TABLE III
HEATS AND ENTROPIES OF ACTIVATION FOR REACTIONS IN 80% AQUEOUS ETHANOL

Substituent on 9-bromofluorene	E_a, kcal./mole	$\Delta S^{\ddagger}$, e.u.
4-$COOCH_3$	22.1 ± 0.7	−14.3 ± 2.0
1-$COOCH_3$	22.9 ± .6	−14.3 ± 1.7
None[a]	24.9 ± 1.3	− 3.5 ± 3.8

[a] The constants reported in this case apply to the reaction of 9-bromofluorene.

Table III, the thermodynamic constants for the reactions of 1-carbomethoxy-9-bromofluorene are almost the same as those for the 4-carbomethoxy isomer. It is interesting to note that 9-bromofluorene is somewhat more reactive (Table I) than its 1- and 4-carbomethoxy derivatives because the activation entropy, rather than the activation energy, for solvolysis of the unsubstituted compound is lower than that for its derivatives. Additional evidence that the transition states in these reactions may not be highly ionic in character is to be found in the fact that the activation energy for 9-bromofluorene is more than for the bromofluorenes which have electron-withdrawing $-COOCH_3$ substituents.

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COMMUNICATIONS TO THE EDITOR

MECHANISM OF CONVERSIONS OF *n*-PROPYL CARBONIUM ION TO CYCLOPROPANE. 1,3-HYDROGEN SHIFT

Sir:

It was reported recently that a fundamental reaction of carbonium ions is their conversion to cyclopropanes.[1,2] For example, nitrous acid deamination of *n*-propylamine and deoxideation of *n*-propoxide ion yield identical C_3H_6 fractions consisting of cyclopropane and propylene in 9:1 ratio.[1] The disconcerting coincidence that ethyl carbene, $CH_3CH_2\ddot{C}H$, produced by thermal decomposition of 1-diazopropane in aprotic media also yields a C_3H_6 fraction of the same composition,[3] raised the possibility that *n*-propyl carbonium ion is deprotonated to ethyl carbene and that cyclopropane and propylene are products of carbene rather than carbonium ion cyclization.

To distinguish between these mechanisms the deoxideation of 1,1-dideuterio-1-propanol was studied. The carbene mechanism, with intermediate $CH_3CH_2\ddot{C}D$, should lead to monodeuteriocyclopropane, while direct cyclization of carbonium ion $CH_3-CH_2-CD_2^+$ should yield dideuteriocyclopropane.

The 1,1-dideuterio-*n*-propyl alcohol was prepared by reduction of benzyl propionate with $LiAlD_4$. Its high isotopic purity was indicated by the failure to observe in the neat sample any proton magnetic resonance absorption characteristic of the $-CH_2-O-$ grouping. The deoxideation of this alcohol was carried out by refluxing with 50% aqueous potassium hydroxide and adding bromoform slowly. The gaseous products were trapped in a −140° trap and then analyzed and separated in pure condition by vapor phase chromatography. Since standards were not available for infrared spectroscopic identification of the deuterium labeled species, mass spectrometry was employed. It was assumed that the cracking probabilities for ordinary and deuterated cyclopropanes were identical. By this means it was found that the cyclopropanes from the deoxideation of $CH_3CH_2CD_2OH$ were $C_3H_4D_2$ (94 ± 2%) and C_3H_5D (5–6%).

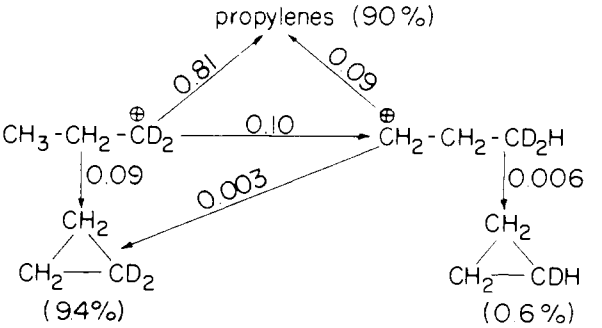
Thus, $CH_3CH_2\ddot{C}D$ is not the intermediate in the major pathway to cyclopropane. The formation of cyclopropane is best explained as a 1,3 ring closure with loss of hydrogen ion.

$$CH_3CH_2CD_2-O^- + \ddot{C}Br_2 \longrightarrow CH_3CH_2CD_2-O-\ddot{C}-Br^- + Br^-$$

$$CH_3-CH_2-CD_2-O-\ddot{C}-Br \longrightarrow CH_3-CH_2-CD_2^+ + CO + Br^-$$

$$CH_3-CH_2-CD_2^+ \xrightarrow{-H^+} \text{propylene and } \begin{matrix} CH_2 \\ / \quad \backslash \\ CH_2-CD_2 \end{matrix}$$

The monodeuteriocyclopropane could be attributed to a carbene intermediate, but more likely it results from a variation of the 1,3-interaction which does not involve proton loss, yielding $^+CH_2CH_2CHD_2$, or 1,3 hydride shift. If this latter interpretation is correct, the partitioning among products (numbers over the arrows) follows from the assumption that on conversion of $^+CH_2CH_2CD_2H$ to cyclopropane, loss of D is twice as probable as loss of H.

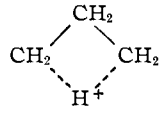


Reutov and Shatkina[4] have reported that nitrous acid deamination of 1-propylamine-1-C^{14} leads to 92% 1-propanol-1-C^{14} and 8% 1-propanol-3-C^{14}. This evidence, taken with the published evidence and unpublished confirmations that 2-propyl cation

(1) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).
(2) M. S. Silver, *ibid.*, **82**, 2971 (1960); **83**, 3482 (1961).
(3) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).
(4) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).

does not lead to 1-propanol,[5] constitutes further conclusive evidence for 1,3-interactions in *n*-propyl carbonium ions. The extents of 1,3-rearrangement of 1-propyl cation are in good accord, 9% in deamination and 10% in deoxideation. Thus, under these irreversible conditions the preferred 1,2 interactions which lead to propylene occur only ten times faster than the 1,3-interactions.

In the Reutov and Shatkina experiment none of the carbon label appears on C-2. Thus, a protonated cyclopropane is excluded in this system,[6] and the transition state is best formulated as shown by the formula



(5) 1-Propanol is not obtained on nitrous acid deamination of 2-propylamine, Mayer and Forster, *Chem. Ber.*, **9**, 535 (1876); Whitmore and Thorpe, *J. Am. Chem. Soc.*, **63**, 1118 (1941); unpublished observations from (a) G. J. Karabatsos and (b) our laboratory. Further evidence is adduced from the failure to observe cyclopropane in deoxideations of 2-propanol.

(6) P. S. Skell, I. Starer and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960).

(7) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Office of Ordnance Research, Contract No. DA-36-061-ODR-607.

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1,3-HYDROGEN SHIFT IN 2-METHYL-1-BUTYL CATION

Sir:

The formation of cyclopropanes in (a) nitrous acid deaminations of *n*-propylamine[1] and 3-methyl-2-butylamine[2] and (b) deoxideations of *n*-propyl and other alcohols[1] are examples of 1,3-interactions in the respective carbonium ions. However, much of the evidence is ambiguous for 1,3-interactions which lead to isomeric carbonium ions, since these rearrangements also can be rationalized by a combination of successive 1,2-rearrangements. Recent publications provide conclusive evidence for 1,3-hydride shift in the *n*-propyl carbonium ion system.[3,4,5]

We wish to report a 1,3-hydride shift in the deoxideation of 2-methyl-1-butanol. Deoxidation of this alcohol with potassium hydroxide and bromoform leads to the products:

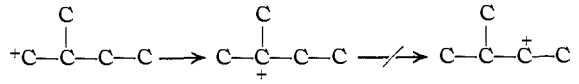
	% of total C_6H_{10}
2-Methyl-1-butene (I)	48.2
2-Methyl-2-butene (II)	11.3
trans-2-Pentene (III)	13.5
cis-2-Pentene (IV)	7.9
1-Pentene (V)	12.3
Ethylcyclopropane (VI)	2.1
trans-1,2-Dimethylcyclopropane (VII)	2.0
3-Methyl-1-butene (VIII)	1.2

(1) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).
(2) M. S. Silver, *ibid.*, **82**, 2971 (1960); **83**, 3482 (1961).
(3) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).
(4) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **84**, 2838 (1962).
(5) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

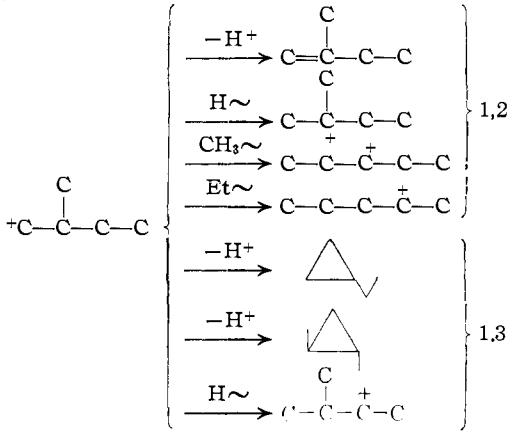
Products I–V are rationalized by assuming 1,2-shifts of H, CH_3 or C_2H_5, yielding *t*-amyl-, 3- and 2-*n*-pentyl cations, respectively. Cyclopropanes VI and VII indicate 1,3-interactions. The formation of 3-methyl-1-butene requires a 1,3-hydride shift (see below).

By gas chromatography the 2-methyl-1-butanol was shown to be free of all isomeric pentanols except 3-methyl-1-butanol, which had the same retention time. Base elimination of toluenesulfonic acid from the tosylate ester of the 2-methyl-1-butanol yielded an olefinic product uncontaminated by 3-methyl-1-butene, whereas the tosylate of 3-methyl-1-butanol yielded 3-methyl-1-butene exclusively. Thus, none of the deoxideation products can be attributed to isomeric alcohols in the 2-methyl-1-butanol.

The formation of 3-methyl-1-butene from 2-methyl-1-butyl cation can be explained by a 1,3-rearrangement or two 1,2-rearrangements. The latter explanation postulates the rearrangement of *t*-amyl cation to 3-methyl-2-butyl cation. This rearrangement has been demonstrated *not* to occur under deoxideation conditions. Deoxideations of *t*-amyl and neopentyl alcohols lead to the *t*-amyl cation, both alcohols yielding the olefins 2-methyl-2-



butene and 2-methyl-1-butene in the same ratio, *uncontaminated by 3-methyl-1-butene*. Thus, the primary reaction paths available to 2-methyl-1-butyl cations are



Thus, under the irreversible conditions of deoxideation a minimum of 8.0%[6] of 2-methyl-1-butyl cation undergoes 1,3-reactions. Undoubtedly 1,3-cyclizations and rearrangements are more common in carbonium ion systems than has heretofore been supposed. We are engaged in efforts to explore the importance of this type of reaction in other carbonium ion systems.

The occurrence of 1,3-interactions in competition with the more exothermic 1,2-rearrangements and proton eliminations implies the presence of free carbonium ions produced in deoxideations and nitrous acid deaminations. In solvolyses, 1,3 interactions are not observed.

(6) The 3-methyl-2-butyl cation is converted to 3-methyl-1-butene to the extent of 38.8% of the C_6H_{10} (R. J. Maxwell, unpublisbed work on deoxideation of 3-methyl-2-butanol).