

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.

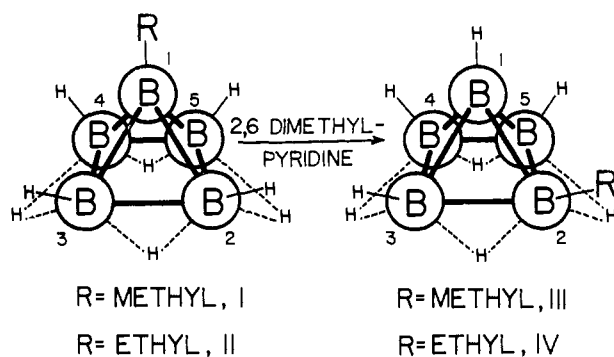


Fig. 1.

A mixture of 0.50 millimole of II¹ and 0.3 ml. of 2,6-dimethylpyridine sealed in a 5-mm. tube exhibited approximately the same B¹¹ nuclear magnetic resonance spectrum as pure II^{1b,2} (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 B¹¹ 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). B¹¹ 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*, **33**, 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(2) J. N. Shoolery, unpublished work.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^{1b} was rearranged to III. The structure of III was confirmed by infrared spectrophotometric and vapor pressure data.⁴

A comparison of the B¹¹ n.m.r. chemical shifts of II, IV and pentaborane^{3,5} reveals a shift of about 13 δ units to lower field when the apex boron of the pentaborane framework is alkyl substituted, and a similar shift of about 14 δ units when a basal boron is alkyl substituted. These "alkyl shifts" are in qualitative agreement with other studies.⁶

The mechanism of the reaction may involve slow "symmetrical" cleavage⁷ of I or II and fast recombination to give III and IV, respectively. Among other possible mechanisms Williams^{6,8} 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.

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(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; B¹¹ and H¹ 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 1954¹ 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 CH₂ group to a free radical center —CH—. This picture of free radical migration has been adopted by Voevodskii, *et al.*² Evidence for the migration of free radicals also comes from the e.s.r. studies of Charlesby and Ormerod.³

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.