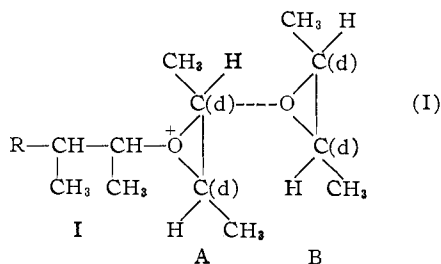


($[\alpha]^{25}_{D} 0.0 \pm 1.0^{\circ}$, 2%, in benzene and CHCl_3 at 5890 and 5461 Å.). This polymer, compared with the high molecular weight crystalline polymer from racemic monomer,⁴ had the same X-ray diffraction pattern, except the third strongest line was at 3.33 Å., replacing the third and fourth 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).

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(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).

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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.

The author is indebted to Dr. C. C. Price and Dr. S. Winstein for valuable discussions on the mechanism aspects of this work and to Dr. F. E. Williams for fractionation of the optically active monomer and its precursors.

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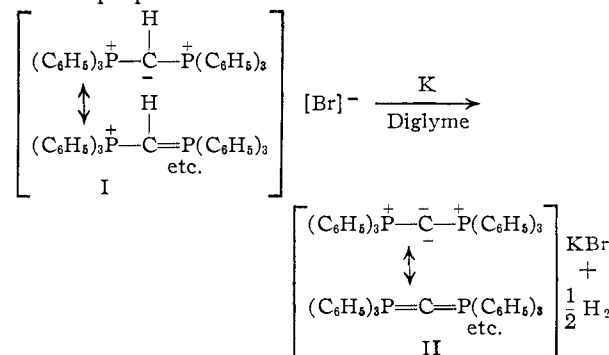
RECEIVED JUNE 28, 1961

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.

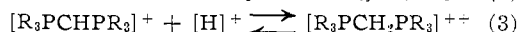
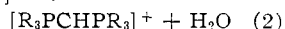
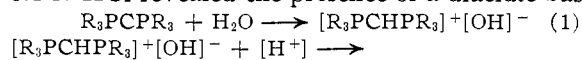
Hexaphenylcarbodiphosphorane (II) is a yellow, high-melting crystalline substance of remarkable stability; however, it is very susceptible to moisture and reacts vigorously with a variety of substances. It was prepared as shown



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.).

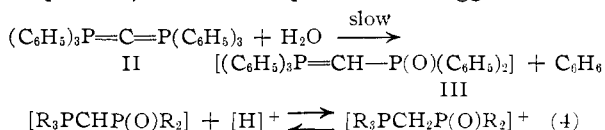
The orange-yellow hot solution was filtered from the potassium bromide and allowed to cool, yielding 6.4 g. (60%) of carbodiphosphorane II, m.p. 208–210°. A second crop of II (1.0 g., 10%) was obtained after concentration of the mother liquid to 25 ml. Moisture was excluded. Hexaphenylcarbodiphosphorane (II) had m.p. 208–210° after one recrystallization from diglyme, (Calcd. for $C_{37}H_{30}P_2$: C, 82.8; H, 5.6; P, 11.5; mol. wt. 536; found: C, 83.3; H, 5.8; P, 11.6; mol. wt. 570 \pm 40, cryoscopic in benzene); its characteristic infrared feature seems to be a strong band at 7.6 μ with a shoulder at 7.8 μ (Nujol mull); it absorbs in the 275–379 $m\mu$ region with λ max. 325 $m\mu$ (ϵ 0.7 $\times 10^4$), also at λ max. 258 $m\mu$ (ϵ 0.6 $\times 10^4$) and λ max. 225 (ϵ 3 $\times 10^4$), all in cyclohexane. The 325 $m\mu$ -band disappears if the solution comes in contact with moisture. Crystalline II did not exhibit electron-spin resonance absorption¹ and appeared to be insensitive to *dry* oxygen.

Pure carbodiphosphorane II dissolves completely in water. Titration of the colorless solution with 0.1 *N* HCl revealed the presence of a diacidic base.



The strength of one of the basic functions is comparable to that of sodium hydroxide, while the pK_a for equilibrium (3) is 5.4 \pm 0.1, extrapolated to infinite dilution. The aqueous solutions formed from II are fairly stable, but eventually colorless crystals deposit.

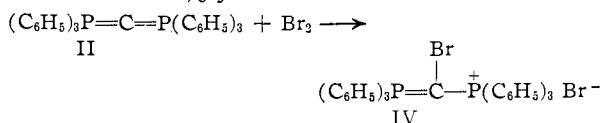
Except under strictly anhydrous conditions, samples of the carbodiphosphorane II become contaminated with a colorless substance III. One sample of II which was treated with water and quickly filtered, gave the water-insoluble III in 6% yield; addition of 0.1 *N* HBr to the clear filtrate (to pH 6) precipitated 80% of the original methylenebis-(triphenylphosphonium) bromide (I) (cf. equations 1 and 2). When crystalline II was exposed for 20 hr. to a stream of nitrogen which had been passed through water, a nearly complete conversion to III took place. Benzene was identified as a second product of this reaction. III had m.p. 157–158° (from benzene-hexane; calcd. for $C_{31}H_{26}P_2O$: C, 78.2; H, 5.5; found: C, 78.6; H, 5.8); it had a strong doublet at 8.50 and 8.56 μ ($>$ PO) and a strong shoulder at 8.3 μ (in CH_2Cl_2); it consumed one equivalent of acid for titration to pH 7 and then no more (slow titration of a water suspension). This interpretation is suggested.



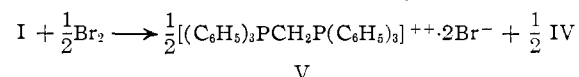
III is, therefore, a new type of stable phosphine-methylene in which the negative charge is stabilized by the adjacent phosphoryl group. The pK_a for equilibrium (4) is probably $>>$ 10.

When one mole equivalent of bromine was added quickly to a *fresh* solution of the carbodiphos-

phorane II in methylene chloride, bromomethylenebis-(triphenylphosphonium) bromide IV was obtained in *ca.* 70% yield.



The same pale-yellow ylid IV can be obtained from the reaction of one-half of a mole equivalent of bromine with the original ylid I in chloroform, since the probable intermediate, $[R_3PCHBr-PR_3]^{++} \cdot 2Br^-$, is a relatively strong acid.



The bromoylide IV had characteristic bands at 9.40 and 11.7 μ in Nujol mull; it retains solvent of crystallization and undergoes some decomposition on drying (a sample obtained from methanol-ether had m.p. 278–279° when dried at 56° and 0.1 mm.; calcd. for $C_{37}H_{30}P_2Br_2 \cdot CH_3OH$: C, 62.3; H, 4.7; P, 8.6; Br, 21.9; found: C, 61.8; H, 4.9; P, 8.5; Br, 21.5).

Methylenebis-(triphenylphosphonium bromide) (V; colorless, m.p. 308–310° from ethanol; characteristic bands at 12.05 and 12.23 μ in Nujol mull; calcd. for $C_{37}H_{32}P_2Br_2$: C, 63.6; H, 4.6; P, 8.9; total Br and ionic Br, 22.9; found: C, 63.7; H, 4.7; P, 8.6; total Br, 22.4; ionic Br, 22.5) was the starting point in this work. V was obtained in 40% yield when triphenylphosphine and methylene bromide, in a 2:1 mole ratio, were heated to 150°. When the phosphine and the bromide, in a 1:5 mole ratio, were kept 18 hr. at 60°, the yield of V was *ca.* 20%; in addition, 40% of bromomethylenebis-(triphenylphosphonium bromide) (VI) was formed [VI, $BrCH_2P^+(C_6H_5)_3Br^-$, m.p. 240–241° from ethanol-ethyl acetate; characteristic bands at 12.13 and 12.70 μ in Nujol mull; calcd. for $C_{19}H_{17}PBr_2$: C, 52.4; H, 3.9; P, 7.1; Br, 36.7; found: C, 52.4; H, 4.0; P, 6.9; Br, 37.3].

Methylenebis-(triphenylphosphonium) bromide (I; colorless, m.p. 270–271° from methylene chloride-hexane; characteristic bands at 8.15 and 12.40 μ in Nujol mull; calcd. for $C_{37}H_{31}P_2Br$: C, 72.0; H, 5.1; P, 10.1; total Br and ionic Br, 13.0; found: C, 71.8; H, 5.0; P, 10.3; total Br, 13.6; ionic Br, 13.7), was obtained from the bis-phosphonium salt V on treatment with aqueous sodium carbonate.

It is conceivable that the reduction of the phosphonium-ylid I with potassium may involve the disproportionation of a phosphoranyl² radical, $[R_3P^{\cdot}CHPR_3]$.

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(2) F. Ramirez and N. McKelvie, *J. Am. Chem. Soc.*, **79**, 5829 (1957).

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(1) We are grateful to Professor G. Fraenkel and Mr. J. Freed of Columbia University for this determination.