B^{11} spectra of Ia,b,c, (Fig. 2) contain three sets of doublets having estimated area ratios of 2:1:1 (low field to high field). The high field doublet has a chemical shift value characteristic of an "apical environment,"[5] whereas the low field doublets have chemical shift values quite similar to the base boron atoms in B_6H_{10}. The H^1 n.m.r. spectra are compatible with the B^{11} n.m.r. spectra and with structure I. A low field quartet and high field quartet are present in the ratio of 3:1 which represent the terminal hydrogens attached to the basal and apical boron atoms, respectively. The bridge hydrogen unresolved multiplet, as well as the sharper absorptions due to the hydrogens attached to carbon, are present where expected. In compounds Ia and Ib a singlet represents the methyl protons. The propyl group in Ic gives rise to three distinct C–H absorptions with barely resolved multiplet structure reflecting the interactions of the adjacent CH_2 and CH_3 groups. In compounds la and lc (where –R equals –H) a single low field peak may be assigned to those hydrogens attached to carbon in the basic molecular skeleton.

The compounds $B_4C_nH_{2n+4}$ (or more generally, $B_mC_nH_{m+n+2}$) may be considered to fit between the boron hydrides which have bridge hydrogens but no carbon in the molecular skeleton and the recently reported carboranes[7] ($B_mC_nH_{m+n}$) which contain carbon and boron but no bridge hydrogens. Perhaps the compounds might be named dihydrocarboranes.

It is interesting to compare the "stable" partial three-center bond character of the carbon atoms in the dihydrocarboranes, as well as in the carboranes, with the relatively unstable bridge (or three center) intermediates normally postulated in carbonium ion chemistry, *e.g.*, protonated double bonds.

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ELECTRON SPIN RESONANCE AND ISOTOPIC EXCHANGE STUDIES IN THE TRITIUM-POLYSTYRENE FLUFF SYSTEM[1]

Sir:

In a recent publication by Ingalls and Wall,[2] a technique was disclosed for stabilizing free radicals at room temperature through the use of finely divided polymer fluff as the reaction medium. Such a rigid and finely spaced system not only has the advantage of minimizing radical recombination, but also permits essentially complete mixing with gases. We wish to report here an application of the above technique to the study of reactions induced by the β-radiation of tritium gas. The use of polymer fluff permits the utilization of tritium gas as an internal radiation source in electron spin resonance (e.s.r.) studies of various model organic systems, and direct observation of radical intermediates is possible as an aid to a mechanistic study of the Wilzbach[3] method of labeling organic compounds by exposure to tritium gas. Advantages arising from such a technique are at least comparable to those for tritiated water as radiation source in condensed media.[4]

Polymer fluffs were cast in thin-walled quartz tubes by freeze-drying dilute benzene solutions of polystyrene.[5] Our experimental apparatus consisted simply of a quartz tube connected through a stopcock to a gas reservoir bulb. Reaction gases were pre-mixed in the reservoir bulb and admitted to the quartz tube containing a fluff capsule. The resulting e.s.r. spectrum in the tritium-polystyrene fluff system is essentially identical with that observed in gamma-irradiated polystyrene.[6] The e.s.r. signal growth for a series of experiments is presented graphically in Fig. 1.[7] As expected, the rate of signal growth is a function of tritium pressure. The presence of xenon or helium enhanced the initial rate of increase in radical concentration. Nitric oxide not only inhibited radical build-up but also caused a change in the e.s.r. spectrum to an asymmetric structure.

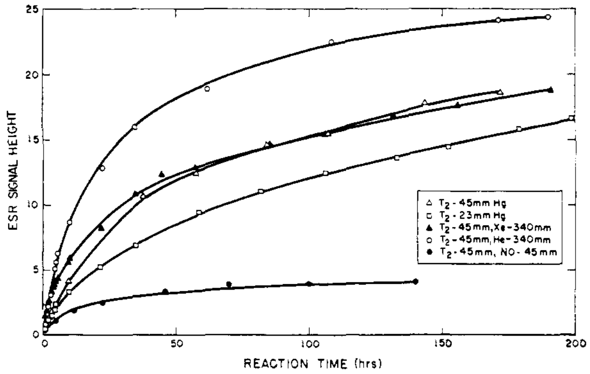

Fig. 1.—E.s.r. signal growth in the T_2–polystyrene system.

Following evacuation of the gas, the observed radicals were found stable at room temperature over periods of weeks. The addition of deuterium or ethylene caused a gradual but small decrease of the e.s.r. signal intensity. On the other hand, nitric oxide appeared to react with the intermediate radicals at a rate faster than our e.s.r. response, and the residue e.s.r. signal was similar in structure and in magnitude to that observed in the tritium–nitric oxide–polystyrene fluff system.

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(7) Each unit of e.s.r. signal height represents radical concentration in the order of 10^{15} spins (for a 3-mg. sample) and the radiation dose rates are approximately 3.4 × 10^{16} ev./hr. for T_2 pressure at 45 mm. and 1.7 × 10^{16} ev./hr. for T_2 pressure at 23 mm.

The degree of tritium labeling in uncross-linked polystyrene was determined by dissolving the reacted fluff in benzene and then subjecting the benzene solutions to liquid scintillation counting. Yields expressed as number of tritium atoms incorporated per 100 ev. energy (G) are summarized in Table I. Wilzbach labeling of organic liquids and solids often suffers from inefficient absorption of radiation energy in the organic matrix. The fact that our observed yields are much higher than even those found for gas phase labeling of similar hydrocarbons[9] must have resulted from inhibited radical recombination[2] in the polymer fluff, thereby promoting competitive tritium labeling processes.

TABLE I

TRITIUM LABELING OF POLYSTYRENE

T_2, pressure, mm.	Additive	Total dose,[a] ev. × 10^{-18}	G(Polystyrene-T
44.2	None	3.0	4.4
23.0	None	2.3	3.7
45.5	NO, 1-45 mm.	3.4	1.5
44.7	Xe, 340 mm.	3.6	14.5
44.5	He, 340 mm.	4.2	9.5

[a] The tritium β-radiation dose was calculated from tritium gas in contact with the fluff, assuming complete absorption of energy in the reaction system. Our assumption is based on the low range of tritium β-particles (7 μ in liquid H_2O) and can be substantiated by estimation from findings of Dorfman[8] on the absorption of tritium β-particles in various gases. Electron density for each fluff capsule is 2×10^{21} electrons per ml., and energy absorption in the gas phase is appreciable only in samples containing xenon or helium as additive.

The apparently similar effects of Xe and He are not readily explainable. The presence of helium is known to enhance the tritium labeling of *n*-hexane,[10] whereas xenon has been shown to exert a scavenging effect in the isotopic exchange between tritium and methane.[11] Our observed enhancement of isotopic exchange due to the presence of xenon may be attributed to gaseous-ions sensitized formation of tritium atoms[12] by reaction (1).

$$X^+ + T_2 \rightarrow XT^+ + T \qquad (1)$$

The high efficiency of xenon sensitization for such a reaction has been demonstrated recently by Lampe.[13] A more critical series of experiments is currently in progress.

A final point of importance is manifested in the relatively high efficiency of tritium labeling observed in our system. A practical method of labeling organic macromolecules by the Wilzbach process is now available with the use of polymer fluffs. Such a technique appears much more promising than the present available methods[14] of tritium labeling of biochemical molecules.

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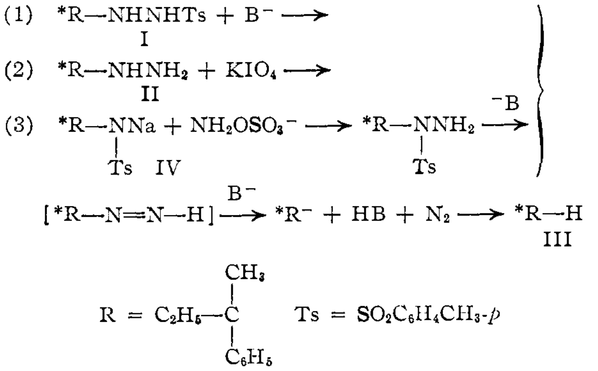
NITROGEN AS LEAVING GROUP IN ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON[1]

Sir:

Carbonium ions, radicals and carbenes formed by loss of a molecule of nitrogen from either compounds or ions have in many instances exhibited different behavior than the corresponding species generated through use of other leaving groups. This communication deals with a comparison of the stereochemical capabilities *of carbanions* produced with nitrogen as distinct from other leaving groups such as carbon,[2a] oxygen[2b] or hydrogen.[2c]

The three reactions used for this purpose are formulated.



$$\text{(1)}\quad {}^*\text{R—NHNHTs} + \text{B}^- \longrightarrow \quad (\text{I})$$

$$\text{(2)}\quad {}^*\text{R—NHNH}_2 + \text{KIO}_4 \longrightarrow \quad (\text{II})$$

$$\text{(3)}\quad {}^*\text{R—N(Ts)Na}\ (\text{IV}) + \text{NH}_2\text{OSO}_3^- \longrightarrow {}^*\text{R—N(Ts)NH}_2 \xrightarrow{^-\text{B}}$$

$$[{}^*\text{R—N=N—H}] \xrightarrow{\text{B}^-} {}^*\text{R}^- + \text{HB} + \text{N}_2 \longrightarrow {}^*\text{R—H}\ (\text{III})$$

$$\text{R} = \text{C}_2\text{H}_5\text{—C(CH}_3\text{)(C}_6\text{H}_5\text{)} \qquad \text{Ts} = \text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$$

Compound II[3] was prepared by a reaction sequence patterned after that reported for the preparation of 2-phenyl-2-propylhydrazine.[4] Resolution of II was accomplished by fractional crystallization of its dibenzoyl-*d*-tartrate salt from water to give (+)-II, $[\alpha]^{25}_{546}$ + 12.8° (l = 1 dm., neat), n^{25}_D 1.5354. Hydrogenolysis of this material, $[\alpha]^{25}_{546}$ + 11.8° (l = 1 dm., neat), in acetic acid with a platinum catalyst produced (+)-2-phenyl-2-butylamine (V), n^{25}_D 1.5124, $[\alpha]^{25}_{546}$ +15.8° (l = 1 dm., neat). Application of the Curtius rearrangement to optically pure (+)-2-methyl-2-phenylbutyric acid[5] (VI) gave (−)-2-phenyl-2-butylamine (V), $[\alpha]^{25}_{546}$ −18.2° (l = 1 dm. neat). Since the configurations of acid VI and hydrocarbon III are known,[5b] these reactions established the configurations of amine V and hydrazine II, as well as the rotation of optically pure II ($[\alpha]^D_{546}$ ±13.5°, l = 1 dm., neat). Sulfon-

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