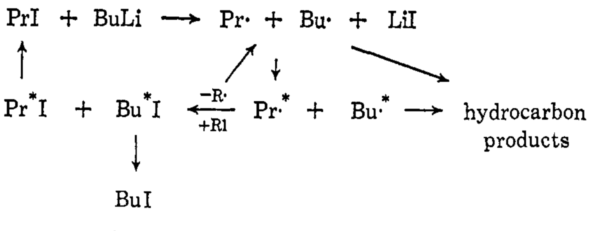
methyl doublet and iodomethine septet of 2-iodopropane (Figure 1b and c) have the same emission–absorption relationship, the reverse of that for the iodomethylene triplet of 1-iodobutane in Figure 1b, c, and e. Negative peaks in the 1.8–0.7-ppm region of Figure 1b may come from 1-iodobutane or hydrocarbon 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

initiation $RI + RLi \longrightarrow 2R\cdot + LiI$ (1)
polarization $R\cdot \longrightarrow R\cdot^*$ (2)
transfer $R\cdot^* + RI \longrightarrow R^*I + R\cdot$ (3)
depolarization $R^*I \longrightarrow RI$ (4)
termination $2R\cdot \longrightarrow R_{-2\mathrm{CH_2}}CH{=}CH_2 + RH$ (5)
termination $2R\cdot \longrightarrow RR$ (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 $-CH_2Li$ 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

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

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

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

$$RLi + R'I \rightleftharpoons RI + R'Li$$

metal exchange process.

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[9] F. S. D'yachkovskii and A. E. Shilov, *J. Gen. Chem. USSR*, **33**, 400 (1963); *Russian Chem. Rev.*, **35**, 300 (1966).

[10] D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963).

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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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[1] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 87, 5250 (1965).

[2] M. Cocivera, *ibid.*, 90, 3261 (1968).

[3] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967).

[4] K. A. Bilevitch, N. N. Pubnov, and O. Yu. Okhlobystin *Tetrahedron Letters*, 3465 (1968).

[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).

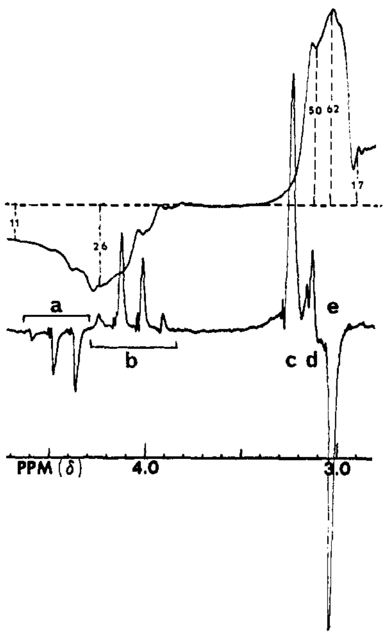

Figure 1. A comparison of the proton magnetic resonance peak and integral scans in the region δ 4.7–2.9 ppm for the reaction of 2-iodopropane with *n*-butyllithium. The emission–absorption septet at δ 4.26 ppm is that of the iodomethine proton in polarized 2-iodopropane, while the 3.17-ppm triplet is the polarized iodomethylene signal from the halogen–metal interchange product 1-iodobutane. Integral values for the peak combinations a–e were used in the calculation of relative changes in amounts of normal and polarized materials present.

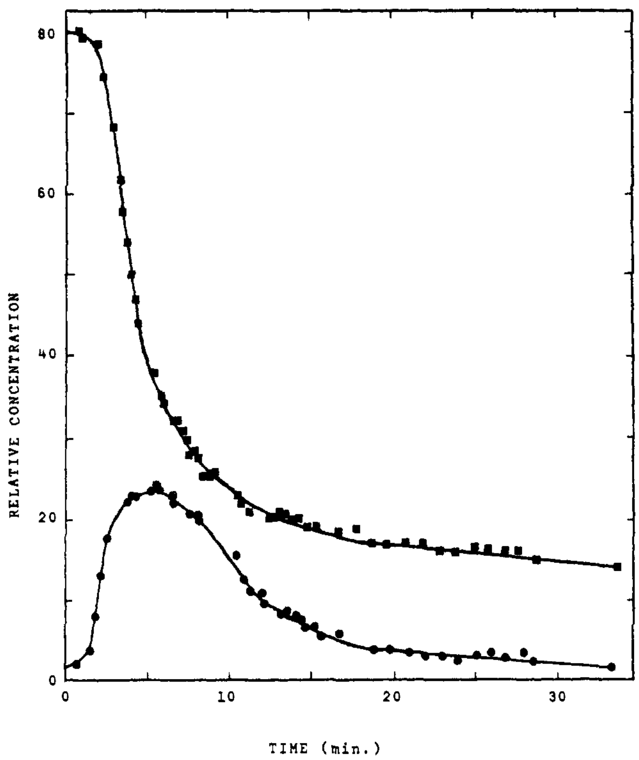

Figure 2. Relative concentration changes with time for the polarized (●) and normal (■) forms of 1-iodobutane from the reaction of 100 μl of the iodide with 0.6 ml of 1.5 *M n*-butyllithium in hexane. Relative integrals for simplified peak areas were assumed in calculation of the concentrations.

Since a theoretical treatment of the polarized species is only available for the pure emission case[7] and since no combination of species with absorption or emission alone would give the observed single signal-peak intensities, the emission–absorption combinations for first-order multiplets are empirically based.[8] At optimum polarization, each signal is composed of two nearly equivalent positive and negative halves, each of which may contain several peaks. The resultant integral for this multiplet is zero.[9] In an A_nX_m multiplet, the symmetrical normal number and location of peaks are retained, but either the upfield or downfield half is negative (*cf.* Figure 1), and the optimum relative intensities, a_{ij}, are duplicated by[8]

$$a_{ij} = (-1)^r c_{i-1,j} + (-1)^s c_{i,j-1}$$

where c_{ij} values are coefficients from the binomial expansion with i as the order and j as the term, and with r and s as any even or odd integers but of opposite quality.[10] Since the relative intensities of a normal species in the same multiplet are given by the coefficients of the binomial expansion, the contribution of normal and polarized species to any measured signal is calculated from the sum of the products of the respective relative intensities[11] with their species concentrations. Reaction dynamics may be followed by repeating the measurements and calculations at various time intervals.

As a test, the method is applied to the iodomethylene pmr signal from a 1-iodobutane reaction with *n*-butyllithium (Figure 2) and to this same band plus the iodomethine signal from a 2-iodopropane reaction with *n*-butyllithium (Figures 1 and 3). First-order coupling in these nine- and seven-spin systems produce a triplet and septet, respectively, with the relative species intensities shown in Table I. The measured integral for individual peaks or groups of peaks in these multiplets compares with the total integral in the triplet (Figure 1c–e) as

$$c = {}^1/_4(\text{BuI}) + {}^1/_2(\text{Bu*I})$$

Table I

	Relative intensities (I)	Absolute total ($\Sigma\lvert I\rvert$)	Species
	Triplet (for CH_2I from *n*-BuI)		
Normal	1:2:1	4	BuI
Polarized	1:0:−1	2	Bu*I
	Septet (for CHI from *s*-PrI)		
Normal	1:6:15:20:15:6:1	64	PrI
Polarized	−1:−4:−5:0:5:4:1	20	Pr*I

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(9) Actual integrals are slightly different because the perturbation in relative transition intensities caused by finite chemical shift separations is similar to that in normal signals.

(10) Even r and s combinations generate the normal intensity pattern for first-order splitting, while if both terms are odd the pure emission pattern obtains.[8]

(11) For this purpose, the relative intensities are normalized with respect to the sum of the absolute values.

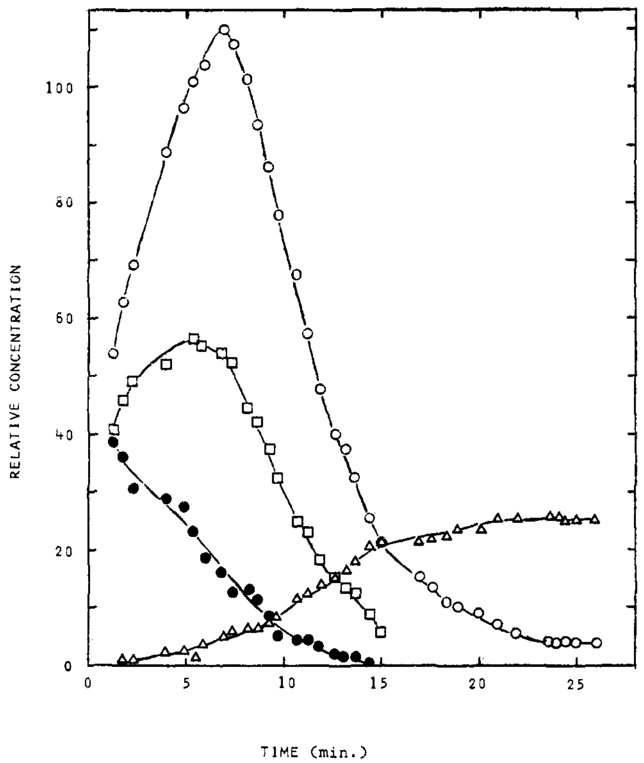

Figure 3. Relative variation with time for the polarized (*) and normal forms of 2-iodopropane (PrI, ●; Pr*I, □) and 1-iodobutane (BuI, △; Bu*I, ○) from the reaction of 150 μl of 2-iodopropane with 0.6 ml of 1.5 *M* *n*-butyllithium in hexane. These values were calculated from the statistical integral intensities for normal spectra and the optimum emission–absorption spectra of the individual species.

and

$$d + e = {}^3/_4(\text{BuI}) - {}^1/_2(\text{Bu*I})$$

where *c*, *d*, and *e* are the measured integrals of the peaks so labeled. The relative concentrations are then

$$(\text{BuI}) = c + d + e$$

$$(\text{Bu*I}) = [3c - (d + e)]/2$$

A similar evaluation of the iodomethine septet gives

$$(\text{PrI}) = a + b$$

$$(\text{Pr*I}) = (11b - 21a)/16$$

Applying the first set or both sets of these equations in Figures 2 and 3, we see that the relative concentrations of polarized species initially increase while the starting iodide is consumed.[5] The 1-iodobutane formed slowly by the halogen–metal interchange between 2-iodopropane and *n*-butyllithium is extensively polarized, but absorption–emission activity in the triplet drops off after 7 min, even though the amount of this material contributing to the normal absorption component continues to increase. These equilibrium steps in reactions terminated by radical coupling and disproportionation give curves for relative changes in polarization or normal contributions of an individual compound which are in good agreement with standard concepts of reaction dynamics.

Since the current method is empirically based, complex multiplets with comparable emission–absorption combination signals[5] may be treated. In addition, the method provides a direct means of comparing rates for radical dissociation–recombination processes with those from optical racemization studies[12] or from other related reactions[13] involving one-electron intermediates if fast reactions[14] can be achieved.

Acknowledgment. The author is indebted to Mr. R. L. Landau for technical assistance and to Marshall University for the opportunity to carry out this work in the absence of financial support.

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Evidence for Homoallylic Stabilization of Carbanions. Reactions of Phosphines with 4-Trihalomethylcyclohexa-2,5-dien-1-ones[1]

Sir:

Although it is well established that carbonium ions can be stabilized by homoallylic conjugation with double bonds,[2] evidence for similar homoallylic stabilization of carbanions by interaction with distant π bonds is scarce. Enchanced acidity of the hydrogens at C-4 in bicyclo[3.2.1]octa-2,6-diene has been ascribed to homoaromatic stabilization of the π-electron system of the anion.[3] Acidity of otherwise unactivated C–H bonds in camphenilone due to formation of homoenolate anions has been demonstrated,[4] but no quantitative estimate of the amount of stabilization afforded the anion by homoallylic resonance has been made.[5]

This communication offers evidence that phosphine derivatives abstract positive halogen ions from 4-trihalomethylcyclohexa-2,5-dienones to give carbanions which are markedly stabilized by homoallylic resonance.

Reaction of the 4-trichloromethylcyclohexadienone **1** with tris(dibutylamino)phosphine in ethanol solution

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(1) Reactions of Cyclohexadienones. XXI. Part XX: *Chem. Commun.*, 1435 (1968).

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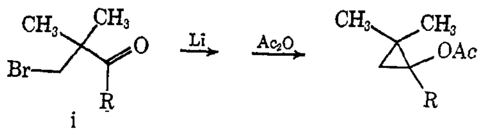
(5) The formation of derivatives of cyclopropanol by the reaction of i with lithium has been described as proceeding *via* a "homoenolate anion" [D. P. G. Hamon and R. W. Sinclair, *Chem. Commun.*, 890 (1968)]. In the absence of any rate data, however, there seems no reason to consider the intermediate lithium reagent to have homoenolate character.



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