

## *p*-Toluenesulfonate Eliminations in Dimethyl Sulfoxide

Sir:

Studies of the olefinic products produced from base-catalyzed eliminations in dimethyl sulfoxide when compared with the products from elimination in ethanol become remarkably definitive of the mechanism of elimination reactions in general. Reported here are preliminary results from the study of some secondary tosylates.

The reactions were carried out at 55° with a ratio base:ester of 2:1. In dimethyl sulfoxide both ethoxide and *t*-butoxide were used as bases. To prevent isomerization of the olefinic products during the eliminations in dimethyl sulfoxide<sup>1</sup> a constant stream of dry nitrogen was bubbled through the mixture to sweep the olefins, as they were formed, from the reaction flask into a collection trap immersed in a Dry Ice-acetone mixture. The reactions were carried out in anhydrous ethanol and dimethyl sulfoxide that had been dried over potassium hydroxide and fractionated through a 30-in. spinning-band column at reduced pressure. Product analysis was by gas chromatography. The results are summarized in Table I.

**Table I.** Products from the Elimination of *p*-Toluenesulfonates at 55°

Alkyl group	Solvent	Base	<i>trans</i> -2-ene: <i>cis</i> -2-ene	
			1-ene	2-ene
2-Butyl	EtOH	KOEt	35	1.95
2-Butyl	DMSO	KOEt	54	2.34
2-Butyl	DMSO	KO- <i>t</i> -Bu	61	2.53
2-Pentyl	EtOH	KOEt	42	1.90
2-Pentyl	DMSO	KOEt	66	3.07
2-Pentyl	DMSO	KO- <i>t</i> -Bu	72	3.26
<i>cis</i> -2-Methylcyclohexyl	DMSO	KO- <i>t</i> -Bu	59	41
<i>trans</i> -2-Methylcyclohexyl	DMSO	KO- <i>t</i> -Bu	0	100

Of particular concern for the eliminations in dimethyl sulfoxide is the nature of the base and the possibility of an E1cB mechanism.

If the base were either hydroxide ion, obtained by reaction of unremoved water in the dimethyl sulfoxide with alkoxide ion, or the anion derived from dimethyl sulfoxide, then regardless of the alkoxide ion added the same base would be present in solution. This predicts the same ratio of olefinic products when ethoxide is replaced with *t*-butoxide. The experimental results are not in agreement with this prediction. Further, since the solutions of base in dimethyl sulfoxide were homogeneous, all but extremely small concentrations of hydroxide are eliminated due to the insolubility of potassium hydroxide. Also, the relative acidities of *t*-butyl alcohol and dimethyl sulfoxide<sup>2</sup> are sufficiently different

(1) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, *J. Am. Chem. Soc.*, **85**, 2111 (1963).

(2) A. Ledwith and N. McFarland, *Proc. Chem. Soc.*, 108 (1964).

to make consideration of the anion derived from dimethyl sulfoxide as the attacking base remote. Although an E1cB-type mechanism was considered a distinct possibility when the study was begun, the total *trans* elimination observed in the *trans*-2-methylcyclohexyl tosylate seems to discount this possibility.

The most striking aspect of the data is the predominance of the 1-ene product in the reactions carried out in dimethyl sulfoxide. That the increase in Hofmann product is *not* a manifestation of the steric requirements of the attacking base, leaving group, or ester structure is shown by a comparison of the data for potassium ethoxide in the two solvents ethanol and dimethyl sulfoxide.

The data from *cis*- and *trans*-2-methylcyclohexyl tosylates eliminate a *cis* elimination<sup>3</sup> and its subsequent increase in nonbonded repulsions in the transition state. All of the data, however, are consistent with a *trans* elimination with a transition state that involves a great deal of heterolysis of the carbon-hydrogen bond and a lesser amount of heterolysis of the carbon-oxygen bond. This type of a transition state is also concordant with the observations that eliminations in dimethyl sulfoxide are many times as rapid as in hydroxylic solvents<sup>4</sup> and the carbanionic character of the transition state in the  $\beta$ -phenylethyl system is increased with an increase in base strength in the same solvent.<sup>5</sup>

These data demonstrate for the first time that it is possible in some elimination reactions to change from essentially Saytzeff products to Hofmann products without changing any of the steric requirements of base, leaving group, or alkyl group.

Based on the evidence at hand, it is reasonable to assume that, as more 1-ene is produced, carbon-hydrogen bond stretching becomes more important in the transition state for tosylate eliminations, and the increase in 1-ene produced by exchanging *t*-butoxide for ethoxide is a manifestation of base strength and not the bulkiness of the base; *i.e.*, carbon-hydrogen bond stretching is so pronounced that steric effects of the attacking base are of little importance.

The increase in the *trans*-2-ene:*cis*-2-ene ratio in dimethyl sulfoxide indicates that eclipsing effects are more pronounced and, concurrent with the greater carbon-hydrogen bond stretching, the double bond is somewhat more developed than in the reactions in ethanol.

The increase in 1-ene and *trans*-2-ene:*cis*-2-ene ratios in the 2-pentyl system can be attributed to the more severe eclipsing effects of ethyl as compared with methyl. However, this may be only part of the answer. *n*-Butyl tosylate has been found to undergo elimination slower than *n*-propyl tosylate<sup>6</sup> in ethanol; thus, some of the rate difference may be electronic in nature.

(3) C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **30**, 673 (1965), suggest this possibility to explain the products from the elimination of 2-octyl benzenesulfonate.

(4) Dimethyl sulfoxide has the unique ability to promote the formation of carbanions by reaction of alkoxide ions with saturated carbon-hydrogen bonds: G. A. Russell and H.-D. Becker, *J. Am. Chem. Soc.*, **85**, 3406 (1963), and references therein.

(5) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960).

(6) D. H. Froemsdorf and W. W. Wilkison, unpublished results.

In conclusion these data show that the products obtained from an elimination reaction can be changed in a predictable way by changing the structure of the transition state.

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## Solvent and Base Effects on the Mechanism of the E2 Reaction

Sir:

Evidence has accumulated that makes it reasonable to assume that the ratio of the extent of carbon-hydrogen to carbon-heteroatom bond stretching in the transition state for E2 reactions may vary with changes in the leaving group, the solvent, and the base.<sup>1</sup> However, the relative importance of the solvent vs. the base is not defined, since almost invariably a change in solvent has resulted in a change in base.<sup>2</sup> Reported here are the results of some preliminary studies of the products formed from elimination reactions using 2-bromobutane as substrate and various solvents and bases.

The reaction conditions were the same as previously reported.<sup>3</sup> The data are summarized in Table I.

Table I. Products from the Elimination of 2-Bromobutane at 55°

Expt.	Solvent	Base	% 1-ene	<i>trans</i> -2-ene: <i>cis</i> -2-ene
1	EtOH	KOEt	19	3.35
2	<i>t</i> -BuOH	KOEt	38	2.19
3	DMSO	KOEt	27	3.57
4	<i>t</i> -BuOH	KO- <i>t</i> -Bu	53	1.64
5	DMSO	KO- <i>t</i> -Bu	31	3.65

These data provide important suggestions concerning the effect of base strength and solvent on C-H and C-Br bond stretching in the transition state for E2 reactions, and hence the Hofmann and Saytzeff orientation rules.<sup>4</sup>

The increase in the % 1-ene in expt. 2-5 as compared with expt. 1 is indicative of an increase in the ratio of C-H to C-Br stretching. The greater the value of % 1-ene the greater the ratio of C-H to C-Br stretching.

An increase in base strength, whether it results from a decrease in the energy of solvation of the base brought about by a change in solvent or a change of base in the

same solvent, should increase the C-H stretching in the transition state. In expt. 2 and 3 in which the base strength is increased by a solvent change as compared with expt. 1, an increase in the ratio of C-H to C-Br stretching is exhibited by an increase in the percentage of 1-ene formed. Thus, as previously observed in tosylate eliminations,<sup>3</sup> the percentage of 1-ene formed is sensitive to solvent effects alone.

In expt. 2 as compared with 4 and expt. 3 as compared with 5, an increase in base strength in the same solvent also results in an increase in the ratio of C-H to C-Br stretching as exhibited by the percentage of 1-ene formed. Thus, in both *t*-butyl alcohol and dimethyl sulfoxide, as base strength is increased the ratio of C-H to C-Br stretching is increased.

However, eclipsing effects, as shown by the *trans*-2-ene:*cis*-2-ene ratios, increase with base strength in dimethyl sulfoxide and decrease with base strength in *t*-butyl alcohol. The magnitude of eclipsing effects in these reactions is dependent upon the dihedral angle between the opposing methyl groups in the transition state. Since the dihedral angle is largely dependent upon the extent of C-Br stretching, these data show that an increase in base strength may result in either an increase or a decrease in C-Br stretching, depending upon the solvent used. This solvent dependence can be interpreted as the ability of the solvent to solvate the leaving group, which in this case is the bromide ion.<sup>5</sup>

In *t*-butyl alcohol then, the C-H to C-Br bond-stretching ratio increases dramatically with an increase in base strength because C-H stretching is increased while C-Br stretching is decreased. Thus the increase in the percentage of 1-ene formed in *t*-butyl alcohol with *t*-butoxide as the base (expt. 4) as compared with the amount formed in ethanol with ethoxide as the base (expt. 1) is mainly the result of two effects: an increase in base strength and a solvent effect complementing each other, and not the size of the attacking base as previously assumed.<sup>2b,6</sup>

These data suggest that the products formed from an E2 reaction are dependent upon the ratio of C-H to C-X bond stretching and the actual extent of bond stretching in the transition state. The Hofmann rule<sup>4</sup> is a manifestation of a transition state in which C-H stretching is much greater than C-X stretching, while the Saytzeff rule<sup>4</sup> is the result of a transition state in which the ratio of C-H to C-X stretching approaches 1 or less. An increase in the extent of both C-H and C-X stretching results in a flattening of the transition state, making eclipsing effects more severe. Carbon-hydrogen stretching in a particular substrate is dependent upon both the solvent and the identity of the base. Carbon-heteroatom stretching in a particular substrate is dependent upon the solvent and the identity of the leaving group.<sup>7</sup> This solvent dependence may be related to the solvent's ability to promote dissociation, *i.e.*, solvate both cations and anions, or it may be related to the solvent's ability to solvate the leaving group only. The degree of solvation of the leaving

(1) For a recent review see D. V. Banthorpe, "Reaction Mechanisms in Organic Chemistry," Vol. 2, E. D. Hughes, Ed., Elsevier Publishing Co., New York, N. Y., 1963.

(2) (a) Alcohol solvents and the corresponding lyate base being the usual conditions; (b) see H. C. Brown, I. Moritani, and Y. Okamoto, *J. Am. Chem. Soc.*, **78**, 2193 (1956); or (c) D. J. Cram, F. D. Greene, and C. H. DePuy, *ibid.*, **78**, 790 (1956).

(3) D. H. Froemsdorf and M. E. McCain, *ibid.*, **87**, 3983 (1965).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 420.

(5) In agreement with previous trends (A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962)), the solvent effect observed in these reactions predicts that the energy of solvation of bromide ion in DMSO is greater than the energy of solvation of alkoxide ions.

(6) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, p. 143.

(7) The dependence of C-H and C-X stretching upon substrate structure and leaving group identity is discussed in ref. 1.