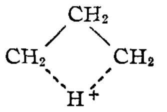
does not lead to 1-propanol,[5] constitutes further conclusive evidence for 1,3-interactions in *n*-propyl carbonium ions. The extents of 1,3-rearrangement of 1-propyl cation are in good accord, 9% in deamination and 10% in deoxideation. Thus, under these irreversible conditions the preferred 1,2 interactions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



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[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 Soc.*, **63**, 1118 (1941); unpublished observations from (a) G. J. Karabatsos and (b) our laboratory.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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RECEIVED JULY 16, 1962

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]

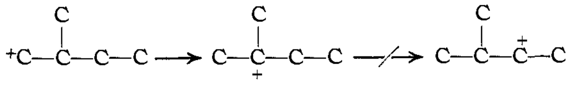
We wish to report a 1,3-hydride shift in the deoxideation of 2-methyl-1-butanol. Deoxidation of this alcohol with potassium hydroxide and bromoform leads to the products:

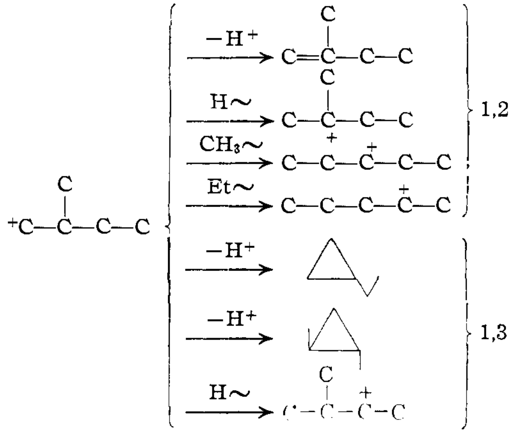
	% of total C$_5$H$_{10}$
2-Methyl-1-butene (I)	48.2
2-Methyl-2-butene (II)	11.3
trans-2-Pentene (III)	13.5
cis-2-Pentene (IV)	7.9
1-Pentene (V)	12.3
Ethylcyclopropane (VI)	2.1
trans-1,2-Dimethylcyclopropane (VII)	2.0
3-Methyl-1-butene (VIII)	1.2

Products I–V are rationalized by assuming 1,2-shifts of H, CH$_3$ or C$_2$H$_5$, 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.

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[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).

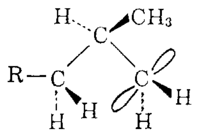
[3] O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962).

[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).

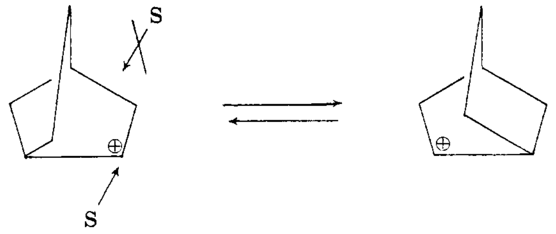
[6] The 3-methyl-2-butyl cation is converted to 3-methyl-1-butene to the extent of 38.8% of the C$_5$H$_{10}$ (R. J. Maxwell, unpublished work on deoxideation of 3-methyl-2-butanol).

The 1,3-interactions are best rationalized as intramolecular hydride transfers made probable by the favorable geometry of the extended chain (minimum non-bonding repulsions) in acyclic paraffinic systems.



The lifetimes of alkyl carbonium ions under the alkaline conditions of deoxideation (15–50% aqueous KOH solution) must be limited by the rates of diffusion of R^+ and OH^-, since it is reasonable to expect this bimolecular reaction to occur at each collision. Thus a lifetime of $<10^{-9}$ second is indicated for R^+. It is significant that within this time interval 1,2-rearrangements, 1,3-hydride shifts and cyclopropane formations have been observed, emphasizing the high mobility of atoms in alkyl carbonium ion systems.

The conclusions that unimolecular rearrangements are occurring with frequencies in excess of solvent and ion-pair relaxations has bearing on a current controversy relative to the postulate of non-classical carbonium ions. Critics of the non-classical concept have suggested that control of stereochemistry can be explained by rapid interconversion of isomeric classical carbonium ions, as illustrated for norbornyl cation. The suggestion is validated by analogy since this interconversion can be faster than reaction with the solvent, so that *endo* attack is precluded, leading to *exo* products exclusively. Control of stereochemistry is a valid argument in favor of a non-classical structure *only* in those cases where it can be demonstrated that equilibration between classical ions is slower than conversions to products.



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[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, Grant No. DA-ARO(D)-31-124-6211.

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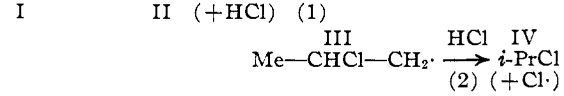
RECEIVED JULY 16, 1962

FREE RADICAL ADDITIONS OF HYDROGEN CHLORIDE TO ALKENES

Sir:

It has long been known that the addition of hydrogen bromide to a 1-alkene may be directed to give 95% or more of either primary or secondary bromide.[1] The high yields of either product demonstrate kinetic control of both products since longer or more strenuous treatment of either bromide with a catalyst for either type of addition leads to the same equilibrium mixture of bromides.[2] Reports of primary chlorides from free radical additions of hydrogen chloride to 1-alkenes are relatively rare. This situation has been ascribed[3] to the difficulty in reaction of an alkyl radical, particularly an allyl radical, with hydrogen chloride in the necessary chain. Recent papers from Madison[4] and Moscow[5] throw new light on this explanation and warrant reconsideration of some previous data.

Benson and Willard[4] found that liquid *n*-propyl chloride is isomerized to isopropyl chloride by gamma radiation, that the reaction is catalyzed by hydrogen chloride and retarded by propylene, that hydrogen in the hydrogen chloride exchanges but chlorine does not, and that *G*-values as high as 150 can be obtained for formation of isopropyl chloride. This work establishes the rearrangement mechanism



$$\underset{\text{I}}{n\text{-PrCl}} \xrightarrow{\text{Cl}\cdot} \underset{\text{II}}{\text{Me—}\dot{\text{C}}\text{H—CH}_2\text{Cl}} \xrightarrow[(+\text{HCl})\ (1)]{}$$
$$\overset{\text{III}}{\text{Me—CHCl—CH}_2\cdot} \xrightarrow[(2)\ (+\text{Cl}\cdot)]{\text{HCl}} \overset{\text{IV}}{i\text{-PrCl}}$$

This reaction must be reversible, and the equilibrium mixture, which is high in isopropyl chloride,[6] would undergo extensive exchange with hydrogen chloride in the presence of radicals without change in proportions of chlorides if side reactions did not interfere. The equilibrium between I and IV does not tell us about the relative concentrations of II and III nor about their relative rates of reaction with hydrogen chloride. However, the rearrangement of the bromine analog of III, $\text{Me-CHBr-CH}_2\cdot$, to the analog of II in the chlorination of isopropyl bromide[7] suggests that II is more stable than III.

Nesmeyanov, Freidlina and co-workers[5] have demonstrated rapid rearrangements of radicals like II. Their simplest example is the peroxide-catalyzed addition of hydrogen bromide to 3,3-dichloropropene. Here, the products show that 90% of the $\text{Cl}_2\text{CH-}\dot{\text{C}}\text{H-CH}_2\text{Br}$ reacting rearranged to $\cdot\text{CHCl–CHCl–CH}_2\text{Br}$ before reaction with hydrogen bromide.

The above considerations suggest: (1) In reactions of both II and III which require little activation energy, the products correspond to the more stable radical, II, at least when the halogen is bromine. (2) In reactions of II and III which are

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[1] M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933); F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] F. R. Mayo and A. A. Dolnick, *J. Am. Chem. Soc.*, **66**, 985 (1944).

[3] F. R. Mayo, *ibid.*, **76**, 5392 (1954), and references therein.

[4] H. L. Benson, Jr., and J. E. Willard, *ibid.*, **83**, 4672 (1961).

[5] A. N. Nesmeyanov, R. Kh. Friedlina, V. N. Kost and M. Ya. Khorlina, *Tetrahedron*, **16**, 94 (1961).

[6] T. I. Crowell and G. L. Jones, Jr., *J. Am. Chem. Soc.*, **73**, 3506 (1951), report that the equilibrium mixture of propyl chlorides contains less than 0.8% primary chloride. R. H. Wiley, W. Miller, C. H. Jarboe, J. R. Harrell and D. J. Parish, *Radiation Research*, **13**, 479 (1960), were able to isomerize *n*-propyl but not *i*-propyl chloride with γ-rays although hydrogen chloride was split out of both chlorides. On the other hand, the 12% primary chloride found by addition of hydrogen chloride[3] is consistent with the negligible difference in heats of combustion of the two chlorides (0.04 kcal./mole, Beilstein, Vol. I, third supplement, pp. 219, 222) and the 9% primary bromide in the equilibrium mixture of propyl bromides.[2]

[7] P. S. Skell, R. G. Allen and N. D. Gilmour, *J. Am. Chem. Soc.*, **83**, 504 (1961).