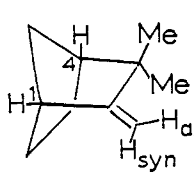
A New Class of Homoallylic ^1H–^1H Coupling Revealed by Multiple Resonance[1,2]

Sir:

There are now several examples in the literature[3] of long-range proton–proton coupling constants of the type termed[4] "homoallylic," which involve coupling through four σ bonds and a symmetrically disposed π bond, *i.e.*, H—C—C=C—C—H. Another homoallylic interaction, however, can be envisaged in which the coupling occurs through the pathway H—C=C—C—C—H. The designation homoallylic for the latter is more closely related to its popular usage in reaction mechanisms, as originally proposed by Simonetta and Winstein.[5] This second type of homoallylic coupling, hitherto unreported, has been revealed in the course of a current investigation of the nmr parameters of *exo*-methylene groups, and we wish to record these observations. In addition, some evidence bearing on the steric dependence of long-range, allylic couplings[3,6,7] is presented.

The proton spectrum (60 MHz) of camphene (**1**) consists of readily assigned multiplets for the *exo*-methylene and bridgehead protons, sharp singlets for the C-methyl protons, and a complex band for the methylene protons. In CCl_4 solutions (5 mole %), the lower field signals, δ 4.65 and 4.44, were shown to arise from the *syn*- and *anti*-*exo*-methylene protons, respectively, by a nuclear Overhauser experiment.[8] Upon saturation of the methyl signals, δ 1.01 and 1.05, the intensity of the 4.44-ppm band increased by 16% while the 4.65-ppm signal was essentially unchanged. The C-1 and C-4 protons absorb at 2.68 and 1.88 ppm, respectively. These assignments follow from the fact that the former is allylic and agree with earlier conclusions.[9]



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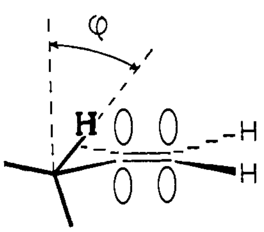

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The *syn*-*exo* proton signal appears as a poorly defined "quartet," suggesting interactions with *three* other nonequivalent protons, having comparable coupling constants, while the *anti* proton gives rise to a broadened band ($W_{1/2} \sim 2$ Hz) of unresolved structure (Figure 1A). To unravel these patterns we have examined the spectrum while simultaneously irradiating at up to *three* other regions. Double irradiation at either bridgehead proton reduced the lowest field signal to a poorly defined "triplet" while the 4.44-ppm signal becomes a crude "doublet" with decoupling at C-1 but merely narrows slightly with decoupling at the C-4 proton (Figure 1B and C). Triple irradiation, *i.e.*, spin decoupling both bridgehead protons, reveals an AX pattern for the *exo*-methylene protons but the higher field components are significantly broader, 0.7 *vs.* 0.4 Hz for the lines of lower field doublet (Figure 1D). This broadening is eliminated by a quadruple resonance experiment in which the methyl and both bridgehead protons are simultaneously irradiated (Figure 1E). In this way, the lines in the AX pattern have widths at half-height < 0.4 Hz, and the geminal coupling is easily measured, J_{gem} = 0.90 Hz. A second experiment[10] in which the *syn*-*exo* proton signal is observed while irradiating the *anti*-*exo*-, the C-1, and the methyl protons simultaneously reveals the homoallylic coupling between the C-4 bridgehead and *syn*-*exo* protons with J = 0.85 Hz. By further quadruple resonance experiments we have determined values for other coupling constants in camphene as listed in Table I.

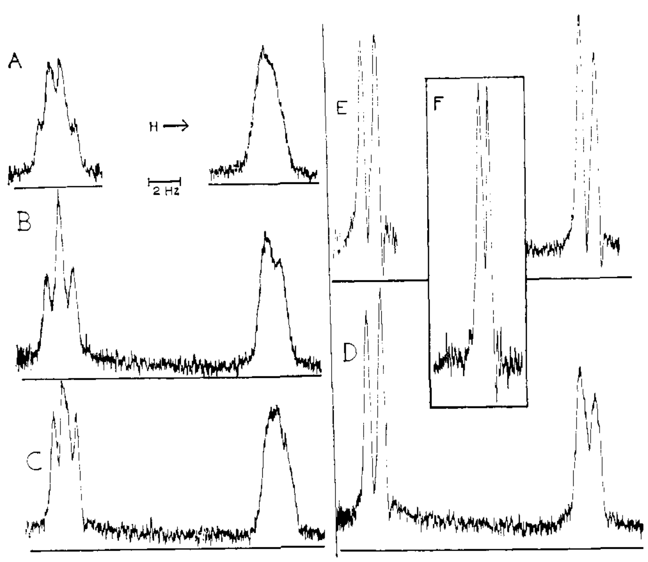

Figure 1. *exo*-Methylene proton spectra (60 MHz) of **1**: (A) normal pattern; (B) decoupling C-1 proton; (C) decoupling C-4 proton; (D) decoupling both bridgehead protons; (E) simultaneous decoupling of C-1, C-4, and methyl protons; (F) (insert) *anti*-proton signal upon decoupling the *syn*, C-4, and methyl protons simultaneously.

Table I. Proton Nmr Parameters for *exo*-Methylene Protons in Camphene (**1**)[a]

Proton	$\delta_H^{CCl_4}$	J_{gem}[b]	$J_{HC_1C=CH}$[b]	$J_{HC_4CC=CH}$[b]	$J_{MeCC=CH}$[b,c]
syn	4.65	0.9	0.55	0.85	<0.02
anti	4.44	0.9	0.55	<0.1[c]	<0.05

[a] Spectra were obtained on a Varian HA-60 instrument with external audio power for the decoupling experiments supplied by a GR-1310A and two HP-200CD oscillators, while the frequencies were measured with a HP-5245L counter. [b] In hertz with an estimated precision of ±0.1 Hz. [c] Estimated from line widths at half-height.

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(1) Part XVII in our series on nmr studies.

(2) Part XVI: D. J. Sardella and J. B. Stothers, *Can. J. Chem.*, in press.

(3) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); W. A. Thomas, "Annual Review of NMR Spectroscopy," E. F. Mooney, Ed., Academic Press, London, 1968, pp 78–84.

(4) J. T. Pinhey and S. Sternhell, *Tetrahedron Letters*, 275 (1963).

(5) M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

(6) E. W. Garbisch, *ibid.*, **86**, 5561 (1964).

(7) G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 6117 (1968).

(8) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

(9) (a) J. A. Claisse and D. I. Davies, *J. Chem. Soc., B*, 679 (1967); (b) G. A. Neville and I. C. Nigam, *Tetrahedron Letters*, 837 (1969).

(10) The multiple irradiation experiments are more readily performed in benzene solution using the solvent signal for "locking" rather than TMS. Our data reveal no measurable effect of this solvent change on the *J* values. In benzene, the positions of the various bands occur in the same relative order, low to high field, with comparable chemical shift differences.

The allylic couplings (column 3, Table I) are of interest in the light of recent discussions[7,11] on their steric dependence. In camphene the "dihedral angle" φ (see 2) is *ca.* 80° and the identical values for the cisoid and transoid couplings disagree with current notions which predict $J_{\text{cisoid}} < J_{\text{transoid}}$. The near coplanarity of the interacting protons, however, represents the case for which experimental data are scarce,[6,7] but the observed values, 0.55 Hz (*e.g.*, Figure 1F), are midway between those predicted, *viz.* +0.35 and +0.65 Hz, although the signs remain to be determined for camphene.

The data in the last two columns of Table I represent values for the homoallylic coupling of a second kind. It is interesting that for this case the *syn*-C_4H interaction is larger than the allylic coupling (*syn*-C_1H) and, furthermore, there is a marked steric dependence since the *anti*-C_4H coupling is much smaller. It may be suggested that the coupling involves principally σ contributions since the protons are nearly in a common plane, but it will be interesting to compare the values for cases in which the sp^3-bonded proton is orthogonal to the π plane. Work to this end as well as the determination of the relative sign of the coupling constant is in progress.

The presence of this homoallylic coupling has been confirmed for other related hydrocarbons by similar experiments, and the effects of alkyl substitution and stereochemistry on these and the geminal couplings are under study. It would appear that measurements of these parameters in appropriate systems may have application for stereochemical assignments besides their inherent theoretical interest.

Acknowledgment. We thank the National Research Council of Canada for financial support of this investigation.

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(11) M. Barfield, *J. Chem. Phys.*, **48**, 4463 (1968).

(12) Holder of NRCC scholarships, 1968–1970.

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Book Reviews

Mechanistic Aspects in Aromatic Sulfonation and Desulfonation. By HANS CERFONTAIN, Laboratory for Organic Chemistry, University of Amsterdam, The Netherlands. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xiii + 314 pp. 16 × 23.5 cm. $14.00.

The book, one of the Interscience Monographs on Organic Chemistry, contains an imposing amount of facts concerning electrophilic as well as nucleophilic aromatic sulfonation, desulfonation, and desulfonylation. The material is systematically arranged according to reaction and the classes of compounds undergoing the reaction concerned. The volume should be most valuable and useful as a reference source.

In view of the fact that the writer has made several important contributions to the field, it is somewhat unexpected to find that his attitude toward the mechanistic problems is a rather noncommittal one. Contrary to what its title may suggest, the book should be considered a bibliography and collection of facts and hypotheses originating from various research workers, rather than a critical mechanistic discussion by the writer himself.

A few obscure passages occur, particularly on pages 188–192. Some use of potential-energy profiles could possibly have been helpful in the representation of mechanistic facts, but this may be a matter of personal taste.

The writer states that he has attempted to cover the literature up to April 1967, and a considerable fraction of the references are from the 1960's.

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Anwendung von Isotopen in der organischen Chemie und Biochemie. Band I. Bestimmung der Isotopenverteilung in markierten Verbindungen. By H. SIMON and H. G. FLOSS. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1967. x + 247 pp. 16 × 23.5 cm. $13.50.

This, the first of three planned volumes on the use of isotopes in organic chemistry and biochemistry, deals with the determination of the distribution of an isotope at the various positions of a labeled molecule, a problem which often has to be faced in respect of both the starting material and end products of a tracer experiment. In some instances the distribution has been determined by physical methods, the account of which occupies only three pages of this book; but in the vast majority of cases, either chemical or enzymic degradation of the molecule has been carried out in a stepwise manner, and isotopic measurements have then been made on the resulting fragments. It is on this latter aspect that almost the entire book is based. The authors have adhered rigidly to the title, and the reviewer wondered whether it would have been straying too far away from this path to have given one or two examples of actual problems which had involved intramolecular double-labeling, or where the possibility of such labeling occurred in the product (see the one-sentence statement, without any reference, on p 3 that mass spectrometry is necessary for the determination of intramolecular double-labeling).

Methods for the degradation, followed by isolation of degradation products in form and purity suitable for isotopic analysis, are described, class by class: carboxylic acids, aliphatic hydrocarbons, alcohols, etc; later sections give examples from the various groups of natural products: carbohydrates, steroids, vitamins, alkaloids, etc. Although completeness is not claimed, the whole range of organic compounds which have been studied by tracer methods seems to be covered in a reasonably representative way. The list of approximately 840 references includes a good many in 1966 and three or four in 1967. However, this is very much more than a mere compilation of facts. The authors, who are themselves established workers in the field, have critically evaluated the various methods and drawn attention to the many pitfalls and traps for the unwary; and this should greatly help other workers to obtain meaningful results from their tracer experiments. This is a thoroughly practical book, and experimental details are given for many procedures of general importance.

The style reminded the reviewer of Houben-Weyl (and this is intended to be not only descriptive, but also complimentary). It is very clearly written, and the text is illustrated by many formula schemes. It is provided with a good subject index, and also with a tabulation of several hundred compounds, arranged according to molecular formula, giving methods of degradation and literature references.

This excellent volume fills a real need and should be available in every laboratory in which organic tracer work is carried out. One may look forward to the appearance of the two remaining volumes of the series (on the isotope effect and analysis).

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