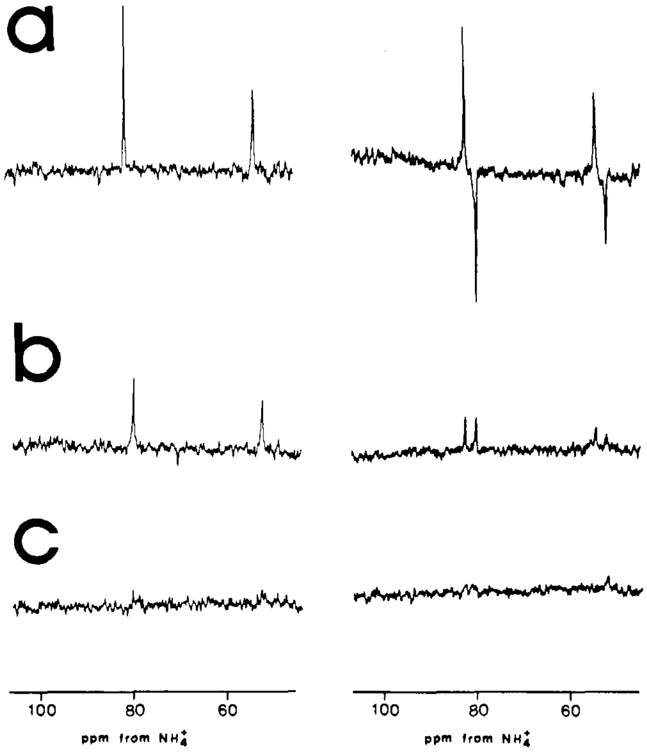

Figure 2. Proton decoupled and coupled spectra of a 1.0 M solution of benzyloxycarboxylglycylglycine methyl ester in deuteriochloroform, obtained (a) using the INEPT pulse sequence, (b) with nuclear Overhauser enhancement, and (c) without Overhauser enhancement. With the exception of the decoupled spectrum c all spectra represent the result of 10-min time averaging; the decoupled spectrum c is equivalent to that which would be obtained in 10 min in the absence of the nuclear Overhauser effect. Chemical shifts measured with respect to saturated aqueous ammonium nitrate were 81.6 and 53.8 ± 0.1 ppm downfield for peptide and amide resonances, respectively.

signal enhancement was obtained. The sensitivity improvement factors for proton coupled and decoupled spectra were 15 and 8, respectively, over the unenhanced spectra, and 4 and 2, respectively, over spectra obtained with nuclear Overhauser enhancement. The INEPT method is thus particularly suited to the measurement of proton coupled spectra and to the study of systems with less than the full nuclear Overhauser effect, offering in some cases an improvement in total acquisition time of more than two orders of magnitude.

Cross-polarization methods in solution cannot solve all ^{15}N sensitivity problems, relying as they do on the existence of resolvable proton-nitrogen couplings which may not be available for unprotonated nitrogens or in chemically exchanging systems. Nevertheless the great sensitivity gains possible in suitable systems make cross polarization a very attractive proposition; the INEPT pulse sequence offers a simple way of making this available on existing instrumentation. Many variations on existing techniques are possible using an INEPT sequence as a preparation, including ^{15}N relaxation studies. A related pulse sequence has been used for detecting multiple quantum transitions with enhanced sensitivity,[12] while recently a modified INEPT sequence has been used in the first two-dimensional NMR experiments on ^{15}N.[13]

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Analysis and Optimization of Gas-Phase Reactions. 13.[1,2] Silatoluene

Sir:

Silabenzene and its derivatives, repeatedly postulated as reaction intermediates[3-5] and one of which was finally generated unambiguously,[3] according to the literature[6] have so far eluded spectroscopic detection and characterization. According to quantum chemical calculations,[7-10] the parent compound is expected to be a thermodynamically stable[7] singlet[8] molecule with Si-C distances shortened by ~0.1 Å[8-10] with respect to the single bond length and should exhibit a first ionization potential of ~8.2 eV.[11]

After numerous futile attempts, tenacity, and especially a newly designed heated inlet system, which allows gas-phase flow pyrolysis of compounds to take place at ~1 cm above the ionization region of the photoelectron spectrometer,[12] helped to achieve the goal. Starting from 1-methyl-1-allyl-1-silacyclohexa-2,4-diene,[3,4] with propene as an advantageous leaving molecule[13] in the thermolysis,[4] the change in the PE spectroscopic molecular fingerprints upon pyrolysis (Figure 1) reveals two bands at 7.7 and 9.1_5 eV. A third band centered at 10 eV coincides with the first band of propene (Figure 1).

The two low-energy bands emerging in the PE spectrum of the pyrolysis mixture are assigned to the lowest radical cation states of silatoluene on the basis of the following arguments. A low first ionization energy is predicted according to first-order perturbation of benzene—inserting a silicon center should yield for C_5H_5SiH 8.2 eV,[11] and additional attachment of a methyl group should further lower the ionization energy by ~0.4 eV[14]—to amount to ~7.8 eV for $C_5H_5SiCH_3$. In contrast, the second ionization potential should remain approximately constant and be comparable to $IE_2 = 9.15$ eV of toluene.[14] Both expectations are in full accord with a Koopmans correlation, $IE_n = -\epsilon_j^{SCF}$, of MNDO eigenvalues (Figure 1).

Additional support is supplied by mass spectroscopic investigation: the oven used in the PE spectrometer heated inlet system could be fixed at a distance of ~18 cm from the ionization chamber of a Varian MAT CH7. The predominant

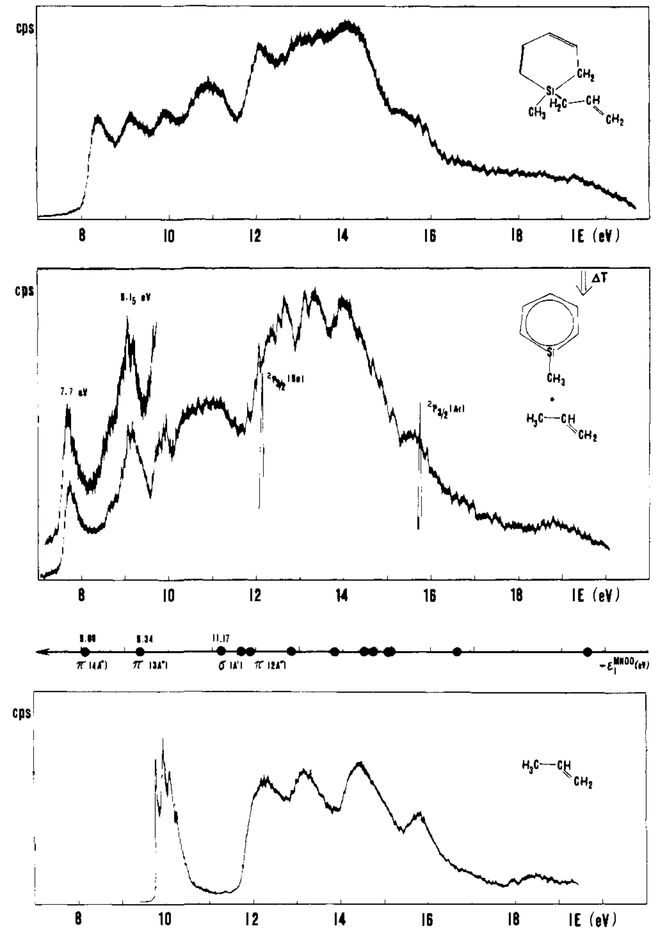

Figure 1. He I PE spectra of 1-methyl-1-allyl-1-silacyclohexa-2,4-diene, of the pyrolysis mixture at 1100 K oven temperature and of propene (calibration with $^2P_{3/2}$ states of Xe and Ar).

changes upon heating are that the parent peak (*m/e* 150) vanishes, the 100% peak (*m/e* 109) assigned to the primary fragmentation radical $C_5H_6SiCH_3^{+\cdot}$ is reduced to 10% intensity, and peaks due to propene (*m/e* 42, 100%; *m/e* 41, 99%) appear. In spite of the rather large distance between heating and ionization zones, a peak at *m/e* 108 (12%), which presumably arises from silatoluene ($C_5H_5SiCH_3$), is also observed upon heating.[15]

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Criteria for Establishing the Existence of Nuclear Spin Isotope Effects

Sir:

Several years ago it was pointed out[1] that the radical pair model, which was then emerging as the correct explanation for the phenomenon of chemically induced dynamic nuclear polarization (CIDNP), carried with it several corollary predictions regarding chemical reactivity. Among these was the possibility of detecting a kinetic isotope effect arising from differences among the nuclear magnetic moments, rather than the masses, of nuclides. This proved to be a seductive idea and was followed by several reports[2] of such effects in reactions usually considered to proceed via radical pair intermediates. Given both the proliferation of modern analytical methods for determining isotope ratios and current high interest in isotope enrichment,[3] it is to be expected that reports of such isotope effects will increase in frequency. The purpose of this communication is to point out that there exist at least three types of criteria for distinguishing true nuclear spin isotope effects from unusually large (but nevertheless interesting and possibly useful) mass isotope effects.[4]

I. It is both expected on theoretical grounds and observed[5] that the magnitude of a mass isotope effect varies monotonically with the atomic weight of the isotope. There is, of course, no correlation between the atomic weight and nuclear magnetic moment of an element. It therefore follows that *a nuclear spin isotope effect should be manifested as an extremum in a comparison of the isotope effects measured for at least* **three** *suitably chosen isotopes with different magnetic moments.* There are numerous examples of such suitable "isotope triplets" for elements which are constituents of common radical pair precursors. These include cases where one ($^{12}C/^{13}C/^{14}C$; $^{16}O/^{17}O/^{18}O$; $^{32}S/^{33}S/^{34}S$; $^{206}Pb/^{207}Pb/^{208}Pb$), two ($^{117}Sn/^{118}Sn/^{119}Sn$),[6] or three ($^1H/^2H/^3H$) of the isotopes have nuclear spins. The isotopes of hydrogen, while chemically attractive, are less suitable than the other examples because the effect arises from differences among the *magnitudes* of nuclear moments of the isotopes rather than the presence or absence of a nuclear spin.

II. The radical pair theory of CIDNP predicts[7] that *the yield of products from a radical pair containing a magnetic nucleus*