

*o*-Xylene (25 cc.) was mixed with varying quantities of acetic anhydride and the complex was slowly added in a manner similar to that above. When mixed at room temperature, the exothermic reaction was not allowed to exceed 30°. The same yellow precipitate mentioned above formed in this reaction from a dark red-brown solution. Washing and vacuum distillation were carried out in the same manner as previously described. No attempt was made to separate the isomeric mixture obtained. Very large amounts of acetic anhydride (eg. 0.35 mole) could not be used because of increasing amounts of tarry oxidation products coating the distilling flask.

The yield of mononitro products obtained in all cases with the uranium nitrate–nitrogen tetroxide–water complex seemed to increase almost linearly with increasing amounts of acetic anhydride between 0.02 and 0.12 mole and then leveled off to an average of approximately 0.04 mole of nitro product. The yield then became independent of the amount of acetic anhydride used. With uranyl nitrate hexahydrate the yield increased linearly with amounts of acetic anhydride between 0.06 and 0.18 mole and the yield increased slowly.

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(8) A. W. Crossley and N. Renouff, *J. Chem. Soc.*, **95**, 202 (1909).

### Poly(diphenylvinylphosphine Oxide)<sup>1</sup>

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In previous studies concerned with cyclic polymerization involving tertiary phosphine oxides it was postulated that a radical could form on a carbon atom adjacent to a phosphoryl function.<sup>3,4</sup> To our knowledge only one report on the polymerization of a vinyl substituted tertiary phosphine oxide has been recorded.<sup>5</sup> Since the completion of the present work, an investigation of the homopolymerization of several vinylphosphonates has been described; low molecular weight polymers were obtained.<sup>6</sup> We now wish to report the synthesis and

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(3) K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.*, **82**, 2712 (1960).

(4) K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **25**, 2006 (1960).

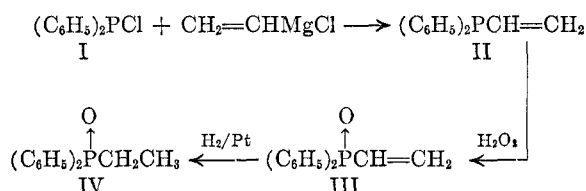
(5) An attempted preparation of di-*n*-propenylphenylphosphine oxide and diisopropenylphenylphosphine oxide via Grignard reaction resulted in polymerization of the monomers *in situ*. See C. G. Gebelein and E. Howard, Jr., Abstracts of Papers, Third Delaware Regional Meeting, Philadelphia, February 25, 1960, p. 79.

(6) R. M. Pike and R. A. Cohen, *J. Poly. Sci.*, **44**, 531 (1960).

results of polymerization of diphenylvinylphosphine oxide. This monomer was specifically selected for the study because: (a) there are no allylic hydrogen atoms in the molecule which could take part in degradative chain transfer<sup>7</sup> and (b) the vinyl group is in conjugation with the phosphoryl group which would be adjacent to the propagation radical.

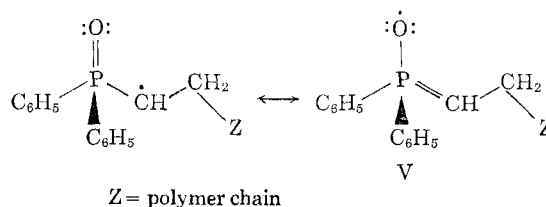
### RESULTS AND DISCUSSION

Diphenylvinylphosphine oxide (III) was prepared as depicted in the scheme. In the final step the phosphine II was oxidized to give white crystals of diphenylvinylphosphine oxide in a yield of 47.2%. In addition to the elemental analysis and infrared spectrum which support the structure III, the oxide was reduced under low pressure to the known diphenylethylphosphine oxide (IV).



In contrast to vinyl phenyl ketone which is unstable and polymerizes upon standing,<sup>8</sup> diphenylvinylphosphine oxides (III) is stable in air and does not polymerize in storage for several months. However, in the presence of radical initiators this monomer homopolymerized in bulk or in solution. The polymer is soluble in dimethylformamide and alcohol, and one sample (m.p. 220–242°) in alcohol gave a value of 0.047 for its intrinsic viscosity.

Although the monomer III does not seemingly contain such active hydrogen as were present in the compounds described in the studies mentioned previously,<sup>3,4,6</sup> the intrinsic viscosity measurement obtained on the sample of poly(diphenylvinylphosphine oxide) suggests the polymer is of low molecular weight. The degree of stabilization of the propagation radical through enolic-like structures involving the phosphoryl function may influence chain growth. Since the *d*-orbitals of the phosphorus atom would participate in the stabilization of the radical, such contributing structures as V may have different steric requirements from those of a carbon-carbon double bond composed of only



(7) R. C. Labile, *Chem. Revs.*, **58**, 807 (1958).

(8) For a discussion of vinyl ketone polymers see: C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley & Sons, Inc., New York, 1952, Chap. 14.

*p*-orbitals. To be specific the requirement that all atoms attached to a carbon-phosphorus multiple bond must lie in or near a common plane may no longer hold.<sup>9</sup> Thus, greater shielding of the propagation radical by the phenyl groups and the oxygen atom might result. Molecular models support this postulation. Efforts are underway to further investigate the chemistry of this oxide III and related monomers.

#### EXPERIMENTAL<sup>10</sup>

*Diphenylvinylphosphine* (II). To 0.4 mole of the vinyl Grignard reagent in 400 ml. of tetrahydrofuran was added dropwise, with stirring and cooling, a solution of 55.1 g. (0.25 mole) of diphenylchlorophosphine<sup>11</sup> in 100 ml. of dry benzene. The addition required 1.5 hr. and was regulated to sustain a gentle reflux which was then maintained for 20 hr. Decomposition was effected with 300 ml. of 10% aqueous ammonium chloride to a chilled reaction mixture. The water layer was extracted three times with ether and finally with 400 ml. of hot benzene. After drying overnight, the organic phase was fractionated to give 30.0 g. (56.8%) of the colorless phosphine II; b.p. 104° (0.25 mm.),  $n_D^{24.5}$  1.6260.

*Anal.*<sup>12</sup> Calcd. for  $C_{14}H_{18}P$ : C, 79.24; H, 6.13; P, 14.62. Found: C, 79.43; H, 6.12; P, 14.43.

The infrared spectrum of the phosphine has major peaks at 3025, 3000, 1580, 1475, 1435 (phenyl-phosphorus), 1385, 1260, 1095, 1065, 1025, 1000, 980, 950, 925, 745, and 700  $cm^{-1}$ .

*Diphenylvinylphosphine oxide* (III). A solution of 42.2 g. (0.2 mole) of diphenylvinylphosphine (II) in 200 ml. of dry benzene was treated dropwise with 28.5 ml. of 30% hydrogen peroxide. The addition (3 hr.) was adjusted to maintain a gentle boil in the solution. After an additional 3 hr. at reflux, the solution was allowed to cool to room temperature and was then poured into 100 ml. of water. The aqueous portion was extracted with ether, the extracts were dried over sodium sulfate, and the organic solvent was distilled under aspirator pressure. The residual oil was treated with a boiling solution of 1:1 benzene-petroleum ether (b.p. 70-90°). Upon cooling the solution deposited white crystals which were washed with petroleum ether; yield 22.0 g. (48.0%), m.p. 115-117°.

*Anal.* Calcd. for  $C_{14}H_{18}OP$ : C, 73.66; H, 5.70; P, 13.59. Found: C, 73.40; H, 5.88; P, 13.60.

An infrared analysis revealed absorption at 3025, 2990 1590 (doublet), 1475, 1435(phenyl-phosphorus), 1375, 1300, 1190 (phosphoryl group), 1100, 1065, 1000, and 970  $cm^{-1}$ . There are also broad bands from 700 to 760  $cm^{-1}$ .

The oxide was reduced in a Paar instrument over platinum at a pressure of 35-45 lb./sq. in. over a 24-hr. period. The yield of diphenylethylphosphine oxide (IV) was nearly quantitative, m.p. 118.5-120.5° (recorded<sup>13</sup> m.p. 121°). The infrared spectrum has major bands at 3025, 2950, 1435, 1175, 1115, 1065, 1025, 995, 750, and 710  $cm^{-1}$ .

*Poly(diphenylvinylphosphine oxide)*. The polymerizations were carried out in an atmosphere of nitrogen at a constant

(9) This type of bonding may find its analogy under the classification of *d*-orbital resonance as was suggested to explain the acidity of an  $\alpha$ -hydrogen in a bicyclic trisulfone: W. Von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

(10) All boiling points are uncorrected. All melting points are corrected.

(11) A generous supply of this compound was obtained from the Victor Chemical Co.

(12) The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(13) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, p. 116.

temperature. The apparatus consisted of a reaction tube which was fitted with a condenser and a nitrogen inlet. Partial purification was achieved by dissolving the polymer in a minimum of absolute alcohol and reprecipitating with cold, dry ether.

*Bulk polymer*. A weighed amount of the monomer III and di-*t*-butyl peroxide (1.0% by weight of the monomer) were placed in the reaction tube which was then immersed in a bath at 140° for 24 hr. The polymer solidified to a mass and was purified as described above. The polymer exhibited absorption in the infrared at 3025, 2975, 1435 (phenyl-phosphorus bond) 1175 (phosphoryl group), 1115, 740, 720 and 700  $cm^{-1}$ . There were also small peaks for water at 3400  $cm^{-1}$  and 1624  $cm^{-1}$ . The yield was nearly quantitative, and the highest melting fraction (m.p. 220-242°) was isolated in 20%. The intrinsic viscosity measurement of the highest melting fraction was obtained with alcoholic solutions (concentrations were less than 1%) using a modified Ubbelohde viscometer.

*Solution polymer*. The same apparatus as described earlier was used. Equal amounts of monomer and dimethylformamide were placed in the reaction tube along with the catalyst (AIBN-1% by weight of monomer). The temperature was maintained at 65° for 120 hr. The infrared spectrum of this polymer was nearly superimposable on that of the bulk polymer. Although elaborate precautions (nitrogen atmosphere) were taken to maintain anhydrous conditions during the purification of the polymer, the hot polymerization mixture was found to be extremely sensitive to moisture. This is reminiscent of earlier work.<sup>3,4</sup> The elemental analysis of the bulk or solution polymer suggested the presence of water as indicated by the infrared spectra also.

*Anal.* Calcd. for  $C_{14}H_{18}OP$ : C, 73.66; H, 5.70; P, 13.59. Calcd. for  $C_{14}H_{18}OP \cdot H_2O$ : C, 68.29; H, 6.09; P, 12.60. Found: C, 67.74; 67.85; H, 5.71, 5.99; P, 11.79.

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## Fluorocarbon Sulfides. II. Synthesis and Physical Properties of Thiaperfluorocyclopentane

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It is well known from careful studies of the reactions of perfluoroalkyl iodides with elementary sulfur<sup>1-3</sup> that bis(perfluoroalkyl) disulfides and trisulfides are formed readily and in good yields at 250° with at best only traces of the corresponding monosulfides being found.<sup>1,2</sup> Above 300°, however, a small amount of monosulfide is obtained.<sup>3</sup>

It was therefore quite surprising to discover that the reaction of 1,4-diodoperfluorobutane with

(1) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 5461 (1951).

(2) G. R. A. Brandt, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1951).

(3) G. V. D. Tiers, *J. Org. Chem.*, **26**, in press.