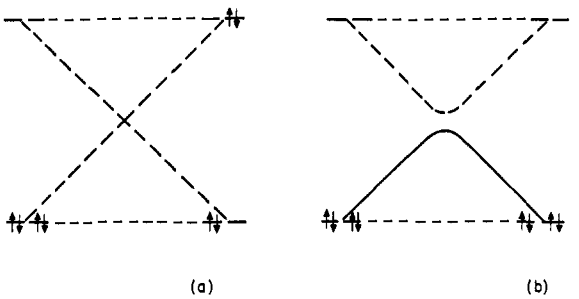

Figure 3. Orbital correlation diagram for dimerization of ethylene to cyclobutane (a) *via* a rectangular transition state; (b) *via* a trapezoidal transition state.

less stable than either. An aromatic system therefore has a unique geometry of minimum energy whereas an antiaromatic system has two distinct geometries that minimize the total energy. In accordance with Evans' principle,[5] pericyclic reactions can be divided into two classes, having their transition states isoconjugate with aromatic or with antiaromatic systems. In the former ones the transition state has a unique geometry; the valleys leading to it from reactant and product must therefore form a continuous depression in the potential surface. In the case of an antiaromatic transition state, however, there will be *two* distinct geometries of minimum energy, separated by a maximum. Since pericyclic reactions necessarily[4] involve a cyclic switching of bonds, the valley from the reactant, and the valley from the product, will lead to the two different forms of the transition state. The transition state is no longer a col separating the heads of two valleys, *i.e.* the highest point in a single continuous groove in the potential surface; here there are two grooves, each containing one of the "classical" structures for the transition state, and the transition state is the lowest point in the intervening ridge (corresponding to the high-energy degenerate "hybrid" form of the transition state). This analysis of course accounts perfectly for the potential surfaces deduced here for antiaromatic reactions; it also of course explains why it is only the antiaromatic reactions that show this anomalous behavior.

The results reported in this series of communications therefore provide further support for the interpretation of pericyclic reactions in terms of Evans' principle[5] and for their consequent classification into aromatic and antiaromatic types. There is of course no reason why an antiaromatic reaction should not be faster than an aromatic counterpart if this particular factor is outweighed by steric or other considerations. The literature shows very clearly that the use of the terms "allowed" and "forbidden" in this connection has proved misleading to organic chemists.

**Acknowledgment.** This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

(5) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 335; *Angew. Chem.*, in press.

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# Alternately Pulsed Carbon-13 and Proton Magnetic Resonance, an Alternative to Nuclear Off-Resonance Decoupling

*Sir:*

It has been noted that when proton decoupling is terminated immediately before a field-sweep passage through the carbon-13 resonance of methyl iodide, $^{13}C$–H spin coupling returns immediately, whereas reequilibration of populations of nuclear energy levels is slower, being determined by relaxation times.[1] Only small Overhauser enhancement of signal was observed. We wish to report that we have successfully modified this experiment for use together with Fourier transform carbon-13 nmr (cmr) methods[2] and that we may obtain signal improvement factors of 2.4–3.0 compared to entirely nonirradiated spectra. Furthermore, we find this alternately pulsed nmr (apnmr) technique to be a superior method for signal assignment compared to the usual off-resonance decoupling or single resonance irradiation methods.[3]

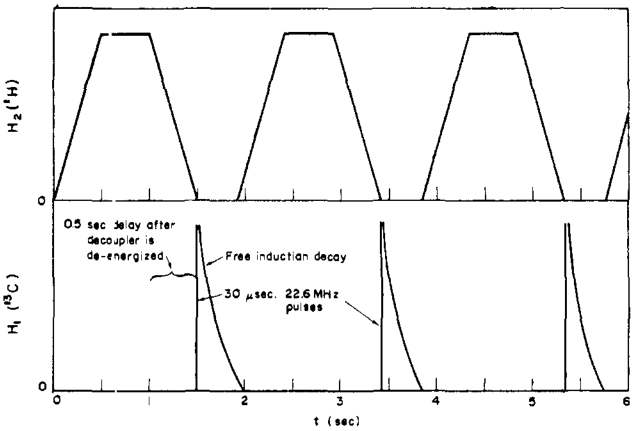

Figure 1. Pulse scheme for alternately pulsed nmr. $H_1$, $H_2$ power levels discretionary. Vertical slopes of $H_2$ represent rise and decay times of decoupler electronics.

Our initial alternately pulsed experiment, sketched in Figure 1, was to gate, in turn, the 90-MHz output of a broad band power amplifier ($^1H$ spin decoupler) and the 22.6-MHz ($^{13}C$) pulse power amplifier of the Bruker HFX-10 nmr spectrometer, storing the $^{13}C$ free-induction decay (fid) in a Fabri-Tek 1080 computer. One pulse channel (B) of a Bruker Model B-KR 300 digital pulse program generator was used along with a Hewlett-Packard 10534A mixer to activate the proton decoupler for 1 sec and to terminate the pulse. A second pulse channel (C) triggered a 30-μsec $^{13}C$ pulse following the 0.5-sec delay found necessary to allow decoupler electronics to deenergize. This trigger voltage also initiated a 0.4-sec computer sweep for storage of the fid. This sequence was made repetitive using the pulse programmer. After 32 pulse cycles, the 1080 computer

(1) J. Feeney, D. Shaw, and P. J. S. Pauwels, *Chem. Commun.*, 554 (1970).

(2) R. R. Ernst, *Advan. Magn. Resonance*, 2, 1 (1966); R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

(3) L. D. Hall and L. F. Johnson, *Chem. Commun.*, 509 (1969); H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 1355 (1969); F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, 60, 1152 (1965); L. D. Hall and L. F. Johnson, *Chem. Commun.*, 509 (1969).

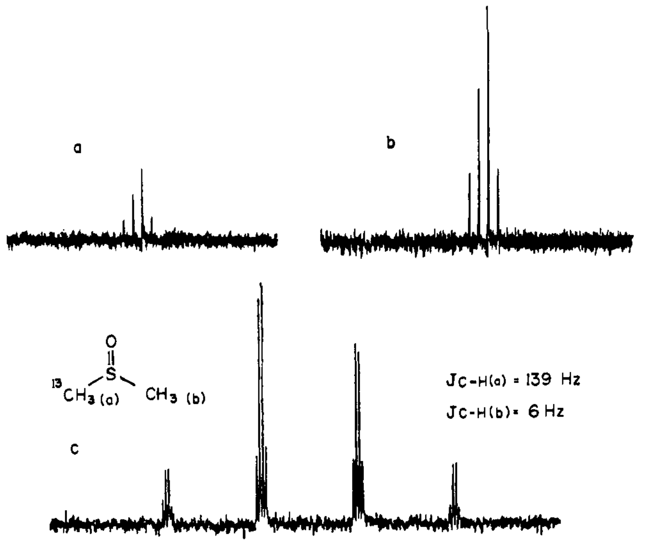

Figure 2. Carbon-13 nmr spectra of dimethyl sulfoxide: (a) no proton irradiation; (b) the apnmr (see text) spectrum; (c) a high-resolution expansion of the apnmr (see text) spectrum.

performed a Fourier transform of the fid to obtain cmr spectra (Figure 2) of a 90% dimethyl sulfoxide–10% hexafluorobenzene solution. With the decoupler power off entirely, Figure 2a was obtained. Alternate power pulsing using the same number of pulse cycles resulted in Figure 2b. The high-resolution spectrum recorded in Figure 2c is an expansion of Figure 2b and demonstrates that even long-range $^{13}$C–H coupling returns immediately after decoupling is terminated. *True values of* $J_{^{13}\mathrm{C}-\mathrm{H}}$ *are obtained.* Off-resonance and single-resonance decoupling frequently distort line shapes and coupling constant values.

A simple application of apnmr resonance to signal assignment can be illustrated by considering the cmr spectra of 2-butanol (not shown). Proton-decoupled, four-resonance signals are observed at −10.4, −23.1, −32.6, and −69.4 ppm *vs.* TMS. The apnmr spectrum shows two quartets ($J$ = 122, 125 Hz), one triplet ($J$ = 120 Hz), and one doublet ($J$ = 134 Hz) allowing immediate assignment of all cmr signals as methyl, methylene, or methine carbons, with, as an additional bonus, the Overhauser enhancement reducing by a factor of 7–9 the time needed to obtain the spectrum. A long-range doublet coupling (not accurately measured) further assigns the resonance at −23.1 ppm to the 1-CH$_3$ carbon illustrating that in apnmr all spin–spin couplings are available for use to assign signals. The other methyl resonance is a complex multiplet. The several superior features of apnmr lead us to believe it will supersede off resonance methods, especially since instrument modifications required are minimal. When, in addition, lanthanide shift reagents are employed, unequivocal assignment of even ambiguous cmr spectra is simple.[4]

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[4] O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **93**, 4295 (1971).

## Carbon Magnetic Resonance. Signal Assignment by Alternately Pulsed Nuclear Magnetic Resonance and Lanthanide-Induced Chemical Shifts

*Sir:*

Assignment of carbon magnetic resonance (cmr) signals has relied on a variety of complex methods such as nuclear off-resonance irradiation, selective proton decoupling,[1] or deuteration studies. Carbon spectra obtained with the newly developed alternately pulsed nmr (apnmr) experiment[2] together with proton-decoupled spectra determined in the presence of lanthanide shift (lis) reagents,[3] in this case tris(dipivaloylmethanato)europium(III) [Eu(DPM)$_3$], illustrate a convenient, rapid, and unambiguous method of assigning $^{13}$C resonances. We demonstrate an application of these two complementary tools by the complete and unequivocal identification of all $^{13}$C signals of isoborneol.

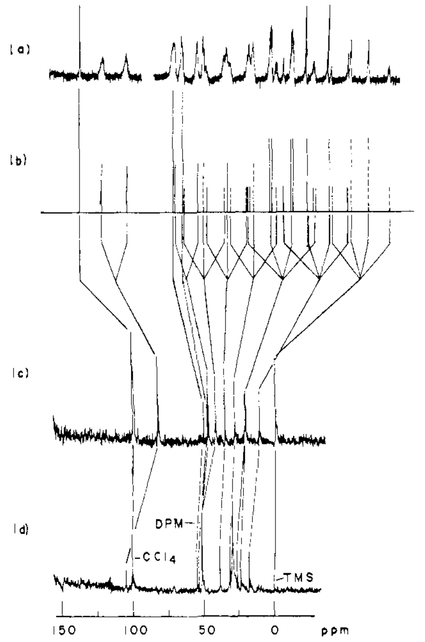

Figure 1. Carbon magnetic resonance spectra of isoborneol: (a) the alternately pulsed nmr spectrum (scale expanded); (b) a histogram of the apnmr spectrum, some lines dashed for clarity; (c) the cmr spectrum of 1.0 *M* isoborneol; (d) a lanthanide-shifted cmr spectrum of isoborneol (1.0 *M* + 523 mg of Eu(DPM)$_3$).

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[1] E. Wenkert, A. O. Clouse, D. W. Cochran, and D. Doddrell, *J. Amer. Chem. Soc.*, **91**, 6879 (1969), and references therein.

[2] O. A. Gansow and W. Schittenhelm, *ibid.*, **93**, 4294 (1971).

[3] (a) C. C. Hinckley, *ibid.*, **91**, 5160 (1969); (b) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5734 5737 (1970); (c) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971).