the signal direction[6,12–14] of the polarized products. For example, the multiplet phase of 1,1,2-triphenylethane[10] (formed *via* a pair initially of triplet multiplicity) was altered to E/A when it was generated from an azo compound (*via* a pair initially of singlet multiplicity).[11] Products derived from phenyl–benzoyloxy[12,13] or chloromethyl–trichloromethyl radical pairs[6] showed alterations of signal directions, when the precursor multiplicity was changed by triplet sensitization. Finally, the benzylic emission signals observed during pyrolysis (singlet reaction) of various hydroxyphenanthrone derivatives were altered when these compounds were photolyzed (triplet reaction).[14]

In the light of these results one would have expected an E/A multiplet during the reaction of $^{1}CH_2$ with toluene to form ethylbenzene, if radical pairs with separations and lifetimes large enough to permit exchange ("singlet–triplet mixing") were involved. The failure to observe any polarization in this reaction indicates a fundamentally different path for the singlet reaction, namely the one-step insertion process previously proposed by Doering and Prinzbach.[5,15]

Richardson, Simmons, and Dvoretzky[17] had suggested that in the analogous gas-phase reactions $^{1}CH_2$ (one-step insertion) and $^{3}CH_2$ (abstraction) attack carbon–hydrogen bonds in different ways. In contrast, DeMore and Benson[18] favored a single reaction mechanism for both species. In their scheme abstraction is chiefly associated with a high-energy precursor. The CIDNP results presented here, the selectivity exerted by triplet methylene,[6b,c] and the almost total lack of selectivity displayed by the singlet species[2] clearly demonstrate that in solution the reaction mechanism is determined by the spin multiplicity and not the energy of the precursor.

The concept of fundamentally different reaction mechanisms for the reactions of $^{1}CH_2$ and $^{3}CH_2$ is in full agreement with results obtained with various other substrates such as chloroform,[6b] 2-chlorobutane,[6c] 2-chloro-2-methylpropane, cyclohexane-d_{12}, and isobutylene. Details of the reactions of CH_2 with these substrates will be discussed in a full paper.

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Intensity Decontrasting in Pulse Fourier-Transform Carbon-13 Nuclear Magnetic Resonance. Effective Signal–Noise–Time Enhancement by New Use of Paramagnetic Additives

Sir:

Carbon magnetic resonance finds rapidly increasing application for complex molecules.[1] Even with the pulse Fourier-transform (PFT) technique, the signal–noise–time problem, determined by the *smallest peaks* in a spectrum, is serious. The intensity of the single lines in proton-decoupled spectra is the outcome of opposing factors. On one hand, favorable nuclear Overhauser enhancement (NOE) occurs mainly for the proton-substituted carbons. On the other hand, saturation decreases the intensity of carbons having long relaxation times, typically those without proton substituent and with minimum NOE. Saturation can be decreased or avoided by driven equilibrium Fourier-transform (DEFT)[2] or spin–echo Fourier-transform (SEFT)[3] techniques or by employing long time spaces between pulses, a time-consuming luxury reserved for special experiments. Typical PFT cmr employs either a short rest time (*e.g.*, 1.5 sec) or no rest time between the end of the scan and the next pulse, leading to extensive saturation of quaternary, substituted aromatic and chlorine- and especially deuterium-bearing carbons. The result is a high "contrast" spectrum, where the intensity ratio between equimolar carbons can easily reach 1:10. This contrast is structurally diagnostic but leads to mistaking peaks for noise and *vice versa*.

We reasoned that a means of correcting this situation is available in the form of odd-electron, paramagnetic additives.[4] Shifts[5] are comparatively small and relaxation enhancement of nuclei is efficient when the electron spin has long relaxation time,[6] *e.g.*, in stable organic radicals and compounds of several members of the first transition metal series. Such additives have been used for selective and nonselective influencing[7,8] of relaxation time, T_1, and for the more specific and relevant decrease and elimination[9] of the NOE enhancement in continuous wave (CW) cmr. We expected that for typical PFT cmr the decrease of saturation experienced by the weaker carbons would be of greater significance than the decrease of NOE enhancement for the stronger carbons. Selectivity of the decrease of relaxation time is to be avoided in the initial and general use by employing a nonpolar, unreactive, nonassociating agent (*e.g.*, with fully occupied coordination sphere and hydrocarbon or fluorocarbon surface); later use will surely exploit specific interactions for diagnostic purposes, as is done for biomolecules with metal ions.[8]

Our preliminary experiments with CW pmr showed that β-diketonates of Cu^{2+} and Fe^{3+} at low concentration in CCl_4 and $CHCl_3$ with a mixture of a large variety of typical organic substrates showed no noticeable chemical shift, but gave nonselective broadening (except for the OH peak). A concentration of the paramagnetic agent was selected which broadened proton peaks to $\sim$2.5-Hz width at half-height, knowing

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Table I. Comparison of Carbon-13 Shifts and Intensities of Two Identical Samples One of Which Contained Paramagnetic Additive (~0.01 M)

	Spectrum of control sample			Spectrum of treated sample		
Assignments	Memory address no.	δ_{CS_2}, ppm	Ht, mm	Memory address no.	δ_{CS_2}, ppm	Ht, mm
Tetramethylsilane	1939	193.1	20	1938	192.9	26
Hexamethyldisiloxane	1920	191.0	63	1920	191.0	76
Methylene	1555	151.6	135	1555	151.6	91
Methyl ester	1458	141.2	68	1458	141.2	66
Chloroform	1218	115.3	72	1217	115.1	189
Aromatic, para	759	65.7	113	759	65.7	109
Aromatic, ortho	745	64.2	168	745	64.2	231
Aromatic, meta	738	63.5	246	738	63.5	242
Aromatic, substituted	691	58.4	28	691	58.4	111
Carbonyl	345	21.1	58	346	21.2	109
Noise			5			5

that the cmr spectrum would have 2.44 Hz per address, and assuming that the ^{13}C peaks would not be more broadened than the ^1H peaks.

Samples were prepared consisting of 654 ± 1 mg of methyl phenylacetate, 300 ± 1 mg of hexafluorobenzene, 159 ± 1 mg of hexamethyldisiloxane, 80 ± 2 mg of tetramethylsilane, and 1.00 ml of spectroquality chloroform. To one of these, 7 mg of iron tris-(pentane-2,5-dionate) was added. The samples were run at probe temperature (45° inside sample) in 10-mm tubes on a Bruker HX-90 spectrometer with a 15-in. magnet, pulse unit, broad-band ^1H decoupler, and fluorine lock. In ~13 min 2048 pulses of 20-μsec duration were given, with 0.4096-sec scanning time and no additional rest time between pulses. The range of 5000 Hz was covered by the 2048 addresses of the transformed spectrum. All other adjustments of the spectrometer and accessories were also kept constant.

Table I lists the spectral data. It shows that: (1) shifts are constant within one memory address absolute; (2) the height of CO, substituted aromatic, and $CHCl_3$ carbon increases dramatically; (3) the height of methylene carbon decreases to about the level of the above ones; (4) no noticeable broadening occurs; (5) a medium effect rather than specific association operates, as the reagent is unbiased toward the COO carbon *vs.* the less coordinating environment of the substituted aromatic carbon.

Further work is to be directed toward determining the best compromise between degree of enhancement of the intensity of weak carbons, loss of NOE enhancement, peak broadening, relaxing efficiency, inertness, and removability of additive, etc.

The results so far are of great practical benefit, since *the weakest, most easily missed peaks are enhanced* by adding only a trace of additive. This tool allows (1) shorter accumulation time (machine time) for a given amount of sample or (2) a smaller absolute amount of or more dilute sample, and (3) indirect benefits, *e.g.*, easier retention of spectrometer lock, since either pulsing time is reduced, or more lock compound (a bad solvent for large molecules) can be employed when the substrate concentration is lower.

The preferred strategy for retaining the diagnostic value of high contrast involves (1) pulsing the untreated sample just enough time to see the intense peaks, then (2) adding the agent and pulsing to locate every carbon. The two together may take less time and offer more and more certain structural information than running the conventional PFT cmr alone to satisfactory signal-to-noise ratios.

The value of equalized intensities for tackling mixtures of unknowns and for quantitative analysis is evident.

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A Photochemical Reaction Induced by Infrared Radiation. The Kinetics of Planar–Octahedral Interconversion in a Nickel(II) Complex

Sir:

Photochemical reactions induced by infrared radiation are rather rare on account of (i) the low energy per quantum in comparison with that normally required to bring about chemical change and (ii) the efficient degradation of vibrational energy into translational energy, particularly in the liquid phase. However, if the irradiation power is high, as in a neodymium Q-switched laser (1.06 μm), and the detection system sufficiently sensitive, it is sometimes possible to observe chemical change in systems having a sufficiently low energy requirement. A recently reported example[1] is the ionic dissociation of *vibrationally* excited water, $H_2O^* \rightarrow H^+ + OH^-$, the reverse recombination being detected conductometrically (τ = 42 μsec at 296°K). We now report an example of a photochemical reaction initiated by 1.06-μm radiation involving the formation of an *electronically* excited species in the primary step.

The species concerned is the blue octahedral complex formed between nickel(II), 1,4,8,11-tetraazaundecane (2,3,2-tet), and water. In aqueous solution this exists mainly as the trans configuration in equilibrium[2] with the yellow, unhydrated, square-planar configuration (λ_{max} 440 nm).

$$\mathrm{Ni(2,3,2\text{-}tet)(H_2O)_2^{2+}} \rightleftharpoons \mathrm{Ni(2,3,2\text{-}tet)^{2+}} + 2\mathrm{H_2O} \quad (1)$$

A 0.1 M solution of the complex chloride was irradiated at 23° with a 2-J (incident energy), 30 nsec, Q-switched pulse of 1.06-μm radiation from a neo-

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