Heteroatom Chemistry
Volume 18, Number 4, 2007

Synthesis of Phenoxy-Substituted Spiro-Ansa Phosphazene Derivatives

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Received 13 March 2006; revised 22 June 2006

ABSTRACT: *In this study, reactions of 2,4,4,6,6-pentachloro-2-(2,4,6-trimethylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (**1**) and 2,4,4,6,6-pentachloro-2-(2,4,6-tritertbutylphenoxy)cyclo-2λ^5,4λ^5,6λ^5-triphosphazatriene (**2**) with 2,2′-dihydroxybiphenyl (**3**) in acetone in the presence of potassium carbonate have been investigated. Mono ansa (**4**) and spiro-ansa (**5**) derivatives were obtained from of **3** with **1**, while mono spiro (**6**) and mono ansa (**7**) derivatives were obtained from **2**.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:372–375, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20322

INTRODUCTION

Many papers deal with reactions of hexachlorocyclotriphosphazatriene with monofunctional reagents [1–5]. Especially, aryloxy-substituted phosphazenes are widely studied [6–12], but the reactions of phosphazenes with difunctional reagents are limited [13–18].

There are four structural types for the reactions of difunctional reagents with cyclophosphazenes: spiro, ansa, bridged, and open chain [19,20].

In the present work, the reactions of phenoxy-substituted phosphazenes **1,2** with difunctional 2,2′-dihydroxybiphenyl ($HOC_6H_4C_6H_4OH$, **3**) have been investigated. Although 2,2′-dihydroxybiphenyl is a difunctional reagent, it might behave as a monofunctional phenol or give transannular-substituted cyclic phosphazenes [19]. Numerous reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with **3** have been investigated by Carriedo and coworkers [20–22]. The reactions of **3** with substituted phosphazenes have been the least investigated [23–25].

RESULTS AND DISCUSSION

Phenoxy-substituted phosphazenes **1,2** were reacted, respectively, at a 1:2 and 1:3 mole ratio with **3** in acetone in the presence of potassium carbonate. From the reaction of **1**, the mono ansa **4** and spiro-ansa derivative **5** were obtained. From the reaction of **2**, a spiro derivative, **6**, and an ansa derivative, **7**, were isolated in approximately equal yields.

The spectra of the former product would also be consistent with the isomeric structure **6′**, which is less likely, however, because of the steric influence of the phenol substituent.

Compounds **5–7** were obtained in good yield except for **4**. Products **5–7** were stable in air and moisture and were obtained as white solids. But product **4** was viscous oil. The structures of compounds **4,5**, and **7** were identified initially by ^{1}H, ^{13}C, ^{31}P NMR elemental analyses and infrared spectroscopy. The structure of compounds **5–7** are consistent with the analytical and spectroscopic data (see the Experimental section). In the IR spectra of **4–7**, the characteristic $\nu_{P=N}$ vibrations occur between 1125 and 1399 cm^{-1}. The P—Cl frequencies of compounds **4–7** were observed between 573 and 699 cm^{-1}. In the FTIR spectra of compounds **4–7**, P—OC stretching

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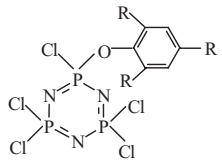
bands were observed between 941 and 1097 cm^{-1}. The peak at 1438–1555 cm^{-1} was assigned as C=C stretching. These data are in good agreement with the literature values [26].



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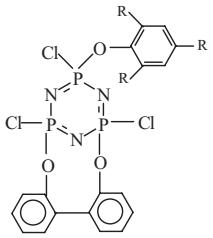
2 R = But



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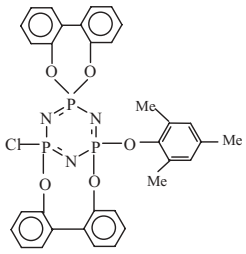
7 R = But



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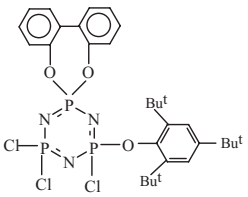

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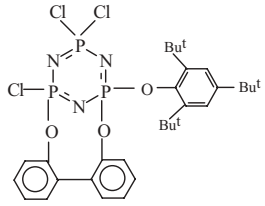

6'

For compounds **4** and **7**, an AB_2 pattern was observed in the ^{31}P NMR consistent with only ansa structures.

The proton-decoupled ^{31}P NMR spectra of the compounds **5** and **6** or (**6′**) had AMX spin system because of three different phosphorus environments within the molecules.

The aromatic protons were observed at $\delta = 6.67$–7.51, $\delta = 6.75$–7.51, $\delta = 7.27$–7.59, and $\delta = 7.23$–7.57 as multiplets for compounds **4,5,6**, and **7**, respectively. The methyl protons resonate at $\delta = 2.23$ (2-CH_3), 2.25 (4-CH_3) and 2.28 (2-CH_3), 2.29(4-CH_3) (in a 2:1 ratio) for **4** and **5** compounds, respectively. For **6**, the protons of the *tert*-butyl group at the ortho position and *tert*-butyl group at the para position gave singlets at $\delta = 1.52$ and 1.33 (in a 2 : 1 ratio). The protons of the *tert*-butyl group at the ortho position and *tert*-butyl group at the para position in **7** gave singlets at $\delta = 1.47$ and 1.28 (in a 2 : 1 ratio), respectively. The ^{31}P NMR spectra of **4** and **7** gave AB_2 spin patterns with $^2J_{PP} = 58$ and 77 Hz, respectively. According to the ^{31}P NMR spectra of compounds **4** and **7**, it is concluded that only ansa structures are possible. Two bond-coupling constants, $^2J_{PP}$, of all the compounds, except for **4**, are nearly the same. These values are between 71.2 and 80.2 Hz and are in good agreement with the literature [20]. $^2J_{PP}$ value of **4** (58 Hz) is lower than others.

EXPERIMENTAL

General Remarks

All the reactions were carried out under dry nitrogen. K_2CO_3 was dried at 140°C prior to use. Acetone used as solvent was distilled from anhydrous $MgSO_4$. 2,2′-Dihydroxybiphenyl, 2,4,6 tri-*tert*-butylphenol, and 2,4,6-trimethylphenol were used as received. Hexachlorocyclotriphosphazatriene was supplied by Aldrich and purified by recrystallization from hexane. Analytical thin layer chromatography (TLC) was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length). Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI Unicam Mattson 1000 spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker ultra shield spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C), and 121.49 MHz (^{31}P). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants, $^2J_{PP}$, in Hz. Elemental analyses were obtained using a LECO 932 CHNS instrument. Melting points were measured in open capillary tubes with an electrothermal-9200 melting point apparatus and were uncorrected. Starting compounds **1** and **2** were prepared as described in the literature [27,28].

Reaction of **1** with 2,2′-Dihydroxybiphenyl

A mixture of **1**, (1.00 g, 2.24 mmol), **3** (0.83 g, 4.48 mmol), and K_2CO_3(3.00 g, 21.74 mmol) in acetone (50 mL) was stirred for 24 h at room temperature, and reaction mixture was refluxed for 6 h. The reaction mixture was followed on TLC silica gel plates using dichloromethane/*n*-hexane 1:3, which showed the absence of starting material and formation of two products. The solvent was removed under reduced pressure, and the resulting

white solid was subjected to column chromatography (silica gel 60 (230–400 mesh) as adsorbent by using dichloromethane/*n*-hexane (1:3) as eluent). Two fractions were obtained. The first fraction is compound **4** (a viscous oil), 0.15 g, 12%. $R_f = 0.487$ (dichloromethane/*n*-hexane 1:2). Elemental analysis calcd (%) for $N_3P_3Cl_3O_3C_{21}H_{19}$ (560.50): C 44.99, H 3.39, N 7.49; Found C 45.95, H 3.79, N 6.66. IR (KBr): ν(CH aliphatic) 2923, ν(C=C dioxybiphenyl) 1501, 1473, 1441, ν(P=N) 1243, 1210, 1125, ν(P—OC) 1097, 941, ν(P—N) 763, ν(P—Cl) 699 cm^{-1}. NMR ($CDCl_3$, δ, ppm): ^1H, 2.23 [s, 3H, C*H*$_3$-*para* (phenol)], 2.25 [s, 6H, C*H*$_3$-*ortho* (phenol)], 6.67–7.51 (m, phenol and dioxybiphenyl); ^{13}C, 149.7, 146.2, 134.8, 130.3, 130.2, 129.5, 129.4 , 121.8. ^{31}P (analyzed as AB_2), $\delta_A = 1.69$ (t, 1P, PClOAr, $^2J_{PP} = 58$ Hz), $\delta_B = 25.2$ (d, 2P, POCl, $^2J_{PP} = 58$ Hz).

The second fraction is compound **5**, a white solid, 0.63 g; 42%, mp = 233–234°C, $R_f = 0.189$ (dichloromethane/*n*—hexane 1:2). Elemental analysis calcd (%) for $N_3P_3ClO_5C_{33}H_{27}$(673.5): C 58.79, H 3.98, N 6.2; Found C 58.32, H 4.14, N 5.98. IR (KBr): ν(CH aryl) 3422, ν(C=C dioxybiphenyl) 1555, ν(P=N) 1363, 1399, ν(P—OC) 1058, ν(P—N) 804, ν(P—Cl) 617, 656 cm^{-1}. NMR ($CDCl_3$, δ, ppm): ^1H, 2.28 (s, 3H, C*H*$_3$-*para* (phenol)], 2.29 [s, 6H, C*H*$_3$-*ortho* (phenol)], 6.75–7.51 (m, phenol and dioxybiphenyl); ^{13}C, 148.1, 148.0, 130.3, 130.2, 129.8, 129.7, 129.6, 129.5, 129.3, 128.5, 125.4; ^{31}P (analyzed as AMX), $\delta_A = 7.69$ (O_2P spiro); $\delta_M = 22.86$ (P(O)OAr); $\delta_X = 29.30$ (POCl). $J_{AM} = 71.3$, $J_{AX} = 80.2$, $J_{MX} = 71.2$ Hz.

Reaction of **2** *with 2,2′-Dihydroxybiphenyl*

Compounds **2** (1.00 g, 1.17 mmol), **3** (0.65 g, 3.49 mmol), and K_2CO_3 (2.00 g, 14.49 mmol) in acetone (50 mL) were used following the same procedure described for **4** and **5**. The solvent was removed under reduced pressure, and the resulting white solid was subjected to column chromatography by using dichloromethane/*n*-hexane 1:3 as eluent. Two fractions were obtained and isolated as white powders; the first is compound **6**, 0.45 g; 38%, mp = 206–207°C. ($R_f = 0.419$ dichloromethane/*n*-hexane 1:3). Elemental analysis calcd (%) for $N_3P_3Cl_3O_3C_{30}H_{37}$ (686.50): C 52.43, H 5.38, N 6.11; Found C 52.43, H 5.43, N 5.51. IR (KBr): ν(CH aryl) 2943, ν(C=C dioxybiphenyl) 1479, 1438, ν(PO—C) 1274, ν(P=N) 1230, ν(P—OC) 1097, ν(P—Cl) 573 cm^{-1}. NMR ($CDCl_3$, δ, ppm): ^1H, 1.31 [s, 9H C(C*H*$_3$)$_3$-*para* (phenol)], 1.57 [s, 18 H, C(C*H*$_3$)$_3$-*ortho* (phenol)]; ^{13}C, 142.29, 142.23, 129.91, 129.64, 128.56, 128.51, 126.51, 124.12, 122.02, 32.09. ^{31}P (analyzed as AMX), $\delta_A = 12.89$ (O_2P spiro); $\delta_M = 17.18$ (PClOAr); $\delta_X = 26.11$ (PCl_2). $J_{AM} = 73.9$, $J_{AX} = 78.7$, $J_{MX} = 73.8$ Hz.

The second fraction is the derivative, **7**, 0.49 g; 42%, mp = 323–325°C (decomp.). $R_f = 0.129$ (dichloromethane/*n*-hexane 1:3). Elemental analysis calcd (%) for $N_3P_3Cl_3O_3C_{30}H_{37}$ (686.50): C 52.43, H 5.38, N 6.11; Found C 51.19, H 5.16, N 6.19. IR (KBr): ν(CH aryl) 3069, ν (CH aliphatic) 2963, ν(C=C dioxybiphenyl) 1477, 1438, ν(PO—C) 1282, ν(P=N) 1238, 1190, ν(P—OC) 1089, ν(P—Cl) 611 cm^{-1}. NMR ($CDCl_3$, δ, ppm): ^1H, 1.30 [s, 9H, C(C*H*$_3$)$_3$-*para* (phenol)], 1.47 [s, 18 H, C(C*H*$_3$)$_3$-*ortho* (phenol)]; ^{13}C, 147.78, 130.03, 129.78, 128.83, 126.55, 121.84. ^{31}P (analyzed as AB_2), $\delta_A = 19.93$ (t, 1P, (PClOAr), $^2J_{PP} = 77$ Hz), $\delta_B = 29.35$ (d, 2P, POCl, $^2J_{PP} = 77$ Hz).

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