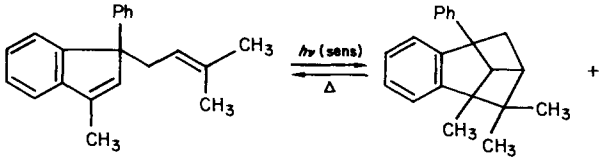
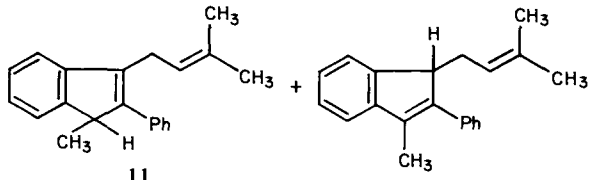
[2.2.0]hexanes) is quite common and is generally thought to be insensitive to the nature and position of substituents on the reacting double bonds.[20] We have found, however, that the normal closure predicted[21] by the "rule of five" does not occur in the photosensitized irradiation of the corresponding phenyl system. Thus, the triplet-sensitized reaction of indene **9** gave rise to a [2 + 2]-



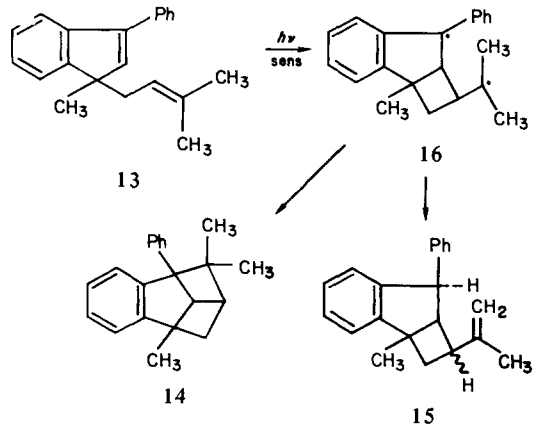
9 10



11 12

cycloadduct, **10** (13%), as well as two rearranged indenes [**11** (34%) and **12** (33%)]. The structures of the latter two compounds were established by comparison with independently synthesized samples. Careful examination of the NMR spectrum of **10** prompted us to assign it as a benzotricyclo[3.2.1.$0^{3,8}$]octane.[22] Thermolysis of cycloadduct **10** at 170 °C led to the rupture of the cyclobutane ring and regeneration of indene **9**.

Subjection of the isomeric phenyl-substituted indene **13** to similar sensitized conditions produced cycloadduct **14**[23] and a



13 16

14 15

mixture of isomeric 2,2a,7,7a-tetrahydro-1-isopropenyl-2a-methyl-7-phenyl-1*H*-cyclobut[*a*]indenes (**15**) (37%). In this case, cyclization of the triplet state of **13** proceeds to give intermediate **16**, undoubtedly a result of the added stabilization of the radical center by the two methyl groups. In simple cases, the activation energies for combination and disproportionation of radicals have been found to be equal.[24] This would explain the formation of both **14** and **15** in the above reaction. It should also be noted that the diradical (i.e., **16**) produced from the sensitized cyclization of **13** is long-lived enough to allow internal disproportionation to compete with radical coupling. This was not the case with indene **9**. The difference in behavior of the two systems parallels the well-documented increase in disproportionation to coupling ratios of free radicals as they become more stable.[24]

The facility with which the intramolecular [2 + 2] indene photocycloadditions occur makes this type of approach particularly attractive for the synthesis of some unusual polycyclic ring compounds.

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(21) R. Srinivason and K. L. Carlough, *J. Am. Chem. Soc.*, **89**, 4932 (1967); R. S. Liu and G. S. Hammond, *ibid.*, **89**, 4936 (1967).

(22) Compound **10**: NMR ($CDCl_3$, 100 MHz) δ 0.59 (s, 3 H), 1.20 (s, 3 H), 1.42 (s, 3 H), 2.24 (ddd, 1 H, J = 9.0, 5.0, and 2.0 Hz), 2.34 (dd, 1 H, J = 12.0, 2.0 Hz), 2.98 (dd, 1 H, J = 12.0, 9.0 Hz), 3.30 (d, 1 H, J = 5.0 Hz), and 6.4–7.3 (m, 9 H). The alternative mode of photocyclization of **9** would lead to a structure having an NMR spectrum quite different from that observed. A detailed analysis of the spectral data will be provided in a later publication.

(23) Compound **14**: NMR ($CDCl_3$, 270 MHz) δ 0.84 (s, 3 H), 1.00 (s, 3 H), 1.60 (s, 3 H), 2.12 (d, 1 H, J = 11.7 Hz), 2.27 (dd, 1 H, J = 8.8, 5.1 Hz), 2.35 (dd, 1 H, J = 11.7, 8.8 Hz), 3.63 (d, 1 H, J = 5.1 Hz), and 7.03–7.36 (m, 9 H).

(24) J. Kraus and J. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

Assignment of Proton-Decoupled Carbon-13 Spectra of Complex Molecules by Using Polarization Transfer Spectroscopy. A Superior Method to Off-Resonance Decoupling

Sir:

Off-resonance proton decoupling is one established assignment aid in ^{13}C NMR spectroscopy. It suffers from two disadvantages when used in assigning the ^{13}C spectra of a complex molecule: the resulting spectra may not be first order, and severe overlap of resonance lines may render the technique of limited value when the spectral region under investigation contains many resonance lines. We point out in this communication that pulse sequences[1] used to induce ^1H–^{13}C polarization transfer (PT) when combined with appropriate delay times (Δ) prior to data acquisition and broad-band decoupling result in (a) spectra containing only CH carbons if $\Delta = (2J)^{-1}$ ($J \equiv {}^{13}C$ and ^1H scalar coupling constant) and (b) predictable phase variations between the resonance of CH_2 carbons and those of CH and CH_3 carbons if $\Delta = 3(4J)^{-1}$. The resonances always appear as sharp singlets, resulting in dramatic time saving for acquiring useful information and enabling a one-to-one comparison to be made to the normal spectrum. We illustrate the technique by using the ^{13}C spectrum of cholesterol.

The polarization transfer pulse sequence is shown in Figure 1; τ is set equal to $(4J)^{-1}$. As pointed out by a number of workers,[1] if data acquistion commences immediately following the ^{13}C $\pi/2$ pulse, a CH resonance appears as a −1:1 doublet, CH_2 resonance as a −1:0:1 "doublet", and a CH_3 resonance as a −1:−1:1:1 quartet. Consequently, if broad-band decoupling is employed, mutual cancellations occur, and no signal is observed. We note, however, that if a delay period (Δ) is introduced, the signal components will undergo *different* intensity cycles, depending on the carbon type. Since J is approximately constant for most CH, CH_2, and CH_3 carbons (in the range 130–150 Hz), broad-band decoupling

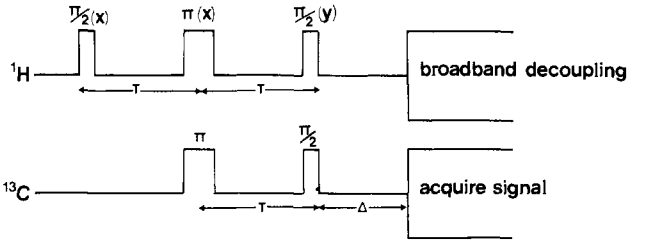

Figure 1. Polarization transfer pulse sequence, $\tau = (4J)^{-1}$. Δ is the decay before proton decoupling and data acquisition. Phase alternation of the final ^1H $\pi/2$ pulse was used.

(1) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979); H. J. Jabobsen and W. S. Brey, *ibid.*, **101**, 775 (1979); A. A. Maudsley, L. Müller, and R. R. Ernst, *J. Magn. Reson.*, **28**, 463 (1977); A. A. Maudsley and R. R. Ernst, *Chem. Phys. Lett.*, **50**, 368 (1977); G. A. Morris, *J. Am. Chem. Soc.*, **102**, 428 (1980).

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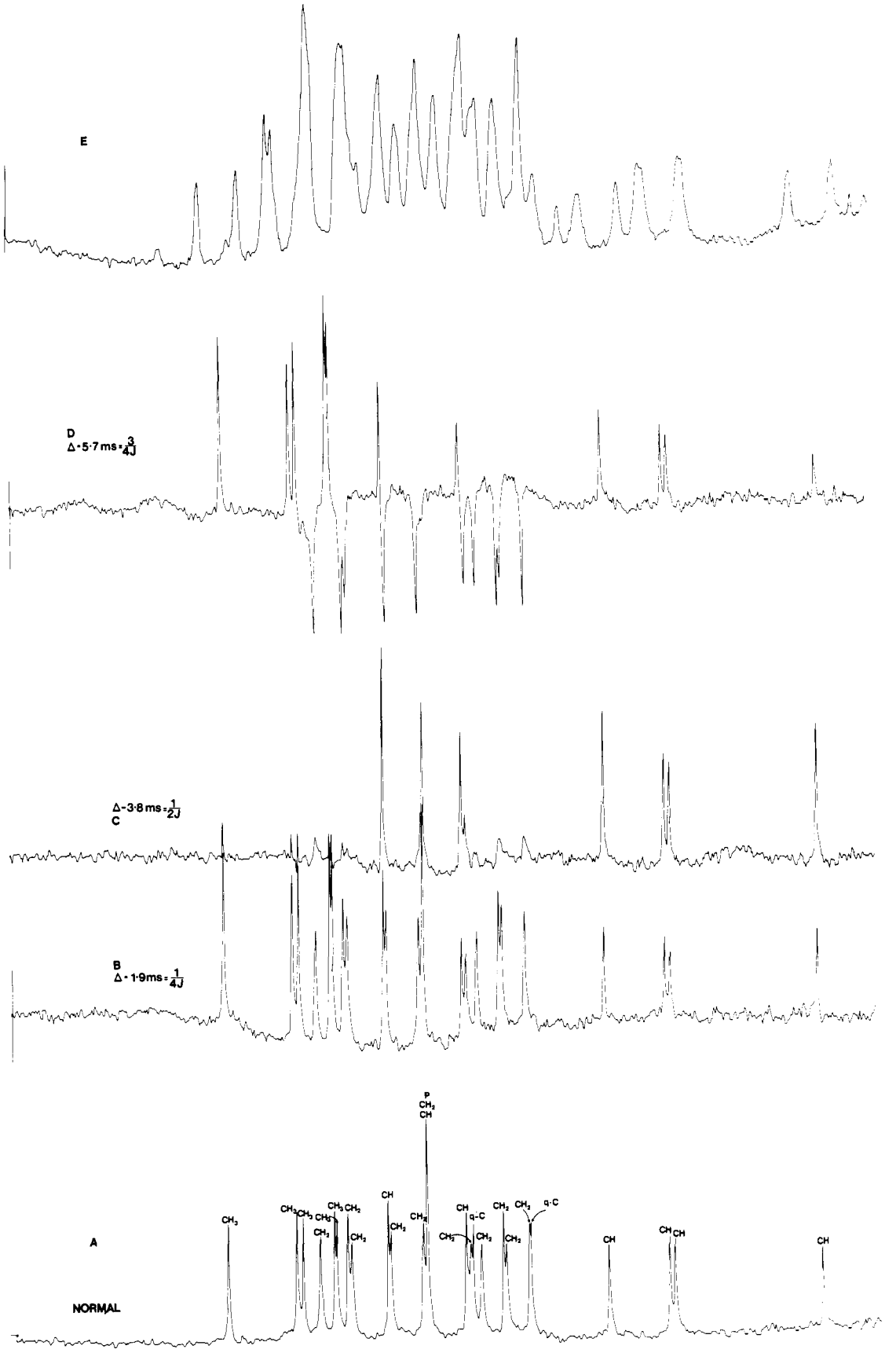

Figure 2. (A) Normal FT spectrum. (B) PT spectrum with $\Delta \simeq (4J)^{-1}$. (C) PT spectrum with $\Delta \simeq (2J)^{-1}$. (D) PT spectrum with $\Delta \simeq 3(4J)^{-1}$. (E) Off-resonance decoupled spectrum, 4000 pulses with ^1H carrier frequency set 3500-Hz upfield.

combined with a suitable Δ value can now be used to either remove resonances or change their relative phases, depending on the carbon type.

We note the following during the delay period: (a) for a CH doublet, the initially opposed carbon spins precess in the rotating frame at rates $J/2$ and $-J/2$, corresponding to a eigenvalue of the proton spin in the particular molecule, and yielding, on proton decoupling, a zero signal at $\Delta = 0$ and $1/J$ and a maximum at

$\Delta = (2J)^{-1}$: (b) for a CH_2 "doublet", the carbon spins precess at rates $\pm J$ and 0, yielding on proton decoupling a zero signal at $\Delta = 0$, $(2J)^{-1}$, and $1/J$ and phase-alternated maxima at $(4J)^{-1}$ and $3(4J)^{-1}$; and (c) for a CH_3 quartet, the spins precess at rates $3J/2$, $J/2$, $-J/2$, and $-3J/2$, yielding a complex signal intensity dependence on Δ *but* a zero signal at $(2J)^{-1}$ and signals with the *same* relative phase at $(4J)^{-1}$ and $3(4J)^{-1}$. The approximate constancy of J combined with the above differences in signal maxima/minima, depending on carbon type, provide a powerful assignment aid *and* a new method of spectral simplification.

These effects are dramatically illustrated in ^{13}C spectra[2] of cholesterol (Figure 2A-D). Spectrum A is the normal FT spectrum. Spectrum B is a polarization transfer spectrum[3,4] determined with $\tau = \Delta = 1.9$ ms $\approx (4J)^{-1}$. Note that non-protonated carbons do *not* appear. Spectrum C is a PT spectrum with $\tau = 1.9$ ms and $\Delta = 3.8$ ms $\approx (2J)^{-1}$. Only CH carbons give intense resonances; seven such carbon nuclei resonate in the spectral region shown; only seven intense peaks are observed. Spectrum D is a PT spectrum with $\tau = 1.9$ ms and $\Delta = 5.7$ ms $\approx 3(4J)^{-1}$. CH_3 and CH resonances appear in-phase; by comparison, CH_2 resonances appear 180° out-of-phase. Note the cancellation of the overlapping CH_2 and CH resonances (marked with a P). Spectra A-D allow a complete and simple breakdown of the resonances into carbon type. The off-resonance spectrum, E, although of some use, is severely broadened and has many overlapping lines. Note as well the greatly increased information content of the PT spectra; the time required to record spectra B-D was less than a quarter of that required to obtain the off-resonance spectrum E.

Acknowledgment. We thank the Australian Research Grants Committee for capital equipment grants. J. M. Field constructed much of the transmitter electronics.

(2) Spectra were determined on a Bruker HX-90 NMR spectrometer fitted with an Aspect 2000 24K computer, and a CXP-type receiver, the pulse programmer and modulator allowing complete computer control over rf phase and timing. Phase alternation of the final ^1H $\pi/2$ pulse was employed.[1] Broad-band decoupling was used during data acquistion. ^{13}C and ^1H pulse widths were $t_C = 12.5$ μs, $t_{\pi/2}{}^H = 60$ μs. All spectra are the result of 200 pulses averaged with a recycle time of 2 s; a spectral width of 2000 Hz is shown. Spectra were determined with the carrier frequency set upfield of the CH_3 resonances; spectra, therefore, run downfield left to right. This was used to suppress the olefinic carbon resonances. The sample was approximately 1.5 M in $CDCl_3$.

(3) Notes of caution: The delay Δ introduces a large linear-phase (LP) variation across the spectrum given by LP $\simeq 180°(\Delta/DW)$ where DW = dwell time. As the utility of PT spectra for assignment purposes depends on phase comparisons, the correct linear-phase correction must be used. For example, for spectrum D, LP $\approx 4500°$. Because an incomplete Fourier transformation is now employed (time-delayed spectra), a slightly distorted peak is recorded. It must be appreciated that for molecular fragments (such as fluoroalkanes, alkynes, etc.) for which J_{CH} varies significantly from 145 ± 15 Hz (the value found is most bonding situations) the spectra resulting from missetting the values of τ and Δ will produce peaks with different phase characteristics than those recorded here: (see: D. T. Pegg, D. T. Thomas, M. R. Bendall, and D. M. Doddrell, *J. Magn. Reson.*, in press.

(4) A referee has raised the question of the homogeneity of the rf pulses used. The spectra were recorded with the normal cross-coil high-resolution probe system; such a system produces extremely inhomogeneous ^1H rf pulses. It is possible to show (unpublished) that the only effect of such an inhomogeneity is a loss of signal-to-noise ratio but no phase information. Our PT spectra are boosted by about a factor of 2.5 compared to the theoretical value of ~4.0 (γ_H/γ_C). It should be possible to introduce PT spectroscopy on most NMR spectrometers; all that is required is pulse programmer control over the ^1H rf channel. Phase alternation of the ^1H channel is not a necessary requirement.

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*Book Reviews**

The Proteins. Volume IV. Edited by H. Neurath (University of Washington) and R. Hill (Duke University Medical Center). Academic Press, New York. 1979. xiv + 679 pp. $49.50.

"The Proteins" is a treatise reviewing protein structure, preparative and analytical techniques, and the molecular basis of protein function. This volume considers protein evolution and three specific protein groups: the chromosomal proteins, the contractile proteins of muscle, and collagen.

In the chapter on Protein Evolution, R. F. Doolittle discusses the mechanisms by which both "neutral" and advantageous changes to proteins can occur, and how these changes become characteristic of the organism. Arguments are presented which favor the concept that amino acid replacements can become fixed in a population despite conferring no apparent reproductive advantage. In the case of proteins with new functions, the author supports the view that they have arisen primarily from related, pre-existing proteins through gene duplication. To illustrate or argue for these theoretical considerations, the author employs often fascinating examples to great advantage. This helps to make the article appropriate for interested readers of all backgrounds.

The chapter entitled Chromosomal Proteins by R. J. DeLange and E. L. Smith focuses on the histones and protamines, the most characterized and understood of the proteins associating with the DNA of all but the most primitive organisms. The stress is on the elucidation of the primary structure of these proteins, the authors' area of expertise, and on the extensive post-translational modifications to which these proteins are subjected. These modifications may prove to be a sophisticated mechanism by which nuclear function is modulated. As noted by the authors, this article was prepared many years ago, and therefore a detailed description of the recent dramatic progress in the definition of the role of the histones in the primary organization of the DNA is not provided.

In the chapter on Contractile Proteins of Muscle by W. F. Harrington, the importance of structure to function is stressed. First, each component of the contractile apparatus is examined in terms of its structure, function, and regulation. Then, in the clearly and concisely presented models for the conversion of chemical energy to mechanical force, the relationship between structure and function is made apparent. Considering the specialized function of the contractile proteins described in this chapter, it is intriguing that they may function in almost every eukaryotic cell. An evaluation of this in the chapter might have been worthwhile in providing a better understanding of these proteins.

Collagen, comprising roughly one-third of the protein content of most vertebrates, functions to maintain shape and resist deformation in a variety of tissues and organs. In the final chapter, the chemistry and biology of this protein are discussed by P. Bornstein and W. Traub. The synthesis of this protein as procollagen, its secretion, and the extensive extracellular modifications which it undergoes are defined. The authors have made this chapter of interest to readers of many backgrounds, especially by including discussions of its involvement in disease and aging.

In the preface to this book, the editors express a desire that "The Proteins" present unifying concepts in protein chemistry. In this volume, they have achieved this to a certain extent. Each of the chapters on the specific protein groups points out the importance of structure and organization to the functions performed by these proteins, and the thorough examination of these proteins provides further insight into the problem of protein evolution.

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Gas Phase Ion Chemistry. Volume I. Edited by M. T. Bowers (University of California, Santa Barbara). Academic Press, New York. 1979. xiii + 435 pp. $39.50.

"Gas Phase Ion Chemistry" consists of two volumes. The dominant theme of the treatise is the chemical physics of gas-phase ion chemistry.

*Unsigned book reviews are by the Book Review Editor.