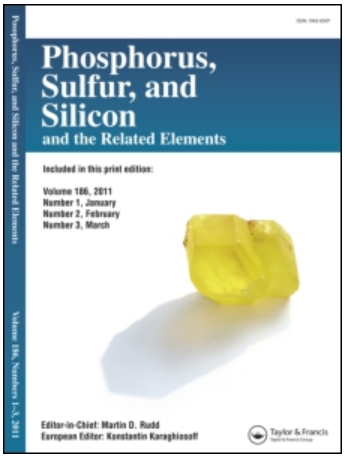

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Arbanov, S. V. , Toshev, T. and Russev, E.(1997) 'FUNCTIONALIZED NITROGEN-CONTAINING TERTIARY PHOSPHINE OXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 127: 1, 27 — 37
To link to this Article: DOI: 10.1080/10426509708040493
URL: http://dx.doi.org/10.1080/10426509708040493

Phosphorus, Sulphur, and Silicon, 1997, Vol. 127, pp. 27–37
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FUNCTIONALIZED NITROGEN-CONTAINING TERTIARY PHOSPHINE OXIDES

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(Received 29 April 1997)

Several new functionalized tertiary phosphine oxides, namely **o**-, **m**- and **p**- dimethylphosphinylmethyleneoxyanilines, bis(dimethylphosphinylmethylene)amine and N-dimethylphosphinylmethylene-ϵ-caprolactam have been synthesized. These compounds were prepared via alkylation of **o**-, **m**- and **p**-aminosubstituted sodium phenolates, aminomethyldimethylphosphine oxide and sodium salt of ϵ-caprolactam with chloromethyldimethylphosphine oxide. The **m**- and **p**- dimethylphosphinylmethyleneoxyanilines and aminomethyldimethylphosphine oxide were acylated with benzoylchloride to the corresponding amides. The new compounds were chatacterized by analytical methods, IR, ^{1}H- and $^{31}P\{H\}$-NMR spectroscopy.

Keywords: Tertiary phosphine oxides; dimethylphosphinylmethyleneoxyanilines; bis(dimethylphosphinylmethylene)amine; N-dimethylphosphinylmethylene-ϵ-caprolactame; ionization constants

INTRODUCTION

The tertiary phosphine oxides functionalized with primary or secondary amino groups are a relatively small group of organophosphorus compounds.[1–10] Due to the high reactivity of the amino group they can be used as phosphorylating agents of polymers as well as a starting material in the synthesis of new organophosphorus compounds.[11] Recently L. Maier[12] and S. Varbanov et al[13–15] have reported the preparation of new tertiary phosphine oxides functionalized with primary amino groups such as aminomethyldimethylphosphine oxide, bis(aminomethyl)methyl phosphine oxide and several aminoalkyloxymethyldimethylphosphine oxides. Later on it has been shown that the first two of these

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Dedicated to Professor Gueorgui Borissov on his 70th Birthday

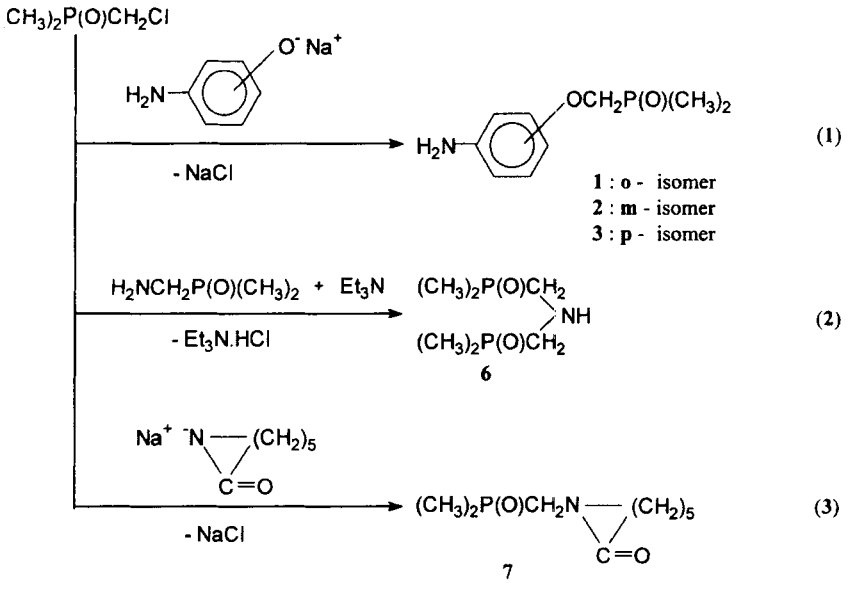
compounds can be used in the synthesis of phosphorus-containing nitrosoureas,[16] bifunctional phosphorus-containing monomers,[14] rigid polyurethane foams,[13] epoxide-amine oligomers and polymers,[17] organometal complex compounds,[18,19] aromatic-aliphatic secondary amines and Schiff bases.[12,20] It has been shown that some of the abovementioned derivatives of the tertiary phosphine oxides have anticancer and herbicidal activity.[16,19,20]

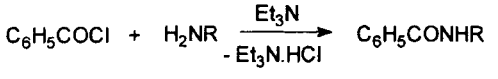
The present paper, being a continuation of our studies on the synthesis, characterization and application of nitrogen-containing tertiary phosphine oxides, reports on the preparation of new tertiary phosphine oxides functionalized with primary and secondary amino groups or with a ϵ-caprolactam ring.

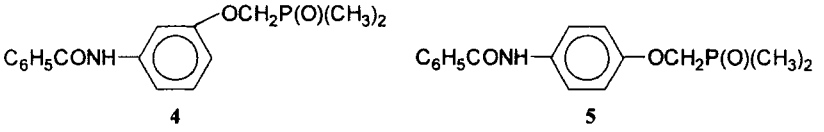
RESULTS AND DISCUSSION

The new nitrogen-containing tertiary phosphine oxides: **o**-, **m**- and **p**- dimethylphosphinylmethyleneoxyanilines **1**, **2** and **3** (Scheme 1, Table I), bis(dimethylphosphinylmethylene)amine **6** and N-dimethylphosphinylmethylene-ϵ-caprolactam **7** were synthesized by alkylation of the **o**-, **m**- and **p**-aminosubstituted sodium phenolates, aminomethyldimethylphosphine oxide and sodium salt of ϵ-caprolactam, respectively with chloromethyldimethylphosphine oxide (CDPO) according to Scheme 1.

The **o**-, **m**- and **p**-aminosubstituted sodium phenolates were prepared immediately before their use through exchange reactions between sodium methoxide and **o**-, **m**-, and **p**-hydroxyanilines, respectively. The sodium salt of the ϵ-caprolactam was also prepared freshly from sodium hydride and ϵ-caprolactam as described elsewhere.[21] It is known that nucleophilic substitution of chlorine atoms in the chloromethyl groups of the tertiary phosphine oxides is running well in aromatic hydrocarbon medium.[22–24] That is why products **1–3** were synthesized in xylene, compound **6** - in benzene, while **7** - in a mixture of toluene and xylene. As seen from Table I, compound **7** was produced with the highest yield, while compounds **1–3** with a little bit lower yields. The yield of compound **6** was the lowest. The different yields can be explained by the variation of the nucleophility of the reagents in the reactions (1), (2) and (3) which decreases in the order: amide anion of ϵ-caprolactam > **o**-, **m**- and **p**-aminosubstituted phenolate anions ≫ nitrogen atom in the aminomethyldimethylphosphine oxide. The higher nucleophility of the first two reagents is due to the presence of a negative charge on their nucleophilic centers. Such a charge is absent in the aminomethyldimethylphosphine oxide. Furthermore, the electronegative phosphoryl group additionally lowers the nucleophility of the nitrogen atom.







$C_6H_5CONHCH_2P(O)(CH_3)_2$

8

SCHEME 1

These suggestions are in good agreement with the data of Glamkowski et al[25] who performed alkylation of several 1-arylpiperazines with the same CDPO reagent under similar conditions and obtained the products with very high yeilds (70–90%). These high yields can be explained by the higher nucleophility of the second nitrogen atom in the 1-arylpiperazines as compared to

TABLE I Preparative and analytical data of tertiary phosphine oxides modified with nitrogen-containing functional groups

No	*Compound*	*Yield (%)*	*M.P., °C (Recryst. solvent)*	*Phosphorus content, %*		*Nitrogen content, %*		pK_a
				Found	*Calcd.*	*Found*	*Calcd.*	
1	**o**-Dimethylphosphinylmethylene-oxyaniline	85	143–145 (Toluene)	15.70	15.56	7.31	7.03	4.07
2	**m**-Dimethylphosphinylmethylene-oxyaniline	82	85–86 (Toluene)	16.13	15.56	6.45	7.03	4.12
3	**p**-Dimethylphosphinylmethylene-oxyaniline	88	115–118 (Xylene)	14.95	15.56	7.23	7.03	5.19
4	**m**-Dimethylphosphinylmethylene-oxyanilinebenzamide	72	173–175 (Acetonitrile)	9,99	10,21	4.01	4.62	–
5	**p**-Dimethylphosphinylmethylene-oxyanilinebenzamide	85	217–219 (Acetonitrile)	10.12	10.21	4.61	4.62	–
6	Bis(dimethylphosphinylmethylene)-amine	52	179–182 (Dioxane)	31.30	31,42	7.16	7,11	2.52
7	N-Dimethylphosphinylmethylene-ϵ-caprolactame	97	B.p. 178–179 (1 mm Hg)	15.01	15,24	6.43	6.89	–
8	Aminomethyldimethylphosphine-oxidebenzamide	89	125–130 (Toluene)	14.28	14.67	6.41	6.63	–

the nitrogen atom in aminomethyldimethylphosphine oxide. In the 1-arylpiperazines there is no electronegative group neighbouring the alkylated nitrogen atoms able to decrease the nucleophility of the latter. The high exothermal effect of reactions (1) and (3) observed on addition of the CDPO also confirms the higher nucleophility of the amide anion of ϵ-caprolactam and of the **o**-, **m**- and **p**-aminosubstituted phenolate anions. The amount of the isolated sodium chloride in the reactions (1) and (3) was almost 100% which was in accordance with the observed high yields of the prepared products.

The preparation of products **1** and **3** has been reported earlier.[8] It was achieved through an intermediate synthesis of the corresponding 2- and 4-dimethylphosphinylmethyleneoxynitrobenzenes and their subsequent reduction with sodium sulfide to produce the corresponding 2- and 4-dimethylphosphinylmethyleneoxyanilines. We consider that the present method for preparation of **1** and **3** is more advantageous since it is performed in a single stage with higher yields.

With a view to prove the structure of the **1–3** as well as to evaluate their probable applicability to further synthesis they were subjected to acylation with benzoyl chloride in the presence of triethylamine {reaction (4)}. The aminomethyldimethylphosphine oxide was acylated in the same way. As seen from Table I, the acylated products **4,5** and **8** were produced with high yields.

Our attempts to perform acylation of **1** in a similar way failed. This is probably due to steric factors. The dimethylphosphinylmethyleneoxy group in **o**-position to the amino group is too bulky and prevents the acylation of **1** according to reaction (4).

The expected composition of the sythesized products was proved by elemental analysis of phosphorus and nitrogen (Table I), and their structure confirmed by IR, ^{1}H and ^{31}P NMR spectroscopy. The molecular mass of **7** was determined by the vapour pressure osmometry and the value obtained agreed satisfactorily with the calculated one ($m.m._{exp.}$ = 196.27, $m.m._{calcd.}$ = 203.32).

In the IR spectra of all studied products (Table II) are present characteristic bands of the phosphoryl group (P=O) at 1135–1178 cm^{-1}, of the CH_3-P bonds at 1294–1310 cm^{-1} and at 938–960 cm^{-1}, of P-CH_2 bond[26] at 754–776 cm^{-1}, of the N-H bonds in the amino groups at 1622–1654 cm^{-1}, 3179–3229 cm^{-1}, 3293–3343 cm^{-1} and 3408–3460 cm^{-1} (products **1**, **2**, **3**, and **6**), of the ether bond neighbouring the aromatic ring at 1043–1055 cm^{-1} (products **1–5**). Bands typical of the amide N-H group are observed in the spectra of **4**, **5** and **8** at 1539–1579 cm^{-1}, 3049–3489 cm^{-1}, respectively and of amide carbonyl group at 1650–1671 cm^{-1}. In the spectrum of **7** there are no bands of the N-H bond.

In the ^{1}H-NMR spectra (Table III) of all studied compounds are observed: characteristic doublets of the methyl group protons $CH_3P=O$ at 1.48–1.67 ppm

TABLE II Characteristic infrared frequences (ν cm^{-1}) of nitrogen-containing tertiary phosphine oxides

No	*P=O*	*CH_3P*	*CH_2P*	*C-O-Ar*	*N-H(Amine)*	*Amide N-H*	*C=O*
1	1172(vs,shp)	1298(m,shp) 950(m,shp)	760(s,shp)	1229(s,shp) 1048(m,shp)	3460(s,shp), 3293(s,shp) 3179(m,shp), 1622(m,shp)	–	–
2	1164(vs,shp) 1154(s,sh) 1135(s,sh)	1294(m,shp) 938(s,shp)	760(m,shp)	1223(m,shp) 1053(m,shp)	3408(vs,shp), 3342(s,shp) 3224(vs,shp), 1634(s,shp)	–	–
3	1148(vs,shp) 1178(w,sh)	1305(m,shp) 938(m,shp)	754(w,shp)	1238(s,shp) 1055(m,shp)	3428(vs,shp), 3343(s,shp), 3229(s,shp), 1637(m,shp)	–	–
4	1168(vs,shp) 1155(s,shp)	1299(m,shp) 940(m,shp)	776(w,shp)	1269(m,shp) 1043(w,shp)	–	3255(w,shp), 3211(w,br), 3151(w,shp), 1557(s,shp)	1661(s,shp) 1670(s,shp)
5	1162(vs,shp) 1177(w,sh)	1298(m,shp) 947(s,shp)	770(w,br)	1220(s,shp) 1048(m,shp)		3489(vs,br) 3227(vs,shp) 3118(vs,shp) 3049(vs,shp) 1550(s,shp)	1657(s,shp)
6	1146(vs,shp)	1298(m,shp) 942(m,shp)	755(w,shp)	–	3423(vs,br) 1654(m,shp)	–	–
7	1175(vs,shp) 1145(vs,sh)	1310(s,shp) 960(s,shp)	765(w,br)	–	–		1650(vs,shp)
8	1146(vs,shp) 1163(vs,sh)	1309(vs,shp) 945(vs,shp)	755(w,shp)	–	–	3289(vs,br), 1539(vs,shp) 1579(m,shp)	

TABLE III ^{1}H and $^{31}P\{H\}$NMR data of tertiary phosphine oxides modified with nitrogen-containing functional groups (δ in ppm, J in Hz)

No	^{1}H-NMR data, protons							$^{31}P\{H\}$
	CH_3-P		CH_2P		HN(Amine)	Ar-H	HN-C=O	
	δ	$^{2}J_{HP}$	δ	$^{2}J_{HP}$	δ	δ	δ	δ
1	1.67(d)	13.0	4.28(d)	7.5	3.75(s)	6.7–6.9(m)		+41.84
2	1.63(d)	13.3	4.19(d)	8.4	3.71(s)	6.2–7.2(m)		+43.25
3	1.63(d)	13.3	4.16(d)	8.2	3.41(s)	6.6–6.8(m)		+43.10
4	1.62(d)	13.2	4.22(d)	8.1		6.1–8.1(m)	8.76(s)	+42.87
5	1.67(d)	13.2	4.23(d)	8.2		6.9–8.0(m)	8.15(s)	+42.73
6	1.56(d)	12.6	3.11(d)	7.3	2.15(s)			+42.11
7*	1.48(d)	12.8	3.79(d)	5.2				+43.36
8	1.48(d)	12.8	4.02(d)	4.9		7.3–8.0(m)	8.35(s)	+45.86

*Signals for: C-$(CH_2)_3$-C - δ 1.70(s), CH_2C=O - δ 2.52(m), C-CH_2N-δ 3.60(m).

and $^{2}J_{HP}$ = 12.6–13.6 Hz, of methylene group protons CH_2P=O at 3.11–4.28 ppm and $^{2}J_{HP}$ = 4.9–8.4 Hz, multiplet signals of aromatic protons of **1–5** at 6.1–8.1 ppm, signals of N-H protons of the amino groups of **1–3** and **6** at 2.15–3.75 ppm, which disappear on deuterium exchange, and signals of protons of the amide groups of **4**, **5** and **8** at 8.15–8.76 ppm. In the spectrum of **7** signals of the $(CH_2)_3$ protons at 1.70 ppm, of the CH_2C=O protons at 2.52 ppm and of C-CH_2N protons at 3.60 ppm are observed, which is in agreement with the available data about the phosphorylated ϵ-caprolactam.[27] In all cases the integral intensities correlate with the number of protons.

The $^{31}P\{H\}$ NMR spectra are singlets and the signals are in the range +41.84–+45.86 ppm typical of the tertiary phosphine oxides containing methyl and methylene groups at the phosphorus atom.[28]

Products **1–3** are pale brown crystals, which change their colour to dark brown on storage, while the remaining substances are white crystals. Products **6** and **7** are hygroscopic. All studied products are soluble in water, chloroform, methylene chloride, methanol, ethanol, acetone, dimethylformamide, etc. but in toluene and xylene only at elevated temperature. They are insoluble in aliphatic hydrocarbons, carbon tetrachloride, diethyl ether. It is worth mentioning, that **o-**, **m-** and **p-** anisidines and phenetidines - the corresponding lower aliphatic analogues of **1**, **2** and **3**, are substances with high boiling but low melting points, sparingly soluble in water.[29,30] The substances from the two types have different physical properties determined by the existance of the dimethylphosphinyl group in **1–3**. As expected benzamides **4**, **5** and **8** have higher melting points if compared to the starting amines.

The dissociation constants of **1–3** and **6** were determined by potentiometric titration (see Table I). It appeared that the pK_a values of **1–3** are similar to that of **o-**, **m-** and **p**-anisidine and phenetidines.[29,31] This fact shows that the electro-

negative phosphoryl group does not affect the basicity of the aminogroups in these compounds. The secondary amine **6** has a $pK_a = 2.52$, which points out that the basicity of its nitrogen atom is very low as compared to that of ammonia ($pK_a = 9.27$).[31] The decreased basicity of **6** is very likely due to the combined effect of the two electronegative phosphoryl groups in its molecule. A similar but weaker effect was observed with the aminomethyldimethylphosphine oxide, whose $pK_a = 6.24$ was determined by $^{31}P\{H\}$-NMR controlled titration.[32]

EXPERIMENTAL

Starting Materials

Chloromethyldimethylphosphine oxide (CDPO), 2-, 3-, and 4-aminophenols, ϵ-caprolactam, sodium hydride (80% in white oil) and benzoyl chloride were commercially available products. Aminomethyldimethylphosphine oxide was synthesized according to.[13] Triethylamine was dried and purified as described elsewhere.[33] All solvents were additionally purified and dried before use by known standard procedures.

Characterization of Synthesized Products

The phosphorus content was determined as described in ref. 34. Nitrogen content was analysed in the Laboratory of Organic Microanalysis of the Institute of Organic Chemistry, Bulgarian Academy of Sciences according to standard method. Melting points were measured on a Boetzius microheating plate PHMK 05 (Germany). Infrared spectra (400–4000 cm^{-1}) were recorded on a Bruker IFS25 spectrometer as KBr pellets and ^1H NMR spectra - on a Bruker WM-250 spectrometer at 250.13 MHz in $CDCl_3$ using tetramethylsilane as internal standard. ^{31}P NMR spectra were taken with decoupling in $CDCl_3$ on a Bruker AC-200 spectrometer at 81.015 MHz. The chemical schifts are given against 85% H_3PO_4. The molecular mass of **7** was determined on a Knauer vapour pressure osmometry instrument in chloroform at 45°C. Dissociation constants of **1–3** and **6** were determined by potentiometric titration of their aqueous solutions with standard solution of HCl. pH measurements were carried out with a Microsyst 2003 pH-meter (Bulgaria), glass and calomel electrodes at 20° $\pm$ 0.1°C at a constant ionic strength $\mu = 0.1$ (KCl) in argon atmosphere.

Preparation of o-dimethylphosphinylmethyleneoxyaniline (1)

A solution of CDPO (1.10 g, 9.0 mmol) in xylene (15 ml) was added dropwise to a refluxing suspension of sodium o-aminosubstituted phenolate in xylene, prepared by addition of o-aminophenol (1.00 g, 9.0 mmol) and sodium (0.21 g, 9.0 mmol) to a mixture of xylene (30 ml) and methanol (15 ml), followed by distillation of the latter. The resulting mixture was refluxed under argon with stirring for 10 hrs and then hot filtered. After cooling to room temperature the precipitate was filtered (yield 1.00 g) and recrystallized.

Products **2** and **3** were prepared in a similar way.

Preparation of p-dimethylphosphinylmethyleneoxyaniline-benzamide (5)

A solution of benzoylchloride (0.44 g, 3.1 mmol.) in methylene chloride (4 ml) was added dropwise at 15–20°C and stirring under argon to a solution of **3** (0.50 g, 2.5 mmol) and triethylamine (0.36 ml, 2.5 mmol) in methylene chloride (11 ml). The mixture was stirred at the same temperature for 4 hrs and the solvent evaporated. The residue was diluted with water (5 ml) and the suspension filtered. The resulting crude solid **5** was dried (yield 0.59 g) and recrystallized.

Products **4** and **8** were prepared in a similar way. Product **8** was isolated by evaporation of the solvent and recrystallization, while **4** was prepared in dimethyl-acetamide at -30°C.

Preparation of bis(dimethylphosphinylmethylene)amine (6)

A mixture of aminomethyldimethylphosphine oxide (2.39 g, 22.3 mmol), triethylamine (3.27 ml, 23.4 mmol) and CDPO (2.95 g, 23.3 mmol) in benzene (70 ml) was refluxed with stirring for 20 hrs. Then the mixture was cooled, filtered and the filtrate evaporated. The residue was washed with dioxane, dried (yield 2.28 g) and recrystallized.

Preparation of N-dimethylphosphinylmethylene-ϵ-caprolactam (7)

To a refluxing suspension of a sodium salt of ϵ-caprolactam, prepared according to[21] from ϵ-caprolactam (6.81 g, 60.0 mmol) and sodium hydride (1.72 g, 57.5 mmol) in toluene (120 ml), was added a solution of CDPO (7.59 g, 60.0 mmol) in xylene (20 ml). The reaction mixture was refluxed for 10 hrs and cooled to ambient temperature and filtered. The filtrate was evaporated and the residue (yield 11.86 g) was subjected to fractional vacuum distillation.

Acknowledgements

The authors thank the National Science Foundation of Bulgaria for financial support (Project CH-626), and Assoc. Prof. Dr. V .Lachkova for very valuable discussions.

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