Hz); ^{13}C NMR ($CDCl_3$) 171.13 (C_3), 34.28 (C_4), 41.68 (C_5), 42.24 (C_6), 5.71 (C_6–CH_3) ppm. The further structural confirmation of both **6b** and **6c** was based on comparisons of ^1H and ^{13}C NMR spectra with those of 3-phenyl-6,6′-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**6d**) (mp 52.5 °C) obtained from the decomposition of **4d** (mp 120 °C)[10] in 59% yield[18] [**6d**: UV (max in EtOH) 254 nm (log ϵ 4.14); *m/e* (rel intensity) 186 (M^+, 4%), 158 (23%), 143 (100%), 128 (62%), 115 (33%); ^1H NMR (60 MHz in CCl_4) δ 2.90 (dd, *endo*-C_4–H, J = 4.0 and 18.0 Hz), 3.10 (*exo*-C_4–H, J = 8.0 and 18.0 Hz), 2.45 (dd, C_5–H, J = 4.0 and 8.0 Hz), 0.92 (s, *endo*-C_6–CH_3), 1.33 (s, *exo*-C_6–CH_3); ^{13}C NMR ($CDCl_3$) 171.03 (C_3), 35.30 (C_4), 50.07 (C_5), 47.07 (C_6), 11.87 (*endo*-C_6–CH_3), 25.87 (*exo*-C_6–CH_3) ppm].

From the above experiments, it was also found that the rates of formation of **6** and disappearance of **5** were in the order $b > d > c > a$. This order coincides with that of relative thermal stability of aziridines **6**. Among four aziridines, **6b** was found to be most stable and gave a 1:4.8 mixture of **5b**[19] and **6b** upon heating in refluxing carbon tetrachloride for 1 h. Similarly, **6d** afforded a 1:2 mixture of **5d**[20] and **6d**. On the other hand, the more labile aziridines **6c** and **6a** afforded a 1.9:1 mixture of **5c** and **6c** and a 2.3:1 mixture of **5a** and **6a**, respectively. These results provide the same thermal reversibility between aziridine and allyldiazomethane as that reported previously by us.[2]

The experimental results shown here, thus, provide the high stereoselective 1,1-cycloaddition reaction of (*E*)-**1** and (*Z*)-**1** and retro-1,1-cycloaddition reaction of *endo*-**2** and *exo*-**2**, supporting a concerted mechanism of an intramolecular 1,1-cycloaddition of diazomethane to the C=C double bond.

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(18) The yield was determined by liquid chromatography using Waters DATA MODULE 730.
(19) **5b**: ^1H NMR (CCl_4) δ 1.6 (CH_3), 3.0 (CH_2), 5.5 (*CH*=*CH*).
(20) **5d**: ^1H NMR (CCl_4) δ 1.7 (CH_3), 3.2 (CH_2), 5.3 (*CH*=*CH*).

Enhancement of ^{29}Si or ^{119}Sn NMR Signals in the Compounds $M(CH_3)_nCl_{4-n}$ (M = Si or Sn, n = 4, 3, 2) Using Proton Polarization Transfer. Dependence of the Enhancement On the Number of Scalar Coupled Protons

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Recently, Freeman and Morris[1] and Morris[2] proposed the use of the nonselective polarization-transfer (PT) pulse train

$$(90_x\mathrm{H})\text{–}\tau\text{–}(180_x\mathrm{H})(180_x\mathrm{I})\text{–}\tau\text{–}(90_y\mathrm{H}) \times (90_x\mathrm{I})\text{–}\Delta\text{–(acquire data, decouple)}$$

as a general technique for enhancing the NMR signals from a nucleus I with a low gyromagnetic ratio. The sequence is particularly useful[3] when the relaxation mechanism of nucleus I arises from nonproton dipolar interactions, a consequence of which is negligible nuclear Overhauser enhancement (NOE) after proton decoupling. Fundamental to NMR is the general rule that, provided the relaxation pathway of a nucleus I is dominated by ^1H–I dipolar couplings, the NOE is independent of the number of relaxing protons, being $1 + \gamma_H/2\gamma_I$ provided the extreme narrowing limit applies.[4]

Recently,[5] we derived an expression for the decoupled enhancement, E_d, following a PT pulse train as a function of τ and Δ for any nucleus of spin l scalar coupled to n spin $^1/_2$ particles (protons). For $l = {}^1/_2$, with τ at its optimum value of $0.25J^{-1}$, this is

$$E_d = 2^{(1-n)}(\gamma_H/\gamma_I) \sum_{M_H=-1/2n}^{1/2n} {}^nC_y M_H \sin(2\pi J M_H \Delta) \quad (1)$$

where $y = M_H + {}^1/_2n$, M_H being the proton spin quantum numbers $n/2, (n/2) - 1, \ldots, -n/2$. This series expression has the simple analytic form

$$E_d = n(\gamma_H/\gamma_I) \sin(\pi J\Delta) \cos^{n-1}(\pi J\Delta) \quad (2)$$

The equivalence of (1) and (2) can be shown by differentiating with respect to Δ the identity

$$\cos^n(\pi J\Delta) = 2^{-n} \sum_{y=0}^{n} {}^nC_y \cos[(2y - n)\pi J\Delta]$$

The first maximum of (2) occurs at $\Delta = \Delta_{opt}$, where

$$\Delta_{opt} = (\pi J)^{-1} \arcsin n^{-1/2} \quad (3)$$

giving the optimum decoupled enhancement factor

$$E_{dopt} = (\gamma_H/\gamma_I) n^{1/2} (1 - 1/n)^{(1/2)(n-1)} \quad (4)$$

This shows that E_{dopt} *increases* as n increases while Δ_{opt} decreases (see Table I). In fact for large n, $E_{dopt} \sim (\gamma_H/\gamma_I)(n/e)^{1/2}$ and $\Delta_{opt} = 1/(\pi J\sqrt{n})$ where e is the exponential number. Thus while $E_{dopt} = \gamma_H/\gamma_I$ for $n = 1, 2$, it can exceed $2\gamma_H/\gamma_I$ for $n \geq 11$. Such behavior is significantly different from that of the NOE, and large enhancements are possible for a variety of interesting systems having large n. While signal enhancements exceeding γ_H/γ_I are known,[6] in this paper we show experimentally that it is possible to obtain larger enhancements and that the PT sequence is likely to be useful to boost the signal to noise ratio (S/N) of NMR of heavy atoms such as Si and Sn for which there appears to be little NOE on proton decoupling.

A coupled PT ^{119}Sn spectrum ($\Delta = 0$) of $(CH_3)_4Sn$ is shown in Figure 1.[7] Note the spectacular improvement in S/N and the change in *relative* intensities between the PT and FT spectra. The relative intensities should change from (FT) 1:12:66:220:495:792:924:792:495:220:66:12:1 (some of the outer lines are too weak to be observed) to 3:30:132:330:495:396:0:−396:−495:−330:−132:−30:−3 (PT). When a proton decoupling field is applied, the experimentally found $\Delta_{opt} \sim 0.095J^{-1}$ and the S/N boost by a factor of 5.3 for the ^{119}Sn resonance compare favorably with the theoretical values of $0.093J^{-1}$ and 5.76 found from 2.147 (γ_H/γ_{Sn}) (see Table I). For $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$ we find that the theoretical Δ_{opt} timings do give the maximum enhancements, but these are about 20% less than predicted, being 3.8 (expt) and 5.0 (theory) and

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(7) ^{119}Sn NMR spectra were determined at 33.56 MHz on a modified HX-90 NMR spectrometer fitted with a CXP-type pulse programmer, modulator, and receiver. A hardware controlled phase shifter was available on the ^1H (90 MHz) channel. Phase alternation of the 90_yH pulse was used.[1,2,9] $(180_xH)(180_xI)$ refocusing pulses were used in the pulse sequence at the middle of the Δ period to obviate the problem of large phase corrections.[3,10,11] Values of $J_{^{119}Sn-H}$ were $(CH_3)_4Sn$ (50%, benzene-d_6), 53.7 Hz; $(CH_3)_3SnCl$ (30%, $CDCl_3$), 59.6 Hz; $(CH_3)_2SnCl_2$ (20%, acetone-d_6), 85.0 Hz.

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Table I. Values of Δ_{opt} To Give the Maximum Decoupled Enhancement E_{dopt} as a Function of the Number of Scalar Coupled Protons[a]

n	1	2	3	4	6	8	9	12	15	18
Δ_{opt}[b]	0.50	0.25	0.196	0.167	0.134	0.115	0.108	0.093	0.083	0.076
E_{dopt}[c]	1.0	1.0	1.155	1.299	1.553	1.772	1.873	2.147	2.389	2.610

[a] τ is set equal to $0.25J^{-1}$. [b] In units of J^{-1}. [c] In units of γ_H/γ_I.

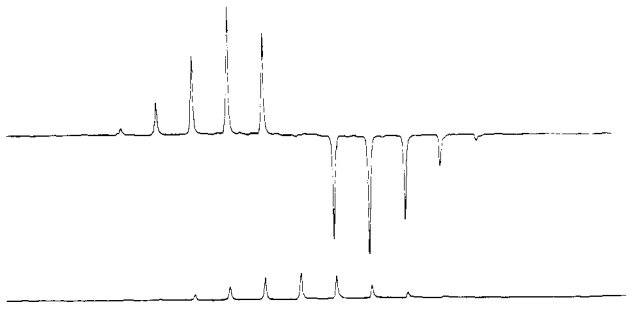

Figure 1. A comparison between the coupled FT NMR spectrum (lower) of $Sn(CH_3)_4$ with the proton polarization-transfer spectrum (upper) determined with τ = 4.66 ms, Δ = 0. Each spectrum is the average of 16 scans. Pulse times were t_{90}^{Sn} = 15 μs, t_{90}^{H} = 24 μs.

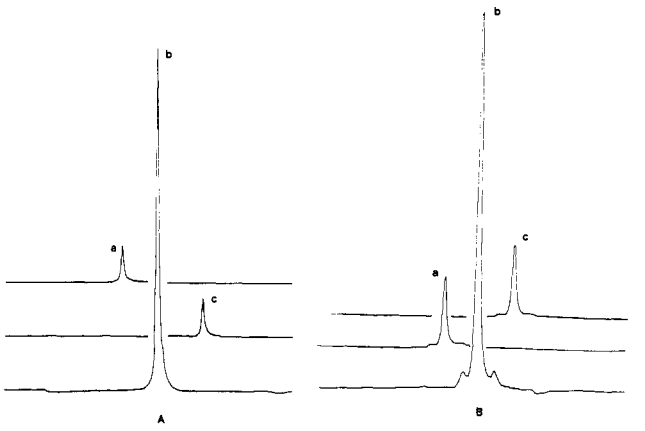

Figure 2. (A) FT (a), PT (b), and reverse proton-decoupled FT (c) spectra of $Si(CH_3)_4$. t_{90}^{Si} was 13 μs. Each spectrum is the average of four scans. E_{dopt} = 9.2 (theory 10.8). (B) Reverse proton decoupled FT (a), PT (b), and FT (c) spectra of $Sn(CH_3)_4$. Each spectrum is the average of four scans. E_{dopt} = 5.3 (theory 5.76).

3.2 (expt) and 4.2 (theory), respectively. The reductions appear to arise from the short ^{119}Sn T_2 values for these compounds. For all three compounds there is no NOE on proton decoupling.

The enhancement factors[8] for the ^{29}Si resonances in $(CH_3)_4Si$ and $(CH_3)_3SiCl$ are much closer to the theoretical value, being 9.2 (expt) (10.8, theory) and 8.5 (expt) (9.4, theory), respectively (Figure 2). The experimental value for $(CH_3)_2SiCl_2$ is 5.0, again somewhat less than the theoretical value of 7.8. For this compound the ^{29}Si T_2 is short and a loss of intensity is to be expected by using the PT sequence.

The enhancement factors presented in this paper are clearly dependent on the number of attached protons; S/N gains of the orders of magnitude measured represent a time-saving factor of 10–100 in obtaining ^{29}Si and ^{119}Sn NMR spectra. It is clear that the PT sequence will be particularly useful for obtaining metal NMR signals (e.g., ^{103}Rh, ^{183}W, ^{57}Fe, ^{199}Hg, ^{29}Si, ^{119}Sn, ^{207}Pb, etc.) in a variety of compounds provided there is a resolvable scalar coupling and the relaxation times (T_i) are not too short, that is, for $(\Delta,\tau) < T_i^{-1}$. Experiments are being performed on a variety of compounds to test the generality of PT NMR to obtain metal NMR spectra.

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(8) ^{29}Si NMR spectra were determined at 17.88 MHz.[7] Values of $J_{^{29}Si-H}$ were (50% in benzene-d_6) $(CH_3)_4Si$, 6.6 Hz; $(CH_3)_3SiCl$, 6.8 Hz; $(CH_3)_2SiCl_2$, 7.7 Hz.

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Functionalized Vesicular Assembly. Enantioselective Catalysis of Ester Hydrolysis

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Several studies on micellar catalysis[1] have been carried out in order to develop stereoselective reaction sites for the hydrolysis of enantiomeric esters and understand the origins of stereoselectivity in proteolytic enzymes,[2] and some of those micellar systems having chiral centers[1b,c] exercised moderate enantioselectivity. We have reported[3] that a zwitterionic double-chained amphiphile involving an amino acid residue may form stable single-compartment bilayer vesicles in aqueous media and suggested that such vesicles may provide asymmetric recognition sites for various guest molecules. In this communication, we report the stereoselective hydrolysis of *simple* enantiomeric esters, L- and D-*N*-benzyloxycarbonylphenylalanine *p*-nitrophenyl esters [L-/D-(*Z*)-Phe-PNP],[4] as catalyzed by a *synthetic functionalized membrane* formed with *N,N*-didodecyl-N^{α}-[6-(trimethylammonio)hexanoyl]histidinamide bromide (**1**).[5] The present substrates would be favorably incorporated into vesicles by their intermolecular hydrogen-bonding interaction[6] with an amino acid moiety placed at the hydrogen belt region and by hydrophobic

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(4) (a) L-/D-(*Z*)-Phe-PNP were synthesized from the corresponding *N*-benzyloxycarbonylphenylalanine and *p*-nitrophenol in the presence of dicyclohexylcarbodiimide. L-(*Z*)-Phe-PNP: mp 128–130 °C (lit.[4b] 126.5–127.5 °C), $[\alpha]^{25}_D$ −9.0° (*c* 2.2, ethyl acetate) [lit.[4b] −8.9° (*c* 2.2, ethyl acetate)]. Anal. ($C_{23}H_{20}N_2O_6$) C, H, N. D-(*Z*)-Phe-PNP: mp 129–131 °C, $[\alpha]^{25}_D$ +8.8° (c 2.2, ethyl acetate). Anal. ($C_{23}H_{20}N_2O_6$) C, H, N. (b) Goodman, M.; Stueben, K. C. *J. Am. Chem. Soc.* **1959**, *81*,3980–3983.
(5) (a) Amphiphile **1** (abbreviated as $N^+C_5His2C_{12}$): liquid crystal with final mp 117 °C; Pauly (for detection of free imidazolyl and phenolic groups)[5b] and Dragendorff (for detection of quaternary ammonium group)[5c] positive; R_f (silica gel 1B of Baker-flex) 0.31 (with 1-butanol–water–acetic acid, 4:2:1 v/v) and 0.22 (with methanol); $[\alpha]^{25}_D$ +40.0° (*c* 1.0, EtOH); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.86 (6 H, t, $(CH_2)_{11}CH_3$), 1.25 (40 H, s, CH_2-$(CH_2)_{10}CH_3$), ~2.00 (6 H, m, $N^+CH_2(CH_2)_3CH_2CO$–), 2.35 (2 H, br t, $N^+(CH_2)_4CH_2CO$–), 2.80–3.62 (8 H, m, $N^+CH_2(CH_2)_4CO$–, $CHCH_2Im$, and $-NCH_2(CH_2)_{10}CH_3$), 3.33 (9 H, s, $(CH_3)_3N^+$–), 5.04 (1 H, br t, –CH–), 6.97 (1 H, s, Im 5-H), and 8.22 (1 H, s, Im 2-H). Anal. ($C_{39}H_{76}BrN_5O_2 \cdot 2.5H_2O$) C, H, N. (b) Hunter, G. *J. Chem. Soc.* **1930**, 2343–2346. (c) Beiss, U. *J. Chromatogr.* **1964**, *13*, 104–110.
(6) Brown and Bunton[1b] suggested that the ability of amide bonds of functional micelles to form intermolecular hydrogen bonds must bring about the high stereoselectivity in the hydrolysis of *N*-acetylphenylalanine *p*-nitrophenyl ester.

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