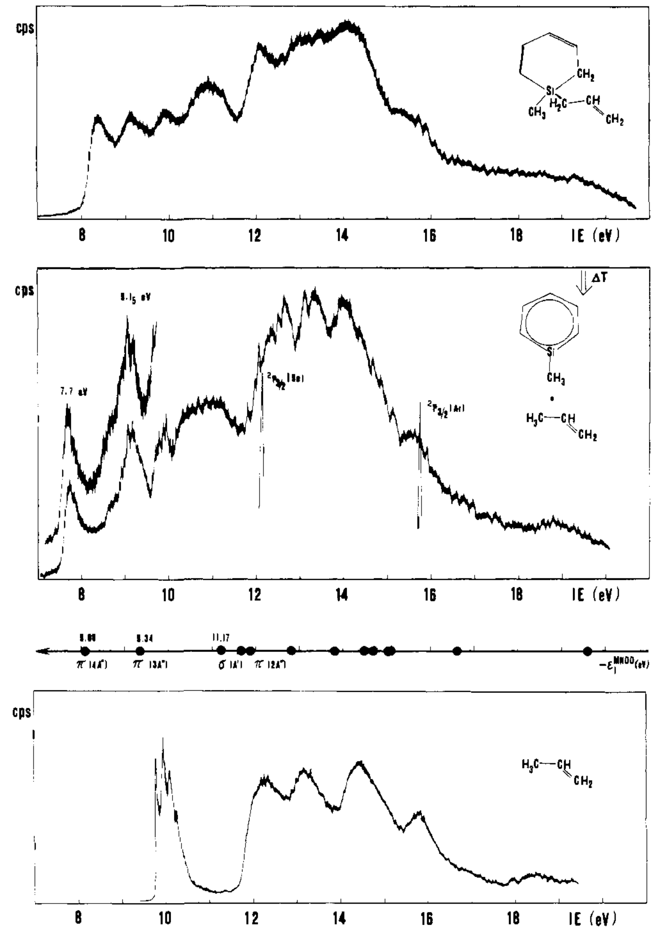

Figure 1. He I PE spectra of 1-methyl-1-allyl-1-silacyclohexa-2,4-diene, of the pyrolysis mixture at 1100 K oven temperature and of propene (calibration with $^2P_{3/2}$ states of Xe and Ar).

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* *should be magnetic field dependent with an extremum near the comparatively low (<1 KG) field corresponding to the hyperfine coupling between the nucleus and the unpaired electron in the radical.* It should be emphasized that this magnetic field effect involves a direct correlation between the magnitude of the hyperfine splitting and the field dependence. It is qualitatively different from the comparison of isotope enrichments in very low and very high fields which has so far been offered as evidence for a nuclear spin isotope effect.[2a,c] The connection between nuclear spins and the (often intriguing) chemical effects of high magnetic fields does not yet appear to be well established.[8] For example, recent calculations[7] show that, at least for a symmetrical triplet-born radical pair with a single $I = {}^1/_2$ nucleus, the isotope effect should be the same in very low and very high fields but still pass through the extremum described above.

III. The theory of isotope effects has progressed to the point where it is feasible to design experiments in which *the spin and mass isotope effects anticipated on chemical grounds should be in opposite directions.* This does not appear to be the case for recently reported photoinduced carbon-13 enrichments in dibenzyl ketone[2a,c,e] and phenylbenzoate.[2b] In both cases the heavier isotope appears preferentially where it would be expected if a mass isotope effect simply retarded photofragmentation. The mass effect could be discounted only by postulating the fragmentation step(s) to be kinetically unimportant or appealing to the unexpectedly large magnitude of the isotope effect.[9] A reasonable way (equivalent to criterion I above) to document the nuclear spin effect in this particular case would be to measure the $^{13}C/^{14}C$ isotope effect since the lighter isotope has the spin in that case. Alternatively, where chemistry permits, the initial multiplicity of the radical pair might be changed, thereby inverting the effect of the nuclear spin on radical pair reactivity.

In view of recent reports of unusually large isotope enrichments observed during free-radical reactions, it becomes important to apply as many of the above criteria as possible to the evaluation of these effects. The extent to which these criteria will be met, and nuclear spin isotope effects fully documented, depends to a large extent on the largely unknown accuracy with which one can extrapolate from the properties of radical pairs, as revealed by CIDNP, to the actual yields of stable products.

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(9) A referee has pointed out that in delocalized radicals the nuclear spin effect should overwhelm secondary mass isotope effects at positions with appreciable spin density which are far removed from the reaction site. Isotope enrichment of *any* detectable magnitude at such positions, regardless of direction, might then serve as evidence for a nuclear spin isotope effect. Furthermore, the magnitudes of the enrichments at different positions in the same radical should depend in some systemic way on the magnitude of the hyperfine splittings at those positions. These two effects, where applicable, are philosophically similar to criteria III and I, respectively.

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A Copper(I)–Bicarbonato Complex. A Water-Stable Reversible CO_2 Carrier

Sir:

The preparation of CO_2-related transition-metal complexes is important in connection with recent research activities in CO_2 coordination chemistry[1] and in organic synthesis using CO_2.[2] Transition-metal–bicarbonato complexes are attracting a considerable interest.[3] Until recently, however, few studies on transition-metal bicarbonato complexes have been reported in spite of their relevance to carbonic anhydrase[4] and to transition-metal-catalyzed organic reactions of CO_2 in aqueous media.[5] Here we report the preparation of a Cu(I)–bicarbonato complex by three routes: (i) hydrolysis of a Cu(I)–alkylcarbonato complex, (ii) hydrolytic carboxylation of a Cu(I)–carbonato complex, and (iii) carboxylation of a Cu(I)–hydroxo complex. The relationship of interconversions among the above various Cu(I) complexes is also shown. The Cu(I)–bicarbonato complex which reversibly decarboxylates in both organic solvents and water acts as a CO_2 carrier to carboxylate cyclohexanone and propylene oxide.

All operations described below were carried out under nitrogen. A reaction mixture of $t\text{-BuOCO}_2\text{Cu(PEt}_3)_3$ (**1a**)[6] and 1.2 equiv of water in *n*-pentane was stirred for 6 h at 0 °C. *t*-BuOH was formed in 98% yield.[17] Evaporation of the solvent in vacuo produced a viscous oil. Crystallization of the oil from *n*-pentane at −78 °C gave a white microcrystalline solid. The solid melted at ambient temperature to produce a colorless viscous oil which was identified as $\text{HOCO}_2\text{Cu(PEt}_3)_3$ (**2a**): Cu content 13.1% (calcd 13.3%); CO_2 evolution by acidolysis 98%; IR (neat) 2621 (ν_{OH}), 1612 cm^{-1} ($\nu_{C=O}$); ^1H NMR (C_6D_6) δ 8.75 ppm (HOCO_2–). The deuterated complex, $\text{DOCO}_2\text{-Cu(PEt}_3)_3$(**2a**-$d_1$), prepared by the reaction using D_2O did not show the IR and NMR absorptions due to the proton of bicarbonate group of **2a**. **2a**-d_1 showed its ν_{OD} band at 2143 cm^{-1}. It is reasonably assumed that **2a** is a coordinatively saturated complex and the bicarbonate group coordinates as a monodentate ligand. The molecular weight of **2a** determined by cryoscopy in benzene was 866 (calcd for dimeric **2a**, 958). The value of molecular weight together with the low IR ν_{OH} absorption suggests that **2a** has a dimeric structure involving a hydrogen bond between the two bicarbonate groups, which may be similar to that of $\text{Pd(Me)(OCO}_2\text{H)(PEt}_3)_2$.[3b] Hydrolysis of $t\text{-BuOCO}_2\text{Cu(}t\text{-BuNC)}_3$ (**1b**)[6] in tetrahydrofuran (THF) at 0 °C quantitatively produced a white precipitate of $\text{HOCO}_2\text{Cu(}t\text{-BuNC)}_3$ (**2b**), which was recrystallized from CH_2Cl_2–*n*-pentane.[7] **2b** reacted with an equimolar amount of EtI in dimethylformamide (DMF) at room temperature to give EtOH in 57% yield and diethyl carbonate in 16% yield with 80% CO_2 evolution. When the amount of water was decreased to 0.5 equiv in the reaction of **1b** with water, a Cu(I)–carbonato