

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.

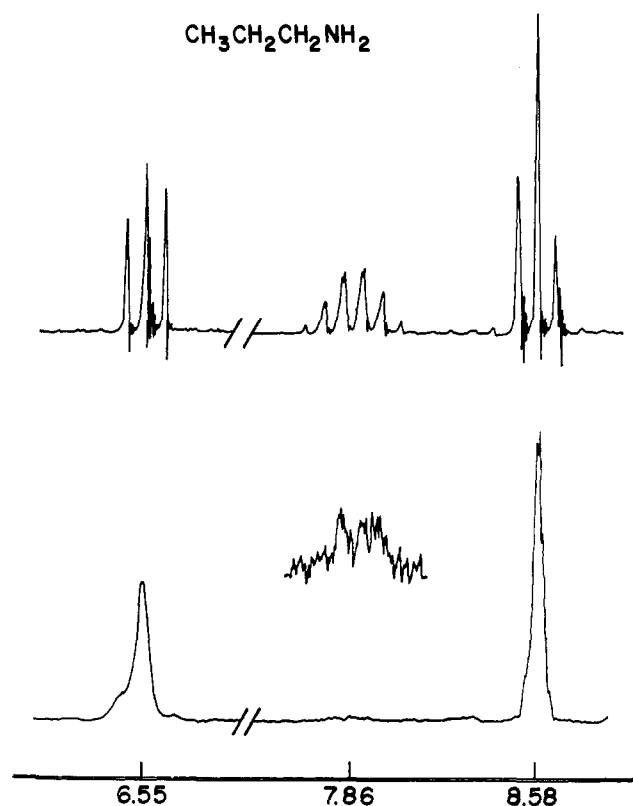


Figure 1. N.m.r. spectra of 1-propylammonium perchlorate and 2,2-dideuterio-1-propylammonium perchlorate in D₂O. Insert drawn at higher spectrometer sensitivity.

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

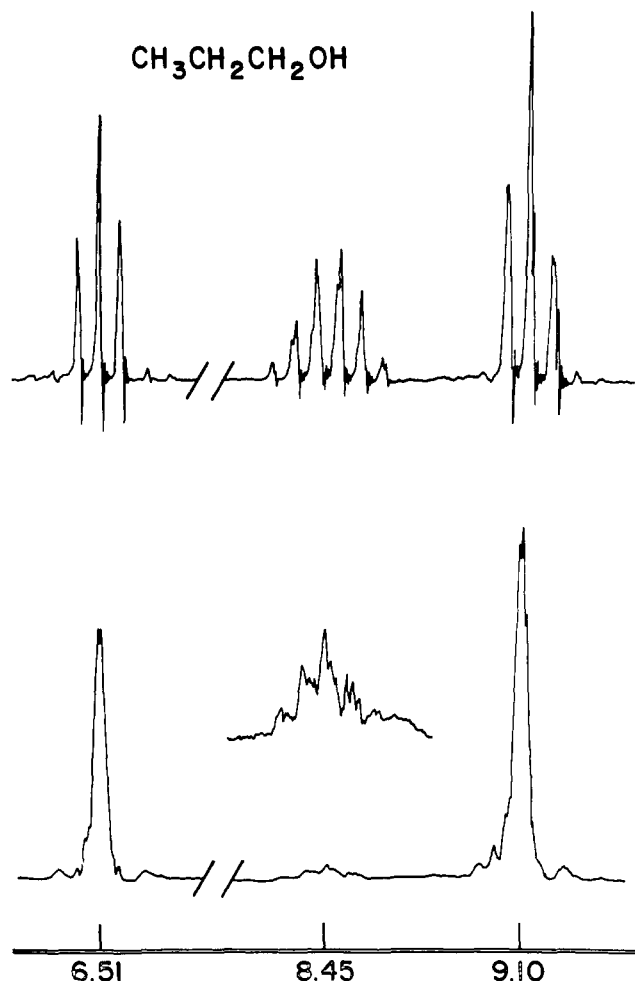


Figure 2. N.m.r. spectra of neat samples of 1-propanol and deuterated 1-propanol from deamination reaction. Insert drawn at higher spectrometer sensitivity.

acetic acid showed the tritium content in C-3. The results are summarized in Table I.

Table I. Activity Data and Tritium Rearrangements in the 1-Propanol from Deamination of 1-Tritio-1-propylammonium Perchlorate.

Compd. assayed	Specific activity, ^a c.p.m./mmole		% T in C-2 and C-3		% T in C-3	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
C ₃ H ₇ OH ^b	3,450,000	2,750,000				
C ₂ H ₅ COOH ^c	101,000	81,000	2.9	2.9		
CH ₃ COOH ^c	55,700	45,400			1.6	1.7

^a Measured by a liquid scintillation counter. Control experiments showed that the degradation reactions cause no rearrangement. ^b Assayed as the α -naphthylurethan. ^c Assayed as the *p*-bromophenacyl ester.

From Table I, it is seen that a total of about 3% rearrangement has taken place, the rearranged tritium being found in both C-2 and C-3. These results are not compatible with a 1,3-hydride shift mechanism. Recently, Karabatsos and co-workers⁹ studied the deamination of 1,1-dideuterio-1-propylammonium perchlorate (I-1-*d*₂) and of I-2-*d*₂ by means of mass spectroscopy.

(9) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, private communications.

copy. Their data for I-1-*d*₂ indicated a total rearrangement of about 3.8% at 40° and about 2% at 0°. In the present study, the deamination of I-1-*t* was carried out at room temperature of ca. 25°, but the actual temperature of the reaction mixture itself was not determined. Taking possible variations due to differences in temperature into account, it may be concluded that the results from the two independent studies, ours with I-1-*t* and that of Karabatsos and co-workers⁹ with I-1-*d*₂, are in substantial agreement.

The results reported in this communication clearly indicate that neither a direct 1,3-hydride shift nor two successive 1,2-hydride shifts can account for the isotopic rearrangements in the 1-propanol from deamination of 1-propylamine. Although the possibility of a protonated cyclopropane as intermediate has apparently been excluded by the ¹⁴C results of Reutov and Shatkina,¹ in the following communication we will report a reinvestigation of the ¹⁴C tracer experiments and show that the observed rearrangements may be best explained by some involvement of a protonated cyclopropane.

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Rearrangement Studies with Carbon-14. XXIII. On the Role of Protonated Cyclopropane in the Deamination of 1-Propylamine¹

Sir:

In 1953, Roberts and Halmann² reported that the nitrous acid deamination of 1-¹⁴C-1-propylammonium perchlorate (I-1-¹⁴C) gave a 1-propanol fraction in which about 8% of the ¹⁴C label was rearranged from C-1 to C-2 and C-3. Years later, Reutov and Shatkina³ repeated this work with a more complete degradation and found about 8% rearrangement of ¹⁴C from C-1 solely to C-3. The possibilities of a 1,3- or two successive 1,2-hydride shifts were suggested. Since the results from the deaminations of 1-tritio-1-propylammonium and 2,2-dideuterio-1-propylammonium perchlorates (I-1-*t* and I-2-*d*₂), reported in the preceding communication,⁴ are not compatible with the either of the hydride shift mechanisms, the possibility of protonated cyclopropane (II)⁵ as an intermediate has to be considered. Involvement of II in the deamination of I-1-¹⁴C would lead to isotope position rearrangement of the label to both C-2 and C-3 of 1-propanol, and not only to C-3.

(1) Supported by a grant from the National Research Council of Canada.

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

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

(4) C. C. Lee, J. E. Kruger, and E. W. C. Wong, *J. Am. Chem. Soc.*, **87**, 3985 (1965).

(5) (a) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964); (b) A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).