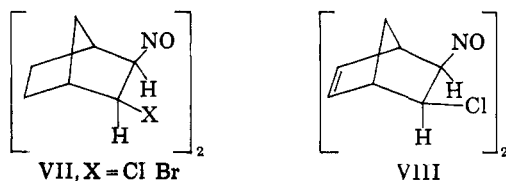
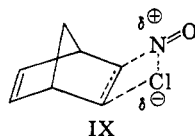


try. Further, it seems reasonable to assume an *exo* configuration for the nitroso group in these adducts, since mechanisms involving attack by NO^+ , $\text{NO}\cdot$, or NOX molecules would all be expected to deliver the nitroso group from the less hindered side of the olefins.¹⁵ Thus, the previously described adducts may be assigned the *cis-exo* stereochemistry shown in VII and VIII.



These results suggest a new view of nitrosyl halide additions. Lack of structural rearrangement and apparent *cis* addition, as well as lack of incorporation of nucleophilic solvent (ethanol or acetic acid) into the products, all speak against the ionic addition mechanism.⁸ A free radical mechanism initiated by $\text{NO}\cdot$ addition is unlikely, since nitric oxide is unreactive toward norbornadiene.¹⁹ This suggests a four-center mechanism, with little carbonium ion character developing in the transition state. In the case of norbornadiene, the transition state may be pictured as shown in IX.



It is interesting that the reaction of dinitrogen pentoxide with olefins, which gives 1,2-nitronitrates, has also been shown to be a *cis* addition; a cyclic transition state analogous to IX has been suggested.²⁰ Similarly, the *cis* course of the addition of acetyl nitrate to olefins, giving 1,2-nitroacetates, has been established.²¹ The *cis* polar addition of hydrogen bromide to acenaphthalene²² has been reported, and most recently, *cis* addition of water and methanol to *endo*-trimethylenenorbornene has been detected.²³ It appears that the nitrosyl halide additions discussed in this paper belong to a rapidly growing group of previously unrecognized *cis* addition reactions.

(19) Private communication from Dr. L. P. Kuhn.

(20) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6008 (1957); T. E. Stevens, *J. Org. Chem.*, **24**, 1136 (1959).

(21) G. Drefahl, H. Crahmer, and W. Thomas, *Chem. Ber.*, **91**, 282 (1958); G. Drefahl and H. Crahmer, *ibid.*, **91**, 745, 750 (1958); F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962).

(22) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **84**, 2012 (1962).

(23) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963); S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

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CORNELL UNIVERSITY
ITHACA, NEW YORK

JERROLD MEINWALD
YVONNE CHU MEINWALD
T. NELSON BAKER, III

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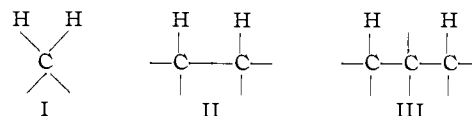
Long-Range Spin-Spin Couplings in the Nuclear Magnetic Resonance Spectra of Some Bicyclo [2.2.1]heptanes¹

Sir:

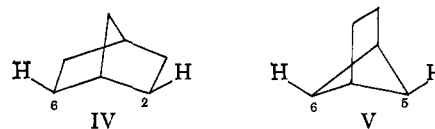
The idea that spin-spin splitting in n.m.r. spectroscopy is dependent upon indirect coupling of neighboring nuclei *via* the electrons in a molecule is generally accepted.² Theoretical and experimental progress

(1) Presented in part at the Eighteenth National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 16-20, 1963. Partial support of this work by the Alfred P. Sloan Foundation is acknowledged with pleasure.

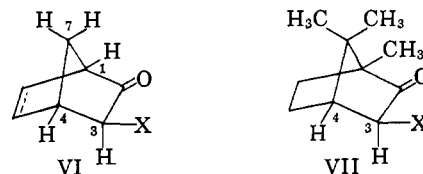
has been made in understanding how spin-spin coupling constants vary with molecular geometry when either two or three bonds (part formulas I and II) separate a pair of interacting protons. Thus, the dependence of J (coupling constant) on the H-C-H angle



in I³ and on the H-C-C-H dihedral angle in II⁴ is known. It is generally stated that coupling between protons which are separated by more than three bonds in saturated systems is negligible (<1 c.p.s.).⁵ However, several counter examples to this rule have been well authenticated in recent years,⁶⁻⁸ and in order to extend the usefulness of n.m.r. spectroscopy as a structural and stereochemical tool, it would be of interest to know what circumstances lead to important (>1 c.p.s.) "long-range" couplings. In the absence of any theoretical treatment of this problem, experimental data concerning long-range couplings in systems of known geometry becomes of interest. Interactions ($J \cong 1$ c.p.s.) between the *exo*-2 and *exo*-6 protons in bicyclo[2.2.1]heptanes (IV)⁷ and between the *endo*-5 and *endo*-6 protons ($J \cong 7$ c.p.s.) in bicyclo[2.1.1]hexanes (V)^{6,8} provide examples of coupling through four single bonds and have proved valuable in analyzing spectra of these systems.



We have found recently that the spectra of a number of *exo*-3 substituted norcamphors and dehydronorcamphors (VI)⁹ show a split *endo*-3 proton ($J \cong 3-4$ c.p.s.) in the n.m.r., in spite of the fact that the analogous camphors (VII) show the *endo*-3 proton as a singlet.¹⁰



Two hypotheses may be entertained to explain this surprising contrast. It might be that the geometry of the camphor skeleton is sufficiently different from that of norcamphor (as a result of nonbonded interactions introduced by the methyl groups) to give two significantly different H-C₄-C₃-H dihedral angles. This possibility appears unlikely, however, in view of

(2) Leading references: J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959; J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961.

(3) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

(4) M. Karplus, *ibid.*, **30**, 11 (1959); see also H. Conroy in R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **2**, 308 (1960).

(5) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 3; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapter 6.

(6) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961), and references cited therein.

(7) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(8) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

(9) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963).

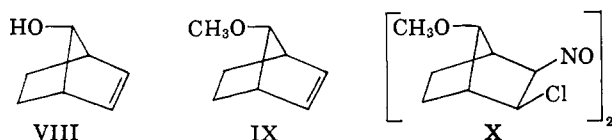
(10) W. D. Kumler, J. N. Shoolery, and F. V. Brucher, Jr., *ibid.*, **80**, 2533 (1958).

the known rigidity of the bicyclo[2.2.1]heptane ring system.¹¹ Furthermore, the model on which a $J_{3,4} \cong 0$ c.p.s. (80° angle) for VII is predicted does not include nonbonded interactions.

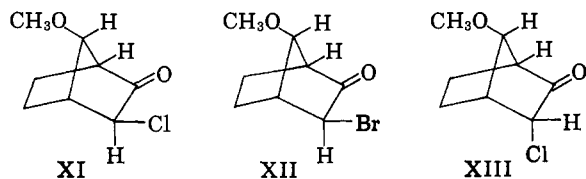
Alternatively, it is possible that $J_{3,4} \cong 0$ even in VI, and that the splitting of the *endo*-3 proton is due to interaction with a more distant proton. We have found this to be the case and would like to call attention to this previously unrecognized long-range coupling in the norbornyl system.

The logical candidates for long-range interactions in VI are the protons at C₁ and at C₇, present in VI but absent in VII. Of these, the *anti*-7 proton bears a geometrical relationship to the *endo*-3 proton rather similar to the relationship between the strongly coupled *endo*-5 and *endo*-6 protons of V. Evidence pointing to this particular interaction was readily obtained by preparing an analog of VI in which the *anti*-7 position was occupied by a methoxyl group, as described in the following section.

The readily available *anti*-7-norbornenol (VIII)¹² was converted by treatment with sodium hydride followed by methyl iodide into *anti*-7-methoxynorbornene (IX),¹³ which gave a crystalline dimeric nitroso



chloride (X)^{9,13} upon treatment with isoamyl nitrite and hydrochloric acid. Levulinic acid-hydrochloric acid hydrolysis^{9,14} of this dimer gave *exo*-3-chloro-*anti*-7-methoxynorcamphor (XI).¹³ The n.m.r. spec-



trum of this compound showed the *endo*-3-proton as a *singlet* at 6.20 τ .¹⁵ The corresponding *exo*-3-bromo-*anti*-7-methoxynorcamphor (XII),¹³ prepared in an analogous way, again showed the *endo*-3 proton as a *singlet* (6.13 τ). As expected, the *endo* chloro epimer XIII,¹³ obtained by chromatography of the base-catalyzed equilibrium mixture derived from XI, showed the *exo*-3 proton as a doublet ($J_{3,4} \cong 4$ c.p.s., 6.00 τ).

We conclude that the n.m.r. spectra of α -haloketones of the general formula VI are characterized by a coupling ($J_{3,7} \cong 3-4$ c.p.s.) between the *endo*-3 and *anti*-7 protons. Whether this coupling is in part dependent on some specific feature of these molecules other than their geometry¹⁶ or whether it is quite general for norbornanes and norbornenes remains to be seen. However, the implications concerning the anticipation of *norbornane* spectra on the basis of *bornane* or other more substituted models are evident.

(11) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 799 (1962).

(12) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(13) All new compounds gave satisfactory elementary analyses.

(14) C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

(15) We are grateful to Dr. E. LeGoff for obtaining some of these spectra for us, using a Varian A-60 instrument at Mellon Institute.

(16) The possibility that the electronegativity of attached groups plays a role in determining the value of coupling constants has been discussed recently by K. L. Williamson.¹¹

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CORNELL UNIVERSITY
ITHACA, NEW YORK

JERROLD MEINWALD
YVONNE C. MEINWALD

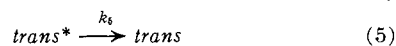
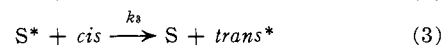
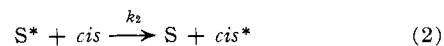
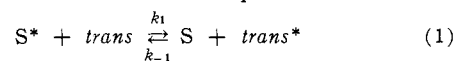
RECEIVED MAY 23, 1963

Mechanisms of Photochemical Reactions in Solution.

XVII. *cis-trans* Isomerization of the Stilbenes by Excitation Transfer from Low Energy Sensitizers

Sir:

We have reported that *cis-trans* isomerization of the stilbenes can be effected by photosensitizers.¹ Evidence is strong that the key step is transfer of triplet excitation from excited sensitizer molecules to the stilbenes. The following mechanism accounts for most of the available data. Asterisks indicate excited triplet states.



Reactions 1, 2, and the reverse of reaction 1 are of the type commonly suggested for energy transfer.² The excitation and deexcitation acts in eq. 1 and 2 involve the same transitions as are observed in emission and absorption spectroscopy.³ Occurrence of reaction 4 is suggested by our observation that, whereas excitation of either of the isomeric stilbenes produces an excited state which can be deactivated to *trans*-stilbene by the reverse of reaction 1 or by other quenching reactions (*vide infra*), the reverse of reaction 2 cannot be detected. Reaction 5 is an ordinary radiationless transition. Reaction 6 is at first startling; however, there is no reason to expect that conversion of electronic excitation to thermal energy will preserve faithfully the geometry of the excited states.⁴

Reaction 3 is demanded by our data. *cis*-Stilbene is a moderately effective acceptor of energy from sensitizer triplets having insufficient excitation energy to promote the substrate to its spectroscopic triplet state.⁵ The process must involve some transformation of the acceptor that does not conform to the Franck-Condon principle.

Sensitizers have been characterized by measurement of the photostationary states established in their presence. Data are presented in Fig. 1 in which photostationary ratios are plotted against triplet excitation energies of the sensitizers. Since results with sensitizers having excitation energies less than that of fluorenone are sensitive to the concentration of the sensitizer, the data plotted are extrapolated values for infinite dilution. Measurements were made in benzene solution at 28°.

If reaction 3 is omitted, the mechanism predicts the photostationary condition

$$\frac{[trans]_s}{[cis]_s} = \frac{k_2(k_5 + k_{-1}[S])}{k_1k_6} \quad (7)$$

High energy sensitizers show no concentration effects indicating that $k_6 \gg k_{-1}[S]$. This condition holds at infinite dilution with sensitizers which show activity as energy acceptors. Under such circumstances, reflected by the data in Fig. 1, eq. 7 reduces to 8.

$$\frac{[trans]_s}{[cis]_s} = \frac{k_2k_5}{k_1k_6} \quad (8)$$

Variation in the stationary state ratio as the sensitizer is changed should depend on the values of k_2/k_1 . Since

(1) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

(2) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962).

(3) Emission and absorption refer to phosphorescence and $S_0 \rightarrow T_1$ absorption, respectively.

(4) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(5) Temperature variation shows that reaction 3 has no appreciable activation energy.