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syn Elimination in 2-Phenylethyl Derivatives

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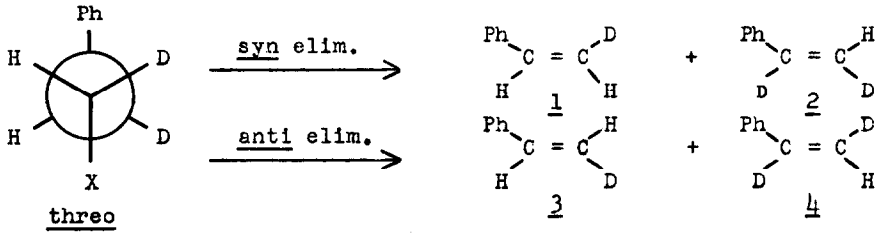
Since the pioneering investigations of Sicher and coworkers[2] the *syn* elimination path in typical E2 reactions has become recognized as an important component. In acyclic systems the *syn* elimination path seems to predominate[2a,b] in systems where there are large steric interactions between vicinal substituents, R and R', it becomes important[3] in systems where such

$$\mathrm{R\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}CH_2\text{-}R'}$$

steric interactions are moderate when bulky bases are used, but the *syn* path seems to be absent when steric interactions are slight. Indeed, the search for a *syn* path in the 2-butyl system ($R=R'=CH_3$) has been fruitless.[4,5] Saunders has attempted to rationalize the *syn* path on the basis of steric repulsions.[3] Recently, two additional groups[5,6] have reported the absence of *syn* elimination in acyclic systems with slight steric interactions. To obviate the conclusion, engendered by the negative observations cited, that *syn* elimination in acyclics is characteristic only of highly branched systems, we report some observations demonstrating the operation of the *syn* path in a sterically unencumbered system.

Our substrate was either *erythro*- or *threo*-PhCHDCHDX. The stereochemistry of the elimination is readily determined from the product distribution. Thus, from the *threo* diastereomer, % *syn* = (1 + 2)/(1 + 2 + 3 + 4). Furthermore, the *intramolecular* deuterium isotope effect for *syn* and *anti* processes are separately measurable, $(k_H/k_D)_{syn} = 2/1$, $(k_H/k_D)_{anti} = 4/3$.



The distribution of products 1 - 4 can be determined from the β-resonances of the deuterium-decoupled styrene nmr spectrum.[7] Some of our results are listed in the Table.

Among the important features of our results to note are the following. 1. The syn elimination path is observed only when benzene is the solvent. Sicher originally suggested[2c] "...the effective species in the syn elimination is not the alcoholate anion as in anti elimination but the $RO^-...K^+$ ion pair"[8] and showed the extent of syn elimination increased significantly on going from dissociating solvents (e.g., DMSO) to ion-pair supporting solvents (e.g., benzene). Our data demonstrate this dramatically (cf. entries 3 and 4). The failure of others[4,5] to observe syn elimination may prove to be attributable to their failure to give Sicher's perception its due cognizance and to their persistent use of dissociating solvents. 2. That syn and anti elimination are associated with different primary deuterium isotope effects requires that each stereochemical path is mechanistically distinct. That is, the syn and anti paths each arise from different activated complexes in the rate determining step. 3. That syn elimination accounts for 20% of the total elimination pathway in a system where steric interactions are minimal shows that a rationale for syn elimination based on repulsive steric interactions[3] is valid only in part, at best. 4. The closeness of primary isotope effects for anti elimination in benzene and tert-butyl alcohol suggests a similar degree of β-CH bond stretching in these solvents, which in turn suggests a similarity of anti transition states in these solvents.[9] If syn eliminations were associated solely with the ability of base to remove the proton at the β-carbon, then one might expect comparable amounts of syn elimination in

Table 1. Eliminations from PhCHDCHDX using tert-BuOK

Diastereomer	X	Solvent	T(°C)	% syn	% anti	$(k_H/k_D)_{syn}$	$(k_H/k_D)_{anti}$
threo	OTs	t-BuOH	30	7	93	a	5.1
threo	OTs	t-BuOH	80	9	91	a	4.2
threo	OTs	DMSO	23	4[b]	96	a	5.6
threo	OTs	benzene	80	18	82	2.3	3.9
threo	OTs	benzene	80	19	81	2.1	4.1
erythro	Cl	benzene	80	25	75	2.9	4.8

a. Not reliable owing to large uncertainty of value. b. Values less than 5% syn elimination probably are not experimentally distinguishable from 0%.

benzene and tert-butyl alcohol, for tert-BuOK seems to be about equally effective a base in anti eliminations in these solvents.[10] Such reasoning again implicates the importance of base structure (e.g., state of aggregation) in promoting syn elimination.

Complete experimental details, complete results, comments on the deuterium isotope effects, and mechanistic implications will appear in a paper currently in preparation.

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(7) We estimate the absolute error of 4% for components present at the 50% level, with an absolute error of 2% for minor components.

(8) It is not clear that the cyclic transition state of Sicher (ref. 2c), involving interaction between the metal cation and leaving group, is equally valid for onium compounds.

(9) We assume explicitly that the degree of double bond character in the transition state of E2 eliminations with $PhCH_2CH_2X$ is small. This seems to be in accord with leaving group isotope effects (e.g., W. H. Saunders, Jr., and S. Asperger, J. Amer. Chem. Soc., 79, 1612 (1957); G. Ayrey, A. N. Bourns, and V. A. Vyas, Can. J. Chem., 41, 1759 (1963)) as well as secondary deuterium isotope effects at C-1 (e.g., S. Asperger, L. Klasinc, and D. Pavlovic, Croat. Chem. Acta, 36, 159 (1964); Chem. Abstr., 63, 2863g (1965); A. F. Cockerill, Tetrahedron Lett., 4913 (1969)).

(10) One must recognize explicitly that comparison of primary deuterium isotope effects for syn elimination with those for anti elimination, for the purpose of assessing the relative degree of β-CH bond breaking, is invalid. This point will be amplified in the full paper.