

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.¹ 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.² 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.³ 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.⁴

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,³ 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.⁵

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.^{2b,6}

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 rule⁴ is a manifestation of a transition state in which C-H stretching is much greater than C-X stretching, while the Saytzeff rule⁴ 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.⁷ 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.

group determines the extent to which the electron pair in the C-H bond assists in the stretching of C-X.

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On the Problem of 1,3-Hydride Shifts during Nitrous Acid Deamination of 1-Propylammonium Perchlorate

Sir:

The work of Reutov and Shatkina¹ and of Karabatsos and Orzech² has led to widespread acceptance of the belief that some 1,3-hydride shift is involved in the deamination of 1-propylamine.³ In 1963, Reutov⁴ stated, without experimental detail, that the deamination of 2-tritio-1-propylammonium perchlorate (I-2-*t*) gave 1-propanol containing tritium only in the C-2 position, as expected for 1,3-hydride shift. One of us has pointed out⁵ that our preliminary data from the deamination of I-2-*t* gave results quite different from those stated by Reutov, the apparent tritium rearrangements from C-2 to C-1 and C-3, respectively, being about 6 and 8%. From more recent work (*vide infra*) we now believe these rearrangements were too high, possibly because of contamination of the 1-propanol by 2-propanol. These early observations, however, led us to a study, by n.m.r., of the products from the deamination of 2,2-dideuterio-1-propylammonium perchlorate (I-2-*d*₂).

Methylmalonic acid was subjected to five successive exchanges with D₂O, and the resulting material was decarboxylated to give 2,2-dideuteriopropionic acid.⁶ I-2-*d*₂ was then prepared from the deuterated propionic acid by conversion to the amide, reduction with LiAlH₄, and neutralization with HClO₄. After deamination in aqueous perchloric acid,⁷ the 1- and 2-propanol fractions were obtained by preparative v.p.c. Figures 1 and 2 show the pertinent parts of the n.m.r. spectra⁸ of I-2-*d*₂ and the 1-propanol from its deamination, as well as the spectra of the corresponding undeuterated compounds. Some C-2 proton absorptions were noted in both the deuterated starting material,

(1) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).

(2) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).

(3) N. C. Deno has strongly emphasized the occurrence of 1,3-shifts in his recent review on carbonium ions in *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(4) O. A. Reutov in "Congress Lectures, XIXth International Congress of Pure and Applied Chemistry," Butterworth and Co. Ltd., London, 1963, pp. 203-227.

(5) Reported by C. C. Lee during a discussion period at the XIXth International Congress of Pure and Applied Chemistry, London, July 10-17, 1963.

(6) A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 1265, 1266.

(7) J. D. Roberts and M. Halmann, *J. Am. Chem. Soc.*, **75**, 5759 (1953).

(8) Obtained by Mr. G. W. Bigam using a Varian Associates HR100 spectrometer at the University of Alberta through arrangements with Professor R. U. Lemieux.

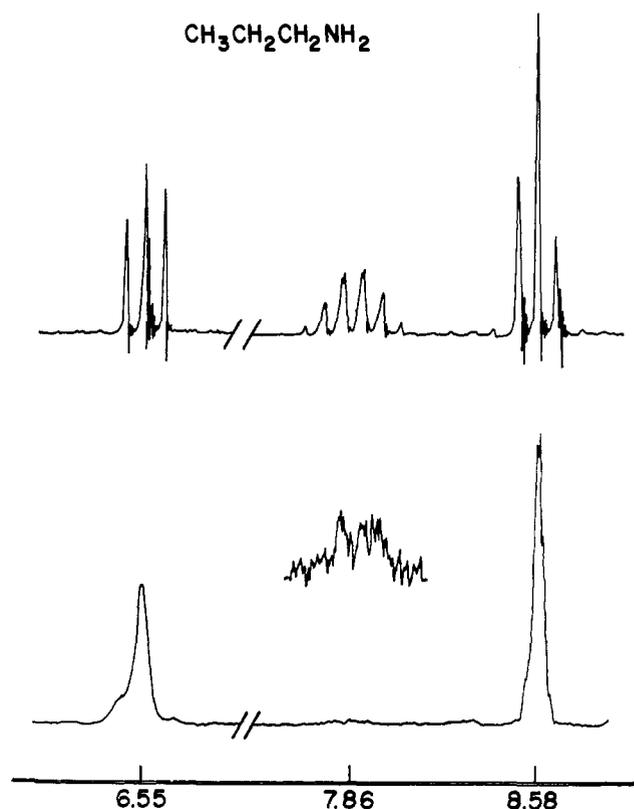


Figure 1. N.m.r. spectra of 1-propylammonium perchlorate and 2,2-dideuterio-1-propylammonium perchlorate in D₂O. Insert drawn at higher spectrometer sensitivity.

I-2-*d*₂ (ca. τ 7.86), and the 1-propanol product (ca. τ 8.45). If only 1,3-hydride shifts were involved, there should be no increase in signal intensity for the C-2 protons in the 1-propanol product. While integration of such low-intensity absorptions would give quantitative data of only doubtful value, qualitatively it is clear that the 1-propanol product shows stronger C-2 proton absorption than I-2-*d*₂, indicating some loss of the deuterium label from C-2, presumably to C-1 and C-3.

The n.m.r. spectrum of the 2-propanol fraction obtained from deamination of I-2-*d*₂ showed the presence of small amounts of unidentified impurities besides the expected signals. The very small amount of C-2 proton absorption was found to be practically identical in intensity with that of the original I-2-*d*₂. This observation is in agreement with the earlier finding of Karabatsos and Orzech,² and it effectively eliminates successive 1,2-hydride shifts as a mechanism during deamination of 1-propylamine.

To obtain a more quantitative evaluation of the extents of isotopic rearrangements, 1-tritio-1-propylammonium perchlorate (I-1-*t*), prepared from reduction of propionitrile with LiAlH₄-*t*, was deaminated. The 1-propanol fraction was purified by v.p.c. and degraded by oxidation, first to propionic acid and then to acetic acid. The degradation procedures were those of Reutov and Shatkina¹ with the exception that, in the oxidation to propionic acid, KMnO₄ in dilute H₂SO₄ instead of KMnO₄ in dilute Na₂CO₃ was used as a precaution to minimize any possibility of hydrogen exchange. The activity of the propionic acid gave the tritium content in C-2 and C-3 and the activity of the