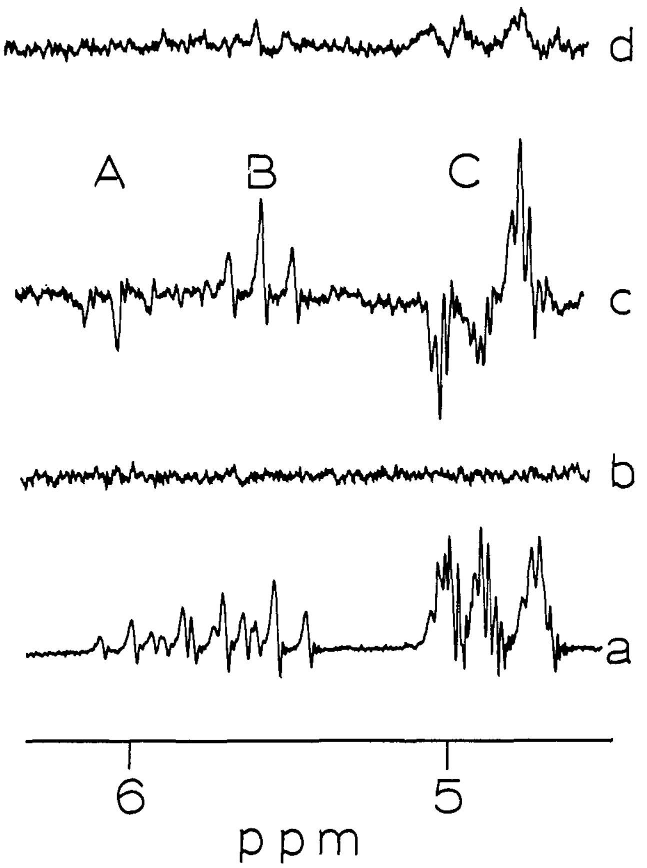

Figure 1.

and emission between δ 4.3 and 6.3 has approximately the same variation with time as that in Figure 1, reaching a maximum in about 1 min.

We see in this spectrum the same enhanced absorption and emission pattern (in regions A, B, and C) as shown in Figure 1c. These undoubtedly arise from butene formed from *n*-butyl bromide and/or *n*-butyllithium (formed by halogen–metal exchange). In addition to these lines there is also the intense line, D, which resembles a dispersion curve or first derivative of the absorption. This peculiar line crosses the base line at the same position as the absorption maximum arising from the vinyl protons of isobutylene. A scan of the *t*-butyllithium solution before addition of *n*-butyl bromide (Figure 2a) shows the spectrum of isobutylene (present as an impurity in commercial *t*-butyllithium). Since isobutylene is present in larger quantities after the reaction than initially, it is reasonable to conclude that isobutylene is the source of this line. The shape of line D is quite insensitive to radiofrequency power and scan rate or direction making it appear unlikely that it arises from a passage effect.[6] One possible explanation for its appearance is that the inhomogeneously broadened isobutylene line (which is a septuplet under high resolution) is undergoing emission in the low-field portion of the multiplet, while the high-field portion exhibits enhanced absorption.

It seems certain that the effects reported here must result from nuclear polarization in a free-radical intermediate[1] which disproportionates to form the olefin from which emission and enhanced absorption are

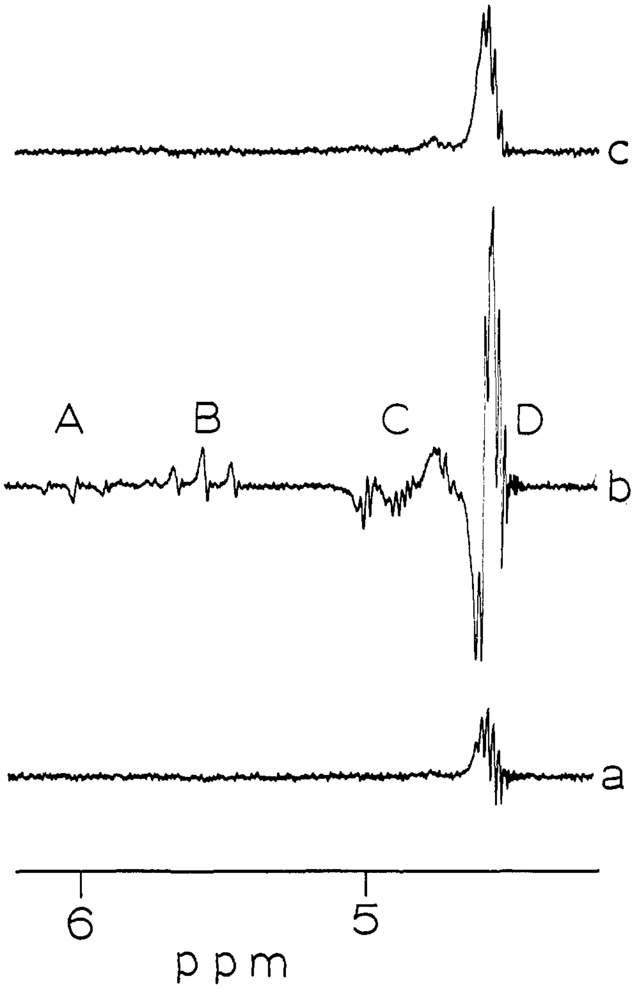

Figure 2.

observed. The formation of 1-butene from *n*-butyl bromide and *n*-butyllithium has been ascribed to just such a radical mechanism by Bryce-Smith.[7] Other protons in the reaction products (for example, the protons on C_4 and C_5 in the *n*-octane which is formed) are also likely to be polarized, but observation of this emission or enhanced absorption is obscured by absorption due to solvent and reagents. Suitable choice of solvents should reveal these effects as well.

Acknowledgments. The Varian A-60A nmr spectrometer was purchased with funds supplied by the National Science Foundation. We wish to thank J. C. Baird and P. H. Rieger for helpful conversations.

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[6] M. Weger, *Bell System Tech. J.*, **39**, 1013 (1960).

[7] D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

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Chemically Induced Dynamic Nuclear Polarization

Sir:

Under the conditions of a conventional, slow-passage, high-resolution nmr experiment, the fractional population difference, or nuclear polarization, p_n, between two Zeeman levels which differ by a single proton spin flip is very nearly that arising from a Boltz-

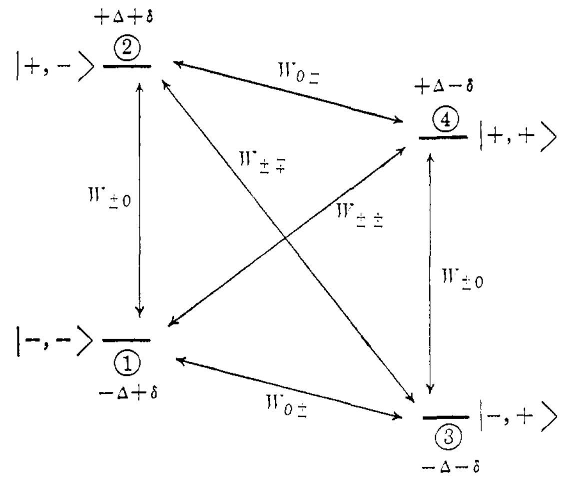


Figure 1. Schematic representation of the energy levels of a spin system consisting of one electron and one proton in a magnetic field. Scalar coupling is neglected. Eigenfunctions, $|m_s, m_I\rangle$, where m_s and m_I are z components of the spin of electron and proton, respectively, and energies, $\Delta = {}^1\!/_2\gamma_e\hbar H_0$, and $\delta = {}^1\!/_2\gamma_H\hbar H_0$, are indicated for each level. W's refer to transition probabilities. Subscripts indicate which spins are flipped in the transition; *e.g.*, $W_{0\pm}$ refers to a transition in which only the nuclear spin flips.

mann distribution and is given[1] by

$$p_n^0 = \frac{n_+^0 - n_-^0}{n_+^0 + n_-^0} = \delta/kT$$

where $\delta = {}^1\!/_2\gamma_H\hbar H_0$, H_0 is the static magnetic field, γ_H is the proton magnetogyric ratio, $n_\pm$'s are populations of the levels, and the superscripts refer to thermal equilibrium. At room temperature p_n^0 for protons in a field of 14 kgauss is approximately 10^{-5} and assures that radiation of the appropriate frequency will be weakly absorbed by the spin system.

The enhanced intensities of nmr absorption and emission observed in reactions of organolithium compounds reported in the preceeding communication[2] are such as to require $p_n \gtrsim \pm 10 p_n^0$. This is clearly a larger change in p_n than may be produced by nuclear–nuclear relaxation processes where the Boltzmann factors driving the level populations never differ appreciably from $1 + 2\delta/kT$. One is therefore forced to conclude that the protons in the emitting species are at some time during the reaction dynamically coupled to an electron spin system.[3] The purpose of this communication is to show that it is possible to produce substantial polarization of protons dynamically coupled to a set of electron spin states which are "saturated" by virtue of their birth with equal populations during a free-radical reaction. This effect is appropriately called chemically induced dynamic nuclear polarization (CIDNP).[3a]

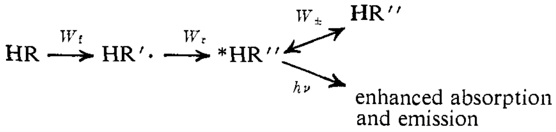
The likelihood that 1-butene is the species responsible for the enhanced absorption and emission during the reaction between n-butyllithium and n-butyl bromide suggests the intermediacy of an n-butyl free radical which then disproportionates to give the olefin.[2,4]

$$C_4H_9Br + RLi \longrightarrow \overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2\cdot + R\cdot + LiBr$$

$$C_4H_9\cdot \longrightarrow C_2H_5\overset{2}{C}H{=}\overset{1}{C}H_2 + C_4H_{10} + C_8H_{18}$$

Presented below is a qualitative explanation of the means by which nuclear polarization may be achieved in a molecule which is formed *via* an intermediate free radical. It should be emphasized, however, that several features of the observed spectra are not predicted by such a simplified model.

The process of polarization may be considered to occur as a proton in the reactant, HR, passes through the "polarizer," HR′·, on its way to product, *HR″, where W_f and W_r are the rate constants for formation



and reaction of the free radical, respectively. Under conditions of steady state in HR′·, the polarization of the protons in the product will depend both on the polarization, P_n, achieved in HR′·, and on the efficiency with which this polarization is transferred to HR″. In the absence of appreciable saturation of the HR″ resonance, the efficiency of transfer depends only on the relative magnitudes of W_f and $W_\pm$, the rate constant for nuclear relaxation in HR″. If $W_\pm \gg W_f$, even a very large polarization in HR′· will be rapidly dissipated in HR″ and p_n will approach p_n^0. As W_f becomes larger relative to $W_\pm$ the rate of change of product polarization is governed by W_f and the efficiency of transfer increases until p_n approaches P_n for $W_f \gg W_\pm$.

The mechanism of nuclear polarization in the free radical is discussed here only for the two-spin case consisting of one electron and one proton. Figure 1 shows an energy level diagram for such a system. At the instant of formation of free radicals, HR′·, from singlet reactants,[5] $n_1 = n_2$ and $n_3 = n_4$, which corresponds to complete saturation of the electron spin-flip transitions. The populations of the four Zeeman levels then decay toward a Boltzmann distribution with a time constant of the order of the electron spin–lattice relaxation time. Once equilibrium is reached

$$P_n^0 = \frac{(n_3 + n_4) - (n_1 + n_2)}{n_1 + n_2 + n_3 + n_4} = \delta/kT = p_n^0$$

and no enhanced polarization results. From this it can be seen that *a necessary requirement for polarization is that W_r be greater than $W_{0\pm}$ and $W_{\pm 0}$*. If, however, the cross-relaxation probabilities $W_{\pm\pm}$ or $W_{\pm\mp}$ are greater than $W_{0\pm}$ and $W_{\pm 0}$, the transitions 4 → 1 or 2 → 3 reach thermal equilibrium before 2 → 1, 4 → 3, 2 → 4, and 1 → 3, and enhanced polarization may occur. In order for polarization to occur, therefore, *it is also necessary that W_r be less than $W_{\pm\pm}$ or $W_{\pm\mp}$*. If the largest transition probability is $W_{\pm\pm}$, levels 1 and 2 become overpopulated relative to 3 and 4 since

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(1) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 133.

(2) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967).

(3) See, for example, R. H. Webb, *Am. J. Phys.*, **29**, 428 (1961).

(3a) Note Added in Proof. The following treatment of nuclear polarization during rapid free-radical reactions is similar to that employed to explain nmr emission from the products of thermal decomposition of peroxides and azo compounds: H. Fischer and J. Bargon, private communication. The name of this phenomenon, which we abbreviate CIDNP, was proposed by H. Fischer.

(4) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

(5) Radical formation by dissociation of photoexcited triplets may require modification of this explanation to include the effects on spin-state populations of large zero-field splittings.

$n_4/n_1 = 1 + (2\Delta - 2\delta)/kT$ at equilibrium, where $\Delta = {}^1/_2\gamma_e\hbar H_0$. Inasmuch as $\Delta/\delta \cong 660$, this may give rise to a large negative value of P_n which, if carried over to the product, would result in stimulated emission. The predominance of $W_{\pm\pm}$ may occur in butyl radicals as a result of the dipole–dipole interaction[6] between the unpaired electron and the protons at the 1 and 2 positions of the radical. This could account in part for the emission lines observed in 1-butene. Where $W_{\pm\mp}$ is the predominant relaxation pathway, states 3 and 4 become overpopulated relative to 1 and 2, and enhanced absorption results. This situation may arise from a time-dependent scalar coupling[7] between a proton and the unpaired electron. This may occur for the protons at the 2 position of butyl radical as a consequence of methylene group rotation which modulates the angularly dependent hyperfine splitting of protons β to an unpaired electron.[8] Such an effect may account in part for the enhanced absorption lines ascribed to 1-butene.

The above qualitative discussion is completely borne out for the one-electron, one-proton case by solution of the classical equations of motion for level populations in $HR'\cdot$ and HR'' in a manner analogous to that employed in treating the steady-state Overhauser effect.[3,9] It is clear, however, that many aspects of both the chemistry and physics of CIDNP remain to be explained. Among other things, the two-spin model cannot explain both emission and enhanced absorption lines from the proton at the 2 position of 1-butene, the presence of enhanced absorption lines from the protons at the 1 position of 1-butene, and the apparent simultaneous emission and enhanced absorption from the isobutylene multiplet.[2] Preliminary calculations[10] make it appear that these effects cannot be explained by a simple extension of the two-spin treatment. Further experimental and theoretical studies of CIDNP phenomena promise to be particularly fruitful because of the predicted sensitivity of these effects to the chemically significant rate constants W_f and W_r.

Acknowledgment. Helpful conversations with J. C. Baird and P. H. Rieger are gratefully acknowledged.

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[6] A. Abragam, *Phys. Rev.*, **98**, 1729 (1955).

[7] A. W. Overhauser, *ibid.*, **92**, 411 (1953); T. R. Carver and C. P. Slichter, *ibid.*, 102, 975 (1956).

[8] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 1963).

[9] R. G. Lawler, unpublished results.

[10] P. H. Rieger and R. G. Lawler, unpublished results.

Book Reviews

Developments in Inorganic Nitrogen Chemistry. Volume 1. Edited by Charles B. Colburn, Rohm and Haas Redstone Research Division, Huntsville, Ala. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. vi + 583 pp. 17.5 × 25 cm. $32.50.

In the Editor's words, "Developments in Inorganic Nitrogen Chemistry" is planned as a two-volume work which "will review in considerable detail the chemical status of one of (the) . . . relatively neglected elements—nitrogen." Volume 1 contains chapters entitled "Bonding in Nitrogen Compounds" (Chapter 1, Michael Green), "The Inorganic Azides" (Chapter 2, A. D. Yoffe), "Developments in the Inorganic Chemistry of Compounds Containing the Sulfur-Nitrogen Bond" (Chapter 3, Margot Becke-Goehring and Ekkehard Fluck), "Nitrogen Ligands" (Chapter 4, W. P. Griffith), "Phosphorus-Nitrogen Compounds (*sans* Cyclic Phosphoronitrilic Compounds)" (Chapter 5, Morris L. Nielsen), "Nitrogen Compounds of Boron, Aluminum, Gallium, Indium, and Thallium" (Chapter 6, John K. Ruff), and "Inorganic Reactions in Liquid Ammonia" (Chapter 7, G. W. A. Fowles). For the most part, the contributions are welcome additions to the review literature since they cover subjects that have not been extensively reviewed relatively recently; however, there are sections in some of the chapters (*e.g.*, Chapter 3) that are essentially repetitions of reviews that are already in the literature. Several of the authors possessed the good judgment to refer to recent reviews which covered subjects that would normally be expected to fall within the purview of their chapter (*e.g.*, the omission of a detailed discussion of borazine chemistry from Chapter 6, the nature of metal-ammonia solutions from Chapter 7, and the phosphoronitrilic compounds from Chapter 5). This is a commendable attempt by the authors to keep from duplicating recent reviews or portions of reviews, especially in view of the spectrum of material which is covered in this volume. Unfortunately, these modest gains are lost elsewhere. There are a number of sections in different chapters which discuss exactly the same subjects (*e.g.*, the ammonolysis of the group III halides which occurs in Chapter 7 on page 538 and in Chapter 6 on page 472; the mechanism of conversion of transition metal–amine complexes into the corresponding amides which appears on page 560 of Chapter 7 as well as on page 250 of Chapter 4). While repetition is sometimes necessary to maintain continuity, a more adamant position by the Editor could eliminate most of this type of duplication. One of the contributions (Chapter 7) covers a subject which has been recently reviewed more extensively (*i.e.*, in "Chemistry in Nonaqueous Ionizing Solvents," J. Jander, Interscience, 1966; "Nonaqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, 1965). The logistics of writing and publishing (being what they are) undoubtedly required that those portions of the various chapters which were, or have been covered, in other places (and that have subsequently been published) be included in this volume.

It appears to this writer that much of the review literature today is an exercise in rearrangement. Authors to contributed volumes become trapped in the delusion (shared on occasion by this writer) that they are really presenting their subject for a unique purpose whereas, in actual fact, they are just casting it in a slightly different light. Thus, the subject of water could appear in collected works devoted to the hydrides of the elements, the oxides of the elements, solvent systems, etc., and each review would probably contain the same basic material except for a slight rearrangement and a shift in emphasis. The price of this type of review gamesmanship is high, for the publisher, the contributors, and the consumer.

In view of this, it is unfortunate that the prospective purchaser is faced with the problem of weighing the positive contribution to the review literature against the material which is essentially repetitious.