

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 Stone<sup>3</sup> and by Seyferth, Wada, and Maciel<sup>6</sup> 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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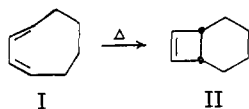
Received July 6, 1965

### The Thermal Cyclization of 1,3-Dienes to Cyclobutenes

Sir:

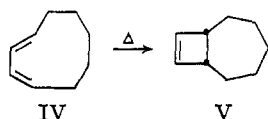
We wish to report what are to our knowledge the first noted examples of the thermal cyclization of hydrocarbonaceous 1,3-butadiene derivatives to cyclobutenes.<sup>1</sup>

When *cis,trans*-1,3-cyclooctadiene (I)<sup>2</sup> 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 cyclization<sup>3</sup> of *cis,cis*-1,3-cyclooctadiene (III) and is converted to III above 300°.

A similar cyclization of *cis,trans*-1,3-cyclononadiene (IV)<sup>4</sup> 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 ( $\tau$  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.<sup>5</sup> V is also obtained as one of several products of the photolysis of *cis,cis*-1,3-cyclononadiene.<sup>5</sup> The *cis,cis*-1,3-dienes of the C<sub>8</sub> and C<sub>9</sub> cyclohydrocarbons exhibit no tendency to undergo thermal cyclization.

The observed stereospecificity of the observed cyclizations is in accord with the recently postulated<sup>7</sup> 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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Received June 2, 1965

### 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.<sup>1</sup>

The reaction has been shown to involve carbon-oxygen coupling of aryloxy radicals<sup>2-4</sup> 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.<sup>2</sup> 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.<sup>2</sup> 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<sup>3d</sup> postulates the formation of quinol ethers by the combination of two aryloxy radicals, followed by rearrangement analogous to the benzidine rearrangement<sup>5</sup> or to the quinamine rearrangement studied recently by Miller.<sup>6</sup> (3) Quinol ether equilibration (without analogy as a polymerization mechanism) has also been postulated.<sup>7</sup> 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.

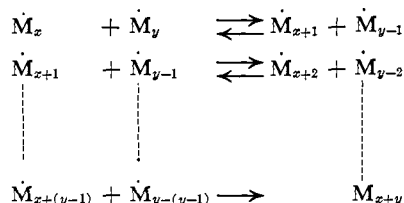
(4) W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

(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).

ether, which in turn dissociates to form two new aryloxy radicals. The suggested process is shown below where  $\dot{M}_x$  and  $\dot{M}_y$  indicate two polymeric aryloxy radicals of degree of polymerization  $x$  and  $y$ , respectively.



The characteristics of such a system would be: (a) the state of oxidation does not change regardless of the number of intervening steps; (b) the degree of polymerization is conserved except in the last step where a tautomerism terminates the equilibration; (c) all steps must be rapid and, except for the last one, reversible; and (d) since any of the aryloxy radicals can be reduced by the phenols in the solution, products containing any number of rings can be produced. The net result is the combination of two polymer chains by the removal of one electron from each.

We wish to report results that confirm the existence of mechanism 3. If the oxidation of xylenol dimer proceeds by mechanism 1 or 2, only products with an even number of rings should be obtained, *i.e.*, tetramer, hexamer, etc. Only mechanism 3 would predict the formation of monomer and trimer.

A solution of 0.020 g. (0.0002 mole) of cuprous chloride in 20 ml. of *o*-dichlorobenzene and 9 ml. of pyridine was stirred under oxygen for 20 min. in a closed reaction flask at 30°, and a solution of 1.935 g. (0.008 mole) of xylenol dimer<sup>2</sup> in 10 ml. of *o*-dichlorobenzene was added. When the oxygen absorption reached 9% of theory, 2.3 ml. of trimethylchlorosilane was added. The chloride ion produced by reaction of the chlorosilane with water formed in the oxidation quenches the reaction immediately. The oxygen was displaced by nitrogen, 2.3 ml. of hexamethyldisilazane was added, and the mixture was refluxed for 1 hr. to complete conversion of the phenols to trimethylsilyl ethers. Dibutyl sebacate and diphenyl ether were added as internal standards. Gas chromatography detected monomer, dimer, trimer, and tetramer (as trimethylsilyl ethers).<sup>8</sup> Their identities were established by comparison of their retention times and infrared spectra of trapped samples with authentic samples prepared by another method.<sup>2</sup> Further confirmation of the identity of the trimer was provided when 7.2 mg. of the trimethylsilyl ether was treated with one drop of 4.5 *M* sodium methoxide,<sup>9</sup> yielding 5.1 mg. (81%) of crude phenol, m.p. 107–109°. A mixture with an authentic sample of trimer, m.p. 112–113°, melted at 109–113°; a mixture with dimer melted at 80–100°.

A series of experiments was carried out varying only the extent of oxidation, with the result shown in Figure 1, in which the weight per cent of the various phenols, based on the weight of dimer originally added, is plotted against extent of oxidation. The amount of monomer increases steadily, reaching a maximum at about 50% oxidation where it is the most abundant species and

(8) Similar results have been obtained in a different system by J. Bussink, O. E. van Lohuizen, J. L. Mulder, and L. Vollbracht, private communication.

(9) G. D. Cooper, *J. Org. Chem.*, **26**, 925 (1961).

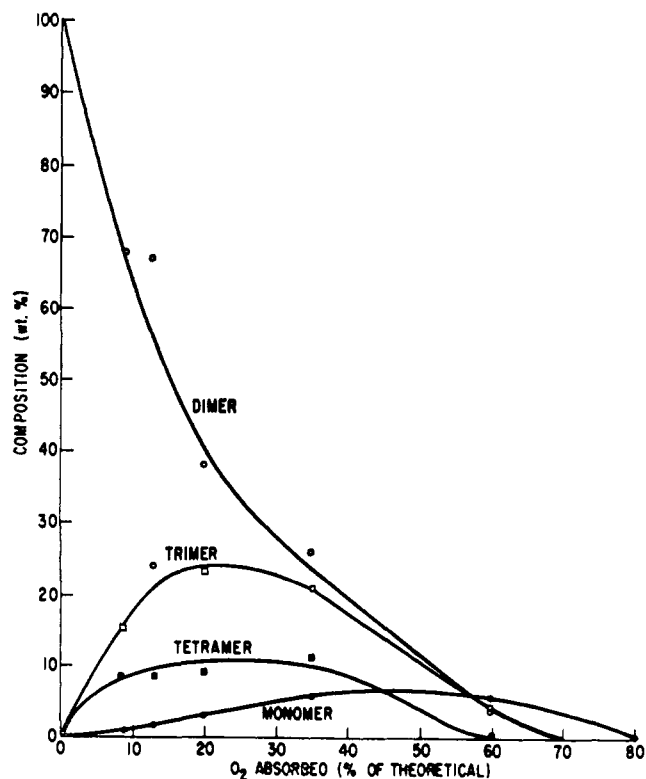


Figure 1. Composition of product from xylenol dimer as a function of extent of oxidation.

makes up 6% of the total weight. Monomer is still detectable at 80% oxidation.

Oxidation of trimer to 30% of theory yielded monomer, dimer, trimer, and tetramer, in a molar ratio of 1:0.36:0.29:0.13. The presence of monomer and trimer in the oxidation product from dimer, and of monomer, dimer, and tetramer in the product from trimer, is inconsistent with mechanisms 1 and 2, but would be expected from mechanism 3.

Other oxidation reactions could lead to the formation of 2,6-xylenol from its dimer or trimer. This seems unlikely because (a) the oxidation utilizes 100–102% of the theoretical amount of oxygen, (b) the yield of xylenol polymer is 92–95% with 3,3',5,5'-tetramethyldiphenylquinone accounting for most of the remaining starting material, and (c) no products other than monomer, dimer, trimer, tetramer, and diphenylquinone are observed.<sup>10</sup>

These experiments show that redistribution of polymeric radicals (or phenols) must occur, but do not prove that the quinol ether is an intermediate. The formation of quinol ethers by oxidation of hindered phenols is well established,<sup>11,12</sup> and there is also evidence<sup>8c,13</sup> for their decomposition to aryloxy radicals as required by mechanism 3.

**Acknowledgment.** We are indebted to J. R. Elliott and A. R. Gilbert for many helpful discussions and

(10) Thin layer chromatography shows a continuous series of higher molecular weight materials which are probably 5-mer to *n*-mer, but no reference materials are available.

(11) C. Martius and H. Erlingsfeld, *Ann.*, **607**, 159 (1957).

(12) E. Müller, K. Ley, and G. Schlechte, *Ber.*, **90**, 2660 (1957), and references cited therein.

(13) W. Theilacker, *Angew. Chem.*, **72**, 211 (1960).

invaluable advice. We are also indebted to Mrs. A. L. Klopfer for much of the experimental work.

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### The Structure of Acetatopentaamminecobalt(III) in $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)^1$

Sir:

The recent suggestion by Fraser<sup>2</sup> that the bonding of the carboxylato groups in carboxylatopentaamminecobalt(III) complexes is an ionic bidentate linkage with both oxygen atoms equivalent led us to investigate the structure of the acetatopentaamminecobalt(III) complex.

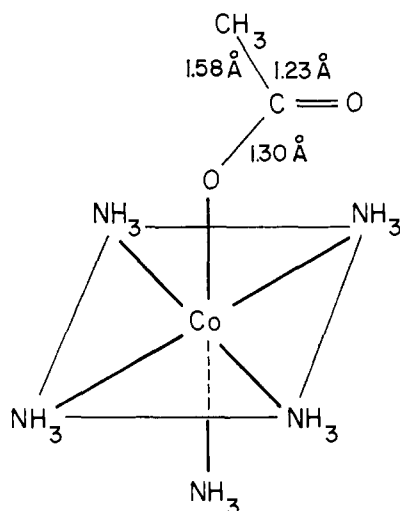


Figure 1. Structure of the acetatopentaamminecobalt(III) ion. The average Co(III)-N distance is 2.00 Å; standard deviations in bond distances  $\sim 0.02$ -0.03 Å.

Although the acetate group is known to act as a bidentate ligand in some of its complexes,<sup>3</sup> the structure proposed by Fraser contradicts some chemical evidence<sup>4</sup>; also, a seven-coordinate cobalt(III) species seemed unlikely. The crystal studied was  $[\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)](\text{Cl})(\text{ClO}_4)$ .<sup>5</sup> The crystal is orthorhombic with cell constants  $a = 22.01$ ,  $b = 9.75$ ,  $c = 11.41$  Å.; the space group is *Pbca*. The measured density is 1.84 g./cm.<sup>3</sup> (the calculated density is 1.83 g./cm.<sup>3</sup>) which requires eight molecules per unit cell. The intensity data were collected with Mo radiation with a set of balanced filters using a GE XRD5 with a scintillation counter. The residual for the 1143 observed

(1) This research was generously supported by grants from the Public Health Service and A.R.P.A.

(2) R. T. M. Fraser, *Nature*, **202**, 691 (1964).

(3) J. van Nieuwekerk, F. Schoening, and J. Talbot, *Acta Cryst.*, **6**, 720 (1953); W. H. Zachariasen and H. A. Plettinger, *ibid.*, **12**, 526 (1960).

(4) H. Taube, private communication; this refers to the fact that in the acetatopentaamminecobalt(III) the two oxygen atoms of the acetate group exchange with solvent oxygens at different rates, suggesting a nonequivalence of the oxygen atoms (see R. B. Jordan, Thesis, University of Chicago, 1965).

(5) The crystals were obtained by recrystallizing a sample of the perchlorate salt of the complex, kindly supplied by J. Halpern, in KCl solution with the intention of preparing the dichloride salt; instead, the chloride-perchlorate salt was obtained.

reflections was 14%. The hydrogen atoms were not included in the calculations.

The structure for the acetatopentaamminecobalt(III) is shown in Figure 1. It is clear that the acetate is bonded to the cobalt by a monodentate linkage and that the two oxygen atoms of the acetate are non-equivalent. The bond distances in the structure are similar to those found in related structures.<sup>6</sup>

The carbonyl oxygen atom of the acetate is about equidistant from two ammonia nitrogen atoms with distances that indicate it is participating in hydrogen bonding with these nitrogen atoms.

The carbonate group was recently found to act as a monodentate ligand in the complex,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3] \cdot \text{Br} \cdot \text{H}_2\text{O}$ .<sup>7</sup>

*Acknowledgment.* We wish to thank J. Halpern for bringing this problem to our attention.

(6) G. Palenik, *Acta Cryst.*, **17**, 360 (1964); Y. Shigeta, Y. Komryama, and H. Kuroya, *Bull. Chem. Soc. Japan*, **63**, 1159 (1963).

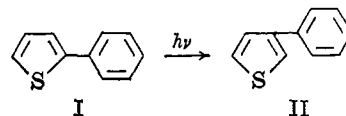
(7) H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 3184 (1965).

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### The Photochemical Rearrangement of Arylthiophenes

Sir:

When 2-phenylthiophene (I) is illuminated with ultraviolet light for 38 hr. at 80° in benzene solution, 3-phenylthiophene (II) is formed in good yield.



Thus when 98 mg. of 2-phenylthiophene, m.p. 34.5-35°,<sup>1</sup> in 87 g. of benzene to which 6.5 g. of crystallized sodium thiosulfate was added was irradiated with a Hanau S-81<sup>2</sup> mercury high-pressure lamp and the reaction monitored using quantitative vapor phase chromatography,<sup>3</sup> nearly all of the 2-phenylthiophene had disappeared after 38-hr. irradiation, while about 40 mg. of 3-phenylthiophene was formed. Preparative v.p.c. then enabled the isolation of the major component 3-phenylthiophene, m.p. 90-91°, mixture melting point undepressed; infrared and ultraviolet spectra are identical with those of authentic 3-phenylthiophene.<sup>4</sup>

(1) The substance was made by the method of J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 314 (1953); melting points: A. S. Brown and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, **59**, 1293 (1948); *Chem. Abstr.*, **43**, 2614 (1949); infrared spectra: A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.*, 3500 (1959); J. S. Sørensen and N. A. Sørensen, *Acta Chem. Scand.*, **12**, 773 (1958); ultraviolet spectrum: L. Bruzzi, J. Degani, and A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **19**, 40 (1961).

(2) A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Vienna, 1958, p. 126.

(3) F. & M. Model 810 apparatus with flame ionization detection; immobile phase diethylene glycol succinate (LAC-728); column temperature 190°, using He as carrier gas (60 ml./min.).

(4) Synthesis and melting point: J. L. Melles and H. J. Backer, *Rec. trav. chim.*, **72**, 491 (1953); infrared spectrum: H. Rosatzin, *Spectrochim. Acta*, **19**, 1107 (1963); J. Degani, M. Pallotti, and A. Tundo, *Ann. Chim. (Rome)*, **51**, 434 (1961); ultraviolet spectrum: see Bruzzi, *et al.*<sup>1</sup>