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Phenolysis of Hexachlorocyclotriphosphazatriene

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ABSTRACT: *The reactions of hexachlorocyclotriphosphazatriene $N_3P_3Cl_6$ (**1**) with the sodium salts of 2,4,6-trimethylphenol (**2a**), 4-tert-butyl-2-methylphenol (**2b**), 2-tert-butyl-4-methylphenol (**2c**) have been investigated, and monoaryloxy-substituted phosphazenes $N_3P_3Cl_5OAr$ (**3–5**) were obtained.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:308–310, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20127

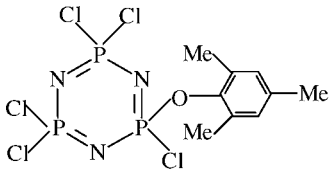
INTRODUCTION

Cyclophosphazenes are an important family of inorganic ring systems and most intensively studied phosphorus–nitrogen compounds. Up to date many compounds have been reported from the interactions of cyclophosphazenes with amines and alcohols [1–11]; however, the reactions of cyclophosphazenes with phenols are highly limited in the literature. Some phenoxy-substituted cyclotri- and -tetra phosphazenes were synthesized and characterized [12]. Hexasubstituted derivatives of hexachlorocyclotriphosphazatriene (**1**) with 4-phenylphenol [13], 4-methyl-, 4-hydroxy-, 4-*tert*-butyl-, 4-phenoxyphenol [14], 2-methyl-, 2-phenylphenol [15], and *o*-dichloro- and *o*-dimethylphenol [16] have been obtained.

We have previously investigated the reactions of **1** with bulky phenols [17,18]. Here we report the reactions of **1** with the sodium salts of 2,4,6-*tri*-methylphenol (**2a**), 4-*tert*-butyl-2-methylphenol (**2b**), and 2-*tert*-butyl-4-methylphenol (**2c**). Monosubstituted phosphazenes were obtained as major products **3–5.** We previously determined the solid-state structure of **3** by single crystal X-ray diffraction analysis [19].

RESULTS AND DISCUSSION

The reaction of **1** with an equimolar amount of sodium salts of **2a–c** in THF gave the monosubstituted products **3, 4, 5**.



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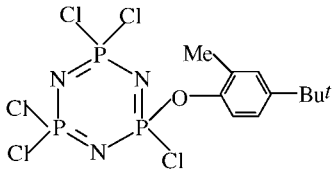

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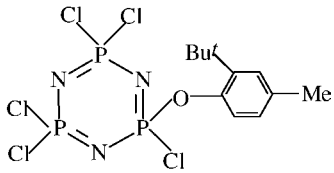

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products were isolated by column chromatography and characterized by elemental analysis, ^{1}H-, ^{13}C-, ^{31}P- NMR spectrometry, and FT-IR. All these compounds are air and moisture stable. No other product could be isolated.

SPECTROSCOPIC STUDIES

The aryl and alkyl C—H stretching frequencies of compounds **3–5** were observed at 3460–3495 cm^{-1} and 2924–2967 cm^{-1}, respectively. P—N bonds have strong infra-red absorbances at 1100–1300 cm^{-1} [8,21,22].

Compounds **3,4,5**, have absorbance bands at 1100–1286 cm^{-1} for ν(P=N) and 593, 590, and 588 cm^{-1} for ν (PCl) respectively. ^{1}H NMR spectra of compounds **3–5** are relatively simple, but informative. The methyl protons resonate at $\delta = 2.25$ (4-CH_3) and 2.34 (2-CH_3) (in a 1:2 ratio) for **3**. For **4**, the protons of the *tert*-butyl group at the para position and methyl group at the ortho position gave singlets at $\delta = 1.29$ and 2.34 (in a 3:1 ratio), respectively. The protons of the methyl group at the para position and *tert*-butyl group at the ortho position in **5** gave singlets at $\delta = 2.22$ and 1.32 (in a 1:3 ratio) respectively. The ^{13}C NMR signals of **3**, CH_3(ortho position) and CH_3(paraposition) are observed at $\delta = 17.67$, 20.72, respectively. The ^{13}C NMR signals of **4**, (CH_3-ortho), (C(CH_3) para), (C(CH_3) para), and (C-ipso) are observed at 21.20, 30.28, 34.54, 147.51 respectively. The ^{13}C NMR signals for **5**, (CH_3 para), C(CH_3)$_3$ ortho), (C(CH_3)$_3$ ortho), C(5)-phenyl, C(3)-phenyl, C(6)-phenyl, and C-ipso are observed at 16.98, 31.44, 34.22, 120.39, 124.03, 128.82, and 149.53 respectively.

The ^{31}P NMR spectra of **3,4,5** gave AB_2 spin patterns with $^{2}J_{PNP} = 60$, 58 and 40.4 Hz respectively. Chemical shifts, δ [P(OAr)Cl] = 11.83, 12.58, 8.89 and δ (PCl_2) = 22.18, 22.51, 22.40 are in good agreement with the literature values [25].

EXPERIMENTAL

General Remarks

All reactions were performed under dry argon-atmosphere using standard Schlenk techniques [23] with previously dried solvents. The tetrahydrofuran (THF) used as solvent was distilled under argon from sodium benzophenone prior to use. Hexachlorocyclotriphosphazatriene (99%) was purchased from Aldrich Ltd. and purified by recrystallization from n-hexane. 2,4,6-*Tri*methylphenol (97%), 4-*tert*-butyl-2-methylphenol (98%), and 2-*tert*-butyl-4-methylphenol (98%) were purchased from Fluka Ltd and used as purchased. Sodium salts were prepared from the reaction of phenols **2a,2b,2c** with metallic sodium [23].

Reactions were monitored by using silica gel 60 F_{254} precoated TLC plates and separating conditions were determined. The separation of products was carried out by column chromatography using silica gel 60 (230–400 mesh, Merck).

The purity of the compounds was checked by TLC and characterized by elemental analysis, ^{1}H, ^{13}C, ^{31}P NMR spectrometry, and FT-IR. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded using a Bruker-Avence 500 NMR spectrometer operating at 500.13, 125 , 202.45 MHz respectively. All data was recorded for solutions in $CDCl_3$. The ^{1}H and ^{13}C NMR chemical shifts were measured using $SiMe_4$ ($\delta = 0$) as an internal standard, and the ^{31}P chemical shifts, using 85% H_3PO_4 as an external standard. Melting points were measured in open capillary tubes with an Elektrothermal-9200 melting point apparatus and were uncorrected. Microanalyses were carried out by the microanalytical service of TÜBİTAK-MAE, Gebze-Kocaeli (Turkey). IR spectra were recorded on an ATI Unicam Mattson 1000-FTIR spectrophotometer in KBr disks and were reported in cm^{-1} units.

Synthesis of **3**

2a (5.37 g, 12 mmol) in THF (20 mL) was over a period of 30 min to small pieces of Na (0.500 g, 24 mmol) in THF (10 mL) with stirring at 298 K, with argon being passed over the reaction mixture. Excess Na was removed by filtration and the solution sodium 2,4,6-*tri*-methylphenoxide was cooled and then frozen with a liquid nitrogen–acetone mixture. To this solution, **1** (4.18 g, 12 mmol) in THF (40 mL) was slowly added and the resulting mixture was allowed to come to ambient temperature with constant stirring [19,25]. After the reaction was completed, the precipitated NaCl was filtered off and the solvent was removed under vacuum. The solid residue was dissolved in *n*-hexane and set aside to crystallize. The compound **3** [2-(2,4,6-tri-methylphenoxo)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene] was obtained in 64% yield, mp 81°C. ($R_f = 0.83$ dichloromethane/*n*-hexane 1:10). Found: C, 24.34; H, 2.46; N, 9.04% Calcd for $N_3P_3Cl_5C_9H_{11}O$:C, 24.13; H, 2.45; N, 9.38%. IR (KBR): ν(CH aryl) 3489, ν(CH) 2924, ν(C=C) 1482, ν(P=N) 1222, 1181 ν(PCl) 593 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 2.25 (s, 3H,CH_3-*para*), 2.34 (s, 6H, CH_3-*ortho*), 7.2 (s, 2H, Ar-*H*); ^{13}C, δ 17.67 (s, 2C, CH$_3$-*ortho*), 20.72 (s, 1C, CH$_3$-*para*), 129.83 (s, 2C, 3-phenyl), 129.87 (s, 2C, 2-phenyl), 146.4 (s, 1C, C-ipso); ^{31}P, AB_2 pattern, δA = 11.83, δB = 22.18, $^{2}J_{AB} = 60$ Hz.

Synthesis of **4**

2b (1.46 g, 8.9 mmol in 20 mL of THF), Na (0.40 g, 17.8 mmol), and **1** (3.1 g 8.9 mmol in 15 mL of THF) were used as for **3**. The reaction mixture vigorously stirred at room temperature 1 h, and refluxed for 7 h. The precipitated NaCl was filtered off, and solvent removed in vacuo. The residue was chromatographed on silica gel: 100 g, (eluent: toluene/*n*-hexane 1:10), 2-(4-*tert*-butyl-2-methylphenoxo)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene **4** was obtained in 78% yield. (R_f: 0.64 dichloromethane/hexane 1:10). Compound **4** was viscous oil. Found: C, 28.32; H, 3.08; N, 8.37%; Calcd for $N_3P_3Cl_5C_{11}H_5O$: C, 27.74; H, 3.15; N, 8.83%. IR (KBr): ν(CH aryl) 3495, ν(CH) 2967, ν(C=C) 1464, ν(P=N) 1119–1168, ν(PCl) 590 cm^{-1}. NMR ($CDCl_3$): ^{1}H, $\delta = 1.29$ (s, 9H, C(CH_3)$_3$-para), 2.34 (s, 3H, CH_3-ortho), 7.20–7.22 (m, 3H, phenyl); ^{13}C, $\delta = 21.20$ (s, 1C, *C*H$_3$-ortho), 30.28 (s, 3C, *C*H$_3$-para), 34.54 (s, 1C, *C*(CH$_3$)$_3$-para), 119.68 (s, 1C, 3-phenyl), 127.68 (s, 2C, 5,6-phenyl), 147.51 (s, 1C, C-ipso) ; ^{31}P, AB$_2$ pattern, δA = 12.58, δB = 22.51, $^2J_{AB} = 58$ Hz.

Synthesis of **5**

2c (2.00 g; 12.1 mmol), Na (0.55 g; 24.2 mmol), and **1** (4.23 g; 12.1 mmol) were used following the same procedure described for **3**. The residue chromatographed (silica gel: 100 g, eluent: dichloromethane/*n*-hexane 3:1), and 2-(2-*tert*-butyl-4-methylphenoxo)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene) (**5**) was obtained in 57% yield. Compound **5** is white crystal mp 59°C. (R_f: 0.71 dichloromethane/*n*-hexane 1:10) (Found: C, 27.83; H, 3.15; N, 8.62%, Calcd for $N_3P_3Cl_5C_{11}H_5O$: C, 27.74; H, 3.82; N, 8.83%). IR (KBr): ν(CH aryl) 3460, ν(CH) 2945, ν (C=C) 1500, ν(P=N) 1100–1286, ν(PCl) 588 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.32 (s, 9H, C(CH_3)$_3$-ortho), 2.22 (s, 3H, CH_3-para) 6.9 [dd, 1H, C(5)-*H*], 7.08[s, 1H, C(3)-*H*], 7.24 [dd, 1H,C(6)-H]; ^{13}C, δ 16.98 (s, 1C, CH_3-para), 31.44 (s, 3C, C(*C*H$_3$)$_3$), 34.22 (s, 1C, *C*(CH$_3$)$_3$), 120.39 (s, 1C, *C*(5)-phenyl), 124.03 (s, 1C, *C*(3)-phenyl), 128.82 (s, 1C, *C*(6)-phenyl), 149.53 (s, 1C, *C*-ipso). ^{31}P AB$_2$ pattern, δA = 22.4, δB = 8.89, $^2J_{AB} = 40.4$ Hz.

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