Interestingly, the δ_{ij}/δ_{nj} for the borneol–Pr(fod)$_3$ case are found to be independent of the shift reagent concentration in the range $0 \leqslant [L_0]/[S_0] \leqslant 5$ for which there are three possible explanations.

1. No LS_1 complexes are formed at all

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{2([LS_2]/[S_0])_j\Delta_{2i}}{2([LS_2]/[S_0])_j\Delta_{2n}} = \frac{\Delta_{2i}}{\Delta_{2n}} \qquad (2a)$$

2. The bound shifts in the 1:1 and 1:2 adducts are equal, $\Delta_{1i} = \Delta_{2i}$

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{([LS_1]/[S_0] + 2[LS_2]/[S_0])_j\Delta_{1i}}{([LS_1]/[S_0] + 2[LS_2]/[S_0])_j\Delta_{1n}} = \frac{\Delta_{1i}}{\Delta_{1n}} \qquad (2b)$$

3. The bound shifts in the 1:1 and 1:2 adducts differ, but are proportional to each other, $\Delta_{2i} = C\Delta_{1i}$

$$\frac{\delta_{ij}}{\delta_{nj}} = \frac{([LS_1]/[S_0] + 2C[LS_2]/[S_0])_j\Delta_{1i}}{([LS_1]/[S_0] + 2C[LS_2]/[S_0])_j\Delta_{1n}} = \frac{\Delta_{1i}}{\Delta_{1n}} \qquad (2c)$$

There is no compelling reason why no LS_1 adducts should be formed. It also seems unlikely that the Δ_{1i} and Δ_{2i} should be exactly equal. One might expect the metal–oxygen distance to be somewhat larger in 2:1 adducts and consequently the Δ_{2i} to be smaller than the Δ_{1i}. It is conceivable that a small stretching of the metal–oxygen distance can give a new set Δ_{2i} of bound shifts, somewhat smaller than the Δ_{1i}, which remain correlated well enough with the Δ_{1i} for eq 2c to be a good approximation. A definite answer requires a multiparameter fit to the experimental data (3). The important result for structure elucidation purposes, however, is the fact that in each of the three cases mentioned above there is a direct correlation between induced and bound shifts.

Thus the following tentative conclusion may be reached: if the ratios of the induced shifts are found to be independent of the shift reagent concentration, there is a direct correlation between induced and bound shifts; *i.e.*, no multiparameter fit is required in this case. Whether it is generally the case that the ratios of the induced shifts are independent of the shift reagent concentration whenever LS_2 complexes are formed is presently under investigation.

Acknowledgments. We thank Professor B. L. Shapiro for making his manuscript available to us prior to publication. Financial support from the National Research Council of Canada is gratefully acknowledged.

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Chemically Induced Dynamic Nuclear Polarization in the Presence of Paramagnetic Shift Reagents

Sir:

Nmr spectra showing the chemically induced dynamic nuclear polarization[1] (CIDNP) phenomenon are often difficult to analyze, because many different reaction products can occur, and their resonance lines overlap frequently. The usual measures taken in nmr spectroscopy to separate overlapping resonances, like changing the solvent or increasing the magnetic field strength, do not qualify for most CIDNP studies. They fail because the chemistry of the reactions often changes with the solvent, and the CIDNP enhancement factors decrease with increasing magnetic fields.[1,2]

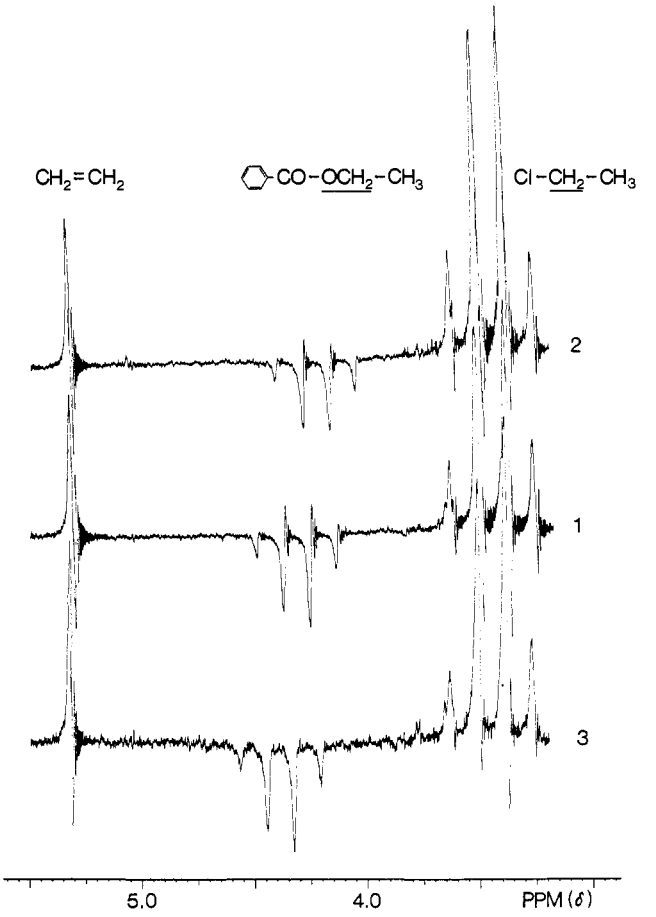

Figure 1. CH_2 resonances during the decomposition of BPPO in CCl_4 at 60 MHz without shift reagent (1), with Pr(fod)$_3$ (2), and with Eu(fod)$_3$ (3).

We have investigated the possibility of simplifying the analysis of CIDNP spectra with paramagnetic shift reagents and found the following important result. In spite of the fact that increasing concentrations of paramagnetic additives decrease the CIDNP intensities rapidly,[1] paramagnetic shift reagents, for example the lanthanides Eu(fod)$_3$ and Pr(fod)$_3$,[3] can successfully be used to selectively shift the resonance lines of CIDNP—showing products with atoms containing lone-pair electrons like O, N, S, and P.

As a characteristic example we have chosen the thermal decomposition of benzoyl propionyl peroxide (BPPO) in CCl_4 as the solvent. The details of this decomposition have been described elsewhere.[4] Figure 1.1 shows the CH_2 resonances of the main products ethylene, ethyl benzoate (I), and ethyl chloride. In the presence of Eu(fod)$_3$ the CH_2 quartet of I is shifted downfield, whereas the other product lines remain unchanged (Figure 1.2). Similarly in the presence of Pr(fod)$_3$ only the quartet of I is shifted upfield (Figure 1.3). The lanthanide-induced shifts of the ester quartet

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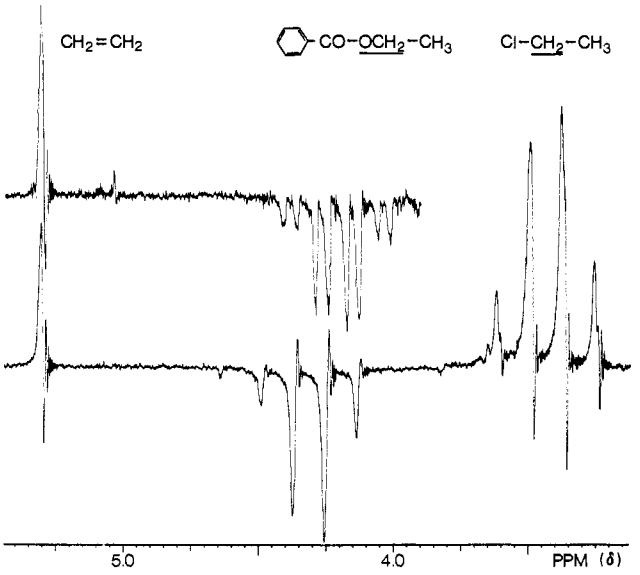

Figure 2. CH_2 resonances during the decomposition of a mixture of BPPO and CBPPO in CCl_4 without shift reagents, and in presence of $Pr(fod)_3$ (upper trace).

in Figure 1.2 and 1.3 correspond to a molar ratio between the shift reagent and the ester of 7.5×10^{-3}. Whereas such low concentrations of the shift reagents cause only small reductions of the CIDNP intensities of the complexing products, higher molar ratios ($>5 \times 10^{-2}$) will eventually quench them.

The CIDNP intensities of the other products which complex less are also reduced less, so that adding shift reagents can be used to simplify CIDNP spectra by removing certain enhanced resonance lines selectively. However, this means a loss of information, and shifting the resonance lines while retaining their CIDNP is more desirable. We found that even if products give coinciding resonances, shift reagents may lift their degeneracy by complexing better with one of the products. We have demonstrated this fact by decomposing equivalent amounts of *m*-chlorobenzoyl propionyl peroxide (CBPPO) and BPPO in CCl_4. Without shift reagents the emission quartets of ethyl *m*-chlorobenzoate (II) and I have identical chemical shifts and coupling constants (Figure 2 lower trace). Upon addition of $Pr(fod)_3$, the quartet of I is shifted to higher magnetic fields more than that of II so that the two resonances can be distinguished (Figure 2 upper trace). Figure 3 shows the case where I was added to a solution of decomposing CBPPO. Whereas I gives an unenhanced absorption quartet, the reaction product II causes an emission quartet. Normally the two quartets overlap and, as their relative intensities have been chosen so that they are equal during the decomposition, emission and absorption cancel (Figure 3.1). In the presence of $Eu(fod)_3$ the degeneracy is removed and the emission and the absorption quartet can be analyzed separately (Figure 3.2). Similarly, $Pr(fod)_3$ shifts the absorption quartet more upfield than the emission quartet (Figure 3.3).

During the reactions the line positions of the shifted lines change, *i.e.*, they approach their original chemical shifts. This is partly explained by the change in ratio between shift reagents and the products with increasing conversion of the reactants. Unfortunately, as some lines move, time-averaging methods cannot be used if

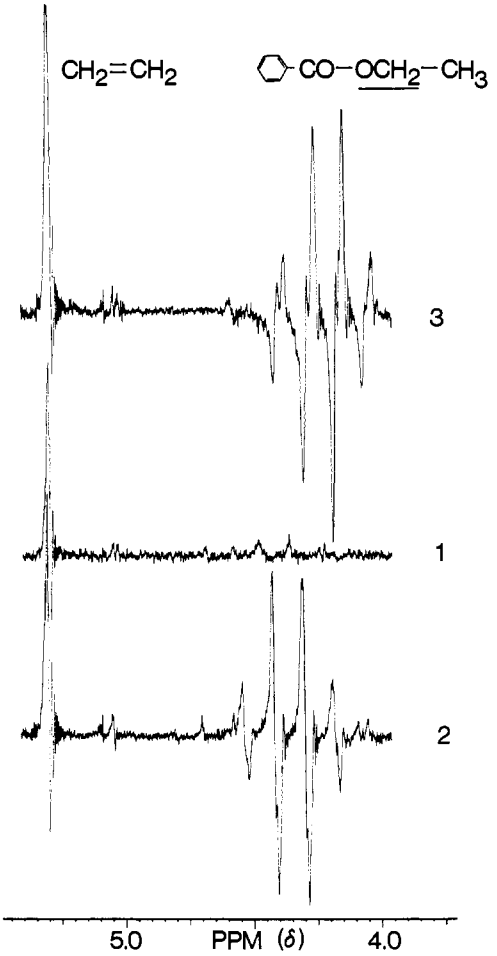

Figure 3. Emission quartet of ethyl benzoate and absorption quartet of ethyl *m*-chlorobenzoate without shift reagent (1), with $Eu(fod)_3$ (2), and with $Pr(fod)_3$ (3).

shift reagents are present. However, the actual line positions reflect the extent of conversion of the reactants. Therefore, the line positions, if calibrated, allow the determination of enhancement factors, which are often difficult to obtain otherwise.

Shift reagent poisons, for example acids, resulting from some reactions as products have to be avoided, since they destroy the lanthanides. Thus during the decomposition of certain benzoyl peroxides a precipitate is formed, and the CIDNP is quenched. The fate of the shift reagents can conveniently be studied by following the shifts of their own resonances during the reactions.

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Received June 1, 1972

Structure and Absolute Stereochemistry of Everheptose

Sir:

Everninomicins[1] are oligosaccharide antibiotics and perhaps related to curamycins[2] and avilamycins.[3] Due

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