

trast in reactivity serves to emphasize the ability of the complex to reduce only the more electrophilic carbonyl groups in polyfunctional compounds, hence this reagent seems to have great potential in organic synthesis.

We are actively examining other selective reductions as well as the further characterization of lithium *N*-dihydropyridylaluminum hydride,⁵ which may be isolated as a pale yellow crystalline solid from concentrated pyridine solutions.

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(6) It is especially desirable to ascertain whether I possesses a 1,2- or a 1,4-dihydropyridine moiety.

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EVIDENCE FOR GA(I) AS AN INTERMEDIATE IN THE REACTION OF GALLIUM METAL WITH AQUEOUS PERCHLORIC ACID

Sir:

Evidence recently has been obtained for the existence of Ga(I) in the gallium dihalides¹ and in certain addition compounds of the gallium dihalides,² as well as in the anodic oxidation of gallium in glacial acetic acid.³ There appears to be no published evidence, however, for the existence of Ga(I) in aqueous solutions,⁴ although reference has been made to the persistence of reducing properties following the dissolution of gallium metal in aqueous hydrochloric acid.⁵

We wish to report certain observations on the stoichiometry of the reaction of gallium metal with perchloric acid which provides strong evidence for the participation of Ga(I) as an intermediate species in the reaction. The pertinent experimental observations are that in the reaction of the metal with hot 11 *M* (72 wt. %) perchloric acid each mole of Ga(III) produced is accompanied by the formation of *one-half* mole of H₂ and *one-fourth* mole of Cl⁻ ion.⁶ No other reduction products are formed in significant amount, in conflict with the implication by Foster that chlorine and other products are formed.⁷ The results from a typical experiment are tabulated

Gallium metal used	3.10 mmoles (0.2164 g.)
Hydrogen gas produced	1.55 mmoles (34.8 ml. S.T.P.)
Chloride produced	0.78 mmole
Cl ⁻ /Ga ratio	0.248
H ₂ /Ga ratio	0.50

The observed stoichiometry can be accounted for quantitatively by the mechanism

(1) R. K. McMullan and J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4761 (1958).

(2) S. M. Ali, F. M. Brewer, J. Chadwick and G. Garton, *J. Inorg. and Nuclear Chem.*, **9**, 124 (1959).

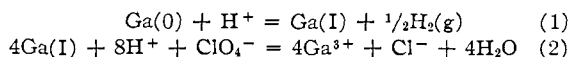
(3) A. W. Davidson and F. Jirik, *J. Am. Chem. Soc.*, **72**, 1700 (1950).

(4) The second edition of Latimer's "Oxidation Potentials," 1952, for example, discusses aqueous gallium chemistry in terms of the +2 and +3 oxidation states.

(5) L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

(6) The original observation concerning the Cl⁻-Ga(III) proportion was made in the course of some work recently carried out in collaboration with L. I. Katzin at the Argonne National Laboratory.

(7) L. S. Foster, "Inorganic Syntheses," Vol. II, 1946, p. 26.



The proposed mechanism involves highly selective behavior of Ga(0) and Ga(I) with respect to oxidation; the metal reacting predominantly with H⁺ rather than ClO₄⁻ or the intermediate chlorine compounds which must be involved in step two of the above mechanism, and the Ga(I) reacting predominantly with ClO₄⁻ rather than H⁺ despite the fact that H⁺ is certainly a sufficiently strong oxidizing agent to convert it to the trivalent state. On the basis of the present interpretation, gallium(I) joins the rather small group of ions which is capable of reducing perchlorate ion in aqueous solution.⁸ The reluctance of Ga(I) to reduce H⁺ provides an explanation for the slow rate of dissolution of the metal in the halogen acids as compared with HClO₄ and for the observed reducing properties of the solution after the metal is completely dissolved.

(8) W. R. King and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

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CRYSTALLINE POLYMERS OF THE 2,3-EPOXYBUTANES—STRUCTURE AND MECHANISM ASPECTS

Sir:

It was suggested previously,^{1,2} based on indirect evidence,³ that the stereoregular polymerization of propylene oxide to high molecular weight isotactic polymer occurs by a front-side displacement at its asymmetric carbon atom. We recently polymerized the *trans*- and *cis*-2,3-epoxybutanes to high yields of different crystalline high polymers.⁴ We now have evidence, based on polymerizing D(+)-2,3-epoxybutane to optically inactive crystalline polymer, which indicates that the stereoregular polymerization of *trans*-2,3-epoxybutane occurs by a rearward displacement on either of its equivalent asymmetric carbon atoms.

D(+)-2,3-epoxybutane, prepared by the procedure of Lucas and Garner,^{5,6} ([α]_D²⁵ +58.8°, lit.⁵ +59.0°) was polymerized (1.0 g.) with an *i*-Bu₃Al-0.5 water catalyst⁷ (0.4 millimole Al) in *n*-heptane (6.1 g.) for 2 hr. at -78°. This polymerization, which was almost instantaneous, gave a 97% conversion to highly crystalline, heptane-insoluble polymer [(ln η_{rel})/C] 1.0 (0.1%, CHCl₃, 25°), m.p. 96°] which was essentially optically inactive

(1) M. Osgan and C. C. Price, *J. Polymer Sci.*, **34**, 153 (1959).

(2) E. J. Corey, *Tetrahedron Letters*, **2**, 1 (1959).

(3) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).

(4) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 489 (1960).

(5) H. J. Lucas and H. K. Garner, *J. Am. Chem. Soc.*, **70**, 992 (1948).

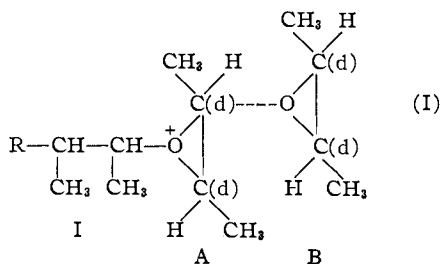
(6) The starting D(-)-2,3-butanediol was kindly supplied (98% purity based on rotation) by Dr. R. W. Jackson and Dr. R. F. Anderson, U. S. D. A., Northern Utilization Research and Development Division, Peoria, Illinois. The final D(+)-2,3-epoxybutane was, by gas chromatography, 96.7% *trans*-2,3-epoxybutane, 0.5% *cis*-2,3-epoxybutane and 3.2% diethyl ether (ether added to remove water by azeotropic distillation).

(7) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 486 (1960).

($[\alpha]_D^{25}$ $0.0 \pm 1.0^\circ$, 2%, in benzene and CHCl_3 at 5890 and 5461 Å.). This polymer, compared with the high molecular weight crystalline polymer from racemic monomer,⁴ had the same X-ray diffraction pattern, except the third strongest line was at 3.33 Å., replacing the third and fourth strongest lines at 3.41 and 3.25 Å.; the same infrared absorption spectrum in the crystalline state and in the amorphous state above its m.p.; and similar solubility properties (soluble in CHCl_3), except that it was insoluble in benzene at room temperature. It dissolved in benzene above its m.p., remained in solution on cooling to room temperature, and then returned to the room temperature, benzene-insoluble form after drying (80°) from the benzene solution. The mixed m.p. of these two crystalline polymers (dissolved in CHCl_3 and then dried) was 92°.

These data indicate that the crystalline polymer from the optically active monomer has essentially the same structure as that from racemic monomer. The optical inactivity of the polymer from active monomer indicates that crystalline poly-(*trans*-2,3-epoxybutane) is a meso-di-isotactic polymer with *dl-dl* carbon atom sequences.⁸ This conforms with the generally observed inversion of configuration in the simple ring-opening reactions of epoxides.⁹ The possibility of an optically active polymer of low rotation appears remote in view of the many examples in the literature of optically active monomers yielding polymers of high specific rotation.^{3,10,11}

It is proposed, based in part on the facile polymerization and the stereochemistry observed, that *trans*-2,3-epoxybutane polymerizes by a cationic mechanism (I) similar to that suggested for polymerizations with Friedel-Crafts catalysts of tetrahydrofuran,¹² of oxacylobutanes,¹³ and of ethylene oxide.¹⁴ This mechanism involves a rearward,



nucleophilic attack of an epoxide molecule, B, on either equivalent carbon atom of the epoxide molecule, A, involved in the propagating oxonium ion. With racemic monomer, A and B must be the same optical isomer to obtain the stereoregular meso-di-isotactic polymer. Molecular models of the transition state, based on the likely assumption that the plane of epoxide ring B is perpendicular to the plane

(8) The configuration of each asymmetric carbon atom is assigned by viewing it from the nearest oxygen atom.

(9) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 758 (1959).

(10) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, **82**, 4745 (1960).

(11) G. I. Schmitt and C. S. Schuerch, *J. Polymer Sci.*, **45**, 313 (1960).

(12) H. Meerwein, D. Delfs and H. Morschel, *Angew. Chem.*, **72**, 927 (1960).

(13) J. B. Rose, *J. Chem. Soc.*, 547 (1956).

(14) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897 (1957).

of epoxide ring A, indicate that steric hindrance inherent in the monomer can bring about this selection process. An occasional failure of this isomer selection process would lead to a stereo-block structure with *-dl-dl-dl-* and *-ld-ld-ld-* carbon sequences. It is likely that the somewhat different solubility and X-ray pattern of the crystalline polymer from racemic monomer result from such a stereo-block structure.

Crystalline poly-(*cis*-2,3-epoxybutane), based on these results with the *trans*-isomer, is not the meso-di-isotactic polymer previously postulated⁴ on the basis of head-to-tail polymerization with retention of configuration. There are three possible structures for this crystalline polymer which is probably formed by a coordinated anionic process.⁴ One is the racemic di-isotactic polymer formed by head-to-tail propagation with inversion. The other two are meso-di-syndiotactic structures with the carbon atom sequences of meso₁, *dl-ld*, head-to-head with retention, or meso₂, *dd-ll*, head-to-head with inversion.

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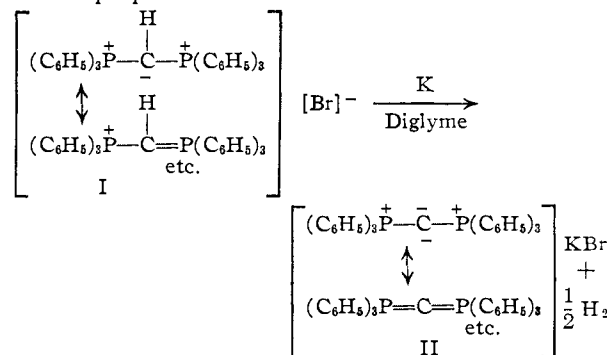
RECEIVED JUNE 28, 1961

HEXAPHENYL CARBODIPHOSPHORANE, (C_6H_5)₃PCP(C_6H_5)₃

Sir:

We wish to describe a new type of phosphorus compound, R_3PCPR_3 , a *carbodiphosphorane*, which is formally related to the carbodiimides and the allenes, and which raises interesting questions of structure and bonding associated with cumulative unsaturation in four-coordinated phosphorus. As double phosphinemetathenes, the carbodiphosphoranes may offer synthetic possibilities.

Hexaphenylcarbodiphosphorane (II) is a yellow, high-melting crystalline substance of remarkable stability; however, it is very susceptible to moisture and reacts vigorously with a variety of substances. It was prepared as shown



Methylidenebis-(triphenylphosphonium) bromide (I) (12.4 g.) was quickly added to a stirred suspension of potassium (1.0 g.) in boiling, purified diglyme (100 ml.). Gas evolution ceased after 20 minutes (total gas collected, 225 ml. at S.T.P.).