

POLYMERIZATION OF CONJUGATED DIENES TO LADDER CYCLOPOLYMERS AND THE CYCLIZATION OF STEREOREGULAR DIENE POLYMERS

Sir:

The polymerization of butadiene and isoprene to stereoregular *cis*- and *trans*-1,4 as well as 1,2(3,4) polymers has been carried out with numerous Ziegler-Natta catalysts.<sup>1</sup>

The polymerization of butadiene, isoprene and chloroprene with a Grignard reagent-titanium tetrachloride catalyst system at a Mg/Ti molar ratio of less than 2, and particularly at 0.5-1, and the polymerization of butadiene and chloroprene with an aluminum triethyl-titanium tetrachloride catalyst system at an Al/Ti molar ratio of 0.5 and less gave insoluble, powdery polymers which contained absorption peaks similar to those observed in cyclized balata (*trans*-1,4-polyisoprene), Hevea (*cis*-1,4-polyisoprene) and 3,4-polyisoprene. The cyclic structure content in the cyclopolymers obtained from the diene monomers ranged from 60-90%. After treatment with dilute sulfuric acid in toluene, the latter polymers gave infrared spectra indicating the disappearance of residual 1,4-units and/or other 1,2(3,4) units and an increase in the peaks attributed to the cyclized units.

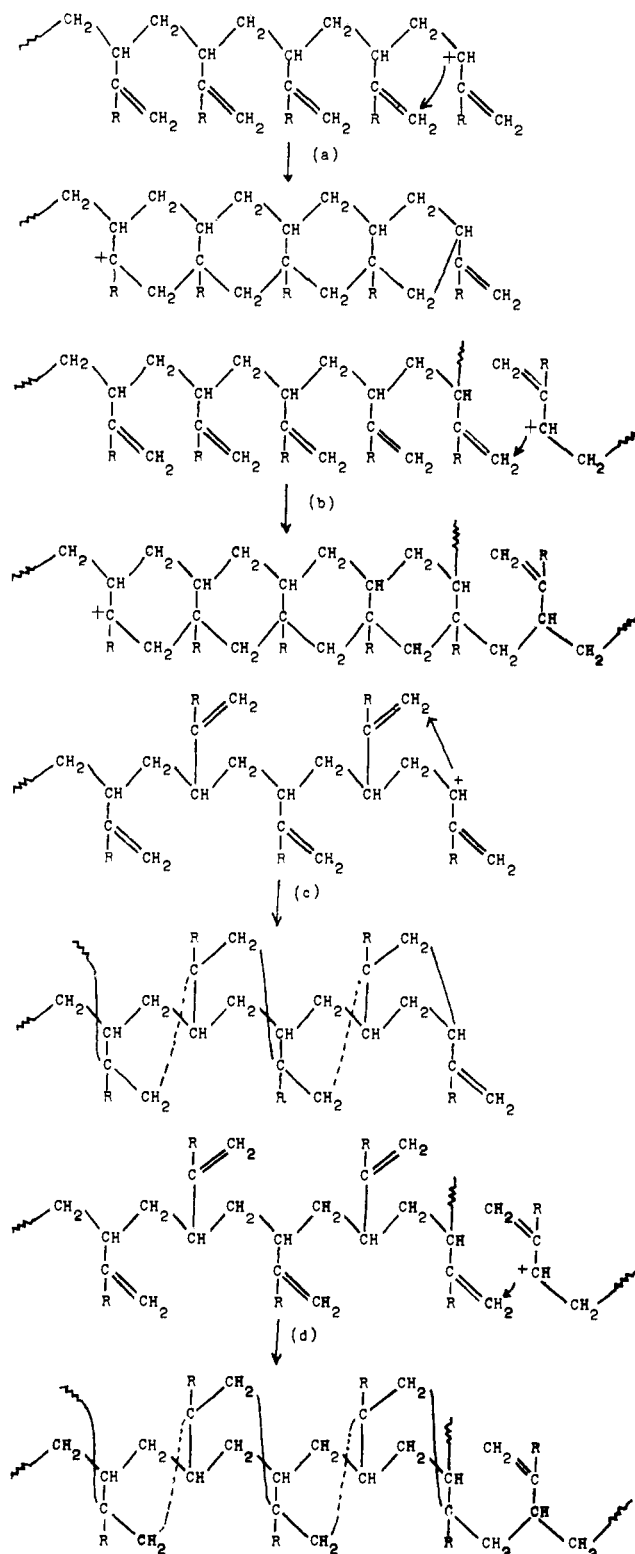
Although cyclopolymers could be obtained directly from the conjugated diene monomers by the use of the organometallic-titanium tetrachloride catalyst system or by means of a titanium tetrachloride-water (trace) catalyst system, these reagents did not cyclize 3,4-polyisoprene or natural *cis*-1,4-polyisoprene under the polymerization conditions. It is believed that the formation of cyclopolymers involves initially polymerization, probably cationic, of *trans*-oriented monomer to isotactic or syndiotactic 1,2-units in the case of butadiene and isotactic or syndiotactic 3,4-units in the case of isoprene and chloroprene. Cyclization may result from either cyclopolymerization by reversal of the direction of the polymerization reaction (a,c) or the copolymerization of additional monomer or a growing chain with pendant 1,2(3,4) groups (b,d). The length of the fused sequence will depend upon the number of isotactic or syndiotactic units in sequence and will be interrupted by the presence of the alternative 1,2 or a *cis*- or *trans*-1,4 unit. In the case of the *isotactic* sequence, the structure of the cyclopolymer is essentially that of a ladder polymer containing fused cyclohexane rings (a,b). In the case of the *syndiotactic* sequence, the structure of the cyclopolymer is essentially that of a spiral ladder polymer containing fused cyclohexane rings in which one chain spirals around the backbone but is connected thereto at every third carbon atom (c,d).

Since the ring-forming reaction can continue through the pendant 1,2(3,4) groups of neighboring polymer chains, the ladder polymers are insoluble, probably highly cross-linked, products.

The solid cyclopolymers obtained directly from the monomers revert irreversibly to liquids at elevated temperatures. The reversion temperatures are 370° for cyclopolyisoprene, 405° for cyclopolybutadiene and 420° for cyclopolychloroprene. The completion of cyclization, probably of 1,4-units, by acid treatment further increases the reversion temperatures.

The infrared spectra of cyclopolymers obtained from isoprene, butadiene and chloroprene all contain the same characteristic bands as the spectrum of cyclized 3,4-, *cis*-1,4, and *trans*-1,4-polyisoprenes. A precise analysis

(1) N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers," Interscience Publishers, New York, N. Y., 1959, pp. 87-229; N. G. Gaylord and H. F. Mark, in "Polymerization and Polycondensation Processes," Advances in Chemistry Series No. 34, American Chemical Society, 1962, pp. 127-136.



of the spectra of the cyclopolymers indicates a closer similarity to the spectrum of cyclized 3,4-polyisoprene than to that of the 1,4-polyisoprenes.

The infrared spectra of the liquids obtained at high temperatures from the cyclopolymers are the same as those of their solid precursors except that the 1,4-units are absent in the former.

The low thermal stability of cyclized 3,4-polyisoprene (softening point less than 200°) and the excellent temperature resistance of the bridgehead chlorine atoms in cyclopolychloroprene point to the spiral ladder structure rather than the linear ladder structure for the cyclopolymers.<sup>2</sup>

In the case of the cyclization of Hevea and balata with sulfuric acid the band for the trisubstituted double bond at 1665  $\text{cm}^{-1}$  shifts to a low intensity broad band at 1670  $\text{cm}^{-1}$  and finally, upon the completion of cyclization, appears at 1653  $\text{cm}^{-1}$ . Simultaneously with the appearance of the band at 1653  $\text{cm}^{-1}$ , representing the vinylidene group, a new band appears at 885  $\text{cm}^{-1}$ .

In the cyclization of 3,4-polyisoprene the band at 1643  $\text{cm}^{-1}$ , characteristic of isopropenyl groups, is replaced by a band at 1650  $\text{cm}^{-1}$  and finally, upon the completion of cyclization, by a band at 1665  $\text{cm}^{-1}$ . The original band at 1378  $\text{cm}^{-1}$  due to the methyl group, during cyclization splits into a doublet at 1385 and 1370  $\text{cm}^{-1}$ , indicating the presence of two methyl groups on the quaternary carbon. This is the major difference between the spectra of the cyclopolyisoprene and the cyclized 3,4-polyisoprene and can be accounted for by a difference in the cyclization mechanism.

Further details of the syntheses of the ladder polymers and their detailed spectral analyses as well as of the cyclization of *cis*- and *trans*-1,4 and 3,4-polyisoprenes, will be published at a later date.

(2) It is recognized that the proposed reaction paths can lead to a number of different cyclopolymers. Cyclization of isotactic sequences (a,b) can lead to a product in which all 1,3-junctures are *cis* or diaxial and all 1,2-junctures are *trans* or axial-equatorial or to a product in which all 1,2-junctures are *cis*. Cyclization of syndiotactic sequences (c,d) can lead to 1,3-*trans*-1,2-*cis* or to 1,3-*trans*-1,2-*trans* products. The referee has pointed out that since both *cis* and *trans* structures are possible at the 1,2-junctures, the failure to remove the bridgehead chlorine atoms by *trans*-elimination involving  $\alpha$ -hydrogen *cis* to the chlorine is insufficient evidence for structural differentiation.

GAYLORD ASSOCIATES, INC.

NEWARK 4, NEW JERSEY

INSTITUTE OF PHYSICAL CHEMISTRY

CZECHOSLOVAK ACADEMY OF SCIENCES

PRAGUE, CZECHOSLOVAKIA

NORMAN G. GAYLORD

IVO KOSSLER

MILAN STOLKA

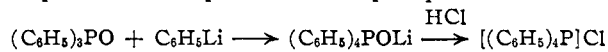
JOSEF VODEHNAL

RECEIVED JANUARY 4, 1963

#### A NEW AND CONVENIENT ROUTE TO ORGANOFUNCTIONAL PHOSPHINE OXIDES AND SULFIDES

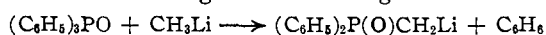
Sir:

Wittig and Rieber<sup>1</sup> have reported the preparation of tetraphenylphosphonium chloride by reaction of triphenylphosphine oxide with phenyllithium in ether, followed by treatment of the reaction mixture with hydrochloric acid. The possibility exists that this reaction proceeds *via* a pentavalent phosphorus intermediate



ate. Our interest in the possible intervention of pentavalent phosphorus intermediates in the generation of phosphinealkylidenes<sup>2</sup> has prompted a more detailed study of this type of reaction. Of particular interest to us was the reaction occurring between triphenylphosphine oxide and methyllithium because of the possible kinetic instability of an intermediate  $(\text{C}_6\text{H}_5)_3\text{CH}_2\text{POLi}$  species.

We have found that the action of methyllithium on triphenylphosphine oxide in diethyl ether produces benzene and a new organolithium reagent.



Thus in one experiment, 50 mmoles of 1.73 *M* methyllithium in ether was added at room temperature under nitrogen to a slurry of 50 mmoles of triphenylphosphine oxide in ether. The phosphine oxide dissolved, and an orange-red solution resulted. The latter was treated with 48% HBr. The organic layer was shown by gas

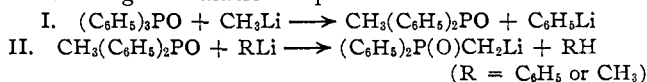
(1) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

(2) D. Seyferth, J. K. Heeren and W. B. Hughes, *J. Am. Chem. Soc.*, **84**, 1764 (1962).

chromatography to contain 43.7 mmoles of benzene (87.5%). Saturation of the aqueous layer with potassium bromide and extraction with chloroform gave 9.0 g. (83.5%) of methyldiphenylphosphine oxide, m.p. and mixed m.p. after recrystallization, 109–111° (lit.<sup>3</sup> m.p. 109–111°). In another experiment the ether solution produced was poured onto solid carbon dioxide to give  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{COOH}$ , m.p. 142–143° (lit.<sup>4</sup> m.p. 142–144°) in 47% yield. Benzene was formed in 86% yield in this reaction. The phosphinyl-substituted lithium reagent also was characterized by its reaction with triphenyltin chloride to give  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$  (76%)<sup>5</sup>; benzene was formed as before.

A similar reaction between ethyllithium and triphenylphosphine oxide resulted in  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CHLiCH}_3$ , which was converted to  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{COOH})\text{CH}_3$ <sup>6</sup> and to  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{CH}_3)\text{Sn}(\text{C}_6\text{H}_5)_3$ .<sup>7</sup>

The mechanism of these reactions appears to involve an exchange-metalation sequence



Experiments in which triphenylphosphine oxide was allowed to react with fresh, ethereal ethyllithium and the resulting mixture was quenched with  $\text{D}_2\text{O}$  demonstrated this. When the ratio of  $\text{C}_2\text{H}_5\text{Li}$  to  $(\text{C}_6\text{H}_5)_3\text{PO}$  was 1:1, the benzene formed in the reaction (97%) ( $\text{C}_6\text{H}_5$  from reaction II plus  $\text{C}_6\text{H}_5\text{D}$  from the reaction of  $\text{C}_6\text{H}_5\text{Li}$  present with  $\text{D}_2\text{O}$ ) contained 14%  $\text{C}_6\text{H}_5\text{D}$ . When the  $\text{C}_2\text{H}_5\text{Li}/(\text{C}_6\text{H}_5)_3\text{PO}$  ratio was increased to 3, the  $\text{C}_6\text{H}_5\text{D}$  content of the benzene formed (98%) rose to 50%. In a similar experiment the phenyllithium remaining in solution due to successful competition by ethyllithium in reaction II was characterized by its reaction with trimethylchlorosilane to give trimethylphenylsilane in 42% yield. A similar situation obtains in the methyllithium-triphenylphosphine oxide reaction. When these reagents were used in 1:1 molar ratio, quenching of the reaction mixture with  $\text{D}_2\text{O}$  gave benzene in 97% yield, which, however, contained only 2%  $\text{C}_6\text{H}_5\text{D}$ . The same experiment with the  $\text{CH}_3\text{Li}/(\text{C}_6\text{H}_5)_3\text{PO}$  ratio increased to 3 gave benzene in 96% yield, which now contained 13%  $\text{C}_6\text{H}_5\text{D}$ . Separate experiments showed that methyl-, ethyl-, and phenyllithium metalate methyl- and ethyldiphenylphosphine oxides in good yield in diethyl ether solution, giving  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{Li}$  and  $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CHLiCH}_3$ , respectively. Further experiments concerning the mechanism of this reaction will be presented when a full account of this work is published.

Triphenylphosphine sulfide also reacts in the same manner with methyllithium, but only in an ether-tetrahydrofuran medium. The  $(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{Li}$  formed was converted to  $(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{COOH}$ <sup>8</sup> (39%) and to  $(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$ <sup>9</sup> (74%). Preliminary experiments show that here also an exchange-metalation sequence is operative.

(3) H. Hoffmann, R. Grunewald and L. Horner, *Chem. Ber.*, **93**, 861 (1960).

(4) K. Issleib and G. Thomas, *ibid.*, **94**, 2244 (1961).

(5) M.p. 141–142°. *Anal.* Calcd. for  $\text{C}_{11}\text{H}_{17}\text{OPSn}$ : C, 65.87; H, 4.82, P, 5.48. Found: C, 65.52; H, 4.68, P, 5.68. N.m.r. in  $\text{DCCl}_3$ :  $\text{CH}_2$  a doublet at 3.60 p.p.m. with  $J = 11$  c.p.s., flanked by two satellite doublets due to splitting by the Sn nucleus with  $J = 29$  c.p.s.; phenyl proton absorption at 8.90 p.p.m. (15 H) and 8.45 p.p.m. (10 H) downfield from tetramethylsilane.

(6) M.p. 138–140°. *Anal.* Calcd. for  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{P}$ : C, 65.69; H, 5.51. Found: C, 65.61; H, 5.66.

(7) M.p. 176–177°. *Anal.* Calcd. for  $\text{C}_{22}\text{H}_{29}\text{OPSn}$ : C, 66.35; H, 5.05; P, 5.34; Sn, 20.60. Found: C, 66.20; H, 4.89; P, 5.27; Sn, 20.88.

(8) M.p. 193–195°; m.p. reported<sup>4</sup>: 188–190°. *Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{SP}$ : C, 60.86; H, 4.74. Found: C, 60.41; H, 5.19.

(9) M.p. 174–176°. *Anal.* Calcd. for  $\text{C}_{21}\text{H}_{27}\text{SPSn}$ : C, 64.05; H, 4.68; P, 5.33. Found: C, 63.84; H, 4.79; P, 5.53.