# Heterocyclic Diamides of Phosphorus from Imidazole and Pyrrole. Synthesis and Utilization in Polymerization Reactions[1]

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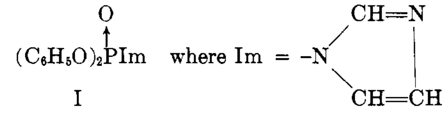
Diimidazol-1-ylphenylphosphine oxide (DIPPO) has been prepared and shown to react transamidatively with monoamines and diamines. 'With the latter, polymeric products were obtained. The polymer obtained from DIPPO and 5,5′-bibenzimidazole is thermally stable to about 360°. Diimidazol-1-yl-N-methyl-N-phenylphosphinic amide and imidazol-1-yl-N-methyl-N-phenylphenylphosphinic amide were found to be exceptionally inert toward hydrolysis and nucleophilic substitution reactions. Dipyrrol-1-ylphenylphosphine oxide has been prepared and found less reactive than DIPPO. It yielded an oligomer with 5,5′-bibenzimidazole.

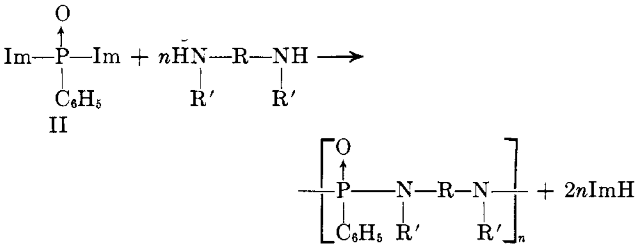
Baddiley and co-workers[3] have reported the synthesis of diphenyl imidazol-1-ylphosphonate (I) and have


$(C_6H_5O)_2\overset{O}{\overset{\uparrow}{P}}Im$ where Im = $-N\langle CH{=}N, CH{=}CH\rangle$

I

described its reactions with amines and alcohols to form the corresponding amides and esters. Staab[4] reported the synthesis of a number of acyl imidazoles and demonstrated their reactivities. In subsequent publications[5] Staab and others described imidazole derivatives of phosphoric acids[6,7] and thionyl chloride,[7,8] as well as carbonyl diimidazole.[9]

On the basis of the preceding work, it was believed that the difunctional compound, diimidazol-1-ylphenylphosphine oxide, DIPPO (II), would be a useful intermediate for transamidative preparation of polymeric phenylphosphonamides.

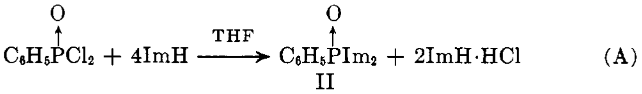

$$Im-\overset{O}{\overset{\uparrow}{\underset{C_6H_5}{P}}}-Im + nH\underset{R'}{N}-R-\underset{R'}{N}H \longrightarrow \left[-\overset{O}{\overset{\uparrow}{\underset{C_6H_5}{P}}}-\underset{R'}{N}-R-\underset{R'}{N}-\right]_n + 2nImH$$

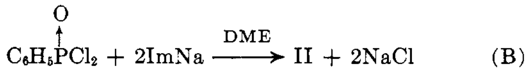
II

The displaced imidazole, unlike the hydrogen halide eliminated from the reaction of a phosphorus halide with an amine, would not react with the amine, thus permitting full utilization of the reactants and simplifying isolation of the main product.

DIPPO, not previously reported, was obtained in good yield by two methods (A and B, col. 2).

For most of our experiments, tetrahydrofuran (THF) solutions of DIPPO were utilized, and the compound was prepared by method A. When a very pure product was required, method B was applied.


$$C_6H_5\overset{O}{\overset{\uparrow}{P}}Cl_2 + 4ImH \xrightarrow{THF} \underset{II}{C_6H_5\overset{O}{\overset{\uparrow}{P}}Im_2} + 2ImH\cdot HCl \qquad (A)$$

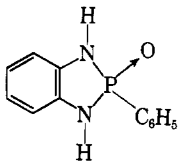

$$C_6H_5\overset{O}{\overset{\uparrow}{P}}Cl_2 + 2ImNa \xrightarrow{DME} II + 2NaCl \qquad (B)$$

DIPPO was found to be thermally stable to *ca.* 360° when heated *in vacuo.* It was, however, quickly hydrolyzed by atmospheric moisture. The latter property necessitated the use of drybox and inert atmosphere techniques during its preparation and handling.

The reactivity of DIPPO toward representative monoamines, which would not yield polymeric products, was determined prior to using it as starting material in condensation polymerization reactions. Substitution of both imidazolyl groups was achieved with cyclohexylamine and aniline, yielding, respectively, N,N′-dicyclohexylphenylphosphonic diamide and N,N′-diphenylphenylphosphonic diamide. These compounds have been described by V. Gutmann, *et al.*,[10] and by Michaelis.[11]

Monosubstitution occurred ordinarily in model reactions between DIPPO and secondary aryl monoamines. Forcing conditions with N-methylaniline resulted in displacement of both imidazolyl groups, but this did not occur with diphenylamine. Failure of the monosubstituted derivative to undergo further substitution in this case is attributed to steric hindrance by the diphenylamino group, and the relatively poor nucleophilicity of aromatic amines. The reduced reactivity due to N-methylanilide substitution on phosphorus was shown further by the properties of diimidazol-1-yl-N-methyl-N-phenylphosphinic amide (III), $C_6H_5(CH_3)NP(O)(Im)_2$, which was synthesized. It has a relatively long half-life (about 4 hr.) in water at room temperature, and does not react readily with aniline in refluxing THF.

With *o*-phenylenediamine, DIPPO reacted to yield 1,3-dihydro-2-phenyl-2H-1,3,2-benzodiazaphosphole 2-oxide (IV) previously reported by another synthesis.[12]



IV

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[2] Central Research Department, Monsanto Chemical Company, St. Louis 66, Mo.

[3] J. Baddiley, J. G. Buchanan, and R. Letters, *J. Chem. Soc.*, 2812 (1956).

[4] H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956).

[5] For a recent review of synthesis and reactions of imidazole derivatives, see H. A. Staab, *Angew. Chem.*, **74**, 407 (1962).

[6] H. A. Staab, H. Schaller, and F. Cramer, *ibid.*, **73**, 736 (1959).

[7] L. Birkofer, W. Gilgenberg, and A. Ritter, *ibid.*, **73**, 143 (1961).

[8] H. A. Staab and K. Wendel, *ibid.*, **73**, 26 (1961).

[9] H. A. Staab, *Ann.*, **609**, 75, 83 (1957).

[10] V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh.*, **91**, 836 (1960).

[11] A. Michaelis, *Ann.*, **293**, 193 (1896).

[12] R. L. Dannley and P. L. Wagner, *J. Org. Chem.*, **26**, 3995 (1961).

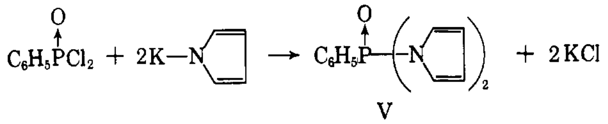
TABLE I

X-RAY POWDER DIFFRACTION DATA

| Name and formula | | Three strongest lines, $d$, Å. | | |
|---|---|---|---|---|
| Diimidazol-1-ylphenylphosphine oxide, $C_6H_5P(O)(C_3H_3N_2)_2$ | | 4.013 (100) | 4.068 (91) | 6.07 (78) |
| Imidazole hydrochloride, $C_3H_4N_2 \cdot HCl$ | | 3.670 (100) | 4.095 (83) | 3.762 (81) |
| N,N′-Dicyclohexylphenylphosphonic diamide, $C_6H_5P(O)(NC_6H_{11})_2$ | | 10.3 (100) | 4.73 (40) | 5.11 (7) |
| N,N′-Diphenylphenylphosphonic diamide, $C_6H_5P(O)(NHC_6H_5)_2$ | | 9.07 (100) | 4.541 (64) | 4.201 (37) |
| 1,3-Dihydro-2-phenyl-2H-1,3,2-benzodiazophosphole 2-oxide, $C_6H_5P(O)NC_6H_4NH$-2 | | 8.63 (100) | 4.439 (40) | 5.44 (37) |
| Imidazol-1-ylsodium, $C_3H_3N_2Na$ | | 4.022 (100) | 5.025 (57) | 2.793 (28) |
| Imidazol-1-yl-N-methyl-N-phenylphenylphosphinic amide, $C_6H_5P(O)(C_3H_3N_2)[N(CH_3)C_6H_5]$ | | 3.995 (100) | 8.0 (80) | 7.2 (50) |
| N,N′-Dimethyl-N,N′-diphenylphenylphosphonic diamide, $C_6H_5P(O)[N(CH_3)C_6H_5]_2$ | | 8.5 (100) | 4.695 (35) | 6.02 (27) |
| | | | | 5.95 (31) |
| Imidazol-1-yl-N,N-diphenylphenylphosphinic amide, $C_6H_5P(O)(C_3H_3N_2)[N(C_6H_5)_2]$ | Form I | 9.24 (100) | 4.004 (90) | 8.49 (75) |
| | Form II | 8.76 (100) | 3.909 (95) | 5.22 (90) |
| Diimidazol-1-yl-N-methyl-N-phenylphosphinic amide, $C_6H_5(CH_3)NP(O)(C_3H_3N_2)_2$ | | 6.03 (100) | 3.715 (65) | 3.453 (65) |
| Pyrrol-1-ylpotassium, $C_4H_4NK$ | | 2.710 (100) | 3.079 (17) | 4.708 (12) |
| Dipyrrol-1-ylphenylphosphine oxide, $C_6H_5P(O)(NC_4H_4)_2$ | | 7.53 (100) | 4.390 (84) | 3.826 (58) |
| 5,5′-Bibenzimidazole, $C_{14}H_{10}N_4$ | | 3.446 (100) | 5.20 (53) | 5.47 (40) |
| 5,5′-Bibenzimidazole monohydrate, $C_{14}H_{10}N_4 \cdot H_2O$ | | 13.7 (100) | 5.053 (97) | 6.84 (76) |
| 5,5′-Bibenzimidazole monohydrochloride, $C_{14}H_{10}N_4 \cdot HCl$ | | 3.363 (100) | 6.01 (94) | 5.081 (71) |
| 5,5′-Bibenzimidazole dihydrochloride dihydrate, $C_{14}H_{10}N_4 \cdot 2HCl \cdot 2H_2O$ | | 4.611 (100) | 8.76 (87) | 6.46 (57) |
| 5,5′-Bibenzimidazole dihydrochloride monohydrate, $C_{14}H_{10}N_4 \cdot 2HCl \cdot H_2O$ | | 3.215 (100) | 6.56 (30) | 4.646 (25) |
| 3,3′-Diaminobenzidine, $(NH_2)_2C_6H_3C_6H_3(NH_2)_2$ | | 4.783 (100) | 5.31 (49) | 9.4 (37) |
| 3,3′-Diaminobenzidine tetrahydrochloride, $(NH_2)_2C_6H_3C_6H_3(NH_2)_2 \cdot 4HCl$ | | 3.700 (100) | 3.597 (78) | 3.414 (53) |

Polymers were prepared from DIPPO and difunctional amines by melt polymerization techniques. 1,6-Hexanediamine gave a polymer comparable to that obtained by interfacial methods from phenylphosphonic dichloride,[13,14] but having a higher softening temperature. With piperazine, DIPPO reacted to give a water-soluble polymer that would form a brittle film. 4,4′-Methylenedianiline yielded a polymer that could be cast into a flexible (though weak) film from dimethylformamide. Aryl diamines, including *p*-phenylenediamine and benzidine, gave polyphosphonamides with higher softening and decomposition temperatures than those made from aliphatic diamines. The secondary aryl diamine, N,N′-diphenyl-*p*-phenylenediamine, yielded no polymer. A low molecular weight polymer, perhaps more correctly called an oligomer, was obtained from DIPPO and 5,5′-bibenzimidazole. Thermogravimetric analysis indicated that this product began to decompose thermally at 360° in helium.

It is desirable in a condensation polymerization that the by-products formed be readily removable from reaction systems at temperatures at which the reactions are conducted. In an attempt to improve our synthesis of polymeric phosphorus amides by meeting this requirement, we synthesized dipyrrol-1-ylphenylphosphine oxide (V).



V

We determined its thermal stability and tested its reactivity toward representative amines. It was hoped that the greater volatility of pyrrole (b.p. 131°) compared with that of imidazole (b.p. 256°) would be advantageous.

The decomposition temperature of V, by the method of Blake and co-workers,[15] is 242°. Compound V proved to be unreactive toward cyclohexylamine and aniline at the respective reflux temperatures. Unlike DIPPO, it is practically inert toward water, with an extrapolated half-life in the order of weeks rather than seconds. This parallels the observation of Staab[5] on the rate of hydrolysis of N-acetylpyrrole and N-acetylimidazole.

In polymer synthesis, dipyrrol-1-ylphenylphosphine oxide was found to be a much less reactive intermediate than DIPPO. An oligomer of low molecular weight (degree of polymerization ~3) was obtained in a reaction with 5,5′-bibenzimidazole when the reaction was conducted at high temperature (*ca.* 300°). N,N′-Diphenyl-*p*-phenylenediamine did not react with V at 220°. Although pyrrole can be readily removed from the system, the low decomposition temperature and relatively low reactivity of V toward nucleophilic reagents greatly limit the usefulness of this reaction. The decreased reactivity of V, compared with DIPPO, is ascribed mainly to increased covalent nature of its P–N bond.

$P^{31}$ nuclear magnetic resonance (n.m.r.) chemical shifts are reported for many of the compounds as an aid to identification. The relationship between the chemical shifts and the structure of these and other phosphorus–nitrogen compounds has been discussed elsewhere.[16]

## Experimental[17]

**Diimidazol-1-ylphenylphosphine Oxide (II) from Phenylphosphonic Dichloride and Imidazole. Method A.**—To a stirred

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[13] D. M. Harris, R. L. Jenkins, and M. L. Nielsen, *J. Polymer Sci.*, **35**, 540 (1959).

[14] M. S. Akutin, L. A. Rodivilova, K. P. Baibakov, and L. P. Nekrasova, Russian Patent 125,566 (April 13, 1959).

[15] E. S. Blake, *et al.*, *J. Chem. Eng. Data*, **6**, 87 (1961).

[16] M. L. Nielsen and J. V. Pustinger, Jr., *J. Phys. Chem.*, **68**, 152 (1964).

[17] All boiling points are uncorrected; all melting points are corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y. The $P^{31}$ n.m.r. spectra were obtained with a Varian Model V-4300-2 high resolution n.m.r. spectrometer at a frequency of 16.192 Mc. and field intensity of approximately 9400 gauss. Chemical shifts are reported with reference to 85% $H_3PO_4$. $H^1$ n.m.r. spectra were recorded with a Varian Model A-60 spectrometer at a frequency of 60 Mc. and field intensity of about 14092 gauss. X-Ray diffraction data of analytically pure compounds were submitted for the A.S.T.M. X-Ray Powder Data File; the three strongest lines are shown in Table I. Infrared spectra were transmitted to the American Documentation Institute.

solution of 17.0 g. (0.25 mole) of imidazole in 400 ml. of THF (dried by distillation from lithium aluminum hydride and stored over sodium wire) was added a solution of 12.2 g. (0.0625 mole) of redistilled phenylphosphonic dichloride in 75 ml. of dry THF over a period of 15 min. under nitrogen. The reaction mixture was stirred at reflux for 3 hr. After cooling to room temperature, the imidazole hydrochloride was collected by filtration, and the product was obtained as its THF solution. Titration of a hydrolyzed aliquot with standard base showed that the reaction was essentially quantitative. Removal of the solvent by distillation left a white solid which, after drying under vacuum, melted at 99–104° and gave a single $P^{31}$ n.m.r. peak at −6 p.p.m. Elemental analysis indicated that the product was somewhat impure.

*Anal.* Calcd. for $C_{12}H_{11}N_4OP$: C, 55.81; H, 4.29; N, 21.70; P, 12.00. Found: C, 52.67; H, 4.66; N, 18.20; P, 12.69.

As a modification of this method, toluene was used successfully in place of THF, the product being obtained as crystals.

**Diimidazol-1-ylphenylphosphine Oxide (II) from Phenylphosphonic Dichloride and Imidazol-1-ylsodium. Method B.**—Imidazol-1-ylsodium was prepared from imidazole and sodium in liquid ammonia at −40 to −33°,[18] with ferric nitrate as catalyst. Upon evaporation of ammonia there remained an occlusion compound of the composition $C_3H_3N_2Na \cdot 0.5NH_3$. Ammonia was removed under vacuum at 70–194°. Yield of the very light tan product was 98.2%.

*Anal.* Calcd. for $C_3H_3N_2Na$: C, 40.01; H, 3.36; N, 31.11; Na, 25.53. Found: C, 40.26; H, 3.50; N, 31.10; Na, 25.33.

Imidazol-1-ylsodium (36.0 g., 0.40 mole) was partly dissolved in 400 ml. of dimethoxyethane (DME). Phenylphosphonic dichloride (39.0 g., 0.20 mole) was added over a period of 42 min. The reaction mixture was stirred at room temperature for 4 hr. and subsequently at reflux for 1.5 hr. Solids were removed by centrifuging, the solvent was evaporated under reduced pressure, and the crude product was recrystallized from hot toluene. There was obtained 23.8 g. (46%) of crystalline II, m.p. 115.5–117.0°, $P^{31}$ n.m.r. shift in DME solution of −6 p.p.m.

*Anal.* Calcd. for $C_{12}H_{11}N_4OP$: C, 55.81; H, 4.29; N, 21.70; P, 12.00. Found: C, 55.78, 55.76; H, 4.26, 4.44; N, 21.71, 21.58; P, 11.99, 12.11.

**N,N′-Dicyclohexylphenylphosphonic Diamide.**—A solution of II in THF reacted at room temperature with excess cyclohexylamine substantially quantitatively to yield N,N′-dicyclohexylphenylphosphonic diamide, m.p. 166–167° (lit.[10] m.p. 167–168°).

**N,N′-Diphenylphenylphosphonic Diamide.**—A solution of 0.0305 mole of DIPPO in 225 ml. of THF reacted with 6.6 g. (0.071 mole) of aniline at reflux for 2 hr. under nitrogen to yield 17.2 g. (78%) of product, m.p. 211.5–213°, from ethanol (lit.[11] m.p. 211°). When the reaction was run at room temperature, a yield of 22% was obtained in 2 hr.

**Imidazol-1-yl-N-methyl-N-phenylphenylphosphinic Amide (VI).**—A mixture of 0.026 mole of DIPPO and 0.026 mole of N-methylaniline was heated stepwise to 235° over a 3-hr. period under nitrogen. Vacuum distillation yielded 0.021 mole of imidazole and 5.9 g. (77%) of product at a pot temperature of 205–215° (1 mm.), m.p. 132–139°, $P^{31}$ n.m.r. chemical shift (in chloroform) of −16.6 p.p.m.

*Anal.* Calcd. for $C_{16}H_{16}N_3OP$: C, 64.64; H, 5.42; N, 14.13; P, 10.42. Found: C, 64.44; H, 5.62; N, 13.89; P, 10.36.

The material is sensitive to moisture; upon standing in air, it was degraded to a viscous brown tar having the odor of N-methylaniline.

**N,N′-Dimethyl-N,N′-diphenylphenylphosphonic Diamide (VII).**—A mixture of 0.0209 mole of DIPPO and 0.0418 mole of N-methylaniline was heated under nitrogen at 180° for 3 hr., then distilled under vacuum to remove excess N-methylaniline and imidazole (0.030 mole). The latter was collected on a cold-finger condenser. The reaction was continued with additional N-methylaniline (0.0274 mole) at 200° for 13 hr., after which the volatile products were distilled. The total amount of imidazole recovered was 0.0390 mole. The main product, b.p. 170–200° (1 mm.) pot temperature, consisted of 5.3 g. (76%) of $C_6H_5P(O)[N(CH_3)C_6H_5]_2$, m.p. 100–101° from heptane, identical by X-ray diffraction analysis with a sample prepared from the reaction of sodium N-methyl-N-phenylamide and phenylphosphonic dichloride.[19] A melting point of 92–93.5° has been reported by Gutmann, *et al.*[20]

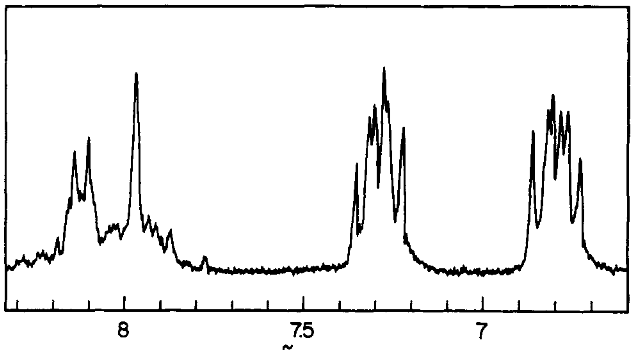

Fig. 1.—$H^1$ n.m.r. spectrum of dipyrrol-1-ylphenylphosphine oxide (14.8 wt. % solution in chloroform).

**Imidazol-1-yl-N,N-diphenylphenylphosphinic Amide (VIII).**—A mixture of 0.0189 mole of DIPPO and 0.0189 mole of diphenylamine was heated at 150° for 15 hr. under nitrogen. Vacuum distillation yielded two fractions: (1) b.p. 150–200° (1 mm.) pot temperature, 1.80 g., largely imidazole (calcd. 1.28 g.) together with diphenylamine; and (2) b.p. 200-250° (1 mm.), 4.90 g. (72%) of colorless crystalline product, m.p. 178–186° from chloroform-heptane, $P^{31}$ n.m.r. chemical shift (in chloroform) of −12.7 p.p.m.

Compound VIII was soluble in chloroform, benzene, ethanol, acetone, or dioxane, slightly soluble in diethyl ether (better warm), and insoluble in heptane, cyclohexane, and water.

*Anal.* Calcd. for $C_{21}H_{18}N_3OP$: C, 70.19; H, 5.05; N, 11.69; P, 8.62. Found: C, 69.97; H, 5.05; N, 11.86; P, 8.44.

Compound VIII was surprisingly stable toward moisture and was recoverable from an ethanol–water solution on evaporation under vacuum.

Two crystalline forms were observed by X-ray diffraction, one from ether extraction or crystallization from chloroform-heptane, the other on melting (under nitrogen). The pattern of the first differed from that of the second in having split peaks (doublets) instead of many of the single peaks found in the second.

**Diimidazol-1-yl-N-methyl-N-phenylphosphinic Amide (III).**—To a stirred solution of 54.4 g. (0.8 mole) of imidazole in 600 ml. of dry benzene at 50–75° was added a solution of 44 g. (0.2 mole) of N-methyl-N-phenylphosphoramidic dichloride[21] in 75 ml. of benzene over a period of 10 min. The reaction mixture was heated at reflux under nitrogen for 2 hr. The solution was removed through a filter stick and cooled to yield 44 g. (92%) of crystals, m.p. 132–134°, $P^{31}$ n.m.r. chemical shift (in dimethylformamide) of +7.6 p.p.m.

*Anal.* Calcd. for $C_{13}H_{14}N_5OP$: C, 54.35; H, 4.91; N, 23.38; P, 10.79. Found: C, 54.06; H, 4.97; N, 24.10; P, 10.50.

Compound III had a half-life in water of *ca.* 4 hr. at room temperature and failed to react with aniline in refluxing THF, or with N-methylaniline at 170°.

**1,3-Dihydro-2-phenyl-2H-1,3,2-benzodiazaphosphole 2-Oxide (IV).**—To 0.057 mole of II in 325 ml. of THF was added with stirring 6.2 g. (0.057 mole) of *o*-phenylenediamine in 110 ml. of THF over a period of 0.5 hr. A white precipitate formed immediately, which dissolved upon heating to reflux. After the solvent was distilled over 2 hr. with the pot temperature reaching 85°, a yellow solid remained. Washing with ether and filtration gave 16.1 g. of crude IV. Its X-ray diffraction pattern showed that the major component was identical with the material reported by Dannley and Wagner.[12]

**Pyrrol-1-ylpotassium** has previously been prepared under a variety of conditions.[22-26] We found it convenient to prepare

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[18] H. H. Strain [*J. Am. Chem. Soc.*, **49**, 1995 (1927)] has referred to unpublished work by Wenzel in the course of which imidazolylsodium was prepared by this method.

[19] M. L. Nielsen, unpublished work.

[20] V. Gutmann, G. Moertl, and K. Utvary, *Monatsh.*, **92**, 1258 (1961).

[21] A. Michaelis, *Ann.*, **326**, 129 (1903).

[22] N. Ljubavrin, *Ber.*, **2**, 100 (1869).

[23] E. C. Franklin, *J. Phys. Chem.*, **24**, 85 (1919).

[24] J. E. Reynolds, *J. Chem. Soc.*, **95**, 505 (1909).

[25] G. R. Clemo and G. R. Ramage, *ibid.*, **49** (1931).

[26] A. Treibs and A. Dietl, *Ann.*, **619**, 80 (1958).

pyrrol-1-ylpotassium in the solvent that was to be used later in the synthesis of dipyrrol-1-ylphenylphosphine oxide. Also, we established the position of potassium substitution of the product spectroscopically. The preparation was conducted in an inert atmosphere. Potassium (15.6 g., 0.40 mole) was suspended in 300 ml. of DME in a 1-l. flask. The flask was equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel which contained 29.5 g. (0.44 mole) of pyrrole dissolved in 100 ml. of DME. The pyrrole solution was added over a period of 2.5 hr. with the reaction temperature maintained at 26–32°. At lower temperatures, potassium became coated with the product and the rate of reaction was prohibitively slow. Finally, the mixture was heated slowly to 63° to complete the reaction and then was cooled and filtered. The colorless solid, pyrrolylpotassium, weighed 35.0 g. after vacuum drying. Solvent was removed from the filtrate under vacuum, leaving 5.4 g. of light tan product. The combined yield was 96%.

*Anal.* Calcd. for $C_4H_4KN$: C, 45.67; H, 3.83; N, 13.32; K, 37.17. Found: C, 45.35; H, 4.14; N, 12.95; K, 37.46.

The reaction, when repeated on a larger scale (1.2 moles), proceeded equally well when no external cooling was applied.

The infrared spectrum of solid pyrrol-1-ylpotassium conclusively indicates the absence of amino hydrogen. A very weak band at 3510 cm.$^{-1}$ is attributed to a rather small degree of hydrolysis. Exposure of the Nujol mull of pyrrol-1-ylpotassium to the atmosphere leads to hydrolysis, evidenced by strong infrared absorption at 1600–3600 cm.$^{-1}$. The infrared spectrum of the hydrolyzed sample is similar to that reported for pyrrol-1-ylpotassium by Treibs and Dietl.[26]

**Dipyrrol-1-ylphenylphosphine Oxide (V).**—To pyrrolylpotassium (21 g., 0.20 mole), partly dissolved in 400 ml. of DME, a solution of phenylphosphonic dichloride (19.5 g., 0.10 mole) in 100 ml. of DME was added over a period of 1 hr. under an inert atmosphere and with ice-bath cooling. External cooling was removed after the addition of phenylphosphonic dichloride had been completed. Although the reaction appeared to be complete, agitation was continued for 15 hr.

The solid was removed from the reaction mixture by centrifuging, and was washed with 400 ml. of DME. The combined DME solutions yielded 22.3 g. of slightly violet solid, m.p. 95–101°, upon removal of solvent by evacuation. Three recrystallizations from cyclohexane (300-ml. each) yielded a purified product, 7.8 g. (30% yield), m.p. 107–108°. The yield of V was later improved (59.5%) by using *n*-heptane as the solvent for recrystallization, $P^{31}$ n.m.r. shift (in DME) solution) of −10.7 p.p.m.

*Anal.* Calcd. for $C_{14}H_{13}N_2OP$: C, 65.62; H, 5.11; N, 10.94; P, 12.09. Found: C, 65.60; H, 5.21; N, 10.82; P, 12.24.

The position of substitution on the pyrrole ring was determined spectroscopically. The infrared spectrum of the compound indicates lack of absorption at 3400 cm.$^{-1}$, the region where absorption attributable to N–H stretching in pyrrole occurs. Consequently, no rearrangement occurred in the reaction and the product was dipyrrol-1-ylphenylphosphine oxide. The proton n.m.r. spectrum of V (Fig. 1) was obtained in $CDCl_3$ solution, with tetramethylsilane as the internal standard. It is characterized by the following chemical shifts: 7.8–8.4 (phenyl group), 7.15–7.45 (pyrrolyl $\alpha$-hydrogens), and 6.7–6.95 p.p.m. (pyrrolyl $\beta$-hydrogens). The integrated areas for these shifts have the ratio 5:4:4. The assignment of the n.m.r. shifts of dipyrrol-1-ylphenylphosphine oxide is based on published data[27] for pyrrole and its methylated derivatives.

The proton n.m.r. spectrum of V substantiates conclusions based upon its infrared spectrum. Additionally it reveals that the phosphorus atom decreases the shielding of ring protons of the pyrrole nucleus, especially in the $\alpha$-positions. The spectral fine structure suggests nuclear spin coupling between the pyrrolyl hydrogen and the phosphorus atom.

Pure V is stable to atmospheric conditions for prolonged periods. We have found it advisable to recrystallize the compound in an inert atmosphere, since the material which has been recrystallized in air has discolored upon standing. Compound V did not react with cyclohexylamine or aniline at reflux, or with N,N′-diphenyl-*p*-phenylenediamine at 220° in a reasonable time.

**Polymerizations.**—In all experiments, except for the piperazine–DIPPO, 5,5′-bibenzimidazole–DIPPO, and 5,5′-bibenzimidazole–dipyrrol-1-ylphenylphosphine oxide polymerization, an aliquot of a THF solution of DIPPO was titrated to determine the concentration. Solvent was then removed by distillation under nitrogen and the solid residue was dried by evacuation. The amine was added to the solid DIPPO in a nitrogen-flushed drybox, and the polymerization reaction mixture was heated in an oil bath.

**1,6-Hexanediamine with DIPPO.**—A mixture of 0.0624 mole of DIPPO and 7.30 g. (0.0624 mole) of 1,6-hexanediamine was heated under nitrogen at 140–145° for 3 hr. The yellow product was washed with water, dissolved in methanol, and decolorized with charcoal. A small amount of a clear, insoluble, jelly-like material was separated and discarded. The polymer was precipitated with hexane as 5.5 g. (35%) of a white solid that softened at 80–85° and decomposed *in vacuo* at 250°, $\eta_{\text{inh}}$ (1% in methanol) 0.08.

*Anal.* Calcd. for $C_{12}H_{19}N_2OP$: C, 60.49; H, 8.04; N, 11.76; P, 13.00. Found: C, 56.98; H, 7.85; N, 10.55; P, 12.67.

**Piperazine with DIPPO.**—To a solution of 0.054 mole of DIPPO in 300 ml. of THF was added a solution of 4.65 g. (0.054 mole) of piperazine (purified by sublimation from sodium hydroxide) under nitrogen. A white precipitate formed immediately. The solvent was removed by distillation under nitrogen over 2 hr. and the residue was heated at 230–240° (0.3 mm.) for 3.5 hr. The product was dissolved in methanol and decolorized with charcoal. The solvent was evaporated and the residue was dissolved in chloroform from which it was reprecipitated twice with hexane to give 5.7 g. of a hygroscopic, slightly water-soluble solid that softened at 185–190°, $\eta_{\text{inh}}$ (1% in *m*-cresol) 0.09. The polymer melted with decomposition at 270° in air; *in vacuo* it decomposed at 310° without melting. The polymer gave a brittle film when cast from water solution.

**4,4′-Methylenedianiline with DIPPO.**—A mixture of 0.057 mole of DIPPO and 11.3 g. (0.057 mole) of recrystallized 4,4′-methylenedianiline was heated at 160° under nitrogen for 2 hr. Heating was continued at 160° (0.3 mm.) for an additional 0.5 hr., then at 190° (0.3 mm.) for 1.5 hr. The addition of methanol seemed to plasticize the product. Leaching successively with ethanol, then ether, afforded 10.5 g. of a fine, yellow powder that softened at 185–190° and decomposed *in vacuo* at 370°, $\eta_{\text{inh}}$ (1% in dimethylformamide) 0.07.

*Anal.* Calcd. for $C_{19}H_{17}N_2OP$: C, 71.2; H, 5.31; N, 8.75; P, 9.69. Found: C, 65.94; H, 5.81; N, 8.39; P, 9.37.

***p*-Phenylenediamine with DIPPO.**—A mixture of 0.058 mole of DIPPO and 6.25 g. (0.058 mole) of recrystallized *p*-phenylenediamine was heated at 160–165° for 1.5 hr. under nitrogen, then at 160–165° (0.3 mm.) for 0.5 hr., and finally at 190° (0.3 mm.) for 2 hr. The methanol-insoluble portion of the product (7.6 g.) was the desired polymer, $\eta_{\text{inh}}$ (1% in dimethyl sulfoxide) 0.05. The product did not melt *in vacuo* at 300°, but decomposed at 345°. It was oxidatively unstable at elevated temperatures. An additional 3.9 g. of solid was isolated from the methanol solution by precipitation with ether. This material softened at 195–200°.

**Benzidine with DIPPO.**—A mixture of 0.061 mole of DIPPO and 11.2 g. (0.061 mole) of recrystallized benzidine was heated at 160° for 1.5 hr. under nitrogen, at 160° (0.3 mm.) for an additional hour, followed by 1.5 hr. at 190° (0.3 mm.). Methanol was added and 11.8 g. of insoluble polymer was isolated. This material softened at 210–215° and decomposed *in vacuo* at 330°. No solvent could be found, hence viscosity was not determined.

*Anal.* Calcd. for $C_{18}N_{15}N_2OP$: C, 70.6; H, 5.9; N, 9.15; P, 10.1. Found: C, 67.66; H, 5.54; N, 9.71; P, 8.17.

Addition of ethanol to the concentrated methanol solution afforded an additional 2.5 g. of solid that softened at 190–195°.

**1,1′-(5,5′-Bibenzimidazolyl)phenylphosphine Oxide Polymer, Prepared from DIPPO.**—DIPPO (3.31 g., 0.013 mole) and 5,5′-bibenzimidazole (3.05 g., 0.013 mole, synthesis reported below) were mixed in the drybox and transferred into the polymerization vessel. This vessel, which was designed for quantitative condensation and recovery of imidazole and the polymer, consisted of a wide test tube fitted on top with a Ŧ $^{29}/_{42}$ male joint. The test tube was connected to a Z-shaped, externally cooled condenser. The system was under a dry nitrogen atmosphere at ambient pressure in the beginning of the experiment. Later, vacuum was applied slowly for removal of imidazole. The vessel was immersed in an oil bath maintained at 110°, and the bath temperature was raised at a slow rate. Melting was observed at 110°, and around 120° imidazole began to sublime from the reaction zone. Over a period of 3.5 hr. the temperature was raised to 225°, and the reaction mixture became homogeneous, setting up

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(27) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

to a solid foam. The product was cooled, transferred into drybox, and crushed mechanically. To force the reaction to completion, the material was again heated under vacuum at temperatures ranging from 217–245° for 2.5 hr. Imidazole continued to sublime from the system, and some sintering was observed at the highest temperature. The amount of imidazole obtained was 1.56 g. The weight of the brown polymer was 4.83 g. Based upon imidazole recovery, the average degree of polymerization (D.P.) was 4.19.

*Anal.* Calcd. (D.P. 4.19): C, 66.78; H, 3.78; N, 16.83; P, 8.31. Found: C, 64.47, 64.36; H, 4.05, 4.01; N, 16.70, 16.59; P, 8.32, 8.39.

The oligomer melts from 244–280°, it begins to decompose thermally at 360°. At room temperature the product is insoluble in toluene, dimethoxyethane, and methyl ethyl ketone; it is soluble in 2-benzoylpyridine.

The experiment was repeated, allowing the reaction to proceed for 5.5 hr. at 275–290°. Imidazole recovery and elemental analysis indicated an average degree of polymerization of 11.0. Again the product solidified at the reaction temperature.

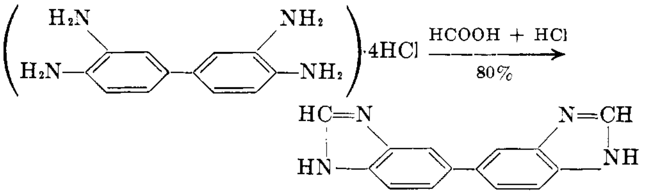
**1,1′-(5,5′-Bibenzimidazolyl)phenylphosphine Oxide Oligomer, Prepared from Dipyrrol-1-ylphenylphosphine Oxide.**—Compound V (5.12 g., 0.020 mole) and 5,5′-bibenzimidazole (4.68 g., 0.020 mole) were transferred into a 100-ml. flask in an inert atmosphere box. The flask was connected through a trap immersed in liquid nitrogen to a dry nitrogen by-pass line. Formation of liquid condensate was observed when the reaction temperature had been raised to 208°. The temperature was increased to 308° in order to melt the reactants and to obtain thorough mixing. Subsequently, the system was evacuated slowly to <1 mm., and heating was continued at 270–310° for 6 hr. The reaction mixture was converted to a dark brown solid product.

The liquid condensate, 2.08 g., was identified as pyrrole by its infrared spectrum. The infrared spectrum of the solid product (7.15 g.) is similar to that of poly[1,1′-(5,5′-bibenzimidazolyl)-phenylphosphine oxide] prepared from DIPPO. By elemental analysis of the solid product, the average degree of polymerization was 3.0 ± 0.3.

*Anal.* Calcd. (D.P. 3.0): C, 67.66; H, 3.90; N, 16.03; P, 8.18. Found: C, 66.41; H, 3.78; N, 15.49; P, 7.96.

**Attempted Reaction of Dipyrrol-1-ylphenylphosphine Oxide with N,N′-Diphenyl-*p*-phenylenediamine.**—Compound V (10.25 g., 0.04 mole) and pure N,N′-diphenyl-*p*-phenylenediamine (10.41 g., 0.04 mole) were heated in redistilled quinoline (40 ml.) solution at 220° for 15.5 hr. The system was evacuated at 80°. Gas chromatographic analysis of the collected quinoline indicated that it contained only 0.5% of the pyrrole expected from the desired polymerization. The nonvolatile solids were identical with starting materials by infrared spectra.

**5,5′-Bibenzimidazole.**—A mixture of 7.0 g. (0.021 mole) of 3,3′-diaminobenzidine tetrahydrochloride, 17.4 g. (0.378 mole) of formic acid, and 38 ml. of 5 *N* hydrochloric acid was heated at reflux for 0.5 hr. The reaction mixture was then poured into 55 ml. of concentrated ammonium hydroxide and 25 g. of ice. The brown solid was filtered off and dissolved in methanol. The solution, after filtration to clarify, was evaporated to dryness and the residue was washed with ether. The product weighed 4.0 g. (80%) and melted at 265–267°. Recrystallization from isopropyl alcohol yielded a 1:1 adduct which was decomposed at 190–200° to yield pure 5,5′-bibenzimidazole, melting at 292–293.5°. The X-ray diffraction pattern was unique.



*Anal.* Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.60; H, 4.18; N, 23.67.

5,5′-Bibenzimidazole is soluble in ethanol, formamide, ethylenediamine, dimethylformamide, pyridine, *m*-cresol, hot diglyme, and hot water. It is insoluble in acetone, ether, benzene, hexane, chloroform, dioxane, ethyl acetate, and tetrahydrofuran.

The neutralization equivalent, determined by titration with hydrochloric acid in glycol–isopropanol solution, was 119.6 (calcd. 117.1).

A sample that had been stirred in water and azeotroped with benzene to dry (m.p. 275–280°) gave a different X-ray diffraction pattern from the material above.

*Anal.* Calcd. for $C_{14}H_{10}N_4 \cdot H_2O$: C, 66.65; H, 4.79; N, 22.21. Found: C, 65.57; H, 4.28; N, 21.56.

This "monohydrate" was unchanged by recrystallization from methanol–benzene, according to the X-ray diffraction pattern. However, extraction with diethylamine converted it to the anhydrous bibenzimidazole as shown by X-ray diffraction.

As a means of identifying 5,5′-bibenzimidazole, the dihydrochloride was prepared for X-ray diffraction analysis. 5,5′-Bibenzimidazole was dissolved in dilute hydrochloric acid. On evaporating part of the water and adding acetone, a crystalline product was obtained, m.p. about 310°. Its X-ray diffraction pattern was unique.

*Anal.* Calcd. for $C_{14}H_{10}N_4 \cdot 2HCl \cdot 2H_2O$: Cl, 20.66; N, 16.32. Found: Cl, 20.57; N, 16.24.

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# Phosphorus Compounds. V. Tautomerism in Phenylphosphinic Acid and Its Anion[1-3]

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Hydrogen isotope exchange in the P(O)H system in aqueous and deuterium oxide solutions of phenylphosphinic acid, its sodium salt, and the corresponding deuterated acid and salt, followed by infrared techniques, has shown the reaction to be both acid and base catalyzed. The almost total lack of exchange in buffered neutral solutions shows that a simultaneous attack by a nucleophile and an electrophile is not a significant factor in the exchange reaction. The proportion of "enol" in neutral phenylphosphinate solution probably does not exceed that found in aqueous acetone solutions.

A previous article[1] of this series reported both acid and base catalysis in the hydrogen isotope exchange reaction with dialkyl phosphonates. This finding is in marked contrast[4] to the same reaction with the parent acid, phosphorous acid, which is usually considered to have a structure somewhat similar to that

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(1) Previous paper in this series: W. J. Bailey and R. B. Fox, *J. Org. Chem.*, **28**, 531 (1963).

(2) Presented before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

(3) Abstracted from a thesis submitted to the Faculty of the Graduate School of the University of Maryland, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1959.

(4) A. I. Brodskii and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **85**, 1277 (1952).