

Synthesis and Reactivity of Alkoxy, Aryloxy, and Dialkylamino Phosphazene Azides

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Supporting Information

Instruments. ^{31}P (144.8 MHz), and ^1H (360 MHz) NMR spectra were recorded with a Bruker AMX360 NMR spectrometer, which employed a broad band CPMAS pencil probe. Chemical shifts are relative to external 85% aqueous H_3PO_4 (^{31}P NMR) or tetramethylsilane (^1H NMR). The ^{31}P NMR spectra were proton-decoupled. Fast atom bombardment mass spectrometry was conducted on a Kratos MS-50 mass spectrometer with a magnetic sector using xenon atoms and a nitrophenyl octyl ether matrix.

Experimental

Synthesis of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$, $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_4\text{Cl}_2$, and $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_3\text{Cl}_3$. These materials were synthesized by a previously reported procedure.¹ The cis form of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_3\text{Cl}_3$ was isolated by crystallization from hexanes at -11°C followed by several recrystallizations from hexanes.

Synthesis of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}_3$. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$ (4.0 g, 6.3×10^{-3} mol) was dissolved in 2-butanone (60 mL) at room temperature. Tetrabutylammonium bromide, $n\text{-Bu}_4\text{NBr}$, (0.28 g, 8.7×10^{-4} mol) was added to the solution followed by solid sodium azide, NaN_3 (0.60 g, 9.2×10^{-3} mol). The reaction was then heated to reflux for 24h, allowed to cool to room temperature, and examined by ^{31}P NMR to check for complete conversion to the azide. The solvent was then removed by rotovap, and the resultant oily, white solid was extracted between diethyl ether (100 mL) and deionized water (100 mL).

The ether layer was washed again with deionized water (100 mL) and then with 4% aqueous NaHCO_3 (100 mL). The ether layer was then dried with MgSO_4 and filtered to yield a clear, pale yellow solution. The ether was removed by rotovap to yield a slightly cloudy oil. The oil was further purified by column chromatography on silica gel with 60% hexanes/40% CH_2Cl_2 as the solvent. The purified fractions were combined, and the solvent was removed by rotovap to yield a colorless oil. The oil was dissolved in hot hexanes (50 mL), filtered, and allowed to cool to room temperature. A clear colorless, oil separated from solution on cooling the mixture to $-11\text{ }^\circ\text{C}$. The hexanes were decanted off, and the oil was dried under vacuum. After several days, the oil crystallized to form a white solid. Yield: 3.6 g (89%). ^{31}P NMR (CDCl_3) $\delta = 13.6$ (t, 1P), 8.6 (d, 2P); ^1H NMR (CDCl_3) $\delta = 7.3\text{--}6.9$ (m, 25H); $\text{C}_{30}\text{H}_{25}\text{N}_6\text{O}_5\text{P}_3$ calculated mass 642.77; FAB(+)-MS: 643.2 [MH^+].

Synthesis of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_4(\text{N}_3)_2$. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_4\text{Cl}_2$ (6.0 g; 0.010 mol) was dissolved in 2-butanone (60 mL). Sodium azide (2.0 g; 0.031 mol) and $n\text{-Bu}_4\text{NBr}$ (0.20 g; 6×10^{-4} mol) were added, and the mixture was heated to reflux for 24h. The solvent was removed by rotovap, and the product was extracted between Et_2O (100 mL) and 5% aqueous K_2CO_3 (100 mL). The ether layer was washed with additional 5% aqueous K_2CO_3 (100 mL). The ether layer was dried with MgSO_4 , filtered, and the ether removed by rotovap to yield an oil. The oil was purified by column chromatography on silica (60% ethyl acetate/ 40% hexanes). The solvent was removed by rotovap. The product oil was then dissolved in hexanes and cooled to $-55\text{ }^\circ\text{C}$ to crystallize the product. The hexanes were decanted off, and the product was allowed to warm to room temperature where it melted to form a clear, colorless oil. The oil was redissolved in hexanes and cooled to $-55\text{ }^\circ\text{C}$ again. The hexanes were decanted off and the product allowed to warm to room temperature. The resultant oil was then dried under vacuum. Yield: 4.9 g (80%). ^{31}P NMR (CD_2Cl_2) $\delta = 13.2\text{--}12.3$ (overlapping d, cis + trans isomers, 2P), 8.5-7.2 (overlapping q, cis + trans isomers, 1P); ^1H NMR (CD_2Cl_2) $\delta = 7.6\text{--}6.9$ (m, 20H); $\text{C}_{24}\text{H}_{20}\text{N}_9\text{O}_4\text{P}_3$ calculated mass 591.40; FAB(+)-MS: 592.1 [MH^+].

Synthesis of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_3(\text{N}_3)_3$. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_3\text{Cl}_3$ (5.0 g, 9.6×10^{-3} mol) was dissolved in distilled toluene (100 mL) under N_2 . $n\text{-Bu}_4\text{NBr}$ (0.26 g, 8.1×10^{-4} mol) was added along with NaN_3 (3.0 g, 0.046 mol). The reaction mixture was then heated at reflux for

72h. After the reaction was allowed to cool to room temperature, the solvent was removed by rotovap to yield a milky, white oil. The product was then extracted between Et₂O (125 mL) and 3% aqueous NaHCO₃ (100 mL). The ether layer was washed with additional 3% aqueous NaHCO₃ (100 mL) followed by distilled water (100 mL). The ether layer was then dried with MgSO₄ and filtered. The ether was removed by rotovap to yield a yellow oil. The product was then purified by column chromatography on silica (10% Et₂O/ 90% hexanes. The purified fractions were combined and rotovapped to yield a clear, colorless oil. The oil was then dried under vacuum for 48h. Yield: 4.2 g (81%). ³¹P NMR (CD₂Cl₂) δ = 13.1-11.3 (m, overlapping singlet, doublet, and triplet for cis and trans isomers); ¹H NMR (CD₂Cl₂) δ = 7.4-6.7 (m, 15H); C₁₈H₁₅N₁₂O₃P₃ calculated mass: 540.33; FAB(+)-MS: 541.0 [MH⁺].

Synthesis of N₃P₃(N(CH₃)₂)₄Cl₂. This compound was synthesized via the literature procedure.²

Synthesis of N₃P₃(N(CH₃)₂)₄(N₃)₂. N₃P₃(N(CH₃)₂)₄Cl₂ (2.0 g, 5.2 x 10⁻³ mol) was dissolved in 2-butanone (50 mL) at room temperature. n-Bu₄NBr, (0.3 g, 9.3 x 10⁻⁴ moles) and NaN₃ (1.0 g, 1.5 x 10⁻² moles) were then added. The reaction was heated to reflux for 48 hours and allowed to cool to room temperature. After confirming complete conversion to the azide by ³¹P NMR, solvent was removed by rotovap. The resulting oily, off-white solid was dissolved in diethyl ether (200 mL) and washed two times with deionized H₂O (100 mL) followed by a washing with a 4% aqueous NaHCO₃ (100 mL). The ether layer was dried with MgSO₄ and filtered to give a clear, colorless solution. The ether was then removed by rotovap giving a clear, colorless oil. The oil was further purified with multiple recrystallizations in hexanes at -55 °C. The product was dried under vacuum for 24 hrs. Yield: 1.1 g (53%). ³¹P NMR (CDCl₃) δ = 24.8 (t, 1P), 21.4 (d, 2P); ¹H NMR (CDCl₃) δ = 2.7-2.6 (m, 18H); C₈H₂₄N₁₃P₃ calculated mass 395.31; FAB(+)-MS: 396.1 [MH⁺].

Synthesis of N₃P₃(N(CH₂CH₃)₂)₃Cl₃. This material was synthesized by a previously reported procedure.² However, THF was used as the solvent instead of benzene.

Synthesis of N₃P₃(N(CH₂CH₃)₂)₃(N₃)₃. N₃P₃(N(CH₂CH₃)₂)₃Cl₃ (1.5 g; 3.3 x 10⁻³ mol) was dissolved in 2-butanone (30 mL). Sodium azide (0.84 g; 0.013 moles) and tetrabutylammonium bromide (0.20 g; 6.2 x 10⁻⁴ mol) were added, and the reaction

mixture was refluxed for 48h. The solvent was removed by rotovap, and the resultant oily solid was extracted between diethyl ether (100 mL) and deionized water (100 mL). The ether layer was rinsed with a second portion of water (100 mL) and then dried with MgSO_4 . The MgSO_4 was filtered off and the ether removed by rotovap to yield an orange liquid. The liquid was further purified by column chromatography (90% hexane/10% diethyl ether) on silica gel. The fractions were combined, and the solvent removed by rotovap to yield a clear, colorless liquid which was dried under vacuum for 48h. Yield: 1.1 g (70%). ^{31}P NMR (CDCl_3) δ = 18.7-17.2 (m) (appears to be a quartet 18.3 (1P) and doublet 17.4 (2P)); ^1H NMR (CDCl_3) δ = 3.3-3.0 (m, 12H), 1.2-0.9 (overlapping triplets, 18H); $\text{C}_{12}\text{H}_{30}\text{N}_{15}\text{P}_3$ calculated mass: 477.42; FAB(+)-MS: 478.4 [MH^+].

Synthesis of $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{Cl}$. This compound was synthesized via literature procedure.³ A mixture of the hexa-, penta- and tetra-trifluoroethoxy/chloro trimer derivatives was obtained.

Synthesis of $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{N}_3$. The mixture of the hexa-, penta- and tetra-trifluoroethoxy trimer derivatives ($\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{Cl}$ 5.0 g, 7.5×10^{-3} mol) was dissolved in 2-butanone (50 mL). To this was added $n\text{-Bu}_4\text{NBr}$ (0.14 g, 4.3×10^{-4} mol) and NaN_3 (1.44 g, 2.2×10^{-2} mol). The reaction mixture was stirred at room temperature for 24 hrs. The solvent was removed by rotovap leaving a clear, colorless oil. The oil was dissolved in diethyl ether (50 mL) and washed twice with deionized H_2O (100 mL). The ether layer was dried with MgSO_4 and filtered. The solvent was removed by rotovap and the product dried under vacuum. ^{31}P NMR showed a mixture of products which appear to be the hexa-, penta- and tetra- trifluoroethoxy/azido trimers. The individual trimers could not be isolated from the mix.

Reaction of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}_3$ with $\text{P}(\text{C}_6\text{H}_5)_3$. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}_3$ was treated similarly with triphenylphosphine, triphenyl phosphite, triethyl phosphite, and hexamethylphosphorous triamide with the exception that triphenyl phosphite required toluene as the reaction solvent and a longer reaction time (48h). For brevity, only the reaction of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}_3$ with triphenylphosphine is detailed. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}_3$ (0.35 g, 5.4×10^{-4} mol) was dissolved in distilled THF (20 mL). Triphenylphosphine (0.23 g, 8.8×10^{-4} mol) was added, and the reaction was heated to reflux for 24h. The reaction was allowed to cool to room temperature, and the solvent was removed by rotovap to

yield a thick oil. The oil was dissolved in diethyl ether (40 mL) and extracted twice with deionized water (30 mL). The ether solution was then extracted with 2% aqueous NaHCO_3 (30 mL), dried with MgSO_4 , and filtered to yield a clear, colorless solution. The ether was partially evaporated until the solution became cloudy. The product was then crystallized by addition of hexanes (10 mL) and cooling to -11°C . The solvent was poured off, and the white crystalline product was rinsed twice with hexanes (10 mL). The product was then dried under vacuum for 24h. Yield: 0.28 g (59%). ^{31}P NMR (CDCl_3) δ = 10.4 (d, 1P), 8.5 (d, 2P), 6.9-5.6 (m, 1P); ^1H NMR (CDCl_3) δ = 7.6-7.2 (m, 15H), 7.1-6.8 (m, 25H); $\text{C}_{48}\text{H}_{40}\text{N}_4\text{O}_5\text{P}_4$ calculated mass: 876.72; FAB(+)-MS: 877.4 $[\text{MH}^+]$.

Reaction of $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{N}_3$ with $\text{P}(\text{C}_6\text{H}_5)_3$. The trifluoroethoxy/azido trimer mixture (5.4 g) was dissolved in 2-butanone. Triphenylphosphine (3.2 g, 1.2×10^{-2} mol) was added, and the reaction was refluxed for 24 hrs. The solvent was removed by rotovap. The resulting cloudy oil was dissolved in diethyl ether (40 mL) and washed twice with deionized H_2O (100 mL) followed by a washing with an aqueous 1% NaHCO_3 solution (100 mL) to yield a clear, colorless oil. The product was further purified via column chromatography on silica gel using 50% dichloromethane/ 50% hexanes as the solvent. Fractions containing the desired product were combined, and the solvent was removed by rotovap. The resultant clear, colorless oil was then dried under vacuum for 24 hrs. Yield: 0.65 g. ^{31}P NMR (CDCl_3) δ = 17.4 (d, 2P), 13.6 (d, 1P), 10.4 (m, 1P); ^1H NMR (CDCl_3) δ = 7.7-7.2 (m, 15H), 4.3-3.9 (m, 6H), 3.8-3.6 (m, 4H); $\text{C}_{28}\text{H}_{25}\text{F}_{15}\text{N}_4\text{O}_5\text{P}_4$ calculated mass: 906.40; FAB(+)-MS: 906.7 $[\text{MH}^+]$.

Reaction of $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_5\text{N}_3$ with $\text{P}(\text{OC}_6\text{H}_5)_3$. The trifluoroethoxy/azido trimer mixture (5.4 g) was dissolved in toluene. Triphenyl phosphite (3.8 g, 1.2×10^{-2} mol) was added and the reaction mixture was refluxed overnight. After confirming complete reaction by ^{31}P NMR, the solvent was removed by rotovap. The resultant oil was dissolved in diethyl ether (40 mL) and washed twice with deionized H_2O (75 mL) followed by a washing with an aqueous 1% NaHCO_3 solution (75 mL). The ether layer was dried with MgSO_4 . The MgSO_4 was filtered off, and the solvent was removed via rotovap yielding a clear, colorless oil. The product was further purified by column chromatography on silica gel using 67% dichloromethane/ 33% hexanes as the solvent.

Fractions containing the desired product were combined, and solvent was removed by rotovap. The resulting clear, colorless oil was dried under vacuum for 24 hrs. Yield: 0.32 g. ^{31}P NMR (CDCl_3) δ = 17.2 (d, 2P), 6.0 (q, 1P), -23.0 (1P); ^1H NMR (CDCl_3) δ = 7.6-7.2 (15H), 4.5-4.2 (m, 4H), 4.2-4.0 (m, 4H), 4.0-3.8 (m, 2H); $\text{C}_{28}\text{H}_{25}\text{F}_{15}\text{N}_4\text{O}_8\text{P}_4$ calculated mass: 954.40; FAB(+)-MS: 954.7 [MH^+].

Reaction of $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)\text{N}_3$ with $\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_2)_7\text{CH}_3$. $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)\text{N}_3$ (0.3 g; 5×10^{-4} mol) was dissolved in 1-phenyl nonane (3.5 g; 0.017 mol), and the reaction was heated to reflux where vigorous gas evolution commenced. After about 5 minutes, the gas evolution slowed, and the reaction was allowed to cool to room temperature. The reaction was purified by column chromatography on silica (20% Et_2O / 80% hexanes). The solvent was removed by rotovap and the product dried under vacuum to yield a clear, colorless oil. Yield: 0.1 g (26%). ^{31}P NMR (CD_2Cl_2) δ = 11.7 (q, 1P), 8.9 (d, 2P); ^1H NMR (CD_2Cl_2) δ = 7.2-6.7 (29H), 4.51 (1H), 2.10 (t, 2H), 1.5-1.0 (m, 14H), 0.80 (t, 3H); $\text{C}_{45}\text{H}_{49}\text{N}_4\text{O}_5\text{P}_3$ calculated mass: 818.79; FAB(+)-MS: 819.8 [MH^+].

References

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