mers reflected the change of configuration of the C_9 hydrogen atom (see Fig. 2). Thus in XVIII a bathochromic displacement of the ellipticity maxima relative to XIX is observed. Similarly, although the O.R.D. curves of XX and of XVI are coincident,[12] the red shift of the dichroism is apparent in epoxynorcafestanone, leading to the assignment of C_9 β-oriented hydrogen.

The remaining exception to C9,10-anti-configuration is eperuic acid.

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1,2,3,4-TETRAMETHYL-2-CHLOROCYCLOBUTENYL CATION

Sir:

The reaction of 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene (Ia) with silver hexafluoroantimonate in liquid sulfur dioxide was studied in an effort to prepare the tetramethylcyclobutadienyl dication (II), a species which it was presumed would be of exceptional stability as a result of the delocalization energy of its π-electron system and the salutary effect of its four methyl substituents.[1] How-

Ia (X = Cl)
b (X = Br)
c (X = F)

II

III

IV

V
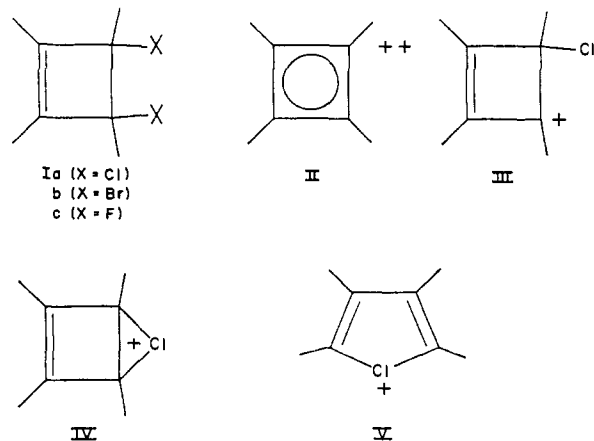
ever, at −70°, although a ready reaction did take place between the reactants (typically, 0.29 mmole of Ia and 0.72 mmole of AgSbF₆ in 0.7 ml. of SO₂), the amount of silver chloride isolable by filtration of the reaction mixture, contained in a sealed tube, through a sintered glass disc, was only one mole per mole of the dichloride.[2]

The derivative formed upon quenching the reaction mixture with an excess of tetramethylam-

(1) (a) Cf. the heptamethylbenzenonium ion of W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, Tetrahedron, 4, 178 (1958). (b) The synthesis of tetraphenylcyclobutadienyl dication has possibly been realized: H. H. Freedman and A. M. Frantz, Jr., "Abstracts of Papers Presented to the American Chemical Society, Washington, D. C., March, 1962," p. 26-O.

(2) The yield in four runs was 1.25 ± 0.04 moles of AgCl per mole of Ia, probably greater than 1.00 as a result of incomplete separation of the filtrate from the AgCl. Allowing the tube to warm to room temperature for the AgCl isolation would then precipitate a second mole.
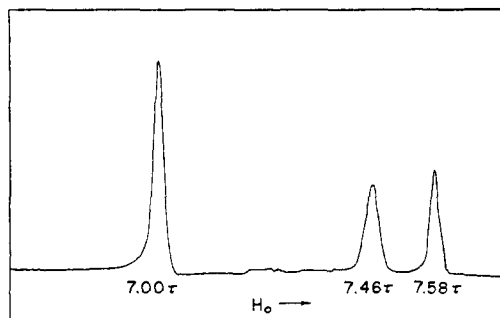
monium chloride (by destroying a break-seal connecting two chambers of a sealed tube) proved to be the initial starting material, Ia (65–69% yield by sublimation), identified by melting and mixed melting points. The structure of the organic moiety produced on treatment of Ia with AgSbF₆ was determined by examination of the nuclear magnetic resonance (n.m.r.) spectrum of the SO₂ solutions at −63° (Fig. 1).[3] Of the possibilities for the nature of the product in solution, II is eliminated by the complexity of the spectrum, and Ic, while not eliminated by the spectral pattern, is excluded by the chemical shifts.[4] Ic and II are also eliminated by the observed precipitation of less than the stoichiometrically required two moles of AgCl. A likely species to be observed in the SO₂ solutions is 1,2,3,4-tetramethyl-2-chlorocyclobutenyl cation (III)—an analogous preparation was used to make the 7-norbornadienyl cation[5]—and the n.m.r. spectrum does speak for a product of this structure.[6]

The ion does not possess the structure IV or V, and if III, IV, and V are in equilibrium, this implies that III is the most stable.[7] The resolution of the components in the n.m.r. spectrum indicates that, although in other cases chloronium ions are presumably more stable than the corresponding α-chlorocarbonium ions, in this case the symmetrical ion, IV, is, compared to the cyclobutenyl cation, III, at a considerable energetic disadvantage. The rate of interconversion of four equivalent structures for III by chlorine migration is less than 10 sec.⁻¹; the corresponding free energy of activation and, therefore, the barrier separating

(3) Tropylium hexafluoroantimonate was used as an internal standard, and a correction was applied for its chemical shift (0.55 τ) with respect to internal tetramethylsilane (TMS), determined separately, for TMS was itself destroyed in the reaction mixture.

(4) The high intensity band should appear at 8.35 τ. The dichloro compound in CCl₄ solution has bands of equal intensity at 8.35 and 8.27 τ relative to internal TMS, and the dibromo compound at 8.35 and 7.97.

(5) P. R. Story and M. Saunders, J. Am. Chem. Soc., 82, 6199 (1960).

(6) The chemical shifts are consistent with those of known methyl substituted alkenyl cations: N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, J. Am. Chem. Soc., 84, 1498 (1962).

(7) Since IV and V are of relatively high energy, it is unlikely that they are true intermediates in the unusual dimerization reaction used to prepare the dichloro compound Ia by chlorination of dimethylacetylene (cf. J. D. Roberts and C. M. Sharts, "Organic Reactions," John Wiley and Sons, Inc., 1962, Vol. 12, p. 17). It is probable that along a reaction path heading for IV or V some displacement irreversibly leads to III and by-passes the former species.

the unsymmetrical and symmetrical ions III and IV is at least 11 kcal./mole. The instability of IV with respect to III may have significance in connection with the synthesis of alicyclic chloronium ions, none of which is known.

The preferential formation of III, rather than II, is of theoretical interest since an analysis employing the Hückel theory suggests that ionization of the first chlorine atom of Ia will require the simultaneous ionization of the second,[8] which, however, contrasts with the experimental observation. Account either of overlap between non-adjacent carbon 2p orbitals,[9] or of change in charge repulsion in the neutral and positively charged molecules[11] decreases the energy gap which favors the double ionization, and the combined effect of the two processes[12] may explain the selectivity for monoionization, although this selectivity should presumably be decreased by solvation.[13]

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(8) If the energy for homolytic cleavage of both the first and second carbon–chlorine bonds to leave localized carbon radicals is the same, and DE_1 and DE_2 are energies yielded on delocalization of these radicals, while I_1 and I_2 are free energies of ionization for removal of one and two electrons from the respective systems, then monoionization should be favored only if $DE_2 + I_2 = -2\alpha + m\beta > 2(DE_1 + I_1) = 2(-\alpha + n\beta)$. According to the Hückel theory, for formation of allyl cation and cyclobutadienyl dication, $m/n = 2/0.828$, and the former should *not* form preferentially.

(9) (a) If $\beta_{13}/\beta_{12} = 0.2$, $m/n = 2.4/1.06$; if 0.5, 3/1.372; if 1.0, 4/2. (b) Exceptional stability predicted for a cyclobutenyl, or homocyclopropenyl, cation has been demonstrated kinetically: E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962). (c) The preference for mono- or di-ionization is not appreciably affected by the methyl substituents. According to the heteroatom model with $\alpha CH_3 = \alpha + 1.65\beta$ and $\beta CH_3 C = 0.64\beta$,[10] if $\beta_{13}/\beta_{12} = 0$, $m/n = 1.481/0.570$; if 0.2, 1.816/0.746; if 0.5, 2.341/1.147; if 1.0, 3.266/1.632.

(10) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 194.

(11) For $\omega = 1.4$ (ref. 10, p. 115) and $\beta_{13} = 0$, $m/n = 3.4/1.656$.

(12) For $\omega = 1.4$, $\beta_{13} = \beta_{12}$, $m/n = 5.4/2.933$.

(13) The effect of solvation on the *reduction* potentials of benzenoid aromatic hydrocarbons is discussed by G. J. Hoijtink, E. de Boer, P. H. van der Meij and W. P. Weyland, *Rec. Trav. Chim.*, **75**, 487 (1956).

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COORDINATION POLYMERS WITH INORGANIC BACKBONES FORMED BY DOUBLE-BRIDGING OF TETRAHEDRAL ELEMENTS

Sir:

In extension of the double-bridging approach to coördination polymers with inorganic backbones that we recently described for octahedral elements,[1] we wish to report similar polymers in which phosphinate anions double-bridge between tetrahedral elements. Although most of the compositions that we have made are insoluble, or only very slightly soluble, in a wide range of solvents and hence not amenable to the usual techniques of polymer characterization, we have found it possible

(1) B. P. Block, J. Simkin, and L. R. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

to determine the molecular weight of one representative of this class and find it to be, indeed, a polymer. On the basis of this finding it is extremely probable that the remaining, insoluble compositions are likewise polymeric. This is very significant in view of the fact that some of these compositions exhibit excellent thermal stability as determined on a thermobalance, making them of great interest as potential thermally stable polymers.

Among the specific compositions that we have investigated are $Be(OPPh_2O)_2$, $Zn(OPPh_2O)_2$, and $Zn(OP(Ph)(Me)O)_2$, which all appear to be novel. Most recently Drinkard and Kosolapoff[2] reported the preparation of several phosphinates of copper-(II), barium, magnesium, calcium, and lead(II), none of which involve tetrahedral configurations for the metal.[3]

We have prepared polymeric metal phosphinates in a variety of ways; however, at this time only a typical mode of preparation will be given for each example. $[Be(OPPh_2O)_2]_x$ was prepared by heating an intimate mixture of 5.0 g. of Be(Ac-CHAc)$_2$ and 21.0 g. of $Ph_2P(O)OH$ to 100° in a microdistillation apparatus at 1 mm. pressure for 3.5 hr. The mixture was cooled, reground, and reheated under the same conditions two more times, yielding, after extensive extraction with EtOH, 8.6 g. of a product containing 2.25% Be, 14.09% P, 65.43% C and 4.60% H; calcd. for $Be(OPPh_2O)_2$: 2.03% Be, 13.91% P, 65.01% C and 4.55% H. $[Zn(OPPh_2O)_2]_x$ was prepared through interfacial polymerization of a 100 ml. aqueous solution containing 2.195 g. of $Zn(OAc)_2 \cdot 2H_2O$ with a 200-ml. benzene solution of 4.36 g. of $Ph_2P(O)OH$ in a Waring Blendor. The mixture was agitated for an hour, then filtered and washed extensively with ethanol. The dried product weighed 4.1 g. and contained 13.4% Zn, 12.14% P, 57.61% C, and 4.18% H, as compared with the calcd. values for $Zn(OPPh_2O)_2$ of 13.08% Zn, 12.40% P, 57.68% C and 4.03% H. $[Zn(OP(Ph)(Me)O)_2]_x$ resulted from the reaction of 1.56 g. of $Ph(Me)P(O)OH$ with 1.10 g. of $Zn(OAc)_2 \cdot 2H_2O$ in 300 ml. of absolute ethanol. The mixture was filtered after one hour of stirring at room temperature to yield, after three ethanol washings, 1.12 g. of a white precipitate containing 17.7% Zn, 16.14% P, 44.88% C, and 4.56% H; calcd. for $Zn(OP(Ph)(Me)O)_2$: 17.40% Zn, 16.49% P, 44.77% C, and 4.29% H. A number average molecular weight of 5600 (15 units) was obtained by ebulliometry in benzene. The white solid turns into a glass at approximately 150°, and softens at about 200°. Long flexible fibers can be pulled from the melt or from the product when wet with benzene at room temperature.

(2) W. C. Drinkard and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **74**, 5520 (1952).

(3) ADDED IN PROOF.—After this communication had been accepted a note appeared, *J. Chem. Soc.*, 2523 (1962), in which G. E. Coates and D. S. Golightly suggested that cobalt (II) methyl- and phenyl-phosphinates have double-bridged polymeric structures. We are indebted to Professor Coates for a preprint of this publication. We had also made these cobalt phosphinates and confirm their results for the most part. Perhaps it is significant, however, that our preparations of $Co(OP(Ph)(Me)O)_2$ start softening just above 200° and exhibit fiber-forming properties similar to those of $Zn(OP(Ph)(Me)O)_2$.