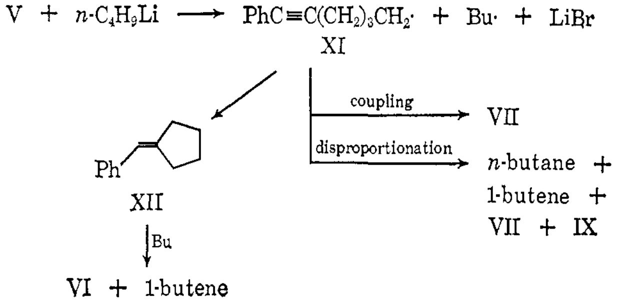
opened for hydrolysis. Addition of D_2O in this case gives only 11% deuterium in VI. Further, if the acetylene VIII is treated with *n*-butyllithium under the same conditions where V reacts completely in 3 min, less than 10% of VIII reacts in 1 hr. Clearly the (intermolecular) addition of a primary organolithium to the phenylacetylene moiety is relatively slow. Even the halogen–metal exchange might not be expected to occur in this system. In an analogous example, Applequist[4] observed no exchange between *n*-propyllithium and ethyl bromide.

These inconsistencies are largely obviated by a reaction scheme in which the cyclizing species is a radical[5] and not a carbanion. If the vinyl radical XII accepted



a hydrogen atom from the butyl radical to give VI and 1-butene, the facts that VI was present in the reaction mixture before hydrolysis and that it incorporated little deuterium on D_2O hydrolysis are explained. The small amount of deuterium incorporation in VI could result from further electron transfer to give the vinyl carbanion by a competing direct carbanionic cyclization or by metalation of VI. 1-Butene is indeed formed in this reaction, and the accompanying communication[6] reports compelling proof (the observation of chemically induced dynamic nuclear polarization CIDNP) that it results from the butyl radical. Further, and by similar proof, the 1-phenyl-5-hexen-1-yne (IX) *must* result from a radical intermediate, and the presence of XI in the reaction solution is established. These facts strongly suggest that cyclization proceeds by a radical pathway.

Bryce-Smith's proposal[7] that the products of the reaction of *n*-butyl bromide with *n*-butyllithium in benzene are best explained by free-radical reactions provides precedence for the suggestion of radical intermediates in the case at hand. Indeed, preliminary investigation of the *n*-butyl bromide–*n*-butyllithium system[6] shows that it also exhibits CIDNP, firmly supporting Bryce-Smith's mechanism. Attempts are in progress, utilizing this effect, to define the generality of this mechanism in other reactions of organometallic compounds.

Acknowledgment. Helpful conversations with R. G. Lawler are gratefully acknowledged. The nmr and mass spectrometers used in the investigation were provided by the National Science Foundation.

---

(4) D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(5) Kandil and Dessy[1b] suggest that radical cyclizations occur with copper derivatives of I and III.

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

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

Harold R. Ward
Metcalf Research Laboratories, Brown University
Providence, Rhode Island 02912

Received August 3, 1967

Nuclear Magnetic Resonance Emission and Enhanced Absorption in Rapid Organometallic Reactions

Sir:

We report here the observation of large positive and negative dynamic polarizations of protons in simple olefins during conventional 60-MHz nmr studies of rapid reactions of organometallic compounds. Although all of the features of the spectra which we have observed are not yet understood, we make this preliminary report because even a simplified analysis[1] of this novel effect, which is appropriately named chemically induced dynamic nuclear polarization (CIDNP), shows that it promises to be of considerable importance in studying reactions involving free-radical intermediates.[1a]

Figures 1 and 2 show two nmr spectra, selected from a number obtained (using a Varian A-60A spectrometer), which clearly show the inverted lines which are a manifestation of stimulated nmr emission. Figure 1b shows a scan of the nmr region from δ 4.5 to 6.3 obtained from 0.5 ml of a hexane solution which is 1.6 *M* in *n*-butyllithium (Foote Mineral Co.), 0.9 *M* in *n*-butyl bromide, and 0.8 *M* in diphenylacetylene.[2] Figure 1c is a scan of the same region 2 min after the addition of 0.2 ml of diethyl ether.[3,4] Repeated scanning of this region shows that the absorption and emission lines of Figure 1c rapidly approach a maximum intensity and slowly decrease, after about 6 min giving the weak absorption spectrum shown in Figure 1d. The spectrum in Figure 1d is consistent with that of the 1 (δ 4.8) and 2 (δ 5.8) protons of 1-butene. The striking correspondence between the positions of the enhanced lines and those of 1-butene (Figure 1a) suggests strongly that this is the chemical species responsible for the intense absorption and emission lines. It is notable, however, that the absorption spectrum arising from the proton at the 2 position in 1-butene consists of four triplets (to first order) while the lines which are enhanced in Figure 1c correspond only to the two outermost triplets. This is an important observation since it shows that the absorption lines are not simply due to an initial surge in 1-butene concentration which then falls to a low value. If this were the case one would reasonably expect to see all of the absorption lines of the olefinic protons.[5]

The spectrum shown in Figure 2b was obtained 30 sec after preparing a pentane solution which was 1.54 *M* in *t*-butyllithium (Lithium Corp. of America) and 0.9 *M* in *n*-butyl bromide. The intensity of absorption

---

(1) R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967).

(1a) NOTE ADDED IN PROOF. Nmr emission has also been observed from the products of thermal decomposition of peroxides and azo compounds by J. Bargon and H. Fischer. We wish to express our gratitude for communication of their results prior to publication.

(2) The presence of a compound containing carbon–carbon unsaturation seems to be necessary to observe CIDNP in this case. When the unsaturated compound is 2-pentyne, the absorption lines shown in Figure 1c become emission lines, and *vice versa*.

(3) The reported time is that at which the scan was started; the scan time for the region of interest was 65 sec.

(4) Ether is known to markedly increase the reactivity of *n*-butyllithium: J. K. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

(5) The chemical logic of such a rapid change in 1-butene concentration might also be questioned in view of the finding that the addition of an olefin such as *cis*-2-pentene, which would compete with 1-butene in most reactions that it might undergo, has little effect on the rate of the reaction and the relative intensities of enhanced absorption and emission.

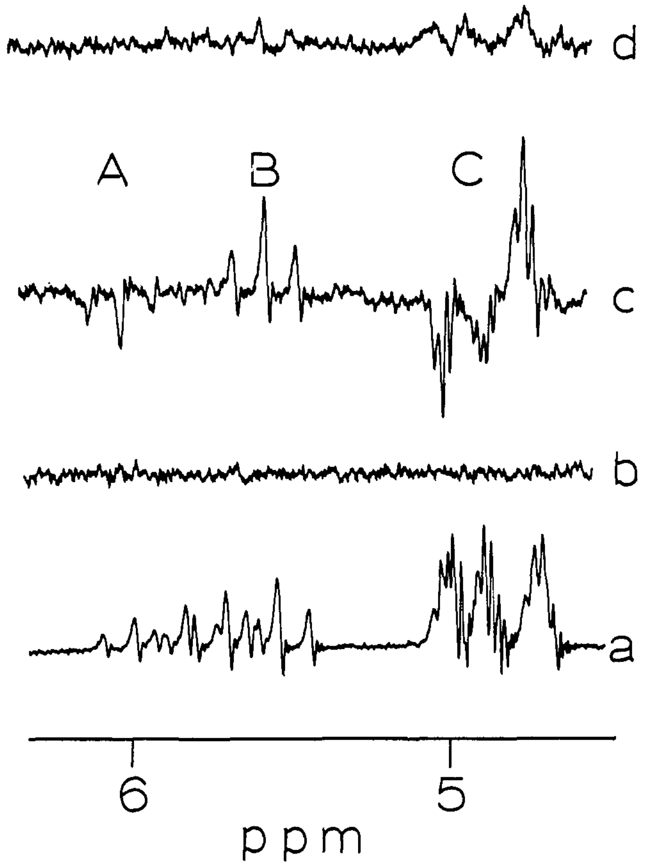


Figure 1.

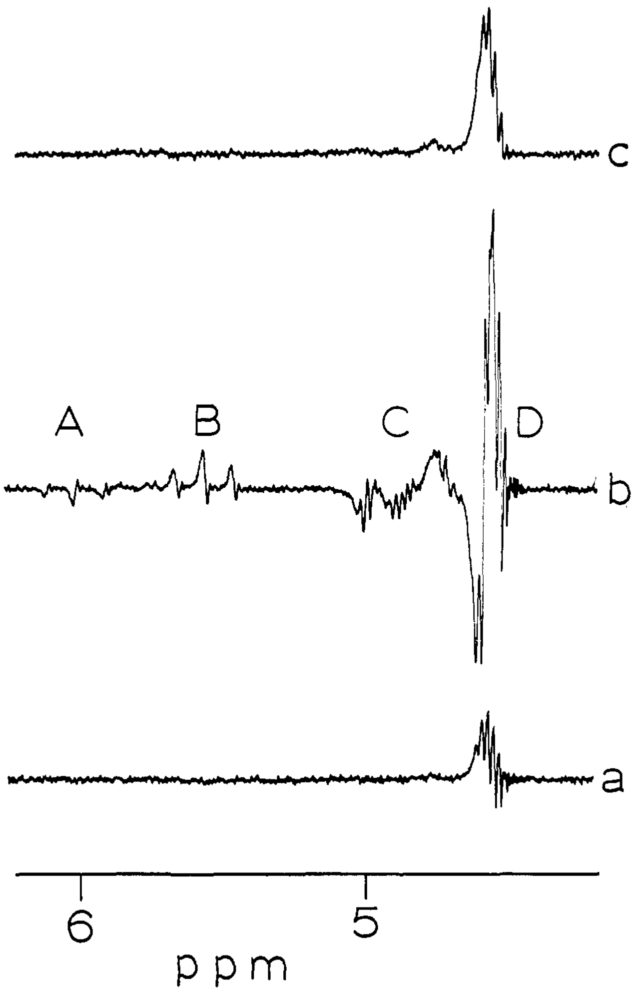


Figure 2.

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 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.

---

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

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

Harold R. Ward, Ronald G. Lawler
Metcalf Research Laboratories, Brown University
Providence, Rhode Island 02912
Received August 3, 1967

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-