that isomerization of the crystallization fraction to another and fractions were obtained served in the proton nmr spectrum. The infrared spectra of tionally different species. The 31P spectrum of suggesting the presence of two isomers despite the singlet ob-

It is proposed that the titanium in these anions is formally with large Boltzmann population differences, to the nuclear species under investigation, the I spins. It provides an alternative to rotating frame cross-polarization experiments, which have recently been used on liquid-phase systems. The pulse sequence for the proposed experiment can be written

Enhancement of Nuclear Resonance Signal Spins by Polarization Transfer

Sir:

We report here a new method for enhancing the intensity of NMR signals from nuclei of low magnetogyric ratio. The method is independent of relaxation mechanisms, unlike the nuclear Overhauser effect, and hence is likely to be particularly useful for nuclei such as 15N and 29Si which have negative magnetogyric ratios. The enhancement arises from the transfer of nuclear spin polarization from the S spins (usually protons) with large Boltzmann population differences, to the nuclear species under investigation, the I spins. It provides an alternative to rotating frame cross-polarization experiments, which have recently been used on liquid-phase systems. The pulse sequence for the proposed experiment can be written

\[ 90^\circ_s(X) - \tau - 180^\circ_s(X), \]

\[ 180^\circ_s(-\tau) - 90^\circ_s(Y), 90^\circ_s(-\tau) \] acquisition

where the transmitter pulses applied to the S spins can be phase shifted so that the first is directed along either the X or Y axes of the appropriate rotating reference frame. This pulse sequence is closely related to one used in heteronuclear two-dimensional Fourier transform spectroscopy but relies on the excitation of spin echoes and employs a fixed delay \( \tau \), equal to 1/(4Jfs) s. For a simple system of two spins I and S, the components of S magnetization \( M(\alpha) \) and \( M(\beta) \) corresponding to the two I spin states can be represented by the vectors \( \alpha \) and \( \beta \) (Figure 1). The first two pulses excite a spin echo for the S

References and Notes

(1) M. T. Pope et al., J. Less-Common Met., 54, 129 (1977), and references therein.
(4) Typical analyses: Calcld (found) for \([\text{Cp}_2\text{TiS}_2\text{H}_2\text{O}_8\] \( \cdot \) \text{H}_2\text{O}: C, 39.92 (39.86); H, 2.32 (2.27); N, 2.09 (2.17); Si, 0.84 (0.79); Sn, 3.84 (3.51); W, 60.39 (60.77); H_2O, 3.23 (2.99); neut equiv, 670 (658, by titration after H\(^+\) ion exchange); \( {\text{C}}_8\text{H}_8\text{O}_8 \) proton ratio, 12:1 (12:1). Calcld (found) for \([\text{Cp}_2\text{Sn}_{11}\text{S}_2\text{H}_2\text{O}_8 \cdot 3\text{H}_2\text{O}: C, 6.88 (7.14); H, 1.62 (1.84); N, 1.81 (1.27); K, 1.28 (1.36); Si, 7.66 (7.22); W, 59.23 (58.90); H_2O, 0.58 (0.50); \( \text{Cp}_2\text{Sn}_{11}\text{H}_2\text{O}_8 \) proton ratio, 8:1 (6.5:1). Calcld (found) for \([\text{C}_{12}\text{H}_{26}\text{N}_{15}\text{H}_7\text{O}_{39}\text{P}_0_3\text{H}_5\text{O}_3\text{H}_2\text{O}: C, 7.61 (6.67); H, 1.91 (1.80); N, 2.17 (2.12); O, 21.95 (22.33); Si, 0.87 (0.84); Sn, 3.69 (3.62); W, 62.79 (62.77); H_2O, 1.68 (1.66).

(5) Acknowledgement is given to F. Davidson for determining the 31P spectra.
(7) Typical analyses: Calcld (found) for \([\text{Cp}_2\text{Ti}_{11}\text{H}_2\text{O}_8 \cdot 3\text{H}_2\text{O}: C, 9.02 (9.29); H, 1.77 (1.82); N, 1.75 (1.82); Si, 2.84 (2.94); W, 63.17 (63.17); H_2O, 1.69 (1.77); \( \text{Cp}_2\text{TiH}_2\text{O}_8 \) proton ratio, 3.1:8 (4.2:1). Calcld (found) for \([\text{Cp}_2\text{Sn}_{11}\text{H}_2\text{O}_8 \cdot 3\text{H}_2\text{O}: C, 6.31 (6.05); H, 1.65 (1.84); N, 1.84 (1.75); Si, 2.12 (2.18); K, 2.77 (2.47); W, 66.41 (66.55); \( \text{Cp}_2\text{SnH}_2\text{O}_8 \) proton ratio, 3.6:1 (3.7:1).
(9) Since this manuscript was first submitted, Professor W. G. Klemperer has published a nonaqueous preparation of \( \text{Cp}_2\text{Ti}_{11}\text{P}_0_3\text{H}_2\text{O}_8 \). [R. K. C. Ho and W. G. Klemperer, J. Am. Chem. Soc., 100, 6772 (1978)].
(10) Typical analyses: Calcld (found) for \([\text{C}_{12}\text{H}_{26}\text{N}_{15}\text{H}_4\text{Cp}_{11}\text{H}_2\text{O}_8 \cdot 3\text{H}_2\text{O}: C, 7.73 (7.76); H, 1.85 (1.81); N, 2.25 (2.26); Ti, 1.54 (1.39); Si, 0.50 (0.68); W, 65.11 (65.15); H_2O, 0.58 (0.53); \( \text{Cp}_2\text{TiP}_0_3\text{H}_2\text{O}_8 \) proton ratio, 9:1 (9.7:1). Calcld (found) for \([\text{C}_{12}\text{H}_{26}\text{N}_{15}\text{H}_4\text{Cp}_{11}\text{H}_2\text{O}_8 \cdot 3\text{H}_2\text{O}: C, 6.31 (6.05); H, 1.65 (1.84); N, 1.84 (1.75); Si, 2.12 (2.18); K, 2.77 (2.47); W, 66.41 (66.55); \( \text{Cp}_2\text{SnP}_0_3\text{H}_2\text{O}_8 \) proton ratio, 3.6:1 (3.7:1).
(13) Professor M. T. Pope has independently prepared several anions belonging to Class I, including \( \text{Cp}_2\text{Sn}_{11}\text{P}_0_3\text{H}_2\text{O}_8 \). [M. T. Pope, private communication; F. Zonnevijlle and M. T. Pope, to be published].
Communications to the Editor

simultaneous transfer experiment, viewed in a frame rotating in synchronism with the radiofrequency field. After an initial 90° pulse (a) the two vectors process continued divergence of the coupling constant such that the divergence between a and b is just 180° and they have spin population differences appropriate to carbon-13 signals by means of proton pulses have been recorded on a Varian CFT-20 spectrometer which had minor hardware modifications to improve the timing stability and to allow a computer-controlled 90° phase shift of the 80-MHz proton transmitter. The delay τ was set equal to 1.5 ms, which is \(1/(4J_{CH})\) for the direct CH couplings in pyridine. Long-range couplings can be used in these experiments, although they require long τ delays; the experiment is however best suited to the enhancement of signals from nuclei directly bonded to protons. Since the range of one-bond couplings is usually relatively small, a value of τ can be selected which gives a good enhancement for all proton-bearing sites in a molecule.

The third pulse applied to the S spins has a relative phase shift of 90°, since it must rotate the magnetization vectors by 180° about the Y axis, leaving them aligned along the ±Z direction (Figure 1f). If relaxation during the short period 2τ is neglected, this corresponds to a population inversion across one transition but equilibrium populations across the other. Because they share common energy levels, the I transitions now have spin population differences appropriate to S spins, larger by a factor \(K = \gamma_S/\gamma_I\). When the I spins are excited by a 90° pulse, one component of the doublet is therefore enhanced by a factor K and the other similarly enhanced but inverted, no overall transfer of magnetization having occurred; if K is negative these positive and negative enhancements are interchanged.

We illustrate this technique using protons as the S spins and carbon-13 as the I spins. Experiments for the enhancement of carbon-13 signals by means of selective proton pulses have been described by several workers; the technique proposed here is effective over a wide band of proton frequencies and requires no knowledge of the proton chemical shifts. When proton-coupled carbon-13 spectra are measured by this method, the normal binomial intensity ratios for multiplets no longer apply, the ratios obtained being -1:1 for doublets, -1:0:1 for triplets, and -1:-1:1:1 for quartets. As a result, mutual cancellation of signals occurs if proton decoupling is employed immediately after the carbon 90° excitation pulse; however, if a suitable delay is introduced between this pulse and the application of the decoupler field, this cancellation is prevented, and an enhanced decoupled spectrum is obtained.

Proton-coupled carbon-13 spectra of pyridine (Figure 2) were recorded on a Varian CFT-20 spectrometer which had minor hardware modifications to improve the timing stability and to allow a computer-controlled 90° phase shift of the 80-MHz proton transmitter. The delay τ was set equal to 1.5 ms, which is \(1/(4J_{CH})\) for the direct CH couplings in pyridine. Long-range couplings can be used in these experiments, although they require long τ delays; the experiment is however best suited to the enhancement of signals from nuclei directly bonded to protons. Since the range of one-bond couplings is usually relatively small, a value of τ can be selected which gives a good enhancement for all proton-bearing sites in a molecule.

Figure 2. Proton-coupled carbon-13 spectra of pyridine (a) enhanced by polarization transfer, (b) enhanced by the nuclear Overhauser effect, and (c) unenhanced. The three experiments utilized the same total instrument time.

nuclei at time 2τ. The 180° pulse applied to the I spins interchanges the spin-state labels α and β (Figure 1d), causing a continued divergence of the α and β vectors throughout the interval 2τ; this is the phenomenon responsible for the modulation of spin echoes. A knowledge of the approximate value of the coupling constant \(J_{CH}\) permits the delay τ to be selected such that the divergence between α and β is just 180° and they are left diametrically opposed along the ±Z axes (Figure 1e). The chemical shift effect is exactly refocussed.

The behavior of the S spin magnetization vectors in a population transfer experiment, viewed in a frame rotating in synchronism with the radiofrequency field. After an initial 90° pulse (a) the two vectors process for a period τ and accumulate a relative phase angle of 90° (b). A 180° pulse about the X axis flips them into mirror-image positions (c) while a simultaneous 180° pulse on the I spins interchanges the spin-state labels (d). Further precession for a period τ leaves the vectors along the ±X axes (e) when a 90° pulse about the Y axis aligns them along the ±Z axes (f). The magnetization represented by the α vector now has inverted spin populations.

Figure 1. Behavior of the S spin magnetization vectors in a population transfer experiment, viewed in a frame rotating in synchronism with the radiofrequency field. After an initial 90° pulse (a) the two vectors process for a period τ and accumulate a relative phase angle of 90° (b). A 180° pulse about the X axis flips them into mirror-image positions (c) while a simultaneous 180° pulse on the I spins interchanges the spin-state labels (d). Further precession for a period τ leaves the vectors along the ±X axes (e) when a 90° pulse about the Y axis aligns them along the ±Z axes (f). The magnetization represented by the α vector now has inverted spin populations.
nuclei such as $^{15}$N and $^{29}$Si where the Overhauser enhanced the signal is inverted and where an incomplete Overhauser effect can result in signal cancellation. One solution to this problem has been to suppress the nuclear Overhauser effect in $^{15}$N spectra; under such conditions the polarization transfer experiment would provide an enhancement factor $K$ of $\sim 10$, in addition to the benefits of faster spin-lattice relaxation.

The proposed polarization transfer experiment bears a superficial resemblance to another technique for sensitivity enhancement which also employs spin echoes and restores the focussed magnetization on the $Z$ axis. This is the "driven equilibrium Fourier transform method" (DEFT). We have consequently adopted the code name INEPT (Insensitive nuclei enhanced by polarization transfer).

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References and Notes

14. The proton spin-lattice relaxation can be accelerated by the addition of polar molecules such as chromium acetylacetonate.

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Stereospecific Synthesis of (±)-Trisporol B, a Prohormone of Blakeslea Trispora, and a Facile Synthesis of (±)-Trisporic Acids

Sir:

Sexual differentiation in Mucoraceous fungi is mediated by a system of $C_{13}$ apocarotenoid hormones based on the trisporic acids (e.g., 1) and congeners such as (9Z)-methyl trisporate B (2). Extensive studies with plus and minus mating types of $B$. trispora has led to the identification of certain prohormones $^2$ which are characteristic of the mating strain and are converted to a trisporic acid by the sexual partner. Trisporol B (3) is produced in very small amounts by minus cultures of this organism and has proven to be the most biologically active of the mating prohormones so far isolated.$^3$ The chemical synthesis of 3 and related members of the trisporic acid group is likely to be a key element in elucidating the reproductive process in fungi of the Mucorales, and we have therefore sought a practical, synthetic solution to the stereochemical and functional group problems posed by these regulatory substances.$^4$

The requirement for 9Z stereochemistry in 3, coupled with the desirability of fashioning the corresponding olefinic link in the trisporic acid and esters in a geometrically defined manner, dictated an approach strategically different from that adopted in previous syntheses of methyl trisporates.$^5$ First, a unit functionally equivalent to the C(8)-C(14) segment of 3 was prepared from ketal aldehyde 4, readily obtainable from ethyl levulinate.$^6$ Thus, 4 was treated with ethylidenetri-

Phenylphosphorane (THF, $-78^\circ$C, 5 min), and the derived oxido ylide ($n$-BuLi, THF, $0^\circ$C) allowed to react with paraformaldehyde (1 h at $0^\circ$C and then 8 h at room temperature) to give the Z alcohol $5(66%); NMR \delta 5.28 (1 H, t, $J = 7$ Hz), 4.10 (2 H, s), 3.92 (4 H, s), 2.66 (1 H, s, disappears in D$_2$O), 1.78 (3 H, s), 1.30 (3 H, s). This alcohol was converted via its tosylate (MeLi, Et$_2$O-HMPA (3:1) and then and then 24 h at $0^\circ$C) to chloride 6 (82%); NMR \delta 5.38 (1 H, t, $J = 7$ Hz), 4.01 (2 H, s) with LiCl (15 h, room temperature) and then to bromide 7 (85%); NMR \delta 5.41 (1 H, t, $J = 7$ Hz), 3.93 (2 H, s) with NaBr (3 h, room temperature).

The diol 8a of $a$-methyltetronic acid (8)$^8$ was generated using sodium hydride (1 equiv, THF-HMPA (1:1)), followed by butyllithium (1 equiv in hexane). A consideration of the resonance forms of this species, which logically include the furanoid structure 8b as a major contributor, suggested that alklylation should occur with high selectivity at the $\gamma$ position.$^9$ In fact, treatment of 8 with 7 (THF, $-60^\circ$C and then 24 h at room temperature) afforded the $\gamma$-substituted tetronic acid 9 (NMR \delta 8.8 (1 H, br), 5.23 (1 H, t, $J = 7$ Hz), 4.67 (1 H, m),