portionation products most probably proceed from such a caged radical pair.[9]

This system provides one more example of what we believe to be a number of reactions in which a formal two-electron transfer can be more accurately described as two one-electron steps.[10]

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(9) (a) In the case where R and R′ are different groups the situation is actually more complicated than pictured above. During the course of reaction the system contains two organolithiums and two organohalides which may therefore undergo a total of four different sets of reactions of the above type. Since these will in general proceed at different rates, the over-all kinetic behavior of the system is very complex and is poorly understood at present. (b) Other reactions of the radicals are also possible, for example, an iodine transfer to give a polarized alkyl iodide and a new free radical.[1]

(10) A similar suggestion has been offered by K. A. Bilevitch, N. N. Bubnov, and O. Yu. Okhlobystin, *Tetrahedron Letters*, 3465 (1968).

(11) National Defense Education Act Trainee, 1967–1968.

Harold R. Ward, Ronald G. Lawler, Robert A. Cooper[11]
Metcalf Research Laboratories
Brown University, Providence, Rhode Island 02912

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Free Radical Iodide–Lithium Interchange[1]

Sir:

The recent method for detecting unpaired electron precursors of reaction products through emission in the proton magnetic resonance spectra (pmr)[2,3] has allowed us to show that interchange reactions between iodoalkanes and alkyllithium reagents involve an unpaired electron intermediate.

The systems considered include *n*-butyllithium reactions with 1-iodobutane (Figure 1e) or 2-iodopropane (Figure 1b–d) in the presence, or absence, of a Lewis base.[4] Figure 1a shows the locations of the normal halide chemical shifts[5] for a mixture of 2-iodopropane, δ 4.26 (septet, 1) and 1.83 (d, 6), and 1-iodobutane, 3.17 (t, 2), 1.5 (m, 4), and 0.8 (m, 3). In addition, *n*-butyllithium (Foote Mineral Co.) contributes a triplet at δ −0.83 ppm[6] and the solvent, hexane, strongly absorbs in the region δ 1.7–0.7 ppm. Although *n*-butyllithium and 1-iodobutane react slowly without a Lewis base, no negative peak, only a distorted (slight upfield decrease and downfield increase) iodomethylene signal, was observed in the absence of the tertiary amine.

Signal combinations differ in upfield or downfield location of the negative portion of multiplets; the

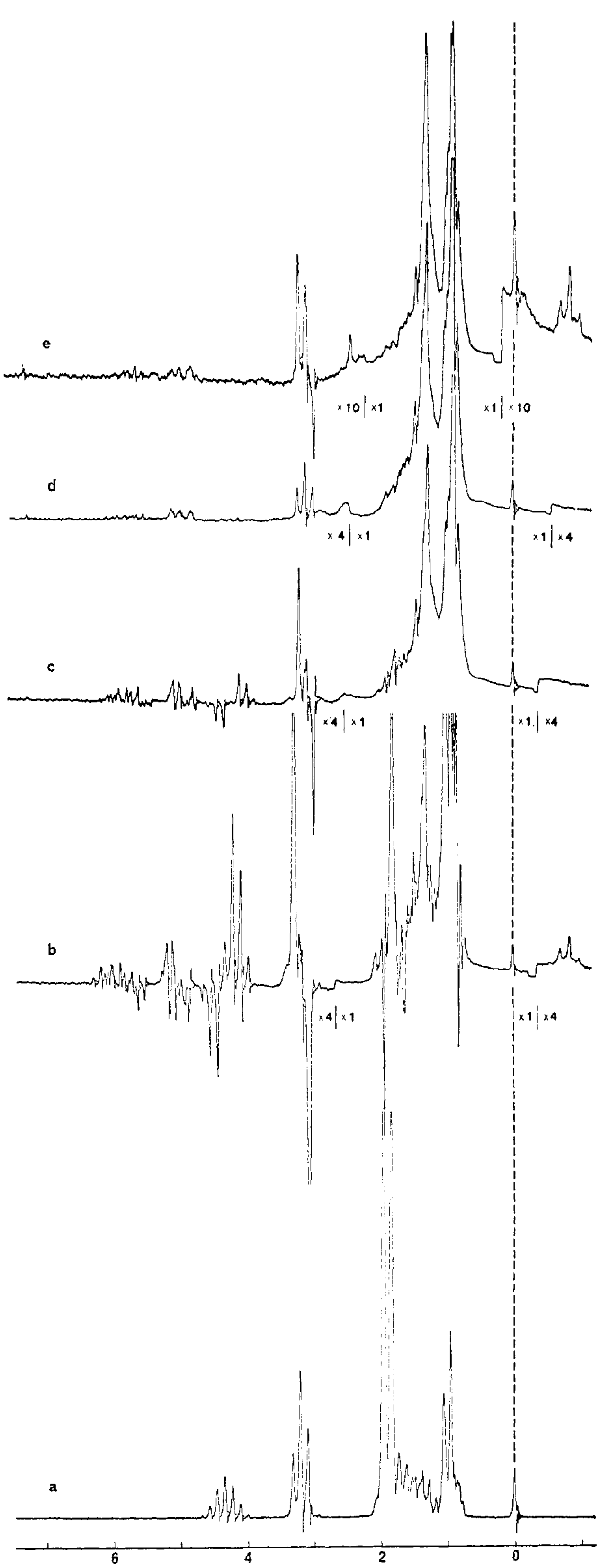

Figure 1. Proton magnetic resonance spectra in the range δ 7.5 to −1 ppm for (a) equimolar quantities of 1-iodobutane and 2-iodopropane in CCl_4, (b–d) 2.4-min scans started at 2.5, 5.3, and 10 min, respectively, after the addition of 150 μl of 2-iodopropane to 0.6 ml of 1.5 *M* *n*-butyllithium in hexane, and (e) 2.4-min scan started at 4.0 min after the addition of 90 μl of 1-iodobutane to a solution of 7 μl of tetramethylethylenediamine and 0.6 ml of 1.5 *M* *n*-butyllithium in hexane. TMS was used as an internal standard; relative amplifications are as shown.

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(1) Presented in part before the Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1968, Abstract ORGN 130.

(2) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967); *Chem. Eng. News*, **46**, 40 (Jan 15, 1968).

(3) A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 2710 (1968).

(4) Alkyllithium depolymerization reagents: C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965), and references cited therein. Amounts of tetramethylethylenediamine larger than 9 μl result in uncontrollable 1-iodobutane reactions. Similar results can be obtained with 15–20 μl of dry triethylamine or anhydrous ethyl ether as catalysts. N,N-Dimethylaniline (0.25 ml) did not significantly enhance the reaction. Very limited amounts of the former reagents have also been used with 2-iodopropane reactions.

(5) Measured with a Varian A-60A. Coupling constants were J = 7–9 cps.

(6) The location of this band shifts in the presence of Lewis bases: *cf.* T. L. Brown, *Advan. Organometallic Chem.*, **3**, 365 (1965).

methyl doublet and iodomethine septet of 2-iodopropane (Figure 1b and c) have the same emission–absorption relationship, the reverse of that for the iodomethylene triplet of 1-iodobutane in Figure 1b, c, and e. Negative peaks in the 1.8–0.7-ppm region of Figure 1b may come from 1-iodobutane or hydrocarbon products. Vinyl protons of the products propene and/or 1-butene are evident in these spectra, bands centered near δ 5.9 and 5.1 ppm. Emission–absorption combinations in all these peaks are evidence for abnormal nuclear spin state distributions (polarization) in chemical species.

The emission phenomena are observable for much longer[7] than in previously reported reactions.[2,3,8] Thus in the 1-iodobutane reaction, after 12 min the polarized triplet was still visible but had disappeared after 16 min in the presence of excess *n*-butyllithium. In excess 2-iodopropane, the 1-iodobutane triplet was only slightly perturbed after 10 min (Figure 1d). The absence of emission or even distortion characterizes the methylenelithium triplet, which disappears long before activity ceases in the iodoalkanes (Figure 1b–d).

In a reaction scheme for cases involving a common R group, the initiation step (1) generates a pair of free radicals. The unpaired electrons become polarized

$$\text{initiation}\qquad \mathrm{RI} + \mathrm{RLi} \longrightarrow 2\mathrm{R}\cdot + \mathrm{LiI} \tag{1}$$

$$\text{polarization}\qquad \mathrm{R}\cdot \longrightarrow \mathrm{R}\cdot^{*} \tag{2}$$

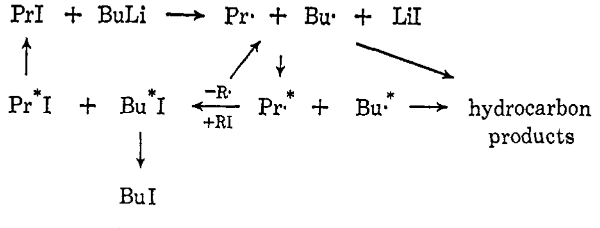
$$\text{transfer}\qquad \mathrm{R}\cdot^{*} + \mathrm{RI} \longrightarrow \mathrm{R^{*}I} + \mathrm{R}\cdot \tag{3}$$

$$\text{depolarization}\qquad \mathrm{R^{*}I} \longrightarrow \mathrm{RI} \tag{4}$$

$$\text{termination}\qquad 2\mathrm{R}\cdot \longrightarrow \mathrm{R_{-2CH_2}CH{=}CH_2} + \mathrm{RH} \tag{5}$$

$$\text{termination}\qquad 2\mathrm{R}\cdot \longrightarrow \mathrm{RR} \tag{6}$$

by the magnetic field and in turn strongly spin couple with nearby protons (2). Iodine atom transfer subsequently gives an iodoalkane (3) with proton spin distributions differing from thermal equilibrium. Pmr measurements aid in nuclear spin relaxation (4). The radical-chain perpetual magnetic pumping process, steps 2–4, is terminated by disproportionation to an olefin plus a hydrocarbon (5), or free-radical coupling (6). Pmr bands of termination products are polarized only if rapid conversion occurs, as for the vinyl multiplets of Figure 1b but not Figure 1e. With two alkyl groups, the 1-iodobutane initially generated is extensively polarized while 2-iodopropane requires several minutes before a comparable degree of polarization is achieved.[7]



The rapid disappearance of the $-\mathrm{CH_2Li}$ pmr band occurs due to signal broadening for all the associated alkyllithium molecules of the minimicellae which bear the unpaired electron.[9] Equivalence of alkyl groups

$$(\mathrm{RLi})_n + \mathrm{R'I} \longrightarrow \mathrm{R(RLi)}_{n-1}\cdot + \mathrm{R'}\cdot + \mathrm{LiI}$$

$$\mathrm{R'}\cdot + (\mathrm{RLi})_{n-1} \longrightarrow \mathrm{R'(RLi)}_{n-1}\cdot$$

in these species and participation of these species rather than R· in step 3 account for the over-all[10] halogen–

$$\mathrm{RLi} + \mathrm{R'I} \rightleftharpoons \mathrm{RI} + \mathrm{R'Li}$$

metal exchange process.

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Arthur R. Lepley, Richard L. Landau
Department of Chemistry, Marshall University
Huntington, West Virginia 25701

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Reaction Dynamics in Nuclear Polarization

Sir:

Recent proton magnetic resonance (pmr) observations include enhanced absorption from the nuclear Overhauser effect[1] and stimulated emission from photochemically[2] or chemically[3] induced dynamic nuclear polarization. However, only the reaction dynamics of pmr emission systems[3] or of unpaired electron precursors[4] for nuclear polarization have been followed. Unfortunately many nuclear polarization signals are combinations of emission and absorption peaks,[5] and thus reaction dynamics are not directly evident from total intensities. Analysis of such signals is therefore needed to provide the means for dynamics studies.

Since nuclear polarization is due to spin coupling with an unpaired electron,[6] chemically induced systems must provide paramagnetic species as a part of their reaction dynamics. The pmr signal from a particular set of chemically equivalent protons in such a reacting system is the net contribution of many molecules which (1) have not yet reacted, (2) have just reacted and are polarized to some degree, and (3) have reacted but have undergone spin relaxation prior to measurement. Reactions which give products with protons distinct from those of the starting materials will only receive contributions from (2) and (3). However equilibrium systems involve contributions from all three categories. Normal signal intensities and relative peak distributions are provided by the thermally equilibrated spin-state populations of normal species (1) and/or (3), while enhanced absorption or stimulated emission comes from the polarized species (2). If it is assumed that there is a new spin-state equilibrium population related to some optimum polarization condition, then measurement of a signal at any particular time would allow calculation of the contribution by normal and polarized species.

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[5] A. R. Lepley and R. L. Landau, *J. Amer. Chem. Soc.*, **91**, 748 (1969), and references cited therein.

[6] For a recent review see: K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance*, **3**, 79 (1967).