

Substituted 1-[(Phosphinyl)methyl]-2,4- and -2,6-Dinitrobenzenes, 1-[(Phosphinyl)methyl]-2,4- and -2,6-Diaminobenzenes: New Starting Materials for Preparation of Fire-Resistant Polymers

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Synopsis

The nitration of the substituted [(phosphinyl)methyl]benzenes by fuming nitric and sulfuric acid gave the substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-dinitrobenzenes (1). The formation of the two dinitro isomers was demonstrated by proton nuclear magnetic ($^1\text{H-NMR}$) and infrared (IR) spectroscopy. The nitration of [di(isopropoxy)phosphinylmethyl]benzene gave mainly the *p*-nitro derivative due to steric hindrance. The phosphinyl ester groups of 1 were hydrolyzed by acids. The substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (2) were synthesized by catalytic hydrogenation of 1. In addition, the corresponding di(benzoylamino) derivatives of 2 were prepared. Some of the synthesized compounds were investigated by gas chromatography–mass spectroscopy (GC–MS). Compounds 2 can be used as starting materials for preparation of phosphorus-containing polymers such as polyamides, polyimides, polyureas, and bismaleimides and as curing agents for epoxy resins.

INTRODUCTION

The science and technology of synthetic polymers has undergone explosive growth during the last few decades, and the number of different polymeric materials in our built environment increases almost daily. All organic polymers burn, thus entailing a certain degree of fire hazard. It has become evident that the problems associated with the flammability of polymeric materials must be attacked and solved.

Flammability problems are faced mainly by the use of fire-retardant compounds.^{1,2} Organophosphorus compounds possess an outstanding position to this respect. The fire-retardant compounds are either added to the polymers during their molding or attached on them with chemical bonds.

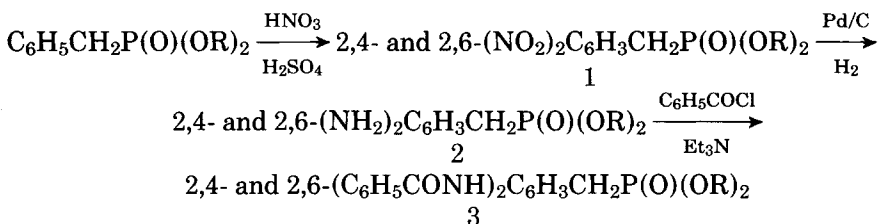
The present investigation deals with the synthesis, isolation, and structure identification of new organophosphorus compounds which may be used as fire retardants for polymer materials. A simple process is described for the preparation of the substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-dinitrobenzenes in satisfactory yield by nitration of the corresponding substituted phosphinylmethyl benzenes. This process is of interest, since, according to the literature,^{3–5} the Michaelis–Arbuzov reaction gives unsatisfactory results with nitro-substituted halides. It has been reported,⁶ for example, that the reaction of 2,4-dinitro-chlorobenzene with triethyl phosphite results in the formation of 2,4-dini-

tro-diethoxyphosphinyl benzene in 11.2% only yield. Previous attempts for the nitration of di(*n*-butoxy)phosphinylmethyl benzene gave mainly the *p*-nitro derivative.⁷

The catalytic hydrogenation of the substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-dinitrobenzenes to the corresponding diamino derivatives is also included in the present investigation. The latter compounds have been used as starting materials for preparation of fire-resistant polymers such as polyamides, polyimides, polyureas, and bismaleimides. The results will be reported later. They have also been used as curing agents for epoxy resins.⁸

RESULTS AND DISCUSSION

The synthesis of the substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-dinitrobenzenes (1) was carried out by nitration of the corresponding phosphinylmethyl benzenes with a mixture of fuming nitric and sulfuric acid. The hydrogenation of 1 over palladium on carbon gave the substituted 1-[(phosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (2). In addition, the di(benzoylamino) derivatives (3) were prepared by reaction of 2 with benzoylchloride in the presence of an acid accept such as triethylamine. The above general reactions are shown as follows:



1a, 2a, 3a: R = CH₃CH₂

1b, 2b, 3b: R = ClCH₂CH₂

The nitration of the substituted phosphinylmethyl benzenes with a mixture of fuming nitric and sulfuric acid gave a product mainly composed of the corresponding 2,4-dinitro and in minor amounts of 2,6-dinitro derivative. It also contained a considerable amount of the 4-nitro derivative. The latter is, of course, intermediate in the formation of the dinitro product and may be separated from this and further nitrated.

All dialkoxyphosphinylmethyl benzenes, except of the diisopropoxy, exhibited nearly the same behavior when nitrated by fuming nitric and sulfuric acid. The composition of the product obtained from the nitration of diethoxyphosphinylmethyl benzene is examined below. Since the nitration intermediate product 1-[(diethoxyphosphinyl)methyl]-4-nitrobenzene was a liquid, it was separated from the solid dinitro product. The latter gave an analytical sample the ¹H-NMR spectrum of which is shown in Figure 1. The main component of this analytical sample was the 1-[(diethoxyphosphinyl)methyl]-2,4-dinitrobenzene. It also contained the corresponding 2,6-dinitro isomer in small amounts as its ¹H-NMR spectrum reveals. The aromatic protons appear in this spectrum as five doublet peaks at 8.32, 8.03, 7.90, 7.42, and 7.27 δ . The peaks at 8.32, 8.03, and 7.42 δ should be attributed to the aromatic protons of positions 3, 5, and 6,

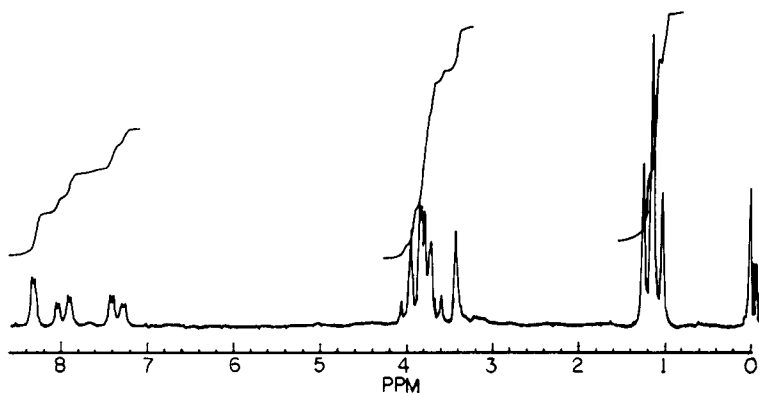


Fig. 1. $^1\text{H-NMR}$ spectrum of 1a.

respectively, of the 2,4-dinitro isomer. The peak at 7.90δ should be attributed to the equivalent aromatic protons of positions 3 and 5 of the 2,6-dinitro isomer and finally the peak at 7.27δ to the aromatic proton of position 4 of the same isomer. Differentiation of the chemical shift values of the methyl protons of 2,4- and 2,6-dinitro isomer cannot be distinguished in this spectrum. It also does not indicate the existence of other dinitro isomers to a detectable amount.

An examination of the aromatic proton chemical shift values shows that it is possible to estimate the amount of the 2,4-dinitro isomer in this mixture of the 2,4- and 2,6-dinitro isomer, by means of the doublet peak at 8.32δ assigned to the aromatic proton of position 3 of 2,4-dinitro isomer. Since this proton lies between two electron-withdrawing nitro groups, it is deshielded most as compared to the other aromatic protons of these isomers hence resonating at lower field.⁹ In this way we have found that the analytical sample consisted of about 90% 2,4-dinitro and 10% 2,6-dinitro isomer. The other peaks of aromatic protons are partially overlapped, and an estimation of the amounts of the two dinitro isomers in the mixture cannot be based on them. Separation of the two dinitro isomers was not attempted.

In addition, the IR spectrum of the same analytical sample reveals the presence of these isomers. It presents weak absorption bands at 780–760 and 825–805 cm^{-1} lying within the characteristic absorption regions of 1,2,3- and 1,2,4-tri-substituted benzene derivatives, respectively.¹⁰

The formation of the 2,4- and 2,6-dinitro isomer conforms with the literature. It has been reported¹¹ that the nitration under medium conditions of the toluene, which may be considered as parent compound of the substituted phosphinylmethyl benzenes, gave a product consisting of 85% 2,4- and 15% 2,6-dinitrotoluene. It has also been shown¹² that the components in mixtures of these isomers, produced by the direct nitration of toluene, can be readily recognized by $^1\text{H-NMR}$.

Upon nitration of the [di(isopropoxy)phosphinylmethyl]benzene with fuming nitric and sulfuric acid the corresponding 4-nitro derivative was mainly obtained whereas the expected 2,4-dinitro derivative was formed in such small amounts as to avoid detection. Apparently, the substitution ortho to the large di(isopropoxy)phosphinylmethyl group becomes difficult. It is known¹³ that the ni-

TABLE I
 Elemental Analysis of the Synthesized Compounds

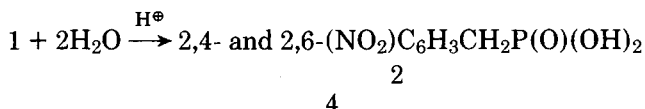
Compound	Formula	Elemental analysis (%)		
		C	H	N
1a	C ₁₁ H ₁₅ N ₂ O ₇ P	41.60 (41.52) ^a	4.92 (4.75)	8.69 (8.80)
1b	C ₁₁ H ₁₃ Cl ₂ N ₂ O ₇ P	34.22 (34.13)	3.45 (3.39)	7.12 (7.24)
Dihydrochloride salt of 2a	C ₁₁ H ₂₁ Cl ₂ N ₂ O ₃ P	39.25 (39.89)	6.21 (6.39)	8.35 (8.46)
2b	C ₁₁ H ₁₇ Cl ₂ N ₂ O ₃ P	40.52 (40.38)	5.39 (5.24)	8.25 (8.56)
3a	C ₂₅ H ₂₇ N ₂ O ₅ P	63.98 (64.37)	5.71 (5.83)	6.08 (6.00)
3b	C ₂₅ H ₂₅ Cl ₂ N ₂ O ₅ P	56.41 (56.09)	4.90 (4.71)	5.49 (5.23)
4	C ₇ H ₇ N ₂ O ₇ P	31.96 (32.07)	2.73 (2.69)	10.52 (10.69)

^a Numbers in parentheses indicate the calculated values.

tration, similarly to other electrophilic substitutions, is also subject to steric hindrance.

The nitration of the substituted phosphinylmethylbenzenes was a strongly exothermic reaction. When the reaction temperature went excessively up, the nitration becomes in some cases violent especially at the beginning of the reaction. Gradual addition of the substituted phosphinylmethyl benzenes to the mixed acids was therefore preferred. On the other hand, if the reaction conditions were sufficiently mild or the concentration of the acid mixture in fuming sulfuric acid was small, the intermediate 4-nitro derivative was obtained in higher yield.

The compounds 1 were hydrolyzed by acids to the corresponding phosphonic acids 4:



Upon hydrogenation of 1 in the presence of a catalytic amount of 10% palladium on carbon under a pressure of 3.5 atm, the corresponding diamino derivatives (2) were prepared in nearly quantitative yields. Generally, alcohols were the best solvents. Uptake was complete within several hours. The dihydrochloride salts of 2 were formed by passing anhydrous hydrochloride gas through their solutions. The structure of 2 was further verified by the preparation and identification of their di(benzolyamino) derivatives (3).

All synthesized compounds were characterized by elemental analysis (Table I), IR and ¹H-NMR spectroscopy (Table II). Typical IR spectra of 1b and 2b are shown in Figure 2. The following characteristic absorption bands appear in the IR spectra of 1: Phenyl (3030 cm⁻¹ and 1600 cm⁻¹); NO₂ (1534–1515 cm⁻¹ and 1344–1333 cm⁻¹); P=O (1264–1256 cm⁻¹); P—O—C (1053–1016 cm⁻¹). The IR spectra of 2 lack the characteristic absorption bands of nitro group and present the strong absorption band of amino group at the region of 3300–3268 cm⁻¹ (Fig. 2).

TABLE II
Physical Characteristics of the Synthesized Compounds

Compound	Solvent	¹ H-NMR		IR KBr (cm ⁻¹)
		PPM		
1a	CDCl ₃	8.23–7.27 (m, 3H, aromatic protons: 8.23 H ₃ of 2,4-isomer, 8.03 H ₅ of 2,4-isomer, 7.90 H ₃ and H ₅ of 2,6-isomer, 7.42 H ₆ of 2,4-isomer, 7.27 H ₄ of 2,6-isomer); 3.83 (m, 4H, CH ₃ CH ₂ O); 3.58 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂); 1.13 (t, 6H, CH ₃ CH ₂ O)	3030 (=CH); 2960–2926 (–CH); 1605 (aromatic); 1534, 1344 (NO ₂); 1264 (P=O); 1053–1019 (P–O–C)	
1b	CDCl ₃	8.23–7.20 (m, 3H, aromatic protons: 8.23 H ₃ of 2,4-isomer, 7.93 H ₅ of 2,4-isomer, 7.80 H ₃ and H ₅ of 2,6-isomer, 7.35 H ₆ of 2,4-isomer, 7.20 H ₄ of 2,6-isomer); 3.93 (m, 4H, ClCH ₂ CH ₂ O); 3.87 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂); 3.43 (m, 4H, ClCH ₂ CH ₂ O)	3012 (=CH); 2920–2850 (–CH); 1595 (aromatic); 1515, 1333 (NO ₂); 1256 (P=O); 1031–1016 (P–O–C)	
2a	CDCl ₃	6.85–5.55 (m, 3H, aromatic protons: 6.85 H ₃ , H ₄ and H ₅ of 2,6-isomer, 6.29 H ₆ of 2,4-isomer, 5.67 H ₅ of 2,4-isomer, 5.55 H ₃ of 2,4-isomer); 3.82 (broad, 4H, NH ₂); 3.68 (m, 4H, CH ₃ CH ₂ O); 2.73 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂); 1.03 (t, 6H, CH ₃ CH ₂ O)	3300 (NH ₂); 2980 (=CH); 2930 (–CH); 1640 (NH deformation); 1340 (C–N); 1222 (P=O); 1040–965 (P–O–C)	
Dihydrochloride salt of 2a	DMSO-d ₆	9.67 (broad, 6H, NH ₃ ⁺ Cl ⁻); 7.13 (m, 3H, aromatic); 3.87 (m, 4H, CH ₃ CH ₂ O); 3.45 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂); 1.17 (t, 6H, CH ₃ CH ₂ O)	2800 (broad, NH ₂); 1630 (NH deformation); 1350 (C–N); 1200 (P=O); 1040–1010 (P–O–C)	
2b	CDCl ₃	7.00–5.70 (m, 3H, aromatic protons: 7.00 H ₃ , H ₄ and H ₅ of 2,6-isomer, 6.47 H ₆ of 2,4-isomer, 5.82 H ₅ of 2,4-isomer, 5.70 H ₃ of 2,4-isomer); 3.93 (m, 4H, ClCH ₂ CH ₂ O); 3.57 (broad, 4H, NH ₂); 3.42 (m, 4H, ClCH ₂ CH ₂ O); 2.90 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂)	3268 (NH ₂); 2980 (=CH); 2850 (–CH); 1620 (NH deformation); 1290 (C–N); 1232 (P=O); 1081–1037 (P–O–C)	
3a	DMSO-d ₆	9.40 (broad, 2H, NHCO); 7.73–7.00 (m, 13H, aromatic); 3.80 (m, 4H, CH ₃ CH ₂ O); 2.97 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂); 1.13 (t, 6H, CH ₃ CH ₂ O)	3195 (NH); 2924 (–CH); 1650 (C=O); 1610 (aromatic); 1520 (NH deformation); 1218 (P=O); 1031–963 (P–O–C)	
3b	CDCl ₃	9.47, 8.62 (broad, 2H, NHCO); 7.70–6.60 (m, 13H, aromatic); 3.83 (m, 4H, ClCH ₂ CH ₂ O); 3.33 (m, 4H, ClCH ₂ CH ₂ O); 2.52 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂)	3205 (NH); 2882 (–CH); 1647 (C=O); 1592 (aromatic); 1517 (NH deformation); 1220 (P=O); 1074–1024 (P–O–C)	
4	DMSO-d ₆	7.98–7.08 (m, 3H, aromatic protons: 7.98 H ₃ of 2,4-isomer, 7.85 H ₅ of 2,4-isomer, 7.72 H ₃ and H ₅ of 2,6-isomer, 7.22 H ₆ of 2,4-isomer, 7.08 H ₄ of 2,6-isomer); 3.30 (d, <i>J</i> _{PCH} = 22 Hz, 2H, PCH ₂)	3050–2080 (broad, P–O–H); 1605 (aromatic); 1527, 1360 (NO ₂); 1200 (P=O); 1064–1016 (P–O–C)	

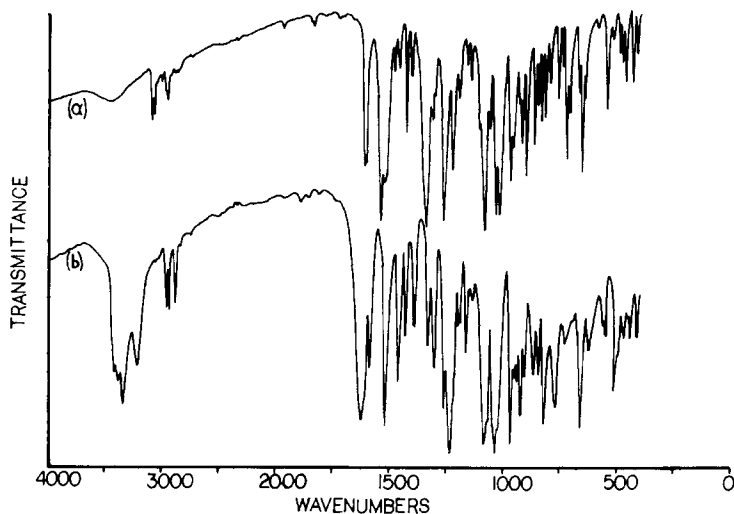


Fig. 2. Infrared spectra (a) of 1b; (b) of 2b.

The $^1\text{H-NMR}$ spectra of 2 compared to the corresponding spectra of 1 show a significant upfield shift of the doublet peak assigned to PCH_2 . Since the NH_2 groups are electron-donating and the NO_2 groups electron-withdrawing, the protons of PCH_2 are shielded more in the compounds 2 and therefore resonate at higher field. The same behavior was also observed in the aromatic protons.

Some of the synthesized compounds were investigated by GC-mass spectroscopy. Figure 3 shows the GC-mass spectrum of 1a analytical sample obtained at an elution temperature of about 200°C . A mass ion is not observed in this spectrum. The peak at m/e 272 assigned to M-46 (M-NO_2) ion has a relative intensity 76%, indicating the high stability of this ion. The base peak at m/e 216 should be attributed to the ion $^+\text{[C}_6\text{H}_3(\text{NO}_2)\text{CH}_2\text{P}(\text{O})(\text{OH}_2)_2$.

The GC-mass spectrum of 2b analytical sample (Fig. 4) obtained at an elution temperature of 193°C shows a M-1 peak at m/e 326 of lesser intensity (9.4%).

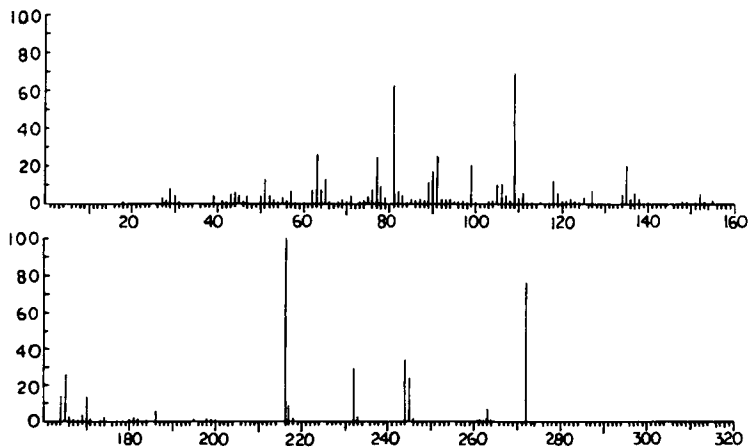


Fig. 3. Mass spectrum of 1a.

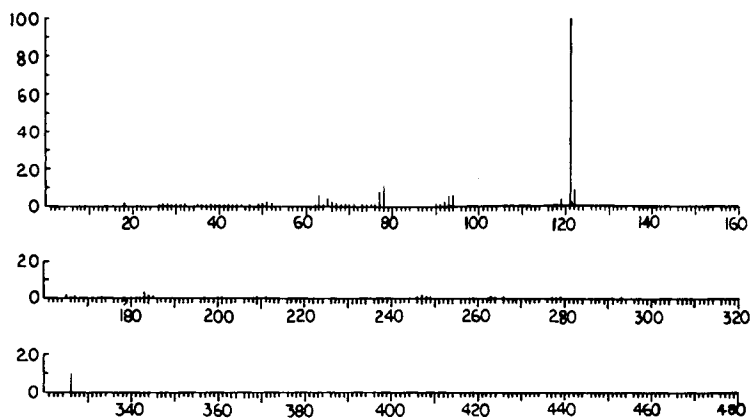


Fig. 4. Mass spectrum of 2b.

As in other aromatic amines the M-1 ion has been mainly arisen from the abstraction of one hydrogen atom from an amino group. The only strong peak appeared in this spectrum is the base peak at m/e 121. This peak is assigned to the ion $(\text{NH}_2)_2\text{C}_6\text{H}_3\text{CH}_2^{\oplus}$ resulted from a direct cleavage of the P—C bond.

Since compounds 3 can be considered as a model system for the polyamides prepared by reaction of 2 with an aromatic dicarboxylic acid, their degradation behavior is of interest. The GC-mass spectrum of 3a (Fig. 5) obtained at an elution temperature 368°C does not show a mass ion. The base peak at m/e 105 and the peak at m/e 361 of relative intensity 76% indicate a direct cleavage of the nitrogen-carbonyl carbon bond. The peak at m/e 77 should be attributed to the fragment resulted by abstraction carbon monoxide from NHCOC_6H_5 .

Phosphorus-containing polymers such as polyamides, polyimides, and pol-

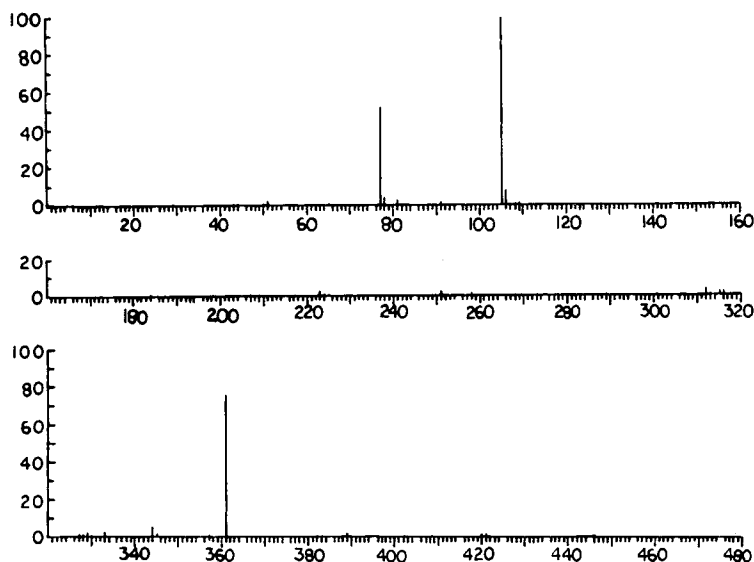


Fig. 5. Mass spectrum of 3a.

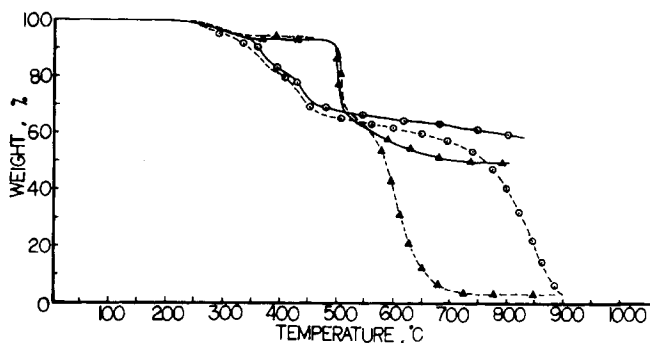


Fig. 6. TGA thermograms of the imide resins 6 (O) and 7 (Δ) in nitrogen (—) and air (---) atmosphere.

yureas based on 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (2) have been prepared and characterized. A remarkable property of the forementioned polymers is their relatively high degree of fire resistance.

Preliminary data concerning phosphorus-containing imide resins prepared by thermal polymerization of 1-[di(2-chloroethoxyphosphinyl)methyl]-2,4- and -2,6-bis(*N*-maleimido)benzene (5) are given below. The bismaleimide (5) was synthesized by reacting of 2b with maleic anhydride. Intermediate bismaleamic acid was cyclodehydrated *in situ* with acetic anhydride using sodium acetate as catalyst in boiling acetone. Imide resin (6) was prepared by heating of 5 at 230°C for 2 h.

In addition, imide resin (7) was prepared for comparative purpose by thermal polymerization of 1,3-bis(*N*-maleimido)benzene which may be considered as the parent compound of 5.

Typical thermogravimetric analysis (TGA) curves of the phosphorus-containing polymer 6 and of the corresponding common polymer 7 in nitrogen and air are shown in Figure 6. It can be seen that the polymer 6 exhibited a lower polymer decomposition temperature and a higher char yield than did the corresponding common polymer 7.

The considerably lower flammability of 6 in comparison to that of 7 was shown by determining their limiting oxygen index (LOI) value. The LOI values of the imide resins 6 and 7 were 71.6 and 41.0, respectively. More data will be reported later.

EXPERIMENTAL

Reagents and Instrumentation

[(Dialkoxyphosphinyl)methyl]benzenes were prepared by the Michaelis-Arbuzov reaction of benzyl bromide or halide with trialkyl phosphites.¹⁴

Melting points were measured on a Büchi apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord Spectrometer. ¹H-NMR spectra were obtained at 60.0 MHz on a Varian T-60A spectrometer with tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ). All NMR spectra were recorded on saturated solutions and at 30°C normal probe temperature. Elemental analyses were performed

by the Microanalytical Laboratory of the National Hellenic Research Foundation in Athens, Greece. GC-mass spectra were recorded by the direct-inlet procedure at 70 eV on a Hewlett-Packard 5980 Mass Spectrometer attached to a 5933A Data System and 2100S Microprogrammable System Computer. The GC-mass spectra were obtained at NASA, Ames Research Center in Moffett Field, Calif. TGA was performed on a DuPont 1090 Thermal Analyzer System. A heating rate of 20°C/min was used in both nitrogen and air atmosphere with a flow rate of 80 cm³/min. The LOI of the polymers was determined with a Stanton Redcroft Flammability Unit (ASTM D 2863-74).

Synthesis of Compounds

1-[(Diethoxyphosphinyl)methyl]-2,4- and -2,6-Dinitrobenzenes (1a). [(Diethoxyphosphinyl)methyl]benzene (21.76 g, 95 mmol) was added dropwise to a mixture of fuming nitric acid (16.3 g) and fuming sulfuric acid (54.30 g), containing 30% SO₃, at 55°C. The addition of the phosphonate lasted 1 h, and, subsequently, the mixture was heated at the same temperature for another hour. The mixture was poured into 1 L of ice water and extracted with chloroform (300 mL). The chloroform solution was washed with 5% NaHCO₃ solution and with water, dried (Na₂SO₄), and concentrated to give a yellowish solid (24.16 g, 80%, mp 78–82°C). An analytical sample was obtained by recrystallizations from ether-chloroform (10:1) having mp 101–104°C.

By concentration of the recrystallizations filtrate a viscous undistillable liquid (4.80 g, 18.5%) was obtained, consisting mainly of 1-[(diethoxyphosphinyl)methyl]-4-nitrobenzene characterized spectroscopically as follows:

¹H-NMR (CDCl₃)δ: 7.53 (d, 2H, aromatic protons H₄ and H₅); 7.03 (d, 2H, aromatic protons H₂ and H₆); 3.77 (m, 4H, CH₃CH₂O); 3.13 (d, J_{PCH} = 22 Hz, 2H, PCH₂); 1.08 (t, 6H, CH₃CH₂O).

IR (KBr) cm⁻¹: 3030 (=CH); 2960–2890 (—CH); 1595 (aromatic); 1530, 1340 (NO₂); 1245 (P=O); 1036–960 (P—O—C).

1-[(Diethoxyphosphinyl)methyl]-2,4- and -2,6-Diaminobenzenes (2a). Recrystallized 1a (2.00 g, 6.28 mmol) was dissolved in 50 mL of absolute ethanol and a small amount of catalyst, 10% palladium on carbon, was added. The hydrogenation was carried out on a Parr apparatus under a pressure of 3.5 atm at room temperature until no more hydrogen was taken up (3 h). After filtration of the catalyst and removal of the volatile components under vacuum, the 2a was obtained as a viscous undistillable liquid (1.57 g, 97%), which could not be induced to crystallize.

The dihydrochloride salt of 2a was formed by passing anhydrous hydrochloride gas through its solution in chloroform. The salt was a nearly white solid, and, after recrystallizations from ethanol-ether (1:6), an analytical sample was obtained which decomposed at a temperature higher than 128°C.

1-[(Diethoxyphosphinyl)methyl]-2,4- and -2,6-di(benzoylamino)benzenes (3a). Recrystallized dihydrochloride salt of 2a (2.19 g, 6.6 mmol) and 20 mL of dried dichloromethane were placed in a flask fitted with a drying tube. The diamine 2a were formed *in situ* by addition of triethylamine (2.67 g, 26.4 mmol). Benzoylchloride (1.86 g, 13.2 mmol) was added to the mixture. An exothermic reaction was observed and the mixture was stirred under nitrogen for 5 min into an icebath. The stirring was continued at room temperature for

2 h. *n*-Hexane (100 mL) was added to the mixture to precipitate the produced 3a as well as the hydrochloride salt of triethylamine. The mixture of these compounds was washed at room temperature with benzene (50 mL) which mainly dissolves 3a. Thus, the benzene filtrate by concentration under vacuum gave a white solid (2.63 g, 77%, mp 230–233°C). An analytical sample was obtained by recrystallizations from ethanol–acetonitrile (1:5) having mp 231–234°C.

1-[Di(2-chloroethoxyphosphinyl)methyl]-2,4- and -2,6-Dinitrobenzenes (1b). [Di(2-chloroethoxyphosphinyl)methyl]benzene (5.13 g, 17 mmol) was added dropwise to a mixture of fuming nitric acid (4.0 g) and fuming sulfuric acid (13.0 g), containing 30% SO₃, at 55°C. The addition of the phosphonate lasted 0.5 h, and, subsequently, the mixture was heated at the same temperature for 4 h, moreover. The mixture was poured into 300 mL of ice water and extracted with chloroform (150 mL). The chloroform solution was washed with 5% NaHCO₃ solution and with water, dried (Na₂SO₄), and concentrated to give a viscous liquid (4.92 g) diluted with 100 mL of acetone–ether (1:10). Upon cooling of the solution, the 1b was crystallized (2.80 g, 42%, mp 79–84°C). The analytical sample obtained by recrystallization from acetone–ether (1:10) had mp 83–85°C.

1-[Di(2-chloroethoxyphosphinyl)methyl]-2,4- and -2,6-Diaminobenzenes (2b). Recrystallized 1b (2.27 g, 58.6 mmol) was dissolved in 40 mL of absolute ethanol, and a small amount of catalyst, 10% palladium on carbon, was added. The hydrogenation was carried out as in 2a compound. A solid product was obtained (1.88 g, 98%, mp 105–109°C). An analytical sample was obtained by recrystallizations from benzene (mp 116–119°C).

1-[Di(2-chloroethoxyphosphinyl)methyl]-2,4- and -2,6-di(benzoylamino)benzenes(3b). Recrystallized 2b (0.44 g, 1.35 mmol), dried dichloromethane (15 mL), triethylamine (0.27 g, 2.7 mmol), and benzoylchloride (0.38 g, 2.7 mmol) were placed in a flask fitted with a drying tube. The reaction as well as the isolation of the product was carried out as in 3a compound. A white solid was obtained (0.58 g, 80%, mp 195–198°C). The analytical sample obtained by recrystallizations from ethanol had mp 198–200°C.

Attempt for Synthesis of 1-[Di(isopropoxy)phosphinylmethyl]-2,4- and -2,6-Dinitrobenzenes. [Di(isopropoxy)phosphinylmethyl]benzene (4.00 g, 15.6 mmol) was added dropwise to a mixture of fuming nitric acid (3.00 g) and fuming sulfuric acid (11.00 g), containing 30% SO₃, which was cooled into an icebath. The addition of the phosphonate lasted 0.5 h, and the mixture was stirred into the icebath for 4 h, consequently into a waterbath of 20°C for 15 h, and finally heated to 90°C for 3 h. The reaction product was isolated by extraction with chloroform (150 mL), washing with 5% NaHCO₃ solution and water, drying (Na₂SO₄), and concentration. A viscous liquid was obtained (0.52 g, 11%) which was mainly consisted of 1-[di(isopropoxy)phosphinylmethyl]-4-nitrobenzene. It was characterized spectroscopically as follows:

¹H-NMR (CDCl₃)δ: 7.48 (m, 2H, aromatic protons H₃, H₅); 6.92 (m, 2H, aromatic protons H₂, H₆); 4.32 (m, 2H, OCH(CH₃)₂); 3.30 (d, J_{PCH} = 22 Hz, 2H, PCH₂); 2.22 (d, 12H, OCH(CH₃)₂).

IR (KBr) cm⁻¹: 3030 (=CH); 2915 (—CH); 1631 (aromatic); 1531, 1351 (NO₂); 1233 (P=O); 1022–1000 (P—O—C).

1-[(Dihydroxyphosphinyl)methyl]-2,4- and -2,6-Dinitrobenzenes (4). [Diethoxyphosphinylmethyl]-2,4- and -2,6-dinitrobenzenes (1a) (2.00 g, 6.3

mmol) was dissolved in 20 mL of concentrated hydrochloric acid, and the solution was refluxed for 4 h. After removal of the volatile components of the mixture under vacuum, a white solid was obtained (1.30 g, 96%, mp 211–214°C). Recrystallizations from acetone–ether (1:4) gave an analytical sample having mp 217–219°C.

1-[Di(2-Chloroethoxyphosphinyl)methyl]-2,4- and -2,6-bis(*N*-maleimido)benzene (5). Maleic anhydride (2.64 g, 26.97 mmol) was added to a vigorously stirred solution of 2b (4.01 g, 12.26 mmol) in acetone under nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. Bismaleamic acid was precipitated as a yellow solid, during the stirring. To the continuously stirred suspension of bismaleamic acid in acetone, acetic anhydride (8.5 mL) and fused sodium acetate (0.70 g) were added, and the mixture was refluxed. A brownish solution was obtained after 0.4 h heating. Refluxing and stirring was continued for about 2 h. The solution was poured in ice water and extracted with chloroform (150 mL). The chloroform solution was washed with 5% NaHCO₃ solution and with water, dried (Na₂SO₄), and concentrated. A brown solid (5.61 g, 94%) was obtained by drying of the concentrate at 50°C in a vacuum oven overnight. Recrystallizations from THF–ether (1:6) gave an analytical sample which did not show a sharp melting point in a capillary tube.

ANAL. Calcd for C₁₉H₁₇Cl₂N₂O₇P: C, 46.85%; H, 3.49%; N, 5.75%. Found: C, 46.32%; H, 3.68%; N, 5.60%.

CONCLUSIONS

Nitration of the (dialkoxyphosphinyl)methyl benzenes with a mixture of fuming nitric and sulfuric acid gave 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-dinitrobenzenes (1). The formation of the dinitro isomers was demonstrated by ¹H-NMR spectroscopy. The nitration product consisted of about 90% 2,4-dinitro and 10% 2,6-dinitro isomer, as was shown by ¹H-NMR spectroscopy. Nitration of the [di(isopropoxy)phosphinylmethyl]benzene gave mainly the *p*-nitro derivative due to steric hindrance. Compound 1 was hydrolyzed by acids to the corresponding phosphonic acids. 1-[(Dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (2) were synthesized by catalytic hydrogenation of 1. In addition, the di(benzoylamino) derivatives (3) were prepared by reaction of 2 with benzoylchloride in the presence of an acid acceptor. All synthesized compounds were characterized by elemental analysis, IR, ¹H-NMR spectroscopy, and some of them by GC–mass spectroscopy. A direct cleavage of the P–C bond and of the nitrogen–carbonyl carbon bond occurred during the pyrolysis of 2 and 3 compounds, respectively, as was shown by GC–mass spectral studies.

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