

Synthesis of Stable Monomeric Metaphosphonimidates, Aryl(oxo, thioxo-, or selenoxo-)iminophosphoranes

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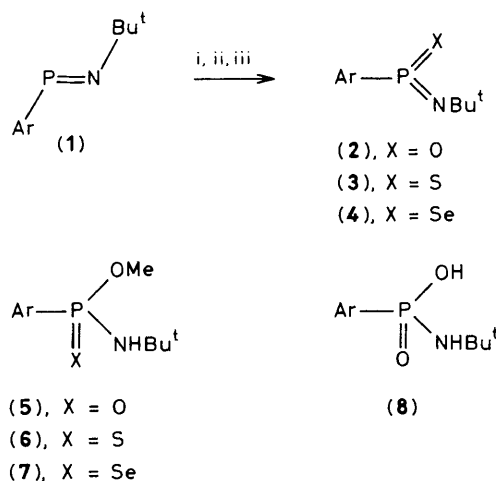
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The title compounds ArP(X)=NBu^t ($\text{Ar} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$; $\text{X} = \text{O}, \text{S}, \text{or Se}$), the first examples of sterically protected stable metaphosphonimidates, have been synthesised in good yield by the reaction of the iminophosphine ArP=NBu^t with ozone, sulphur, or selenium.

Although the chemistry of phosphorus compounds with $p_\pi\text{-}p_\pi$ double bond has been an exciting area of development in the last ten years, little information is available concerning monomeric metaphosphonates. The majority of these unusually hybridized phosphorus derivatives have a very short lifetime and they rapidly polymerize in the absence of trapping agent.^{1,2} Important recent developments include the isolation of sterically protected stable three-co-ordinate pentavalent organophosphorus compounds ArPS_2 ,^{3,4} ArP(O)=PAr ,⁵ and ArP(S)=PAr .⁶ However attempts to isolate the metaphosphonates ArPO_2 ⁷ and ArP(O)=NAr ⁸ were unsuccessful.

We recently reported the first isolation of the thermally stable iminophosphines ArP=NR , containing a sterically protected phosphorus–nitrogen double bond.⁹ Starting from these compounds we have now synthesized the metaphosphonimidates, which are stable as monomers. Treatment of (1)[†] in dry benzene with 1 equiv. of sulphur at 50 °C for 3 h under argon gives after evaporation the solid (3) which can be recrystallized from pentane in 62% yield, m.p. 54–56 °C. Similar reaction of (1) with selenium affords (4), (72%), m.p. 68–70 °C (from pentane). The compounds (3) and (4) form pale yellow crystals which are sensitive to atmospheric moisture but which are fairly stable at 20 °C. Unlike sulphur and selenium, molecular oxygen does not react with the iminophosphine (1). However the oxidation of (1) (10 mmol) with ozone in CH_2Cl_2 (30 ml) at –78 °C leads to the metaphosphonimidate (2) as a colourless viscous oil in ca. 87% yield (³¹P n.m.r.). The latter observation provides an interesting contrast with the diphosphene ArP=PAr in which the P=P bond is cleaved by ozone under the same conditions.¹⁰

The composition and constitution of the products of the addition of oxygen, sulphur, and selenium to the iminophosphine (1) were confirmed by elemental analysis, cryoscopic



$\text{Ar} = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$ throughout

Scheme 1. Reagents and conditions: i, ozone (1 equiv.), CH_2Cl_2 , –78 °C; ii, sulphur, C_6H_6 , 50 °C, 3 h; iii, selenium, C_6H_6 , reflux, 4 h.

molecular weight determinations, spectral data, and by chemical conversions. That compounds (2), (3) and (4) are the metaphosphonimidates, and not the 1,2,3-oxa-, thia-, or seleno-azaphosphiridines is evident from n.m.r. and i.r. data (Table 1).[‡] In particular, the low ³¹P chemical shifts are only compatible with a three co-ordinate, sp^2 -hybridized state of phosphorus.¹¹

The metaphosphonimidates (2), (3), and (4) smoothly add methanol to produce virtually quantitative yields of the corresponding phosphonic amides (5)–(7). Similarly, the

[†] Prepared according to ref. 9 from $(\text{Me}_3\text{Si})_2\text{NP=NBu}^t$ and 2,4,6-tri-*t*-butylphenyl-lithium, 36% yield, b.p. 125–130 °C at 0.02 mmHg. Spectroscopic data for (1): ¹H n.m.r. (C_6D_6) δ 7.45 (s, 2H, ArH), 1.48 (s, 18H, *o*-Bu^t), 1.44 (d, *J* 1.9 Hz, 9H, Bu^tN), and 1.22 (s, 9H, *p*-Bu^t); ³¹P n.m.r. (CH_2Cl_2) δ 451.8 p.p.m.

[‡] The metaphosphonimidate (2) is stable for several days at 0 °C but shows significant polymerization at 25 °C. Unlike compounds (3) and (4) which were purified without difficulty, compound (2) could not be completely freed of small amounts of unidentified impurities.

Table 1. ^{31}P and ^1H N.m.r.^a and i.r.^b data for compounds (2), (3), and (4).

	(2) ^c	(3)	(4)
^{31}P	93.5	162.4	154.8 ^d
^1H (J_{HP})			
Bu ^δ N	1.46 (0.85)	1.53 (1.5)	1.52 (1.5)
<i>p</i> -Bu ^δ	1.30	1.12	1.13
<i>o</i> -Bu ^δ	1.74	1.67	1.65
C_6H_2	7.50 (6.0)	7.25 (5.5)	7.30 (5.0)
i.r., $\nu(\text{P}=\text{X})$	1240	730	700

^a N.m.r. spectra were recorded on a Bruker WP-200 spectrometer operating at 81.0 (^{31}P) and 200 MHz (^1H); 30% solution in C_6D_6 unless otherwise specified, 85% H_3PO_4 as external standard for ^{31}P and Me_4Si as internal standard for ^1H ; δ in p.p.m., J in Hz. ^b Nujol, cm^{-1} . ^c ^1H n.m.r. in CDCl_3 . ^d $^1\text{J}(\text{P}=\text{Se})$ 903 Hz.

metaphosphonimidate (2) reacts with H_2O in tetrahydrofuran to give an 83% yield of the amide (8). Compounds (5)–(8) were characterized by elemental analysis and ^1H and ^{31}P n.m.r. spectroscopy.

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