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.[9] 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[10]

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[11] 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.), $n^{24.5}$ 1.6260.

Anal.[12] Calcd. for $C_{14}H_{13}P$: 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 $C_{14}H_{13}OP$: 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[13] 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 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.[3,4] The elemental analysis of the bulk or solution polymer suggested the presence of water as indicated by the infrared spectra also.

Anal. Calcd. for $C_{14}H_{13}OP$: C, 73.66; H, 5.70; P, 13.59. Calcd. for $C_{14}H_{13}OP.H_3O$: 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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[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 α-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.

Fluorocarbon Sulfides. II. Synthesis and Physical Properties of Thiaperfluorocyclopentane

GEORGE VAN DYKE TIERS

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It is well known from careful studies of the reactions of perfluoroalkyl iodides with elementary sulfur[1-3] 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.[1,2] Above 300°, however, a small amount of monosulfide is obtained.[3]

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

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[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.

(excess) sulfur, which proceeded smoothly at 250° provided an extremely high yield of the cyclic monosulfide $(CF_2)_4S$, thiaperfluorocyclopentane.[3a] This compound, owing to its "globular" shape and weak intermolecular forces, resembles cyclohexane and perfluorocyclohexane in having a relatively high freezing point (−6.5°) and a very low entropy of fusion (*ca.* 2 e.u.), which corresponds to very little inhibition of motion in the crystal. At −127.2° there is a solid state transition with an entropy change of 18 e.u., a more nearly "normal" value for the immobilizing of fluorocarbons.[4]

EXPERIMENTAL

Thiaperfluorocyclopentane. Into each of five 30-ml. heavy-walled borosilicate glass ampoules was placed 7.0 g. of 1,4-diiodoperfluorobutane,[5] n_D^{25} 1.4265, (total 0.077 mole) and 1.0 g. of sulfur (total 0.156 g.-atom). These were sealed *in vacuo*, heated for 20 hr. at 250° in a rocking tube-oven, then chilled in liquid air, opened cautiously, and warmed to room temperature. The crude liquid reaction product, decanted from the solid lumps of iodine and unchanged sulfur, weighed 17.0 g. A portion, 11.7 g., was distilled in an efficient 10-cm. packed[6] fractionating column, and from it there was obtained 9.8 g. of thiaperfluorocyclopentane, $(CF_2)_4S$, (0.042 mole), corresponding to a yield of 79% from the diiodide.

Anal.[7] Calcd. for C_4F_8S; C, 20.70; S, 13.82. Found: C, 20.8; S, 13.9.

Thiaperfluorocyclopentane has b.p. 40.7°, n_D^{25} 1.3052, d_4^{25} 1.6339 ± .0003, f.p.[4,8,9] −6.5°, and solid state transition point,[4,9] −127.2°. The heat of fusion was estimated as 0.5 kcal./mole (entropy of fusion *ca.* 2 e.u.) and the heat of transition as approximately 2.6 kcal./mole (entropy of transition *ca.* 18 e.u.) by the relative area method,[9] the equipment having been calibrated with cyclohexane, toluene, and other similar materials. The observed molar refraction, 26.92 cc., leads[10] to an atomic refraction of 7.40 for sulfur, a value lower than the usual Eisenlohr values due to electron withdrawal by the perfluorinated group. The strongest bands in the infrared spectrum of the vapor are at 7.42, 7.76, 8.22, 8.75, and 10.10 microns.

The ultraviolet spectrum (0.1% in isooctane) shows a single band having λ_{max} = 2211 Å., ϵ_{max} = 50, and width at half-height $W_{1/2}$ = 6920 cm.$^{-1}$

Acknowledgment. I thank B. W. Nippoldt, P. B. Olson, and A. Duncan for elementary analysis and especially for the development of a modified procedure for compounds of this type[7]; and Dr. J. J. McBrady for infrared spectroscopy.

CONTRIBUTION NO. 185 FROM THE
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MINNESOTA MINING AND MFG. CO.
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[3a] ADDED IN PROOF: This compound was recently claimed in U.S. Patent **2,931,803** (C. G. Krespan, to the Du Pont Co.), and was made by the thermal reaction of tetrafluoroethylene with sulfur.

[4] L. L. Burger and G. H. Cady, *J. Am. Chem. Soc.*, **73**, 4243 (1951); also V. E. Stiles and G. H. Cady, *J. Am. Chem. Soc.*, **74**, 3771 (1952).

[5] M. Hauptschein, C. S. Stokes, and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 1974 (1952).

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[7] H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27**, 146 (1955). Furnace temp. 1200°.

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Phenol-Formaldehyde Condensations

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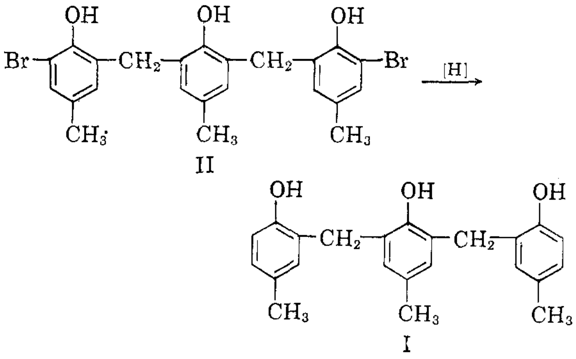
The condensation of 2-6-dihydroxymethyl-*p*-cresol with excess *p*-cresol gives a well defined crystalline product, m.p. 215°.[1–3] The structure of this compound has been in some doubt since both a linear "tri-nuclear" dibenzylphenol structure[1,3] and a cyclic "tetra-nuclear" structure[2] have been suggested. Very recently, Hayes and Hunter[4] presented good evidence for the linear "tri-nuclear" structure.

We have confirmed the findings of Hayes and Hunter by the unambiguous synthesis of 2,6-bis-(2-hydroxy-5-methylbenzyl)-*p*-cresol, I, *via* debromination of 2,6-bis(2-hydroxy-3-bromo-5-methylbenzyl)-*p*-cresol, II.



The condensation product of 2,6-dihydroxymethyl-*p*-cresol and excess *p*-cresol was identical by microanalysis, melting point, mixed melting point, and infrared absorption spectrum with I.

As supporting evidence for the "tetra-nuclear," 2:2 (2,6-dihydroxymethyl-*p*-cresol: *p*-cresol) structure, Niederl and McCoy[2] reported that the equimolar condensation of 2,6-dihydroxymethyl-*p*-cresol with *p*-cresol yielded a crystalline, well defined product. We attempted to repeat this experiment, although we could not reproduce the

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