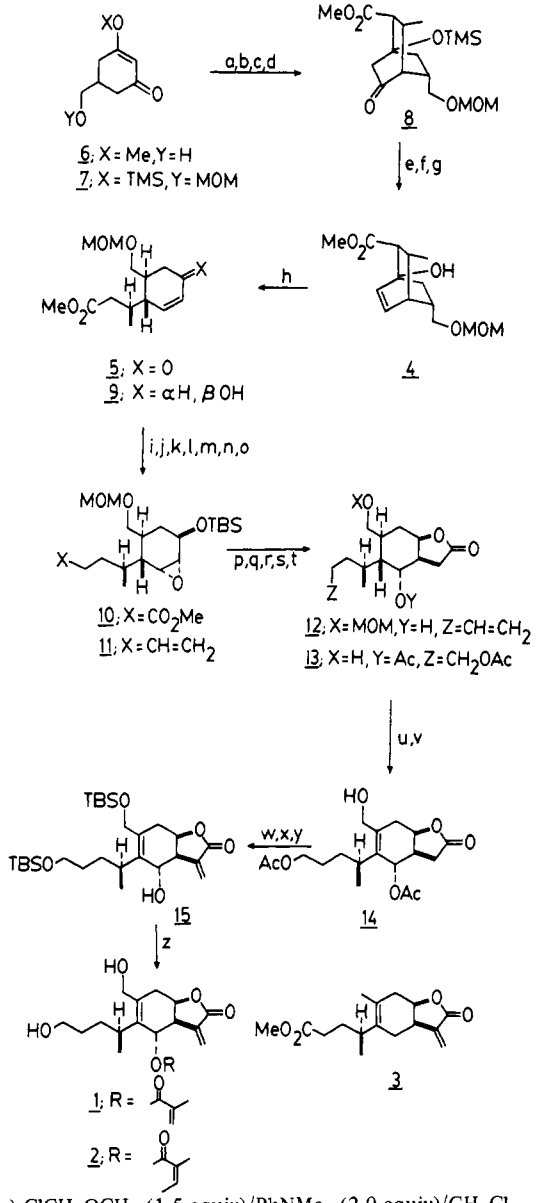
Scheme I



[a] (a) $ClCH_2OCH_3$ (1.5 equiv)/$PhNMe_2$ (2.0 equiv)/CH_2Cl_2 (1.5 M)/22 °C, 48 h; (b) KOH/H_2O/50 °C; Me_6Si_2/toluene/110 °C; (d) LDA (1.0 equiv), 1 M in THF/methyl crotonate (1.1 equiv)/-78 °C, 10 min/-20 °C for 8 h; (e) LDA, 1 M in THF/rapid addition of Br_2 (10 equiv) in CH_2Cl_2 (3 M) at -78 °C/stirring 1 min/inverse quench into aqueous $NaHCO_3$ and Na_2SO_3; (f) $NaBH_4$/EtOH/22 °C, 2 h; (g) Zn^0/EtOH/75 °C, 10 h/H^+; (h) *t*-BuOK (0.1 equiv) 0.25 M in *t*-BuOH/1 min; (i) $(t\text{-BuO})_3$-AlLiH (1.1 equiv)/THF (1 M)/22 °C, 8 h; (j) TBSCl/DMF/imidazole/22 °C, 2 h; (k) NBS (1.1 equiv)/acetone-H_2O (0.5 M)/0 °C, 1 h; MeOH/K_2CO_3/22 °C, 10 h; (l) DiBAl-H, 1 M in hexane diluted to 0.5 M with THF/-78 °C, 10 min/0 °C, 10 min; (m) MsCl (1.3 equiv)/THF (1 M)/Et_3N (2.0 equiv)/0 °C, 1 h; (n) NaI (5.0 equiv)/acetone (0.3 M)/40 °C, 2 h; (o) $(CH_2{=}CH)_2CuLi$, 0.5 M in THF/-78 °C, 30 min/-20 °C, 10 min/0 °C, 10 min; (p) Et_3NHF (2.1 equiv) in CH_3CN (0.4 M)/Et_3N (1.0 equiv)/60 °C, 10 h; (q) $LiCH_2CO_2Li$ (7 equiv)/THF (0.5 M)/HMPA (7 equiv)/50 °C, 6 h/*p*-TSA (0.01 equiv)/benzene (0.25 M)/80 °C, 4 h; (r) O_3/CH_3OH (0.1 M)/-78 °C, 5 min/$NaBH_4$/-20 °C, 20 min; (s) Ac_2O (3 equiv)/pyridine (0.4 M)/DMAP (0.2 equiv)/22 °C, 8 h; (t) $(CH_2SH)_2$ (2.0 equiv)/BF_3Et_2O (2.0 equiv)/CH_2Cl_2 (0.5 M)/0 °C, 1 h; (u) PCC (1.1 equiv)/CH_2Cl_2 (0.5 M)/22 °C, 10 h; (v) PhSeCl (4.4 equiv)/EtOAc (0.25 M)/60 °C, 8 h/workup with H_2O and CH_2Cl_2/$NaBH_4$/EtOH/0 °C, 5 min; (w) K_2CO_3 (2.2 equiv)/CH_3OH (0.1 M)/0 °C, 30 h; (x) TBSCl (3.2 equiv)/pyridine (0.4 M)/imidazole (2.0 equiv)/0 °C, 2 h/TMe_3SiCl (3.4 equiv)/0 °C, 40 min; (y) LDA (1.1 equiv)/THF (1 M)/CO_2/40% CH_2O/Et_2NH/HOAc; (z) methacrylic anhydride (1.05 equiv)/pyridine (0.5 M)/DMAP (2.0 equiv)/22 °C, 8 h.

Ozonolysis of the olefinic side chain of **12** followed by reductive workup gave the corresponding side-chain alcohol, and it along with the secondary ring alcohol were acylated with acetic anhydride in pyridine containing (dimethylamino)pyridine (DMAP). Removal of the methoxymethyl moiety was readily accomplished by employing ethanedithiol and $BF_3{\cdot}Et_2O$: the product, **13** (oil), was obtained in 70% yield from **12**. We now commenced introduction of the ring olefin by pyridinium chlorochromate oxidation of **13**. The unstable aldehyde formed in this reaction was immediately combined with phenylselenyl chloride in ethyl acetate at 65 °C. Contrary to the usual course of this reaction, selenylation under these conditions was accompanied by loss of the elements of PhSeH under nonoxidizing conditions, and a mixture of unsaturated aldehydes became the ultimate products of this reaction.[13] Without purification, these substances were reduced with sodium borohydride in ethanol and the desired alcohol **14** (mp 124-125.5 °C) was isolated after chromatography in 40% yield from **13**.

The terminating steps of the synthesis (α-methylenation of the lactone residue and esterification of the secondary ring alcohol) were addressed starting with removal of the acetate residues of **14** by using K_2CO_3 in methanol at 0 °C for 30 h. The resulting crude triol was then selectively protected in a single-flask operation by initial treatment with TBSCl in a mixture of pyridine and imidazole (primary alcohols react) followed by addition of Me_3SiCl (secondary alcohol reacts). The lithium enolate of this substance (LDA, THF, -78 °C) was carbonated with CO_2 and the resulting acid lactone treated with a mixture of 40% formalin and diethylamine to afford the corresponding α-methylene lactone.[14] Treatment of this substance with acetic acid hydrolyzed the Me_4Si protecting group of the secondary alcohol, giving rise to **15** (mp 121-122.5 °C) in 51% yield from **14**. Esterification of **15** with methacrylic anhydride in pyridine containing DMAP followed by removal of the TBS groups with 10% HCl in ethanol gave synthetic eriolanin (**1**) in 90% yield (mp 113-114 °C; lit.[15] mp 113-114.5 °C). The physical properties of this substance were identical with those of a sample of synthetic eriolanin kindly provided us by Professor Paul Grieco.[16]

Additional examples of tandem conjugate addition reactions potentially useful in the construction of natural products will be reported in the future.

Acknowledgment. This work was supported by a Public Health Service Research Grant (CA 23257) from the National Cancer Institute. We also thank the Syntex Corporation for financial support.

(13) This type of reaction, under similar conditions, has been observed by Professor Dennis Liotta, Department of Chemistry, Emory University. We thank Professor Liotta for sharing his results with us.

(14) For a detailed description of this highly useful methylenation sequence, see W. H. Parker and F. J. Johnson, *J. Org. Chem.*, **38**, 2489 (1973).

(15) See ref 3.

(16) We thank Professor Paul Grieco, Department of Chemistry, Indiana University, for a generous sample of synthetic eriolanin as well as spectral data on natural eriolanin.

Concerted Mechanism of Intramolecular 1,1-Cycloaddition Reaction of Allyldiazomethane[1]

Tsutomu Miyashi, Yôsuke Fujii, Yoshinori Nishizawa, and Toshio Mukai*

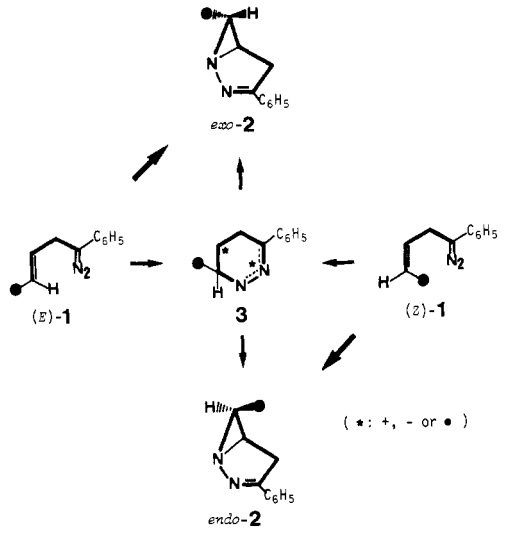
Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received June 12, 1980

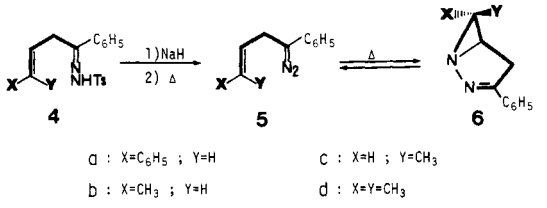
In our previous report,[2] we demonstrated a novel intramolecular reactivity of the terminal nitrogen of diazomethane, that is, various

(1) Organic Thermal Reaction, part 50. For part 49, see ref 2.

Scheme I



Scheme II



allyldiazomethanes thermally undergo a formal nitrene-type 1,1-cycloaddition to give 1,2-diazabicyclo[3.1.0]hex-2-enes instead of the usual 1,3-dipolar cycloaddition to give 2,3-diazabicyclo-[3.1.0]hex-2-enes.

One possible mechanism to account for this cyclization is a concerted one where the 4π system of diazomethane makes the aziridine σ and N=C π bonds, and the π orbital orthogonal to the 4π system of diazomethane enters the lone pair at the nitrogen next to the pyramidal aziridine nitrogen, while the lone pair of the terminal nitrogen of diazomethane remains that of the pyramidal aziridine nitrogen. Thus, (*E*)-**1** and (*Z*)-**1** undergo the stereoselective 1,1-cycloaddition to give *exo*-**2** and *endo*-**2**, respectively. An alternative stepwise pathway from (*E*)-**1** and (*Z*)-**1** involves a six-membered dipole **3** which, in turn, collapses, randomizing the stereochemistry at the C_6 position to afford a mixture of *exo*-**2** and *endo*-**2** (Scheme I).

In order to gain insight into the mechanism which directly concerns the latent nature of the terminal nitrogen of diazomethane as a 1,3-dipole,[3] the thermal decomposition of the sodium salts of tosylhydrazones **4a–4d** was investigated. Herein we report strong evidence to support a concerted mechanism.

Heating the sodium salt of **4a** (mp 141 °C)[4] in refluxing carbon tetrachloride immediately produced a red coloration due to the generation of diazomethane **5a**,[5] which slowly faded upon standing at room temperature under argon atmosphere (Scheme II). The crude reaction mixture obtained after 1 h of heating followed by immediate workup was found to include a 1.9:1 mixture of **5a** and *exo*-3-phenyl-6-methyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**6a**) (mp 138 °C dec).[6] After 10 days the ratio **5a**/**6a** was observed to be 0.4 by ^{1}H NMR analysis.[7] When diazomethane **5a** almost completely disappeared, **6a** was isolated in 45% yield. The endo isomer, however, could not be detected in the crude reaction mixture by ^{1}H NMR analysis. The structure of **6a** was unequivocally determined by its spectral properties [**6a**: UV (max in EtOH) 255 nm (log ϵ 4.11); *m/e* (rel intensity) 234 (M^+, 5%), 206 (100%), 205 (20%), 191 (52%), 128 (36%), 91 (68%); ^{1}H NMR (90 MHz in $CDCl_3$) δ 3.58 (d, C_4–H, 2 H, J_{gem} = 18 Hz), 3.07 (ddd, C_5–H, J = 3.0, 4.5, and 6.0 Hz), 2.43 (d, *endo*-C_6–H, J = 4.5 Hz); ^{13}C NMR[8] ($CDCl_3$) 168.30 (C_3), 168.30 (C_3), 39.07 (C_4), 49.30 (C_5), 54.06 (C_6) ppm].

On the other hand, diazomethane **5b** generated from the sodium salt of **4b** (mp 121 °C)[9] was found to cyclize rapidly and upon standing for 1 day at room temperature afforded *exo*-3-phenyl-6-methyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**6b**) (mp 52 °C) in 72% yield[11] [**6b**: UV (max in EtOH) 253 nm (log ϵ 4.07); *m/e* (rel intensity) 172 (M^+, 3%), 144 (30%), 129 (100%), 128 (49%), 103 (4.2%); ^{1}H NMR (200 MHz in $CDCl_3$) δ 3.40 (d, C_4–H, 2 H, J_{gem} = 20 Hz), 2.70 (ddd, C_5–H, J = 3.0, 4.2, and 6.0 Hz), 1.54 (dq, *endo*-C_6–H, J = 4.2 and 5.8 Hz), 1.34 (d, *exo*-C_6–CH_3); ^{13}C NMR ($CDCl_3$) 168.27 (C_3), 37.90 (C_4), 46.71 (C_5), 48.82 (C_6), 16 .89 (C_6–CH_3) ppm].

Judging from these experimental results, the 1,1-cycloaddition reaction of (*E*)-**1** appears to occur stereoselectively, but a concerted mechanism need not be necessarily supported by these results because of supposed stereochemical inconveniences of their endo isomers. Thus, the direct stereochemical comparison of the stereochemical course was examined by using the *Z*-isomer **4c** (mp 130 °C)[12] which was prepared from 5-phenylpent-2-yn-5-one[13] by catalytic reduction over Pd–$BaSO_4$. The reaction sequence could be cleanly monitored by ^{1}H NMR analysis. Thus, heating the sodium salt of **4c** in refluxing carbon tetrachloride for 1 h followed by immediate workup under argon atmosphere affored a wine-red colored pyrolysate which is exclusively composed of diazomethane **5c**[14] and *endo*-3-phenyl-6-methyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**6c**) in the ratio 1.5:1. ^{1}H NMR analysis of the crude reaction mixture after 4 days revealed the formation of **6c** in 51% yield.[15] Although ^{1}H NMR analysis could not detect the exo isomer **6b**, liquid chromatographic analysis[16] detected a trace of **6b**. The ratio **6b**/**6c** was 1/84.4, which indicates the occurrence of 98.8% high stereoselective 1,1-cycloaddition. Aziridine **6c**[17] separated by liquid chromatography shows the following spectral properties: UV (max in EtOH) 252 nm; *m/e* (rel intensity) 172 (M^+, 3%), 144 (12%), 129 (100%), 128 (45%), 103 (7.6%); ^{1}H NMR (200 MHz in $CDCl_3$) δ 3.08 (dd, *endo*-C_4–H, J = 2.6 and 18.4 Hz), 3.32 (dd, *exo*-C_4–H, J = 8.4 and 18.4 Hz), 2.86 (ddd, C_5–H, J = 2.6, 6.4, and 8.4 Hz), 1.00 (d, *endo*-C_6–CH_3, J = 6.4 Hz), 2.66 (dq, *exo*-C_6–H, J = 6.4 and 6.4

(2) Y. Nishizawa, T. Miyashi, and T. Mukai, *J. Am. Chem. Soc.*, **102**, 1176 (1980).

(3) R. Huisgen, R. Grashey, and J. Sauer, "Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, 1964, p 806; A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976).

(4) Melting points were not corrected. Satisfactory elemental analyses were obtained for all new compounds except diazo compounds and **6c**.

(5) **5a**: ^{1}H NMR ($CDCl_3$) δ 3.4 (2 H, CH_2), 6.5 (2 H, CH=CH).

(6) Y. Nishizawa, T. Miyashi, and T. Mukai, *J. Am. Chem. Soc.*, **102**, 1176 (1980); ref 19; see also A. Padwa and H. Ku, *Tetrahedron Lett.*, 1009 (1980).

(7) NMR analysis was done by using veratrole as an internal standard.

(8) For ^{13}C chemical shift of aziridine, see, for instance, P. Mison, R. Chaabouni, Y. Diad, R. Martino, A. Lopez, A. Lattes, F. M. Wehrli, and T. Wirthlin, *Org. Magn. Reson.*, **8**, 79 (1976).

(9) The corresponding ketone was prepared according to the procedure of Steglich.[10] **4b**: ^{1}H NMR ($CDCl_3$) δ 1.53 (m, CH_3), 5.13 (dq, =C*H*CH_3, J = 4.5 and 15 Hz), 5.33 (dt, *CH*=$CHCH_3$, J = 4.5 and 15 Hz), 3.23 (m, CH_2).

(10) N. Engel, B. Kübel, and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, **16**, 394 (1977).

(11) The yield was determined by liquid chromatography using Waters DATA MODULE 730. Neither liquid chromatographic nor ^{1}H NMR analyses of the crude reaction mixture could detect the endo-isomer **6c**.

(12) **4c**: ^{1}H NMR ($CDCl_3$) δ 1.73 (dd, CH_3, J = 1.5 and 6.0 Hz and small couplings with CH_2), 3.36 (br d, CH_2, J = 1.8 and 6.0 Hz), 5.60 (dqt, =C*H*CH_3, J = 1.8, 6.0, and 10.5 Hz), 5.20 (dqt, C*H*=$CHCH_3$, J = 1.5, 6.0, and 10.5 Hz).

(13) This ketone was prepared from propyne and styrene oxide in lithium–liquid ammonia.

(14) **5c**: ^{1}H NMR (CCl_4) δ 1.7 (CH_3), 3.20 (CH_2), 5.3 and 5.8 (C*H*=C*H*, J_{vic} = 10.5 Hz).

(15) NMR analysis was done by using diphenyldimethylsilane as an internal standard.

(16) The liquid chromatographic analysis was done by using Waters DATA MODULE 730 (retention time **6b**, 3.93 min; **6c**, 8.70 min; column Radial Pak B; solvent ether/THF 4:1, 2 mL/min).

(17) Aziridine **6c** is relatively stable in solution. Evapolation of solvents, however, caused polymerization of **6c** to form ether-insoluble compounds.

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.

Acknowledgment. We gratefully acknowledge support of this work by the grant-in-aid for Chemical Research in Development and Utilization of Nitrogen-Organic Resources sponsored by the Ministry of Education, Tokyo, Japan.

(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

David M. Doddrell,* David T. Pegg, William Brooks, and M. Robin Bendall

School of Science, Griffith University Nathan, Queensland, 4111 Australia

Received August 18, 1980

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

(1) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762.
(2) Morris, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 428–429.
(3) Doddrell, D. M.; Bergen, H.; Thomas, D.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1980**, *40*, 591–594.
(4) Kuhlmann, K. F.; Grant, D. M.; Harris, R. K. *J. Chem. Phys.* **1970**, *52*, 3439–3448.
(5) Pegg, D. T.; Doddrell, D. M.; Brooks, W. M.; Bendall, M. R. *J. Magn. Reson.*, in press.
(6) Chingas, G. C.; Garroway, A. N.; Moniz, W. B.; Bertrand, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2526–2528.
(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.

0002-7863/81/1503-727$01.00/0