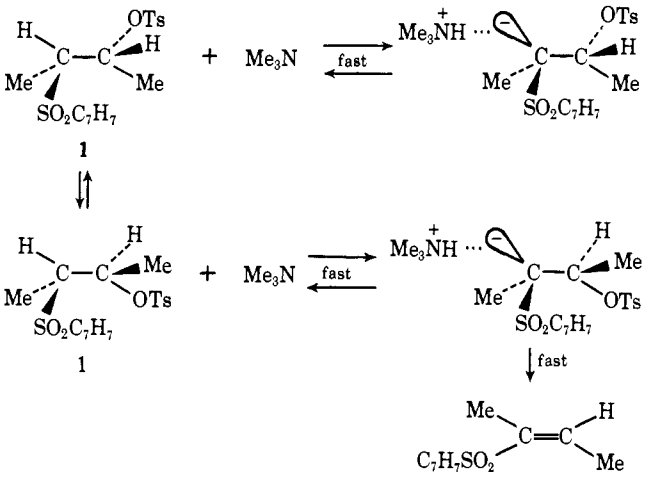
tron-withdrawing groups and have adopted the view, as a working hypothesis, that all such activated eliminations proceed by carbanion rather than concerted mechanisms.[10c] Let us see whether or not the data with respect to eliminations activated by a sulfone group can be accommodated by this point of view.

The evidence from leaving group effects summarized above clearly favors the carbanion mechanism.[9,13] On the other hand, the acceleration observed for elimination *vs.* deuterium exchange,[23] and the high degree of stereoselectivity of the eliminations of **1** and **2**,[11,12] would appear on the surface to clearly favor a concerted process. It is possible, however, to reconcile these latter two observations with a carbanion mechanism if internal return from the carbanion is assumed to be important. There is good evidence to indicate that the formation of strongly basic carbanions is often accompanied by extensive internal return;[24,29] it is important to note that the carbanion from *n*-HexCH(Me)$SO_2C_6H_5$ is included in this group,[24] and that even for a disulfone, $(CH_3SO_2)_2CH_2$, where the acidity has been increased by *ca.* 15 pK_a units relative to a monosulfone, it is estimated that between one-tenth and one-half of the ion pairs formed by water deprotonation undergo internal return.[30] If internal return is extensive under the conditions (50% aqueous dioxane) used to study deuterium exchange with cyclopentyl and cyclohexyl *p*-tolyl sulfones (**21** and **22**), *i.e.*, if $k_{-1} \gg k_2$, the observed rate of exchange will be much less than the actual rate of carbanion formation (k_{-1}), since $k_{obsd} = k_1k_2/k_{-1}$.[24,29a]

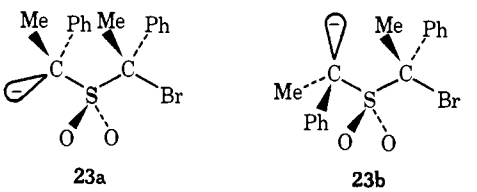


If expulsion of the OTs^- ion from the carbanion in the analogous reactions of the corresponding sulfone tosylates is better able to compete with internal return than is exchange with solvent, *i.e.*, if k_3 is much greater than k_2, the relative rates of the exchange and elimination reactions can be explained by a carbanion mechanism. This interpretation is given credence by the observation that hydroxide initiated 1,3 elimination of HBr from $C_6H_5CHBrSO_2CH(CH_3)_2$ in 40% aqueous dioxane occurs at 560 times the observed rate of deuterium exchange at the isopropyl group of $C_6H_5CH_2SO_2CH(CH_3)_2$.[31] This was interpreted to mean that expulsion of the bromide ion from the $[C_6H_5CHBrSO_2C(CH_3)_2]^-$ carbanion is over 100 times as rapid as is solvent exchange with the $[C_6H_5CH_2SO_2C(CH_3)_2]^-$ carbanion.[31] If interception of internal return is possible in these 1,3 eliminations it should be even more likely in the 1,2 eliminations under present discussion. We saw above that only *ca.* 10^3 of the 10^5–10^7 rate acceleration observed for syn and anti eliminations from 2-*p*-tolylsulfonylcyclohexyl and 2-*p*-tolylsulfonylcyclopentyl tosylates could be accounted for on the basis of an inductive effect of the OTs group in carbanion formation. We believe that the remainder of the rate difference can be attributed to internal return.

The high degree of specifity in eliminations from **1** and **2**[11,12] can also be interpreted in terms of a carbanion mechanism involving internal return. (It may be significant in this respect that these stereoselective eliminations are initiated by tertiary amines, reagents known to promote internal return,[29a] whereas the stereoconvergent eliminations of Cristol and Pappas[5] were initiated by lyate ions, which are less likely to favor internal return.) There is an evident preference for anti eliminations in these systems, but this does not require a concerted mechanism. Rather, it could mean that elimination competes effectively with internal return only when the carbanion is generated from a conformation where anti elimination can occur.



Analogy can be drawn here to comparable high stereoselective base-initiated 1,3 eliminations of HBr from *erythro*- and *threo*-$C_6H_5CH(Me)SO_2C(Br)(Me)C_6H_5$. For example, for the erythro isomer the results require that deprotonation occurs from a conformation that gives carbanion **23a** rather than from one that gives carbanion **23b**.[32]



23a **23b**

(29) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter I; (b) J. E. Hoffman, A. Schriesheim, and R. E. Nickols, *Tetrahedron Lett.*, 1745 (1965); (c) H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, **92**, 2445 (1970); (d) J. A. Zoltewicz and L. S. Helmick, *ibid.*, **92**, 7547 (1970).

(30) J. Hine, J. C. Philips, and J. I. Maxwell, *J. Org. Chem.*, **35**, 3943 (1970).

(31) F. G. Bordwell and M. D. Wolfinger, *J. Amer. Chem. Soc.*, in press.

(32) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *ibid.*, **92**, 2581 (1970).

Table VII. 2-(*p*-Tolylsulfonyl)cyclohexyl Para-Substituted Benzenesulfonates

Benzenesulfonate	Alcohol	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-Nitro	Trans	147–150	$C_{19}H_{21}S_2O_7N$	51.93	4.82	51.71	4.76
p-Nitro	Cis	159–161	$C_{19}H_{21}S_2O_7N$	51.93	4.82	51.82	4.67
p-Bromo	Trans	129–131	$C_{19}H_{21}S_2O_5Br$	48.11	4.46	48.12	4.25
p-Bromo	Cis	112–114	$C_{19}H_{21}S_2O_5Br$	48.11	4.46	47.83	4.47
p-H	Trans	95–96	$C_{19}H_{22}S_2O_5$	57.86	5.63	58.20	5.67
p-H	Cis	135–142	$C_{19}H_{22}S_2O_5$	57.86	5.63	57.47	5.28

We conclude that all of the data concerning sulfone-activated 1,2 eliminations can indeed be accommodated by a carbanion mechanism. It is of interest to note in this connection that the sulfonyl group is one of the weaker electron-withdrawing groups, judging from equilibrium acidities. (The pK_a's of CH_3NO_2, CH_3COCH_3, and $CH_3SO_2CH_3$ are *ca.* 16, 24, and 28, respectively, in DMSO.) The present results are, therefore, consistent with the postulate that most 1,2 elimination reactions proceed through carbanion or carbonium ion intermediates, and that truly concerted eliminations are relatively rare.[28]

Experimental Section[33]

***trans*- and *cis*-2-(*p*-Tolylsulfonyl)cyclohexyl Para-Substituted Benzenesulfonates.** These esters were prepared from the corresponding sulfone alcohols[3] and the appropriate para-substituted benzenesulfonyl chloride by mixing the reagents in cold pyridine, allowing the mixture to stand at 2° for 3 days (*cis*-alcohol) and for 5 days (*trans*-alcohol), and then pouring the reaction mixture into an excess of cold 6 *N* hydrochloric acid. The acidic solution was extracted with cold chloroform, the chloroform layer washed with water and dried over anhydrous magnesium sulfate, and the solvent evaporated under vacuum at room temperature. Addition of hexane to the residue usually caused crystallization. The products were recrystallized from methanol or hexane to a constant melting point. The infrared spectra of chloroform solutions of the individual isomer pairs were in general similar, but the cis isomers showed strong peaks at 10.7 and 11.2 μ which were absent in the trans isomers. The melting points and analysis of the compounds are given in Table VII.

***trans*-2-Phenylsulfonylcyclohexyl Bromide.** A mixture of 5.0 g (0.023 mol) of *trans*-2-phenylthiocyclohexanol and 60 ml of 48% hydrobromic acid was stirred at room temperature for 9 hr. A thin layer of chloroform was kept over the reaction mixture to keep bromine formation at a minimum. The solution was then extracted with chloroform, and the chloroform layer washed successively with water, sodium bicarbonate solution, and thiosulfate solution. After drying over anhydrous magnesium sulfate, the solvent was removed under vacuum to give 6.2 g of product which had no peaks in its infrared spectrum due to the hydroxyl group. A solution of 2.0 g (0.007 mol) of the crude *trans*-2-phenylthiocyclohexyl bromide in 10 ml of glacial acetic acid was treated with 10 ml of 40% peracetic acid keeping the temperature below 28°. After 2 hr water was added and a white crystalline product was obtained. After washing with water 1.9 g of a white product was obtained, mp 54–56°. After recrystallization from methanol the product melted at 61–62°.

Anal. Calcd for $C_{12}H_{15}SO_2Br$: C, 47.53; H, 4.99. Found: C, 47.36; H, 4.93.

***trans*-2-Phenylsulfonylcyclohexyl Chloride.** A mixture of 5 g (0.023 mol) of *trans*-2-phenylthiocyclohexanol and 60 ml of 12 *N* hydrochloric acid was stirred at room temperature for 24 hr. Working up as described above gave 5.4 g of a product which showed an absence of hydroxyl function by infrared analysis. Oxidation in the same manner as described above gave white cyrstals, mp 74–80°. Recrystallization from methanol gave fine white crystals, mp 82–83°.

Anal. Calcd for $C_{12}H_{15}SO_2Cl$: C, 55.70; H, 5.84. Found: C, 55.99; H, 5.61.

(33) Analyses were by Miss H. Beck. Melting points and boiling points are uncorrected.

Kinetic Measurements. A. pH Method for Rapid Reactions with Hydroxide Ion. This method was used for determining the rates of reaction of the *cis*-2-(*p*-tolysulfonyl)cyclohexyll arylsulfonates with hydroxide ion which were too rapid to be measured by conventional procedures. Separate solutions of the reacting substances in 50% by volume dioxane–water were placed in separate arms of a Y tube fitted with a set of Beckman Model G pH meter. The initial concentration of compound was 2.43×10^{-3} *M* and the initial hydroxide ion concentration was 2.43×10^{-3} *M*. The electrodes were allowed to equilibrate in the alkaline solution at 0° for about 10 min before the start of a run. The solutions were mixed as the timer was started and the times at which successive changes in pH of 0.05 unit occurred were recorded. The first reading was usually obtained in 15 sec. The pseudo-first-order rate constant was obtained by multiplying the slope of a pH *vs.* time plot by 2.303. The second-order rate constant was obtained by dividing the pseudo-first-order rate constant by the average concentration of sulfonate present.

The validity of this method was established by measuring the rate of the hydroxide ion catalyzed hydrolysis of ethyl acetate in water and comparing it to the literature value. We also measured the rate of reaction of *trans*-2-(*p*-tolylsulfonyl)cyclopentyl *p*-toluenesulfonate with hydroxide ion in 50% by volume aqueous dioxane and comparing it to the value previously determined by a conductometric procedure. These data are summarized in Table VIII.

Table VIII. Verification of pH Kinetic Method Reaction

Reaction	Rate found by pH method, M^{-1} sec^{-1}	Reported rate, M^{-1} sec^{-1}
Hydrolysis of ethyl acetate (water, 25°)	1.0×10^{-1}	1.07×10^{-1} [a]
Elimination from *trans*-2-(*p*-tolylsulfonyl)cyclopentyl tosylate (50% dioxane, 25°)	2.14	2.17[b]

[a] F. Daniels, "Outlines of Physical Chemistry," Wiley, New York, N. Y., 1948, p 352. [b] Reference 8.

Some detailed data for a kinetic run of this type may be seen in the original thesis.[1]

B. Conductometric Method for Reactions with Hydroxide Ion. This method was used for determining the hydroxide promoted rates of elimination of *trans*-2-(*p*-tolylsulfonyl)cyclohexyl arylsulfonates and *trans*-2-phenylsulfonylcyclohexyl halides. Dioxane purified by the method of Fieser[34] was diluted only slightly in advance of use to prevent decomposition. Equimolar concentrations (generally about 5×10^{-3} *M*) were always used. The solutions of each reactant were equilibrated in separate arms of a Y tube for at least 10 min before mixing. The conductances were measured in a modified Jones and Ballanger conductance cell equipped with platinum electrodes coated with platinum black. Resistances were measured using an Industrial Instruments, Inc. Model RC 16 conductivity bridge. The rate constants were obtained by dividing the slope of the line obtained by plotting $R/(R - R_\infty)$ *vs.* time by the product of the zero time intercept and the original concentration.

C. Conductometric Method for Reactions with Amines. The method previously described[8] was used. In this method the rates were determined using pseudo-first-order conditions in which the base is present in large excess in a buffered system. Three different concentrations of buffer were used, and a plot of the observed rate constant *vs.* buffer concentration gave as the zero intercept

(34) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p 368.

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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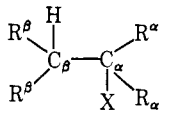
Received May 25, 1970

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]



I

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

(1) Part I: G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).
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(3) Research School of Chemistry, Australian National University, Canberra, Australia.
(4) Author to whom enquiries should be addressed at the Research School of Chemistry.
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