

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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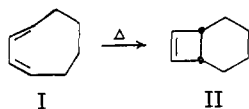
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The Thermal Cyclization of 1,3-Dienes to Cyclobutenes

Sir:

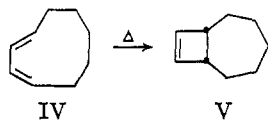
We wish to report what are to our knowledge the first noted examples of the thermal cyclization of hydrocarbonaceous 1,3-butadiene derivatives to cyclobutenes.¹

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.

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(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).

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