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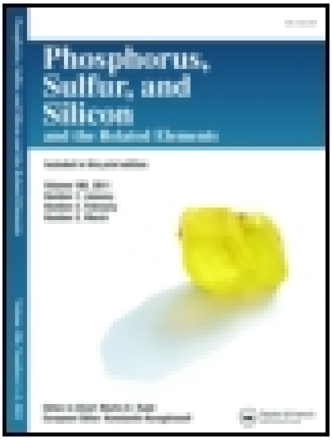

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SCHIFF BASES DERIVED FROM AMINOMETHYL-DIMETHYL-PHOSPHINE OXIDE

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SCHIFF BASES DERIVED FROM AMINOMETHYL-DIMETHYL-PHOSPHINE OXIDE

S. VARBANOV[a], A. GEORGIEVA[b], G. HÄGELE[c*], H. KECK[c] and V. LACHKOVA[b]

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(Received August 19, 1999)

A group of Schiff bases **1** – **18** derived from aminomethyl-dimethyl-phosphine oxide with aromatic aldehydes have been synthesized. Structure and purity of the new compounds were determined by IR, ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy, mass spectrometry and elemental analysis.

Keywords: Tertiary phosphine oxides; aminomethyl-dimethyl-phosphine oxide; Schiff bases; synthesis

Dedicated to Professor Reinhard Schmutzler on occasion of his 65th birthday

INTRODUCTION

Aminomethyl-dimethyl-phosphine oxide (AMPO) is a very interesting functionalized tertiary phosphine oxide. It has been synthesized independently by L. Maier[1] and the Sofia team[2,3] from chloromethyl-dimethyl-phosphine oxide using different methods. It was shown that this phosphorus-containing primary monoamine has a pK_a value of 6.23[3] and possesses high reactivity and nucleophilicity to be used as an organic intermediate reagent, flame retardant for polymers and organic ligand for the synthesis of complexes with metal salts[2,4–10].

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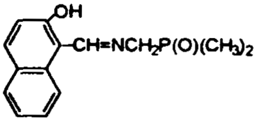
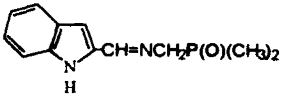
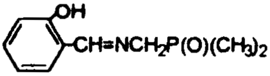
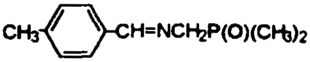
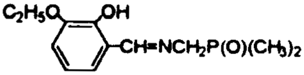
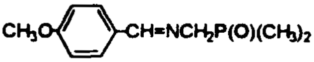
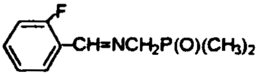
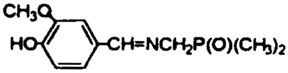
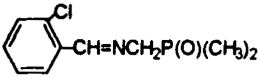
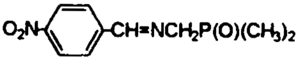
[*] Author to whom correspondence should be addressed Prof. Dr. G. Hägele – Heinrich Heine Universität Düsseldorf. Inst. für Anorg. Chemie Universitätsstr. 10 D-40225 Düsseldorf, Germany

TABLE I Molecular structures of Shiff bases derived from aminomethyl-dimethyl-phosphine oxide

Compound	*No.*	*Compound*
 roxy-1-naphthylmethylene-imino-methyl)-dimethyl-phosphine oxide	**10**	 (2-Indolylmethylene-iminomethyl)-dimethyl-phosphine oxide
 roxyphenylmethylene-iminomethyl)-dimethyl-phosphine oxide	**11**	 (4-Methyl-phenylmethylene-iminomethyl)-dimethyl-phosphine oxid
 xy-2-hydroxyphenylmethylene-iminomethyl)-dimethyl-phosphine oxide	**12**	 (4-Methoxy-phenylmethylene-iminomethyl)-dimethyl-phosphine oxi
 rophenylmethylene-iminomethyl)-dimethyl-phosphine oxide	**13**	 (3-Methoxy-4-hydroxy-ohenylmethylene-iminomethyl)-dimethyl-ph oxide
 rophenylmethylene-iminomethyl)-dimethyl-phosphine oxide	**14**	 (4-Nitro-phenylmethylene-iminomethyl)-dimethyl-phosphine oxide

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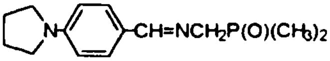
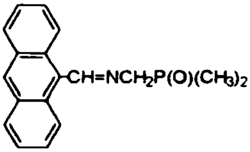
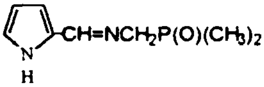
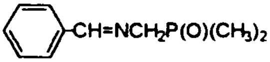
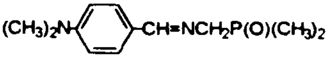
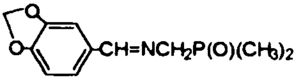
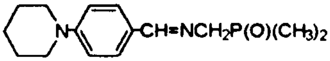
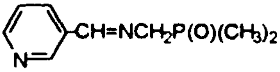
Compound	No.	Compound
 olidinyl)phenylmethylene-imino-methyl]-dimethyl-phosphine oxide rolidinyl)-phenylmethylene-imino-methyl]dimethyl-phosphine oxide	**15**	 (9-Anthracenylmethylene--iminomethyl)-dimethyl-phosphine oxide
 yl-methylene-iminomethyl)-dimethyl-phosphine oxide	**16**	 (Phenylmethylene-iminomethyl)-dimethyl-phosphine oxide
 thylamino-phenylmethylene-imino-methyl)-dimethyl-phosphine oxide	**17**	 [3,4-(Methylenedioxy)phenylmethylene-iminomethyl)-dimethyl-pho oxide
 eridinyl)-phenylmethylene-imino-methyl]-dimethyl-phosphine oxide	**18**	 (3-Pyridinyl-methylene-iminomethyl)-dimethyl-phosphine oxide

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A part of the compounds reported previously exhibits biological activity, e.g. the nitrosourea derivative[5] and the platinum complexes[9] exert antitumor activity being of low toxicity, while the phenoxyphenylalkylphosphine oxides, prepared by L. Maier are proved to be active herbicides[4].

The present work is a continuation of our investigations on synthesis and characterization of functionalized tertiary phosphine oxides, based on aminomethyl-dimethyl-phosphine oxide[2,3,5–10] and reports the preparation and characterization of its Schiff bases with aromatic aldehydes **1–18** (Table I). They are expected to show biological activity and complex-forming properties with metal ions as well. They could be used as organic intermediates for preparation of new organophosphorus-compounds similarly to known azomethyne derivatives[1,11–14].

RESULTS AND DISCUSSIONS

The Schiff bases **1–18** were prepared by condensation of AMPO with corresponding aldehydes in benzene solution at room temperature according to the reaction:

$$(1)\quad R{\cdot}CHO + H_2N{\cdot}CH_2P(O)(CH_3)_2 \longrightarrow R{\cdot}CH{=}N{\cdot}CH_2P(O)(CH_3)_2 + H_2O$$

The yields of the majority of the reaction products proved to be very high, in general about or more than 90%. No catalyst is required. Most of the reactions observed were exothermic. The azomethyne derivatives crystallized from the reaction mixture after mixing the reagents and stirring for 3–4 hrs, usually without azeotropic distillation of the water.

Some preparative and analytical data on Schiff bases **1–18** are given in Table 2. The compounds are colourless or coloured crystalls with characteristic melting temperatures. Most of the compounds **1–18** are hygroscopic, easily dissolved in DMFA, methanol, ethanol, dichloromethane, chloroform, but sparingly soluble in diethyl ether, dioxane, tetrahydrofurane, aliphatic and aromatic hydrocarbons.

Molecular structure and purity for **1–18** were confirmed by IR, ^{1}H NMR and ^{31}P{^{1}H} NMR spectroscopy and mass spectrometry. In addition results from the elemental analysis (phosphorus) are given in Table II.

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TABLE II Preparative and analytical data on Schiff bases of aminomethyl-dimethylphosphine oxide

No	*Yield %*	*M.p., °C / (Recr. solv.) / Colour*	*General formula Mol. mass*	*Phosphorus Content %*	
				Found	*Calcd.*
1	86	153–155 / (Ethyl acetate) / White	$C_{14}H_{16}NO_2P$ 261.26	11.72	11.86
2	86	102–105 / (Ethyl acetate) / Light yellow	$C_{10}H_{14}NO_2P$ 211.20	14.47	14.67
3	87	120–122 / (Ethyl acetate) / Yellow	$C_{12}H_{19}NO_3P$ 256.26	11.86	12.09
4	69	45–48 / (Ethyl acetate) / Cream	$C_{10}H_{13}FNOP$ 213.19	14.45	14.53
5	82	124–126 / (Ethyl acetate) / White	$C_{10}H_{13}ClNOP$ 229.05	13.36	13.49
6	94	111 146 / (Ethyl acetate) / Yellow orange	$C_{14}H_{21}N_2OP$ 264.30	11.55	11.72
7	85	142–144 / (Ethyl acetate) / Beige	$C_8H_{13}N_2OP$ 184.18	16.73	16.82
8	97	135–137 / (Ethyl acetate) / White	$C_{12}H_{19}N_2OP$ 238.27	12.82	13.00
9	50	134–137 / (Ethyl acetate) / White	$C_{15}H_{23}N_2OP$ 278.33	11.05	11.13
10	98	205–207 / (Dichloromethane) / White	$C_{12}H_{15}N_2OP$ 234.24	13.08	13.22
11	96	43–45 / (Benzene) / White	$C_{11}H_{16}NOP$ 209.23	14.67	14.80
12	90	245–246 / (Ethyl acetate) / White	$C_{11}H_{16}NO_2P$ 225.23	13.62	13.75
13	95	189–191 / (Benzene) / White	$C_{11}H_{16}NO_3P$ 241.23	12.73	12.84

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No	*Yield %*	*M.p., °C / (Recr. solv.) / Colour*	*General formula Mol. mass*	*Phosphorus Content %*	
				Found	*Calcd.*
14	90	159–160 / (Ethylacetate) / White	$C_{10}H_{13}N_2O_3P$ 240.20	12.80	12.90
15	98	130–134 / (Ethyl acetate) / Yellow	$C_{18}H_{18}NOP$ 295.31	10.38	10.49
16[a]	92	30–32 / (Benzene) / White	$C_{10}H_{14}NOP$ 195.20	15.72	15.87
17	74	36–37 / (Ethyl acetate) / Yellow	$C_{11}H_{14}NO_3P$ 239.21	12.81	12.95
18	82	119–120 / (Ethanol) / White	$C_9H_{13}N_2OP$ 196.19	13.36	13.49

a. The compound was reported before us by L. Maier[11]: b.p. 133–138°C/0.06 torr.

The infrared spectra (Table III) showed characteristic bands assigned to the phosphoryl group (P=O) at 1138–1199 cm^{-1}, methyl (CH_3-P) and methylene (CH_2P) groups bonded to a phosphorus atom at 1288–1305 cm^{-1} and 741–769 cm^{-1}, respectively. Bands at 1459–1521 $cm^{-1}$and 1550–1615 cm^{-1} are typical for aromatic rings. The Ar-O-R bonds of **3, 12, 13** and **17** were confirmed by bands at 1024–1047 cm^{-1} and 1252–1269 cm^{-1} while the Ar-OH group in **1, 2, 3** and **13** was supported by bands at 1204–1213 cm^{-1}Very strong, sharp bands at 1608–1644 cm^{-1} are characteristic for the monoconjugated CH=N groups[15,16]. Additional bands of the phosphoryl group (P=O) have been observed in the spectra of most of the compounds. This phenomenon was reported by many authors and could be ascribed to different spatial isomers[17,18].

^1H NMR spectra of **1–18** (Table IV) showed resonance signals for all protons in the compounds: doublets for a) methyl protons $C\underline{H}_3P{=}O$ at $\delta = 1.29$ to 1.63 ppm and $^2J_{PH} = -12.6$ to -13.2 Hz, b) methylene protons $C\underline{H}_2P{=}O$ at $\delta = 3.80$ to 4.42 ppm and $^2J_{PH} = -11.9$ to -13.8 Hz, c) $C\underline{H}{=}N$ protons at $\delta = 8.08$ to 9.55 Hz and $^4J_{PH} = 1.9$ to 4.7 Hz. The complex resonance signals for the aromatic ring protons were found in the region of

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δ = 6.00 to 8.70 ppm, while the Ar-O**H** protons in **1–3** occurred as singlets at δ = 9.82 to 14.48 ppm. The relatively high δ-values of Ar-OH in 1–3 is indicative for intramolecular hydrogen bonds formed with the nitroger atom of -CH=N-groups, an observation which is typical for o-hydroxysubstituted Schiff bases[16,19–21]. The resonance signal of the Ar-O**H** proton in **13** was found at 1.78(s) ppm. No intramolecular hydrogen bond is formed, since the OH group is in p-position to the CH=N group[21]. It is worth mentioning that $^2J_{PH}$ of $CH_2P=O$ for all **1–18** were found to higher absolute values than reported previously for similar units having $^2J_{PH}$ in a range –3 to –8 Hz[2,6,22–25].

$^{31}P\{^1H\}$ NMR spectra of **1–18** were singlet resonance signals at δ = +41.01 to +45.03 ppm typical for tertiary phosphine oxides binding two methyl and one methylene groups to the phosphorus atom[25,26].

All compounds were characterized by mass spectrometry and significant mass spectrometric data are presented in Table V. EI mass spectra that show signals for $[M]^+$were obtained for compounds **1–3, 6–10, 13** and **15**only. Two fragmentations are typical for the molecular ions. Loss of $(CH_3)_2PO$ radicals (-77u) takes place that leads *via* α-cleavage to even-electron ions $[RCHNCH_2]^+$. Base peaks in all the EI mass spectra are signals for $[(CH_3)_2P^+(OH)CH_2^\bullet]$ (m/z 92). This ylidion with positive charge located on the phosphorus and the unpaired electron on the adjacent carbon atom is formed from $[M]^+$. by elimination of RCN *via* McLafferty rearrangement. It should be noted that this ion is an isomeric form of the molecular ion of trimethylphosphine oxide $[(CH_3)_3PO]^{+\bullet}$. It has been shown by *ab initio* MO calculations that the unconventional ylidion lies 86 kJ/mol lower in energy than the ion with conventional structure and is separated from the latter by a substantial isomerization barrier of about 195 kJ/mol[28].

Not all the Schiff bases could be measured by EI mass spectrometry possibly due to thermal decompositions of the compounds prior to ionization. However, in case of the remaining compounds **4, 5, 11, 12, 14, 16–18** FAB mass spectrometry proved to be a powerful method. The FAB mass spectra that have been measured with 3-nitrobenzyl alcohol as matrix are characterized by intense signals for $[M+H]^+$ (base peaks). A typical fragmentation under FAB conditions is the elimination of $(CH_3)_2POH$ (-78 u) leading to cations $[RCHNCH_2]^+$. The formation of the latter ions has been observed in the EI mass spectra as well.

TABLE III Characteristic infrared frequences (ν cm^{-1}) of Schiff bases derived from aminomethyl-dimethyl-phosphine oxide

No	*P=O*	*CH_3P*	*CH_2P*	*C=N*	*Ar*	*Ar-O-R*	*Ar-OH*
1	1145(w) 1169(vs)	1298(m)	763(m)	1624(s)	1497(w) 1595(w)	–	1211(m) 3350(w) 3500(w)
2	1157(s) 1164(vs)	1292(w)	750(s)	1629(s)	1489(m) 1574(m)	–	1213(w)
3	1173(vs)	1297(m)	750(m)	1629(s)	1495(w) 1582(w)	1047(w) 1252(vs)	1205(w)
4	1138(vs) 1147(vs)	1295(m)	756(s)	1633(s)	1484(s) 1557(w)	–	–
5	1144(m) 1167(vs)	1288(w)	769(vs)	1630(s)	1467(m) 1591(w)	–	–
6	1178(vs)	1299(m)	768(w)	1610(vs)	1491(w) 1550(m)	–	–
7	1156(vs) 1193(s)	1295(s)	759(w)	1635(vs)	–	–	–
8	1175(vs)	1300(w)	743(w)	1612(vs)	1449(w) 1551(w)	–	–
9	1162(s) 1179(vs)	1302(m)	750(w)	1608(vs)	1452(w) 1560(w)	–	–
10	1156(vs) 1169(s)	1301(m)	750(s)	1627(vs)	1459(m) 1579(w)	–	–
11	1161(vs) 1189(s) 1199(s)	1304(m)	750(w)	1647(m)	1461(w) 1573(w)	–	–
12	1166(vs) 1179(vs)	1303(m)	759(w)	1642(m)	1511(w) 1577(w)	1027(m) 1253(vs)	–
13	1154(vs)	1288(vs)	759(w)	1635(m)	1521(s) 1591(m)	1039(m) 1256(s)	1204(w)
14	1166(vs) 1171(vs)	1298(w)	746(s)	1634(m)	1511(s) 1602(m)	–	–
15	1139(s) 1158(m) 1174(vs)	1295(m)	741(s)	1629(m)	1520(w) 1615(m)	–	–
16	1163(vs)	1290(m)	754(m)	1638(s)	1491(w) 1579(w)	–	–
17	1139(s) 1161(vs)	1291(m)	750(m)	1636(s)	1513(vs) 1599(m)	1024(s) 1269(vs)	–
18	1161(vs) 1194(s)	1305(s)	749(s)	1611(s)	1478(m) 1586(m)	–	–

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TABLE IV ^{1}H and $^{31}P\{^{1}H\}$ NMR data of Schiff bases of aminomethyl-dimethyl-phosphine oxides

^{1}H-NMR								^{31}P
$C\underline{H}_3P=O$		$C\underline{H}_2P=O$		$C\underline{H}=N$		Ar-$\underline{H}$	Ar-$O\underline{H}$	
δ_H	$^{2}J_{PH}$	δ_H	$^{2}J_{PH}$	δ_H	$^{4}J_{PH}$	δ_H	δ_H	
1.63(d)	12.6	4.17(d)	11.9	9.27(d)	2.5	7.10 – 8.10(m)	14.47(bs)	+4
1.59(d)	12.6	4.09(d)	12.0	8.43(d)	3.1	6.85 – 7.40(m)	12.47(s)	+4
1.58(d)	13.2	4.09(d)	13.2	8.43(d)	3.8	6.00 – 7.00(m)	12.82(bs)	+4
1.58(d)	13.2	4.14(d)	13.2	8.63(d)	4.4	7.00 – 8.00(m)	–	+4
1.58(d)	13.2	4.16(d)	13.2	8.77(d)	3.8	7.26 – 8.05(m)	–	+4
1.54(d)	12.6	4.03(d)	13.8	8.15(d)	3.8	6.50(d), 7.60(d)^{c}	–	+4
1.53(d)	12.6	3.98(d)	12.6	8.08(d)	3.8	–	–	+ 4
1.54(d)	13.2	4.03(d)	13.2	8.16(d)	3.8	6.69(d), 7.59(d)^{c}	–	+4
1.54(d)	12.6	4.04(d)	13.2	8.17(d)	4.7	6.68(d), 7.59(d)^{c}	–	+ 4
1.29(d)	13.2	3.80(d)	12.6	8.31(d)	3.1	6.90 – 8.10	–	+4
1.56(d)	13.2	4.08(d)	13.2	8.27(d)	3.8	7.23(d), 7.63(d)^{c}	–	+ 4
1.56(d)	12.6	4.06(d)	12.6	8.25(d)	3.7	6.93(d), 7.68(d)^{c}	–	+ 4
1.57(d)	12.6	4.06(d)	12.6	8.19(d)	3.8	6.91 – 7.34(m)	1.78(s)	+4
1.61(d)	12.6	4.16(d)	12.6	8.43(d)	3.8	7.91(d), 8 28(d)^{c}	–	+ 4

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^{1}H-NMR								
$C\underline{H}_3P=O$		$C\underline{H}_2P=O$		$C\underline{H}=N$		$Ar\text{-}\underline{H}$	$Ar\text{-}O\underline{H}$	δ_P
δ_H	$^{2}J_{PH}$	δ_H	$^{2}J_{PH}$	δ_H	$^{4}J_{PH}$	δ_H	δ_H	δ
1.69(d)	13.2	4.42(d)	12.6	9.55(d)	4.4	7.40 – 8.60(m)	–	42
1.57(d)	13.2	4.11(d)	13.2	8.33(d)	3.8	7.40 – 7.80(m)	–	43
1.57(d)	13.2	4.07(d)	12.6	8.23(d)	3.8	6.85 – 7.50(m)	–	43
1.58(d)	12.6	4.12(d)	12.6	8.90(d)	1.9	7.30 – 8.70(m)	–	42

s: δ_H and δ_P [ppm]. J [Hz]. The sign of $^{2}J_{PH}$ is negative. Data for $^{2}J_{PH}$ are given as absolute values. bs-broad singlet, d- doublet, m-mu
riplet, q -quartet, qw-quintet.

als of $C\underline{H}_3C\underline{H}_2OAr$ protons were found at δ=1.49 ppm(t), $^{3}J_{HH}$=6.9 Hz and δ=4.13(q), $^{3}J_{HH}$=6.9 Hz;
als of pyrolidine methylene protons were at δ=2.02(qw), $^{3}J_{HH}$=3.1 Hz and δ=3.34(qw) and $^{3}J_{HH}$=3.5 Hz.
blets.
ons from pyrol at: δ=6.26(t) ppm, $^{3}J_{HH}$=3.1 Hz; δ=6.54(d) ppm, $^{3}J_{HH}$=3.7 Hz; δ=6.92(s) and for N**H**pyrol proton at δ=9.28(bs) ppm.
al of $C\underline{H}_3$-N protons was at δ=3.03(s) ppm.
$_3$-C protons at δ=1.60–1.75(m) ppm and $C\underline{H}_2NC\underline{H}_2$ protons at 3.29(t) ppm, $^{3}J_{HH}$=5.2 Hz.
otons at δ=2.85(s) ppm.
protons at δ 3.85(s) ppm and 3.93(s) ppm.
protons at 3.93(d) ppm and $^{2}J_{HH}$=2.5 Hz.

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TABLE V Significant mass spectrometric data (m/z / rel. Int. %) of Schiff bases **1** – **18** derived from aminomethyl-dimethyl-phosphine oxide (results of EI-MS are indicated by [a)], those of FAB-MS by [b)])

compound	*method*	*$[M+H]^+$*	*$[M]^+$*	*$[RCHNCH_2]^+$*	*$[(CH_3)_2P^+(OH)CH_2^{\bullet}]$ (m/z 92)*
1	a)		261/10	184/13	/100
2	a)		211/9	134/13	/100
3	a)		255/23	178/12	/100
4	b)	214/100		136/41	
5	b)	230/100		152/39	
6	a)		264/20	187/92	/100
7	a)		184/12	107/47	/100
8	a)		238/14	161/58	/100
9	a)		278/19	201/76	/100
10	a)		234/7	157/20	/100
11	b)	210/100		132/44	
12	b)	226/100		148/39	
13	a)		241/6	164/6	/100
14	b)	241/100		163/19	
15	a)		295/8	218/11	/100
16	b)	196/100		118/46	
18	b)	197/100		119/35	

EXPERIMENTAL

Starting materials

Aminomethyl-dimethyl-phosphine oxide was prepared according to reference[2]. Aromatic aldehydes were commercially available products. Liquid aldehydes were purified by distillation prior to use. Solvents were dried by standard procedures.

Characterization of the prepared compounds 1–18

The elemental analysis for phosphorus content was performed according to reference[27]. Melting point temperatures, measured on a Boetius micro-heating plate PHMK 05 (Germany), were uncorrected. Infrared spectra

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(400 – 4000 cm^{-1}) were recorded on a Bruker IFS-113V spectrometer using KBr pellets. The ^1H NMR spectra for solutions of **1** – **9** and **11** – **18** in $CDCl_3$ were obtained from a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz. **10** was dissolved in DMSO-d_6. The chemical shifts are referenced vs. int. TMS. $^{31}P\{^1H\}$ NMR spectra were obtained at 202.45 MHz. Chemical shifts δ_P are given vs. ext. 85% H_3PO_4. The electron impact (EI) mass spectra were measured on a Varian MAT 311A at 70 eV using the direct inlet system. Fast atom bombardment (FAB) mass spectra were obtained with a Finnigan MAT 8200 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Argon was used as the particle source. The FAB gun was operated at 2 mA discharge current with an acceleration voltage of 8 kV.

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General procedure for the preparation of 1–18

To a stirred solution of the aldehyde (2.0 mmol) in dry benzene (5 ml) at room temperature was added dropwise a solution of AMPO (2.0 mmol) in dry benzene (5 ml). The mixture was stirred at room temperature for 3–4 hrs. In some of the cases the reaction water was distilled azeotropically. The precipitate formed was isolated by filtration, washed with fresh solvent and dried. The prepared crude product was recrystallized from the corresponding solvent till a constant melting temperature. The preparative and analytical data of **1–18** are presented in Table II.

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