

initial equilibrating solution permit the calculation of the LiCl activity in any of these mixtures. Data of this type for other cations permit the calculation of exchange selectivities in concentrated solutions. Work is now being extended to more accurate determinations of the osmotic coefficients of mixed resin-electrolyte systems and to measurement of selectivity as a function of mole fraction exchanged in the lower molality region (1-6 molal for NaCl and LiCl systems) where aqueous phase activity coefficients are accurately known.

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REARRANGEMENT OF 1-METHYL- AND  
1-ETHYLPENTABORANE-9 TO 2-METHYL- AND  
2-ETHYLPENTABORANE-9

Sir:

An apparently quantitative conversion of a 1-alkylpentaborane-9 (R = methyl, I; R = ethyl, II) to a 2-alkylpentaborane-9 (R = methyl, III; R = ethyl, IV) in the presence of 2,6-dimethylpyridine (Fig. 1) suggests a general reaction to obtain 2-substituted pentaboranes.

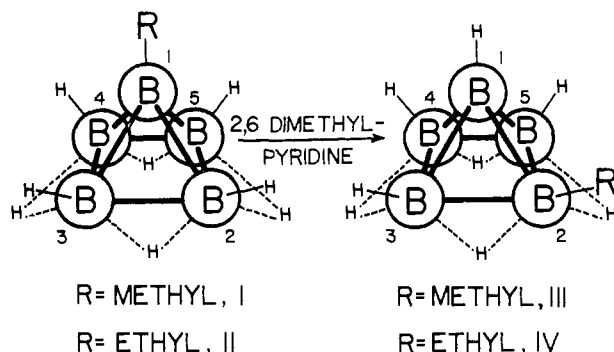


Fig. 1.

A mixture of 0.50 millimole of II<sup>1</sup> and 0.3 ml. of 2,6-dimethylpyridine sealed in a 5-mm. tube exhibited approximately the same B<sup>11</sup> nuclear magnetic resonance spectrum as pure II<sup>1b,2</sup> (doublet  $\delta = +13$ ,  $J = 155$  c./s.; singlet  $\delta = +39^3$  with area ratios 4:1, respectively). After a period of four hours at room temperature the rearrangement was essentially complete and the B<sup>11</sup> n.m.r. profile was that of IV (singlet  $\delta = -2$ ; doublet  $\delta = +16$ ,  $J = 160$  c./s.; doublet  $\delta = +52$ ,  $J = 170$  c./s.; with area ratios of 1:3:1 respectively). B<sup>11</sup> n.m.r. spectra taken periodically during the course of the rearrangement indicated a gradual change from II to IV with no detectable buildup of intermediate substances. The  $\delta = +16$  doublet of IV was not quite as sharp as the corresponding

(1) (a) R. E. Williams, U. S. Patent 2,917,547, Dec. 15, 1959; (b) B. N. Figgis and R. L. Williams, *Spectrochimica Acta*, **331**, No. 5 (1959); (c) N. J. Blay, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 424, 430 (1960).

(2) J. N. Shoolery, unpublished work.

(3) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

doublet of II. This probably is because of the slight environmental non-equivalence of the two types of basal borons with terminal hydrogens in IV (4 and 3,5 positions). Pure IV (0.48 millimole) was isolated after addition of excess boron trifluoride ethyl etherate to the reaction mixture and a subsequent separation of the volatiles by vapor phase chromatography.

Similarly, a mixture of I<sup>1b</sup> was rearranged to III. The structure of III was confirmed by infrared spectrophotometric and vapor pressure data.<sup>4</sup>

A comparison of the B<sup>11</sup> n.m.r. chemical shifts of II, IV and pentaborane<sup>3,5</sup> reveals a shift of about 13  $\delta$  units to lower field when the apex boron of the pentaborane framework is alkyl substituted, and a similar shift of about 14  $\delta$  units when a basal boron is alkyl substituted. These "alkyl shifts" are in qualitative agreement with other studies.<sup>6</sup>

The mechanism of the reaction may involve slow "symmetrical" cleavage<sup>7</sup> of I or II and fast recombination to give III and IV, respectively. Among other possible mechanisms Williams<sup>6,8</sup> has suggested a plausible internal rearrangement facilitated by hydrogen tautomerism. An extension of the present study into the mechanism of the rearrangement and to other related reactions will be reported subsequently.

The author is indebted to Dr. R. E. Williams for use of Varian nuclear magnetic resonance equipment.

(4) J. H. Lamneck and S. Kaye, National Advisory Committee for Aeronautics, research memorandum E58E12, Sept. 1958.

(5) W. D. Phillips, H. C. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(6) R. E. Williams, private communication.

(7) R. W. Parry and I. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(8) R. E. Williams, "Tautomerism and Exchange in the Boron Hydrides; B<sup>11</sup> and H<sup>1</sup> NMR Spectra," *J. Inorg. and Nuclear Chem.*, accepted.

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MECHANISM OF FREE RADICAL DECAY IN  
IRRADIATED POLYETHYLENE. EVIDENCE FROM  
DEUTERIUM-HYDROGEN EXCHANGE

Sir:

In 1954<sup>1</sup> we postulated that free radicals produced in polyethylene by ionizing radiations decayed by reaction following a random walk migration of the free radical centers through the solid polyethylene. We visualized the jumping of hydrogen atoms along or across molecular chains from a saturated CH<sub>2</sub>-group to a free radical center —CH—. This picture of free radical migration has been adopted by Voevodskii, *et al.*<sup>2</sup> Evidence for the migration of free radicals also comes from the e.s.r. studies of Charlesby and Ormerod.<sup>3</sup>

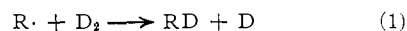
In this note we wish to present a new mechanism for the migration of free radicals in solid poly-

(1) M. Dole, C. D. Keeling and D. G. Rose, *J. Am. Chem. Soc.*, **76**, 4304 (1954).

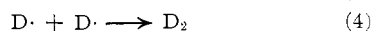
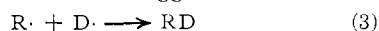
(2) A. T. Koritskii, Yu. N. Molin, V. N. Shamshev, N. Ya. Bulen and V. V. Voevodskii, *Acad. Nauk, S.S.S.R. High Molecular Compounds*, **1**, 1182 (1959).

(3) A. Charlesby and A. Ormerod, paper presented at a conference on "Physics of Polymers," British Physical Society, Bristol, England, Jan. 12, 1961.

ethylene. Evidence for it is based on studies of hydrogen isotope exchange between gaseous deuterium and gamma ray irradiated Marlex-50 polyethylene. Such exchange *during the irradiation* has been studied by Varshavskii, *et al.*<sup>4</sup> These authors postulated a chain reaction



Additional reactions can be suggested



However, in the Russian work reaction (1) might have involved electronically excited or ionized methylene groups because of the existence of these species rather than the free radical  $R \cdot$  during the irradiation. In order to clarify this point we have irradiated Marlex-50 at liquid nitrogen temperature and *in vacuo*, warmed the sample to room temperature, pumped off the evolved hydrogen gas and then introduced deuterium gas subsequent to the irradiation. During this treatment probably two thirds of the free radicals decayed<sup>5</sup>; nevertheless copious exchange up to 25% conversion of  $D_2$  to HD involving the remaining free radicals occurred over a period of about 100 hours. During this period there was less than 0.2% decrease in the total gas pressure; thus reactions (3) and (4) may be considered negligible.<sup>5</sup>

Letting  $y$  represent  $P_{HD}/P_{D_2}^0$ , where  $P_{D_2}^0$  is the initial deuterium pressure, it can be shown that for various mechanisms

$$y = \frac{1}{(b/a) - 1} [e^{-\alpha} - e^{-\beta}]$$

where  $2b/a$  is the D-H fractionation factor, and  $\alpha$  and  $\beta$  have the values:

	$\alpha$	$\beta$
No free radical decay	$at$	$bt$
First order $R \cdot$ decay	$(a/k_3)(1 - q)$ $q = e^{-k_3 t}$	$(b/k_3)(1 - q)$
Second order $R \cdot$ decay	$(a/B) \ln(1 + Bt)$	$(b/B) \ln(1 + Bt)$

The meaning of the kinetic constants  $a$ ,  $b$ ,  $B$  and  $k_3$  will be discussed in the complete paper;  $t$  is the time. Suffice it to say that for  $t$  very small, for the three sets of  $\alpha$  and  $\beta$  values Eq. (6) reduces to  $y \approx at$ . At long times, however, there is a marked difference between the three possibilities. Our evidence indicates that  $R \cdot$  decays by a first order process at least at long times (the mechanism of this will be considered later); the extensive and excellent work of Lawton, Balwit and Powell<sup>6</sup> also demonstrates a first order decay of the alkyl free radical in irradiated Marlex-50.

Referring to Eqs. (1) and (2) it is now evident that these reactions must occur provided that excited or ionized methylene groups no longer

(4) Ya. M. Varshavskii, G. Ya. Vasil'ev, V. L. Karpov, Yu. S. Lazurkin and I. Ya. Petrov, *Doklady Akad. Nauk. S.S.S.R.*, **118**, 315 (1958).

(5) The possibility of a back thermal reaction between molecular hydrogen and irradiated polyethylene suggested by the work of Arvia and Dole, Proc. 2nd Conf. Peaceful Uses of Atomic Energy, United Nations, Geneva, 29, 171 (1958) is being further investigated.

(6) E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Chem. Phys.*, **33**, 395 (1960).

existed in the polyethylene subsequent to the irradiation. It is further evident that the  $R \cdot$  of Eq. (2) is not at the same location in the solid polyethylene as the  $R \cdot$  of Eq. (1). Thus we have an additional mechanism for free radical migration in solid polyethylene. Increase of deuterium gas pressure should not increase  $dy/dt$ , for reasons to be discussed later, but should lower the extent of D-H exchange because of acceleration of  $R \cdot$  decay. This prediction of the mechanism postulated here is borne out by the data.

There is a possibility that some of the exchange may be the result of a reaction in which the D-atom replaces the H-atom on the alkyl free radical without free radical migration as suggested by Voevodskii, *et al.*,<sup>7</sup> in a study involving exchange between deuterium gas and ethyl radicals. While such exchanges may occur to a small extent, evidence will be given later that this mechanism cannot account for the major effect.

By  $R \cdot$ -decay in this note we include also the possibility of conversion of the alkyl to the allyl free radical.<sup>1,2,3</sup> Because of the greater stability of the allyl free radical, reaction (1) involving it would be less likely by a factor of about  $10^{-11}$ .

This research was supported by the U. S. Atomic Energy Commission.

(7) V. V. Voevodskii, G. K. Lavrovskaya and R. E. Mardalefshvili, *Doklady Acad. Nauk. S.S.S.R.*, **81**, 215 (1951).

(8) Fulbright travel grantee from the University of Louvain, Belgium.

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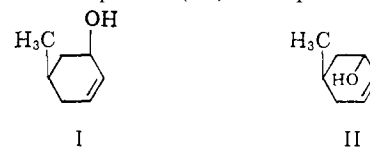
MALCOLM DOLE  
FRANCIS CRACCO<sup>8</sup>

RECEIVED MARCH 30, 1961

#### THE ACID-CATALYZED ISOMERIC REARRANGEMENT OF *cis* AND *trans*-5-METHYL-2-CYCLOHEXENOL-O<sup>18</sup>

Sir:

Several years ago the acid-catalyzed ( $HClO_4$ ) rearrangement of *cis*- (I) and *trans*-5-methyl-2-cyclohexenol (II) in 35% aqueous acetone was investigated in these laboratories and it was found that with both isomers the pseudo first-order rate of loss of optical activity ( $k_a$ ) is several times larger than that of geometric isomerization ( $k_i$ ). This means that the acid-catalyzed allylic rearrangement is stereospecific in the sense that each isomer is converted to its enantiomer faster than to its geometric isomer—in this symmetrical system, allylic rearrangement without geometric isomerization results in the interconversion of enantiomers. It was suggested that the racemization with preservation of geometric configuration may involve either an  $S_Ni$  intramolecular rearrangement of the conjugate acids of the alcohols or an intermolecular stereospecific (*cis*)  $S_N2'$  process.



We have now reexamined this rearrangement and have confirmed the earlier report<sup>1</sup> that  $k_a > k_i$

(1) H. I. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, **79**, 348 (1957).