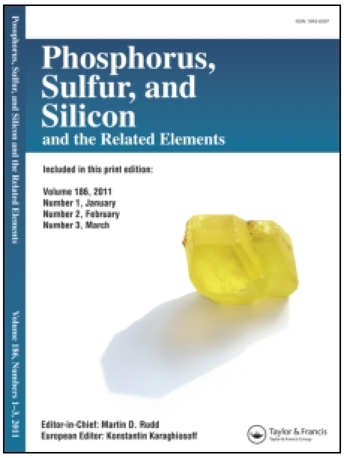

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Ozonization: An Efficient Method for the Oxidation of Halophosphines

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COMMUNICATION
Ozonization: An Efficient Method for the Oxidation of Halophosphines

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The ozonization of various halophosphines **1a–j** leads with quantitative yields to the corresponding phosphine oxides **2a–j**.

Ozonization is a convenient method of oxidation, in particular of compounds with bulky ligands (**1c**, **1d**, **1e**).

Few methods are known which quantitatively convert halophosphines into the corresponding halophosphine oxides (1). In the case of dichlorophosphines the reaction with oxidants such oxygen or dimethyl sulfoxide requires rather drastic conditions, (1) consequently by-products are usually formed. Alternative routes, employing nitrogen oxides or sulfuryl chloride have also been described (2) whereas the use of ozone remains essentially unknown (3).

Ozone does, in fact, oxidize phosphines (4) and based on our previous research describing the reactivity of ozone towards organophosphorus compounds (5), it became apparent that this oxidant should be excellent for conversion of halophosphines to the phosphine oxides.

Indeed, we report here that the halophosphines **1a–j** are readily oxidized by ozone to the corresponding oxides **2a–j** in near quantitative yield. The reaction occurs under mild conditions, at low temperatures in dichloromethane or toluene solvent:

$$\underset{\substack{\mathbf{1a\text{–}j}\\(X{=}Cl,\ N_3)}}{R_nX_{3-n}P} + O_3 \xrightarrow[\substack{\text{toluene}\\(0^\circ,\ -80^\circ C)}]{CH_2Cl_2\ \text{or}} \underset{\mathbf{2a\text{–}j}}{R_nX_{3-n}P = O}$$

The nature of the substituents R has little influence upon the yield of this reaction as shown in Table I:

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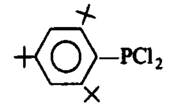
TABLE I

^{31}P NMR chemical shifts of **1a–j** and **2a–j**, ozonization temperature and yields of **2a–j**

	1 : R_nPX_{3-n}	$\delta^{31}P$ réf. H_3PO_4 85% 1	2	(Réf)	Temp. °C	Yield % 2
a	$(Ph)_2PCl$	82	44	(6)	−80	> 99
b	$(Me_2N)_2PCl$	159	30	(6)	−80	95
c	$(iPr_2N)_2PCl$	134	20		−80	90
d	$(iPr_2N)_2PN_3$	105	14		−80	90
e		152	33	(7)	−80	> 99
f	$PhOPCl_2$	177	3	(6)	0	> 99
g	$iPrOPCl_2$	174	5		0	85
h	Me_2NPCl_2	166	18	(6)	0	90
i	iPr_2NPCl_2	170	15		0	85
j	PCl_3	219	5	(6)	−80	> 99

All the compounds **2** are obtained in very good yields, even for previously unknown **2c**, **2d** and **2i**. This is of significant interest because the oxidation of **1c** and **1d** by O_2 or DMSO does not occur, even upon heating (8). An excessive steric hindrance which apparently lowers the reactivity of the lone pair at phosphorus may explain this rather singular fact. Unlike these classical oxidants, ozone reacts readily with **1c–d** even at −80°C to give almost quantitatively the corresponding oxides. Surprisingly, the azido group (often considered as a pseudo halogen) of **1d** is not attacked by ozone. We have not observed explosive decomposition reactions, neither for **1d** nor for any of the halophosphines that we have ozonized.

So, the wide range of substituents used (e.g., aryl, alkoxy, amino) shows that the conversion of halophosphines into halophosphine oxides by ozone is a quite general reaction. Furthermore, this method is simple, efficient, safe, and compares favorably with the hitherto reported methods.

EXPERIMENTAL SECTION

Ozonizations are performed by passing a stream of ozone/oxygen ($[O_3] = 8.10^{-4}M$) through a cooled solution of **1a–j** in dichloromethane or toluene ($[\mathbf{1}] \sim 0.5$ M). Oxygen alone reacts also with some halophosphines but much more slowly. The completion of the reaction is indicated by coloration of a potassium iodide solution.

Spectroscopic characteristics of **2** (^{31}P NMR and IR) are consistent with available literature data.

Recrystallization of **2c** from benzene/hexane (50/50 v/v%) affords colorless crystals : m.p. 202°C.

^{31}P NMR (CH_2Cl_2) δ 20; ^{1}H NMR ($CDCl_3$)δ 1.4 (d, $^3J_{HH} = 7$ Hz, CH_3, 24H) and 3.65 (sept. d., $^3J_{HH} = 7$ Hz, $^3H_{PH} = 21$ Hz, CH, 4H). **2d** is purified by column chromatography on silicagel (ether/light petroleum ether 40/60 v/v%, Rf : 0.64) and gives colorless crystals : m.p. 44°C; ^{31}P NMR (toluene) $\delta + 14.5$; ^{1}H NMR

($CDCl_3$) δ 1.24 (d, $^3J_{HH} = 7$ Hz, CH_3, 12H), 1.27 (d, $^3J_{HH} = 7$ Hz, CH_3, 12H), 3.45 (sept. d., $^3J_{HH} = 7$ Hz, $^3J_{PH} < 0.3$ Hz, CH, 4H); I.R. (KBr pellet): 2150 (ν_{N_3}), 1240 ($\nu_{P=O}$), 1000 (ν_{P-N}) cm^{-1}; mass spectroscopy 289 (M^+), 273 ($M—O^+$), 189 ($M—(iPr)_2N^+$).

Recrystallization of **2i** from (benzene/hexane 50/50 v/v %) gives colorless crystals: m.p. 46°C; ^{31}P NMR (CH_2Cl_2): δ 12; ^1H NMR ($CDCl_3$)δ 1.38 (d, $^3J_{HH} = 7$ Hz, CH_3, 12H); 3.7 (sept. d. $^3J_{HH} = 7$ Hz, $^3J_{PH} = 28, 5$ Hz, CH, 2H).

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