

the general changes observed in ${}^1J_{C_{18}-H}$ and that very large changes in the hybridization parameters are not required, as assumed earlier, to fit the experimental couplings in these near tetrahedral systems. The substituent parameters of Malinowski⁶ also may be explained better by additive incremental changes in $(Z_K)^3$ for a substituted carbon atom. Cautious application of hybridization criteria for molecules which have similar geometry is recommended until variations in the effective nuclear charge upon the radial wave function of a substituted carbon atom are better understood.

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A Correlation of F^{19} - F^{19} *gem* Coupling Constants with Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Fluoroalkenes

Sir:

The geometrical relationship between any two fluorine atoms in a polyfluoroalkene molecule can often be determined by the magnitude of the spin-spin coupling constants obtained from the F^{19} n.m.r. spectrum. Values of J^{FF}_{trans} are distinctive, being more than 110 c.p.s.,¹ and provide a ready means for the proper assign-

Table I. Chemical Shifts^a and Fluorine-Fluorine *gem* Coupling Constants for $F_1F_2C=CX_1X_2$

	Compd.		δ_{F_1} , p.p.m.	δ_{F_2} , p.p.m.	$J^{F_1F_2}_{gem}$, c.p.s.	Ref.
	X_1	X_2				
1	F	H	101.6	129.4	87	b, c
2	F	CF=CFY ^d	107	119	82	e
3	F	Cl	105	121	78	c, f
4	F	CF ₂ Y ^e	104	112	72	e
5	F	Br	96.4	116.8	71.3	b
6	F	CF ₃	93	107	57	h
7	F	CF ₂ Cl	95	106	56	h
8	F	CF ₂ Br	95.3	105.4	55.0	i
9	F	CF ₂ I	95.0	104.1	53.4	i
10	H	CH=CF ₂	$1/2(\delta_{F_1} + \delta_{F_2}) = 87.6$		36.6	j, k
11	H	H	81.3	81.3	36.4	b, l
12	Br	H	81.9	82.8	34.5	b
13	CF ₃	Cl	78.2	78.5	16.7	m
14	F	COF	77.1	88.8	6.6	i

^a Chemical shifts are given relative to CCl₃F. ^b J. Reuben, Y. Shvo, and A. Demiel, to be published. ^c Reference 1. ^d Y = Ni(Ph₃P) π -C₆H₆. ^e D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964). ^f Reference 3. ^g Y = Ni(CO) π -C₆H₆. ^h E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **17**, 1244 (1961). ⁱ Reference 4. ^j J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961). ^k K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1339 (1965). ^l G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 226 (1963). ^m Reference 5.

ment of the correct geometrical configuration.² Both *gem* and *cis* F^{19} - F^{19} coupling constants are, however, spread over wide and overlapping ranges. In some

(1) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

(2) See, for example, D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

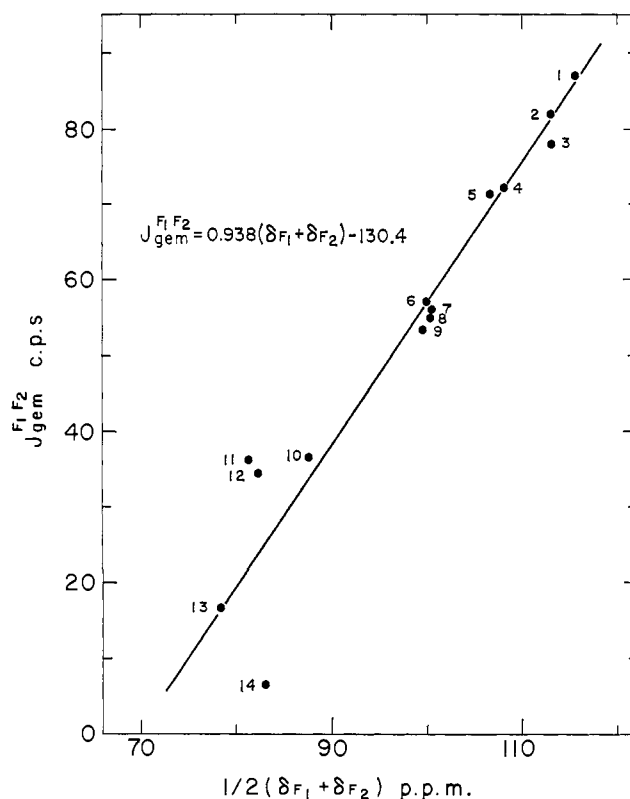


Figure 1. A plot of $J^{F_1F_2}_{gem}$ vs. the mean chemical shift of the interacting nuclei for compounds of the type $F_1F_2C=CX_1X_2$. Numbers refer to Table I.

cases, as¹ in $F_2C=CFH$, $F_2C=CFBr$, $F_2C=CFCl$, etc., J^{FF}_{gem} is greater than J^{FF}_{cis} . In other instances, as in $F_2C=CFCN$,¹ $F_2C=CFBCl_2$,³ and $F_2C=CFCOF$,⁴ the inverse relation has been found, J^{FF}_{gem} being smaller than J^{FF}_{cis} . The ambiguity thus arising is most disturbing when F^{19} - F^{19} coupling constants are used for the elucidation of molecular structure.

In Table I n.m.r. data compiled from the literature and completed with some of our measurements are presented for fluoroalkenes containing a 1,1-difluorovinyl radical.

Low values of J^{FF}_{gem} have been noted by several authors,³⁻⁵ but no satisfactory explanation has been offered. In molecules bearing a mesomerically electron-withdrawing group, bonded to 1,1-difluorovinyl, the contribution of valence-bond resonance structures, such as $F_2C^+-CF=C=N^-$, $F_2C^+-CF=B-Cl_2$, $F_2C^+-CF=CF-O^-$, have to be considered. By this mechanism electrons are removed from the terminal carbon atom, and if these carry nuclear spin information the *gem* coupling constant between the fluorine atoms bound to it will be reduced. At the same time a decreased shielding of the interacting nuclei is expected. Mesomerically electron-releasing substituents will have an opposite effect, owing to contributions of resonance forms of the type $F_2C^--CF=X^+$.

From the above considerations a direct relationship between the magnitude of the coupling constants and the chemical shifts of the geminal fluorines may be anticipated. In Figure 1 J^{FF}_{gem} is plotted vs. the mean

(3) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961).

(4) K. C. Ramey and W. S. Brey, Jr., *J. Chem. Phys.*, **40**, 2349 (1964).

(5) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961).

chemical shift of the interacting nuclei for the compounds listed in Table I. Indeed a linear dependence is obtained. A similar plot for perfluorovinyl derivatives of some metals and metalloids studied by Coyle, Stafford, and Stone³ and by Seyferth, Wada, and Maciel⁶ also yields a straight line, but of different slope [$J^{F_1F_2}_{gem} = 1.4(\delta_{F_1} + \delta_{F_2}) - 217$], suggesting that other factors, besides the relative weights of the valence bond resonance structures, are also important in determining the relationship between coupling constants and chemical shifts.

The observations and correlations presented here should be useful for unambiguous interpretation of n.m.r. spectra of compounds containing the $F_2C=C<$ grouping.

(6) D. Seyferth, T. Wada, and G. E. Maciel, *Inorg. Chem.*, **1**, 232 (1962).

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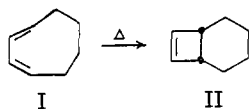
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The Thermal Cyclization of 1,3-Dienes to Cyclobutenes

Sir:

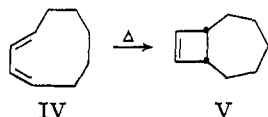
We wish to report what are to our knowledge the first noted examples of the thermal cyclization of hydrocarbonaceous 1,3-butadiene derivatives to cyclobutenes.¹

When *cis,trans*-1,3-cyclooctadiene (I)² is heated at temperatures of 80° or higher it is converted essentially quantitatively to II. The latter is identical in all re-



spects with the material obtained by photochemically induced cyclization³ of *cis,cis*-1,3-cyclooctadiene (III) and is converted to III above 300°.

A similar cyclization of *cis,trans*-1,3-cyclononadiene (IV)⁴ to V takes place at temperatures above 175° and leads to an equilibrium mixture of IV and V in which V predominates up to 250°. At temperatures in excess of 250° an irreversible isomerization of V to *cis,cis*-1,3-



cyclononadiene occurs. The structure of V is assigned on the basis of its n.m.r. spectrum (τ 3.95, 6.9, and 8.5 (area ratio 2:2:10)), mol. wt. 122 (mass spectrum), and its quantitative hydrogenation to the known *cis*-

(1) The cyclization of halogenated butadiene to the corresponding cyclobutene is well documented: E. W. Shlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964).

(2) A. C. Cope and C. L. Bumgardner, *ibid.*, **78**, 2812 (1956).

(3) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962).

(4) R. W. Fawcett and J. O. Harris, *J. Chem. Soc.*, 2673 (1954). The material obtained by these authors is a mixture of *cis,cis* and *cis,trans* isomers in which the latter predominates.

bicyclo[5.2.0]nonane.⁵ V is also obtained as one of several products of the photolysis of *cis,cis*-1,3-cyclononadiene.⁵ The *cis,cis*-1,3-dienes of the C₈ and C₉ cyclohydrocarbons exhibit no tendency to undergo thermal cyclization.

The observed stereospecificity of the observed cyclizations is in accord with the recently postulated⁷ orbital symmetry control of electrocyclic reactions which predicts the observed conrotatory mode of cyclization of these dienes in their ground electronic states.

Acknowledgment. The authors are indebted to the Robert A. Welch Foundation for financial support.

(5) N. Allinger, M. Nakasaki, and V. Zalkow, *J. Am. Chem. Soc.*, **81**, 4074 (1959). We are indebted to Professor Allinger for assistance in obtaining the infrared spectra of the isomeric bicyclo[5.2.0]nonanes.

(6) The detailed results of our studies of the photochemistry of the isomeric 1,3-cyclononadiene will be reported shortly.

(7) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

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The Oxidative Coupling of 2,6-Xylenol, a Novel Mechanism

Sir:

2,6-Xylenol reacts with oxygen in the presence of a cuprous chloride-amine catalyst to yield a high molecular weight linear polyarylene ether.¹

The reaction has been shown to involve carbon-oxygen coupling of aryloxy radicals²⁻⁴ but cannot occur simply by coupling of polymeric aryloxy radicals to monomer radicals. Reactions of this type presumably occur, but the sharp increase in the degree of polymerization near the end of the reaction is not consistent with stepwise addition of monomer units.² Furthermore, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol ("xylenol dimer") as well as low polymers polymerize readily to a high polymer identical with that obtained from xylenol.² Three mechanisms have been suggested:

(1) End-linking of polymer radicals: polymeric aryloxy radicals may couple directly, the oxygen atom of one attacking the *para* position in the terminal ring of the other. (2) Quinol ether rearrangement^{3d} postulates the formation of quinol ethers by the combination of two aryloxy radicals, followed by rearrangement analogous to the benzidine rearrangement⁵ or to the quinamine rearrangement studied recently by Miller.⁶ (3) Quinol ether equilibration (without analogy as a polymerization mechanism) has also been postulated.⁷ In simplest terms, two aryloxy radicals combine to form a quinol

(1) (a) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance *J. Am. Chem. Soc.*, **81**, 6335 (1959); (b) A. S. Hay, *J. Polymer Sci.*, **58**, 581 (1962).

(2) G. F. Endres and J. Kwiatek, *ibid.*, **58**, 593 (1962).

(3) Preprints, Division of Polymer Chemistry, American Chemical Society, Vol. 2, Sept. 1961: (a) A. S. Hay, p. 319; (b) G. F. Endres, A. S. Blanchard, H. L. Finkbeiner, and G. F. Endres, p. 331; (d) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, p. 340.

(4) W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

(5) C. K. Ingold and H. V. Kidd, *J. Chem. Soc.*, 984 (1933); D. H. Smith, J. R. Schwartz, and G. W. Wheland, *J. Am. Chem. Soc.*, **74**, 2282 (1952).

(6) B. Miller, *ibid.*, **86**, 1127 (1964).

(7) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *Soc. Plastics Eng. Transl.*, **2**, 112 (1962).