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 nonadjacent 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]

Acknowledgments.—We are grateful to Professor B. P. Dailey for making available the facilities of his n.m.r. laboratory, and to the National Science Foundation (NSF G-15561 and 19113), and to the Socony Mobil Oil Company for supporting this research.

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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 $\beta CH_3C = 0.64\beta$,[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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RECEIVED APRIL 30, 1962

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 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 $Be(AcCHAc)_2$ 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.

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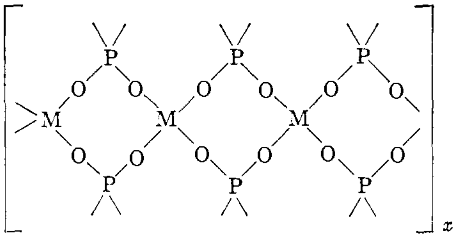
(1) B. P. Block, J. Simkin, and L. R. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

(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 $Zn(OP(Ph)(Me)O)_2$.

The structure of these polymers probably is related to that which we postulated for $[Cr(AcCHAc)(OPPh_2O)_2]_x$,[1] with double phosphinate bridges between metal atoms, *i.e.*



Evidence for this structure is afforded by the isolation and characterization of the beryllium dimer, $[Be(AcCHAc)(OPPh_2O)]_2$.[4] This was produced by a procedure similar to the one used to prepare $[Be(OPPh_2O)_2]_x$, except that the $Be(AcCHAc)_2$ rather than the $Ph_2P(O)OH$ was present in excess. The product gave an ebulliometric molecular weight in benzene of 661 (calcd. 650). The fiber-forming properties of $[Zn(OP(Ph)(Me)O)_2]_x$ constitute additional evidence that the structure is predominantly linear as opposed to crosslinked.

Thermogravimetric analysis indicates that initial weight loss starts at 530° for the polymer of composition $Be(OPPh_2O)_2$, at 495° for polymeric $Zn(OPPh_2O)_2$, and at 415° for polymeric $Zn(OP(Ph)(Me)O)_2$. In significant contrast we have found that $Cu(OPPh_2O)_2$ starts to lose weight at 293°. The Be and Zn polymers probably are more stable thermally than the Cu polymer, since a structure based on a square planar central atom offers a more facile decomposition mechanism than one based on a tetrahedral central element.

Acknowledgment.—This work was supported in part by the Office of Naval Research. Analyses were performed by our Analytical Department, and Dr. J. R. Soulen supervised the thermogravimetric analyses. Experimental assistance was provided by Mr. G. Mincarelli.

[4] B. P. Block, E. S. Roth, C. W. Schaumann and J. Simkin, *Inorg. Chem.*, **1**, in press (1962).

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ROTATORY DISPERSION AND ULTRAVIOLET ABSORPTION PHENOMENA OF SOME CONJUGATED KETONES[1]

Sir:

We have studied the rotatory dispersion (R.D.) curves of several diterpenoids of general structure I in which a keto group is in conjugation with an aromatic ring. Previously the R.D. curves of two such ketones, sugiol methyl ether and nimbiol methyl ether, had been reported as plain curves above 350 mμ.[2] We have found that using the acetate or the benzoate of these two ketones in place of their methyl ethers, measurements at lower wave length become feasible, revealing Cotton effect curves.

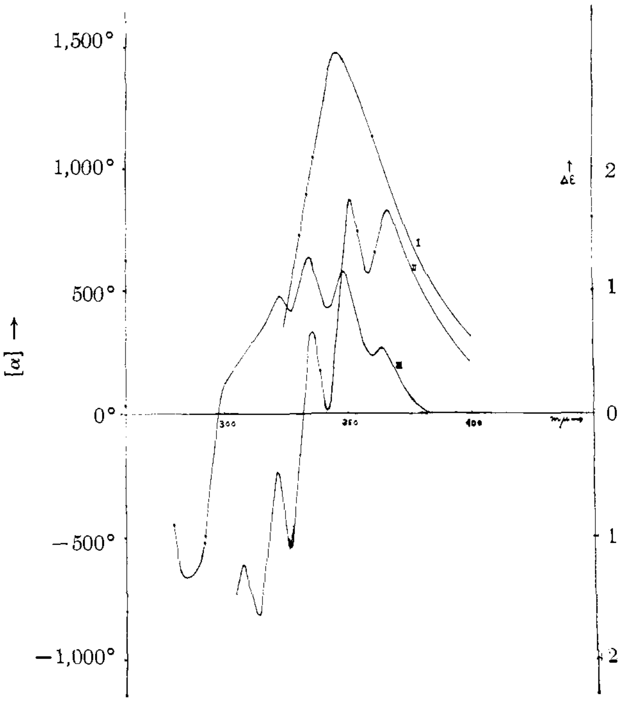
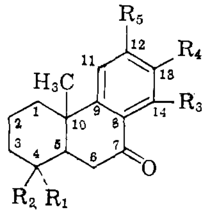


Fig. 1.—I, R.D. of methyl 7-oxo-O-methyl-podocarpate in methanol; II, R.D. of methyl 7-oxo-O-methyl podocarpate in isoöctane; III, C.D. of 7-oxo-O-acetyl-podocarpic acid in dioxane.



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In Table I are shown the results of R.D. measurements in methanol solution of a series of diterpenoid ketones. The corresponding ultraviolet absorption data in the 300–350 mμ range are reported in Table II. The close relationship between ultraviolet and R.D. spectra which is expected on theoretical grounds[3,4] has been demonstrated[5,6] experimentally for many types of compounds. The data in Tables I and II, however, show an apparent lack of correspondence between the ultraviolet spectra and R.D. curves in methanol solution. We have studied therefore the circular dichroism (C.D.) spectra of two diterpenoid ketones, sugiol benzoate and 7-oxo-O-acetylpodocarpic acid and

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[1] Molecular Rotation and Absolute Configuration, Part IV (presented at the Metropolitan Meeting of the New York and New Jersey sections of the American Chemical Society in New York, January 27, 1962). For Part III, see A. K. Bose, *Tetrahedron Letters*, no. 14, 461–467 (1961).

[2] P. Sengupta, S. N. Chaudhuri and H. N. Khastgir, *Tetrahedron*, **10**, 45 (1960).

[3] L. L. Jones and H. Eyring, *Tetrahedron*, **13**, 235 (1961).

[4] A. Moscowitz, *ibid.*, **13**, 48 (1961).

[5] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Company, Inc., New York, 1960.

[6] E. C. Olson and C. D. Alway, *Anal. Chem.*, **32**, 370 (1960).