

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).

This communication presents results from reinvestigating once more the nitrous acid deamination of I-1-¹⁴C.

I-1-¹⁴C was prepared from potassium ¹⁴C-cyanide and deaminated by nitrous acid in aqueous perchloric acid as described by Roberts and Halmann.² The 1-propanol fraction was isolated by preparative v.p.c. Degradation was effected according to the procedures of Reutov and Shatkina,³ involving oxidation of the 1-propanol to propionic acid and then to acetic acid followed by conversion of the latter to methylamine *via* the Schmidt reaction. The propionic and acetic acids were converted to the corresponding *p*-bromophenacyl esters and the methylamine was converted to N-methyl-*p*-toluenesulfonamide. The radiochemical purity of these solid derivatives was assured by repeated recrystallizations until their specific activities were constant. The data on the rearrangements of ¹⁴C are summarized in Table I.

Table I. Activity Data and Rearrangements of the ¹⁴C-Label in the 1-Propanol from Deamination of I-¹⁴C-1-Propylammonium Perchlorate

Compd. Assayed	Specific activity, ^a c.p.m./mmole		% ¹⁴ C in C-2 and C-3		% ¹⁴ C in C-3	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
CH ₃ CH ₂ COOH ^b	7340	194,700				
CH ₃ COOH ^b	297	8,030	4.1	4.1		
CH ₃ NH ₂ ^c	109	3,600			1.5	1.9

^a Measured by a liquid scintillation counter. ^b Assayed as the *p*-bromophenacyl ester. ^c Assayed as N-methyl-*p*-toluenesulfonamide.

Of the two runs summarized in Table I, data from run 2 are likely more reliable because of the higher activities. The results indicate a total of about 4% rearrangement, with the rearranged ¹⁴C approaching equal distribution in C-2 and C-3. This distribution is in very close agreement with that predicted by Karabatsos and co-workers⁶ on the basis of their results from studies of deaminations of 1,1-dideuterio-1-propylammonium perchlorate (I-1-*d*₂) and 2,2-dideuterio-1-propylammonium perchlorate (I-2-*d*₂) by mass spectroscopy. The difference between the presently observed total rearrangement of 4% from the earlier reported 8% possibly may be due, at least in part, to inadequate purification of the compounds assayed by the previous workers.^{2,3} In the course of the present work it was noted that apparently higher activity contents were observed if the solid derivatives of the degradation products were not repeatedly recrystallized until the specific activities were constant.

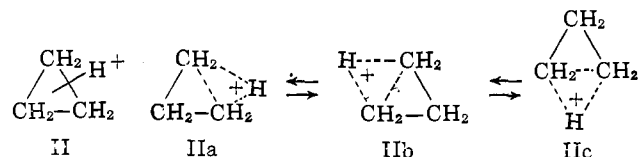
The finding of almost equal distribution of the rearranged ¹⁴C in C-2 and C-3, together with the results from deaminations of I-1-*t* and I-2-*d*₂ recorded in the previous communication,⁴ clearly support the involvement of protonated cyclopropane (II) as an intermediate or a transition state in giving rise to the isotopic rearrangements observed in the 1-propanol. A completely symmetrical protonated cyclopropane was first suggested in 1960 by Skell and Starer,⁷ although these workers later preferred the 1,3-hydride shift.⁸ The pre-

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

(7) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

(8) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

sent data and those of Baird⁵ and Karabatsos⁶ suggest a situation where the three carbon positions are equivalent or approaching equivalence. The experimental results, however, do not differentiate between "face-protonated" (II) and "edge-protonated" (IIa-c) cyclopropanes.



From the present work and others already reported in the literature, it may be concluded that the 1-propyl cation from deamination of 1-propylamine may react with solvent to give 1-propanol, deprotonate to propene, undergo irreversible 1,2-hydride shift leading to 2-propanol, and cyclize to II which may deprotonate to cyclopropane or collapse to give isotopically rearranged 1-propanol. The results from deamination of I-1-*t*⁴ and I-1-¹⁴C indicate a total of about 3-4% isotopic rearrangements from C-1 to C-2 and C-3, which means that about 4-6% of the 1-propanol obtained in the deamination is derived from protonated cyclopropane.

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Carbametallic Boron Hydride Derivatives. III. The π -C₅H₅Fe(π -B₉C₂H₁₁) System

Sir:

In the first communication of this series¹ we reported the synthesis of (B₉C₂H₁₁)₂Fe⁻ (I) and (B₉C₂H₁₁)₂Fe⁻² (II). Evidence available at that time suggested the possibility of "sandwich" bonding between each B₉C₂H₁₁⁻² ion¹ (III) and Fe^{II} and Fe^{III}. A more recent report² was concerned with probable analogs of π -C₅H₅M(CO)₃; (B₉C₂H₁₁)M(CO)₃⁻ (IV) where M = Mn and Re. We now wish to report the preparation and properties of π -C₅H₅Fe(π -B₉C₂H₁₁) containing Fe^{II} (V) and Fe^{III} (VI) which appears to be analogous to the ferrocene-ferricinium ion system. The accompanying communication³ describes the single crystal X-ray diffraction study which confirms the "sandwich" structure of VI.⁴

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).

(3) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

(4) Existing nomenclature systems are not capable of generating reasonably brief names for compounds such as I, II, IV, V, and VI. Accordingly, we suggest that the parent B₁₁H₁₁⁻⁴ ion, which is isoelectronic with the isomeric series of B₉C₂H₁₁⁻² ions, be called ollide ion after the Spanish noun, *olla* (jar or kettle). The isomeric B₉C₂H₁₁⁻² ions would then become (1)-2,3-dicarbollyl ion, etc., where the number in parentheses denotes the position of the missing BH unit which generates the "hole" in the icosahedron. The prefix π - or σ - would be employed to denote the mode of attachment of the (1)-2,3-dicarbollyl, etc., group to other atoms. Thus, VI becomes π -cyclopentadienyl- π -(1)-2,3-dicarbollyliron(III). The use of π - and σ -terminology rests upon the obvious geometrical analogy found in organometallic compounds. The actual bonding arrangement in the so-called π -derivatives remains as an open question which is under examination.