# Routes to Nuclear Polarization of Alkyl Iodides during Halogen–Metal Exchange

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THE detection of nuclear polarization after free-radical transfer recently demonstrated[1] that stimulated emission and enhanced absorption in $^1$H n.m.r. spectra are not limited to the primary products from free-radical reactions.[2,3] A rapid halogen–metal exchange occurs[4] during the reactions of alkyl iodides with organolithium compounds.

The emission absorption characteristics of the bands for the spin–spin coupled multiplet splitting of the iodomethylene protons in the ethyl iodide (Figure 1a) produced from ethyl-lithium have a reversed-phase relationship to those of the iodomethine protons in the reacting 2-iodobutane (Figure 1b). The band locations (a and b) and even
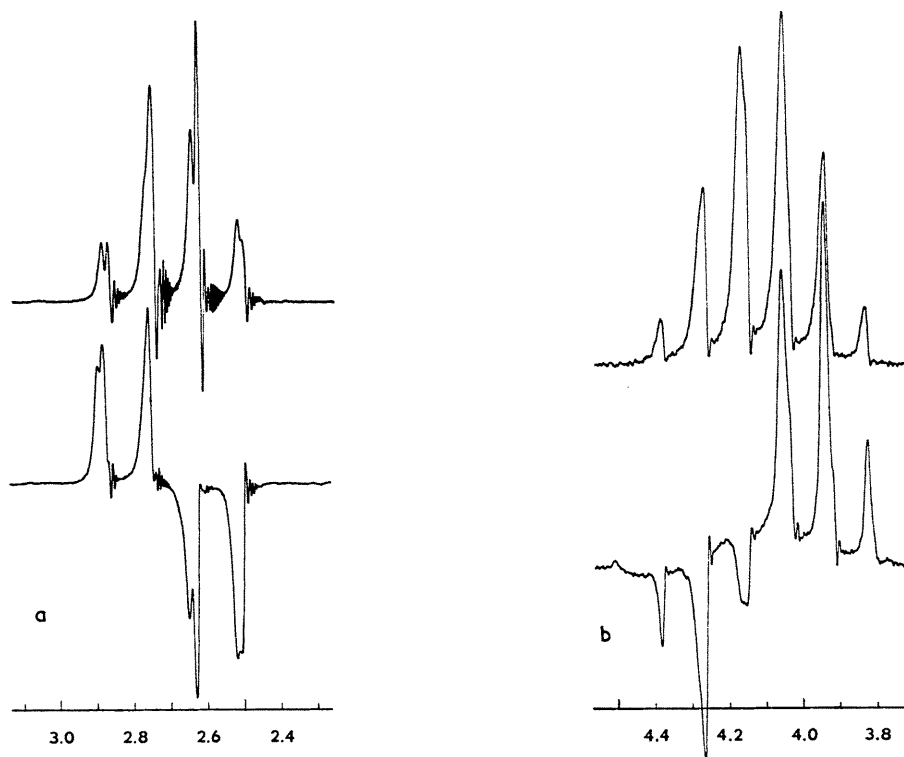


FIGURE 1. A comparison of the normal absorption (upper) and nuclear polarized (lower) proton magnetic resonance bands for the iodomethylene quartet (a) of ethyl iodide and the iodomethine sextet, (b) of 2-iodobutane. Nuclear polarization of these bands occurs during halogen–metal exchange.
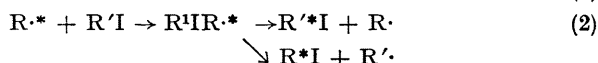
This exchange has been considered as an ionic or molecular-complex process even though the competing reactions which consume starting reagents follow free-radical mechanisms.[5,6] Since nuclear polarization is evident[7] in both iodo-compounds involved in the exchange, it is important to recognize routes which account for the polarization.

second-order splitting (b) of the polarized spectra closely parallel the normal absorption chemical shifts (upper spectra of Figure 1). Although polarization of the new alkyl iodide is evident in the earliest scans, the reacting halide multiplet only gradually increases its polarization to that shown after 5 min. The optimum intensity ratios of
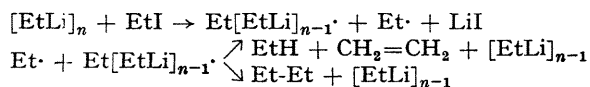
$1:1: -1: -1$ and $-1: -3: -2:2:3:1$ contrast with the normal absorption relationships of $1:3:3:1$ and $1:5:10:10:5:1$. The close-to-optimum appearance of the 2-iodobutane band is near the maximum polarization activity[7] for the 2-iodopropane reaction with n-butyl-lithium in hexane. However the lithomethylene protons show no nuclear polarization in these reactions and in the latter case (Fig 2) have essentially disappeared after 3 min. (e). Since the iodomethylene bands maintain some activity for at least 5 min. after reaching maximum intensity, it would seem that the lithium compound does not participate in the nuclear polarization steps for the iodoalkane.

$$RLi + R'I \rightarrow R\cdot + R'\cdot + LiI$$
$$R\cdot \rightarrow R\cdot^* \qquad (*\text{nuclear polarization})$$
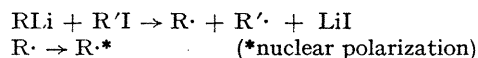
If the free-radicals generated by reaction of iodoalkane and alkyl-lithium become polarized, they may produce active iodoalkanes by exchange with a second alkyl halide molecule either directly (1) or via an intermediate complex (2). The proton signals from the radical or radical–iodoalkane complex are extremely broad[8] and therefore will neither be seen in, nor interfere with, normal $^1$H n.m.r. measurements.

$$R\cdot^* + R'I \rightarrow R^*I + R'\cdot \qquad (1)$$
$$R\cdot^* + R'I \rightarrow R^1IR\cdot^* \rightarrow R'^*I + R\cdot \qquad (2)$$
$$\searrow R^*I + R'\cdot$$

A similar signal broadening may account for the disappearance of the lithomethylene band and the non-appearance of lithomethine peaks. The pertinent free-radical steps leading to hydrocarbon products for iodoethane and ethyl-lithium were:[6]

$$[EtLi]_n + EtI \rightarrow Et[EtLi]_{n-1}\cdot + Et\cdot + LiI$$
$$Et\cdot + Et[EtLi]_{n-1}\cdot \nearrow EtH + CH_2=CH_2 + [EtLi]_{n-1}$$
$$\searrow Et\text{-}Et + [EtLi]_{n-1}$$

In a magnetic field, the unpaired electron of the radical species rapidly aligns itself, to establish an intense local field. The polarizable nuclear spins in this environment couple with the electron spins, causing the nuclear resonance signal to broaden extensively. When this polarized species is rapidly converted into a compound containing only paired electron spins, the polarized nuclei with the slow dipole coupled relaxation time, $T_1$, are capable of radio frequency emission or enhanced absorption as their spins return to thermal equilibrium. Thus the generalized form of the lithium complex $R[RLi]_{n-1}\cdot$ would not be measurable, although its loss of an unpaired electron should make it both observable and polarized. The rapid trapping of other radicals would account both for the alkyl-group

$$R'\cdot + [RLi]_{n-1} \rightarrow R'[RLi]_{n-1}\cdot$$
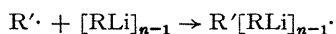
exchange in the lithiated species and the quick disappearance of the alkyl-lithium proton signal.

The complexed radical may now participate in a reaction analogous to (1) or (2) with the overall effect as shown in (1′), of generating the polarized iodoalkane. Evidence for

$$R'I + R[RLi]_{n-1}\cdot^* \rightarrow R^*I + R'[RLi]_{n-1}\cdot \qquad (1')$$
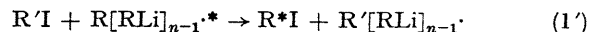
an intermediate with a cyclic four-centred transition state is not inherent in these experiments but an intermediate of this type would be in agreement with other studies.[9] However, low electrical conductivity[6] seems to rule out alternative radical-cations or radical-anions which might be envisaged.
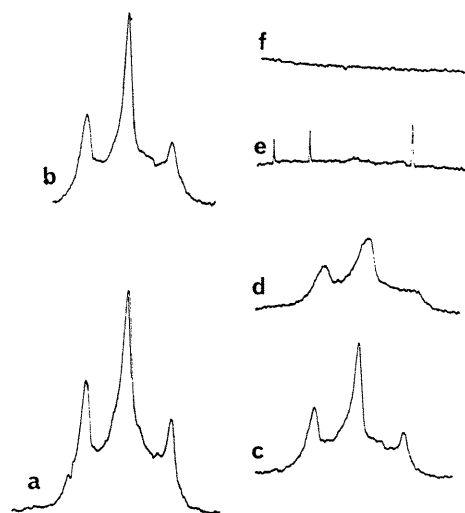


FIGURE 2. *A sequence displaying the disappearance of the lithiomethylene proton magnetic resonance multiplet at $\delta$ $-0.82$ p.p.m.; (a) before halide addition and with scans started at 0.50 (b), 1.25 (c), 2.00 (d), 3.00 (e) and 4.00 (f) min. after the addition of 150 $\mu$l. of 2-iodopropane to 625 $\mu$l. of 1.5 M-n-butyl-lithium in hexane.*

It is not clear whether the maximum of $n = 6$ for normal alkyl-lithium compounds in hydrocarbons[10a] or of $n = 2$ for these compounds in Lewis-base solvents[10b] are the actual forms participating in the equations outlined. However, the polarization results do call for a significant amount of halogen-metal exchange by a free-radical process.

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