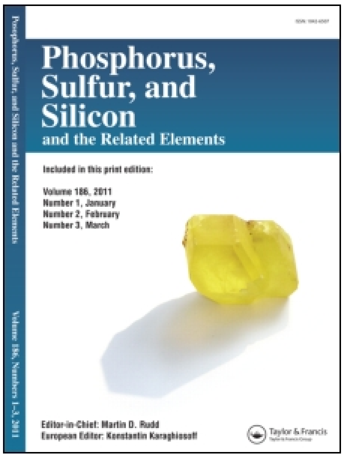

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SYNTHESIS OF A NOVEL EXCEEDINGLY STRONG NONIONIC SUPERBASE

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SYNTHESIS OF A NOVEL EXCEEDINGLY STRONG NONIONIC SUPERBASE*

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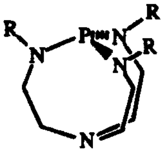
The synthesis of a novel superbase $P(HNCH_2CH_2)(i\text{-}PrNCH_2CH_2)_2N$, **2a**, is discussed. The conditions for the preparation and purification of $H_2NCH_2CH_2N(CH_2CH_2N\text{-}i\text{-}Pr)_2$, **4a**, starting from commercially available $(H_2NCH_2CH_2)_3N$ (tren) were optimized. The existence of the novel zwitterion $HP(N^-CH_2CH_2)(i\text{-}PrNCH_2CH_2)_2N^+$, **2b**, was substantiated by NMR spectroscopy. The superbase **2a** crystallizes from its melt when cooled slowly to -4 °C, and then remains as a solid at room temperature for several days. Hence it can be handled as a liquid or as a solid.

Keywords: Nonionic base; strong base; synthesis; zwitterion

INTRODUCTION

As a consequence of our interest in developing applications of our recently synthesized and commercially available proazaphosphatrane **1a** to organic transformations, we have embarked on a program aimed at evaluating derivatives of **1a** with various alkyl substitution patterns on the nitrogens adjacent to phosphorus. This paper focuses on the synthesis of the novel derivative **2a** by the retrosynthetic path shown in Scheme 1. Compound **2a** has the potential of behaving as an amide base **2b** if equilibrium 1 is appreciable. We have demonstrated that the nucleophilicity and basicity of phosphorus in **1a** stemming from transannular



1a, R = Me
1b, R = *i*-Pr
1c, R = H

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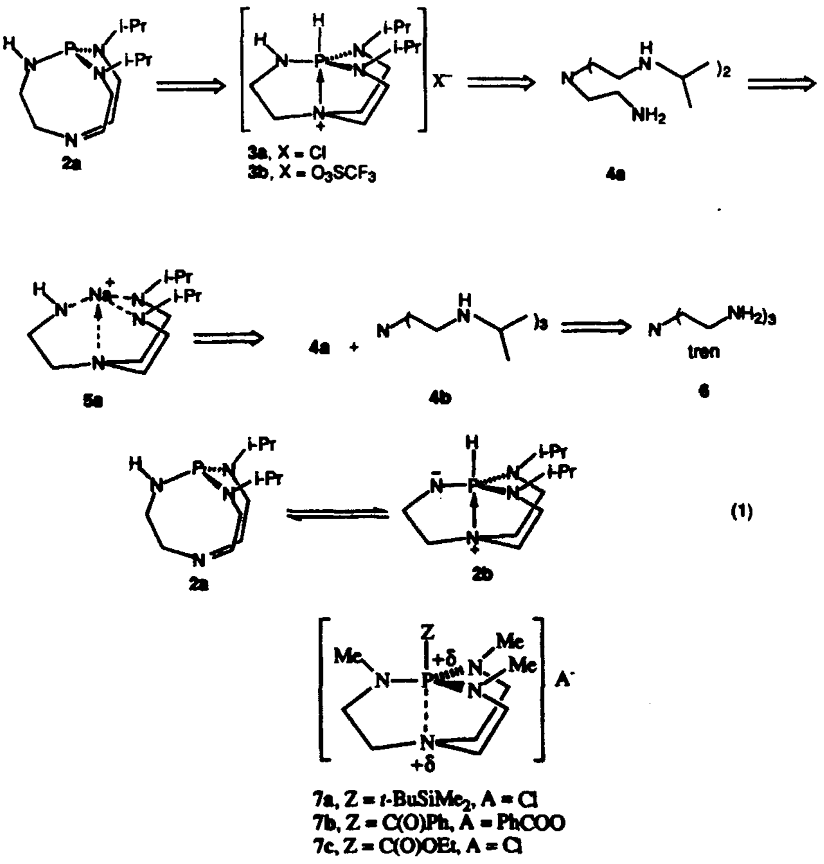
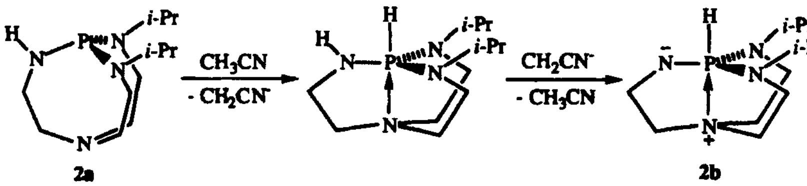
* Dedicated to Professor Robert Wolf



SCHEME 1

bond formation play an important role in the formation and stability of cation intermediates of type **7**.[1,2] It should be noted that the photoelectron spectra of the proazaphosphatranes **1a** and **1b** exhibit a rather low first ionization energy, in accord with expectations.[3] This behavior indicates that there is no substantial interaction between the phosphorus and the axial nitrogen atom in proazaphosphatranes of the type **1a** and **1b** whereas in azaphosphatranes there is a weak but well-defined bond between phosphorus and the axial nitrogen.[3] The transannulation process involved in the formation of such cations can be viewed as a model for S_N2 formation of a five-coordinate intermediate, which has the unusual feature that the nucleophilic atom (axial nitrogen) is forced to invert by virtue of its bridgehead position in the bicyclic structure **1a**.[4] The synthesis of esters,[1] silyl ethers,[2,5]a chiral fluorescent auxiliary,[6] alkenes (via dehydrohalogenation),[7] pyrroles,[8] oxazoles,[8] porphyrins,[8] C-acyl-α-amino acid esters,[8] and isocyanurates[9,10] using **1a** as a catalyst or as a base, and the failure of such reactions employing acyclic $P(NMe_2)_3$ has established the importance of transannular bond formation in **1a** during these transformations.[2] It is known that 1a deprotonates acetonitrile.[9] This strong basicity of **1a** is in agreement with its photoelectron spectra.[3] We speculated that **2a** could deprotonate acetonitrile giving rise to **2b** (Scheme 2) which could act as an amide base. This unique property would thus transform a nonionic superbase **2a** to an ionic superbase **2b** that is overall charge neutral.

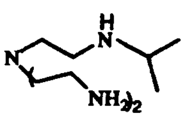


2a **2b**

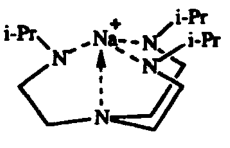
SCHEME 2

RESULTS AND DISCUSSION

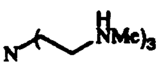
The key steps in the retrosynthetic analysis of the target molecule **2a** shown in Scheme 1 are the optimization of the yield of di-isopropyl tren **4a** in the mixture of **4a** and **4b** obtained from commercially available tren (**6**) and the separation of **4a** from the mixture of **4a** and **4b**. Recently **4b** was synthesized in our laboratories by the reduction of the corresponding imine with sodium borohydride, formed from the reaction of **6** with acetone in an acidic medium.[11] The crude mixture containing **4b** indicated the presence of small amounts of **4a** and **4c**.[11] Preliminary experiments indicated that the yield of **4a** in a mixture of **4a** and **4b** could be maximized by adjusting the amount of sodium borohydride and acetone



4c



5b



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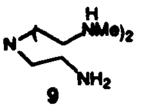

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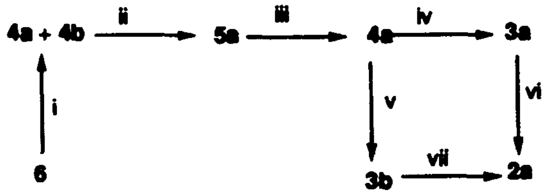
and also the reaction time and temperature. The synthesis of **2a** is given in Scheme 3. Tren was reacted with acetone in an acidic buffer to give the corresponding imine which was subsequently reduced with sodium borohydride to afford a mixture of **4a** and **4b**. The average yield of **4a** in a mixture of **4a** and **4b**

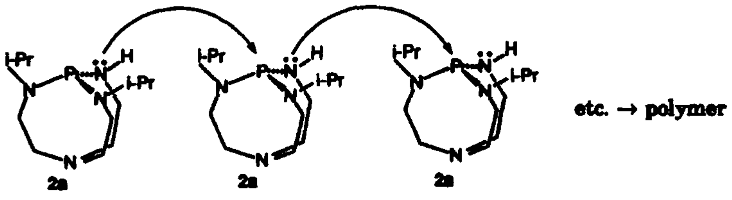


SCHEME 3 (i) H_2O, AcOH, AcONa, -8 °C to -2 °C acetone; $NaBH_4$, -2 °C (ii) 2 equiv. NaI, hexanes (iii) heat to 200 °C at 200 mtorr with simultaneous distillation of **4a** (iv) $P(NMe_2)_3$, PCl_3 (v) $P(NMe_2)_3$, TfOH (vi) *t*-BuOK, CH_3CN (vii) *t*-BuOK, THF

was 32% under optimum conditions as determined by ^1H NMR integration. This yield was found to decrease when more than the optimum amount (45 g) of sodium borohydride was used, whereas a mixture of **4a**, **4b** and **4c** was obtained when less than 40 g of sodium borohydride was used. The optimum temperature was found to be -2 °C. At temperatures lower than -5 °C a mixture of **4a**, **4b** and **4c** was obtained and also the yield of the distilled mixture of **4a**, **4b** and **4c** decreased significantly. When the reaction was run at 10 °C only **4b** was obtained. The optimum amount of acetone was found to be 95 mL. Higher or lower amounts of acetone decreased the yield of the desired product **4a** as did longer or shorter reaction times compared with the optimum time.

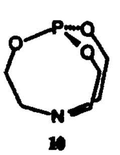
Attempted purification of **4a** by fractional distillation of the crude mixture of **4a** and **4b** with a packed column failed. It is known, that amines can form adducts with alkali and alkaline earth metal salts, and that these complexes dissociate at elevated temperatures liberating the amine.[12] Attempts to prepare **8** from less expensive commercially available starting materials gave rise to mixtures of **8** and **9**.[13] Although efforts to separate **8** from a mixture of **8** and **9** using their sodium iodide complexes failed, since both amines formed almost equally strong complexes with sodium iodide,[13] we believed that it might be more difficult for **4b** to form a sodium iodide complex than for **4a** owing to greater steric hindrance among three isopropyl groups in **5b** then among two such groups in complex **5a**. A series of experiments was conducted in which the reaction time, the concentration of **4a** in a hexanes solution of a mixture of distilled **4a** and **4b**, the amount of NaI used and the rate of stirring were varied in order to determine a set of optimum conditions for the preferential formation of the complex of **4a** with NaI. It was observed that the use of larger amounts of NaI, higher concentrations of **4a** in the hexanes solution of **4a** and **4b**, and longer reaction times compared with the optimum conditions, resulted in more pronounced entrainment of **4b** in the solid residue. Complex **5a** decomposed rapidly at 200 °C under reduced pressure to liberate **4a** which distilled out, thereby separating **4a** from the sodium iodide.

Compound **4a** was converted to **3a** (method A in the Experimental Section) and to **3b** by a procedure used to synthesize **1a** in high yields.[14] Suprisingly **3a** was also obtained from a mixture of distilled **4a** and **4b** (method B in the Experimental Section). Deprotonation of **3a** using *t*-BuOK in acetonitrile resulted in only a 28% yield of the desired product **2a**. The low yield of **2a** may be associated with the observation (see later) that **2a** deprotonates acetonitrile ($pK_a = 25^{15}$). The sparing solubility of **3a** in THF prompted us to synthesize **3b**, which was deprotonated using *t*-BuOK in THF to give a 55% yield of **2a**. It was observed that **2a** polymerizes slowly on standing at 24 °C, presumably by successive transaminations as depicted in Scheme 4. This reaction is not observed for **1a** or **1b** in which all three of the P-N nitrogens are substituted with alkyl groups that can sterically inhibit this reaction. Noteworthy in this respect is the rapid polymerization of **10** and **1c** (an analogue of **2a**) by a transesterification[16]and transamination pathway, respectively.[17,18] However, no appreciable polymerization was observed for **2a** for several months at -4 °C when it was stored under a nitrogen atmosphere.



SCHEME 4

The ^{31}P NMR spectrum of **2a** in CD_3CN revealed a singlet at 109.3 ppm (**2a**) and a 1:1:1 triplet (ca. 16%) at 5.1 ppm (^1J = 76 Hz) which we assign to a deuterated zwitterion (i.e., the deuterated-phosphorus analogue of **2b**) rather than the deuterated-phosphorus analogue of cation **3a**, namely **11** (δ ^{31}P -21.7, ^1J = 76 Hz). The ^{31}P NMR spectrum of **2a** in C_6D_5N revealed a singlet at



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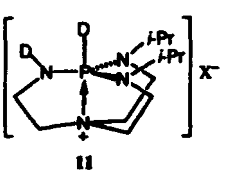
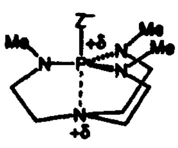


11



12a, Z = PhNCO
12b, Z = CS_2
12c, Z = PhNCS

110.95 ppm (**2a**) and a singlet at 3.35 ppm (ca. 1%) which we assign to **2b**. It is interesting that zwitterions such as **2b** constitute a second variety of such ions in azaphosphatrane systems, the type of zwitterion described earlier by us being represented by **12a-c.**[4] What we believe is cation **11** is a species formed in an equilibration reaction between **3a** and **1a** in CD_3CN. In that mixture ^{31}P NMR peaks for **1a** and the presumably deuterated analogue of **2a** (namely, **13** in Scheme 5) were detected, as well as ^{31}P peaks and one-bond P-D spin-spin coupling constants for **14**[14,17] and **15** in Scheme 5. Since **1a** is known to deprotonate acetonitrile in an equilibrium reaction[18] and we have shown here that tautomer **2b** forms from **2a** in this solvent, the pathway shown in Scheme 5 to **13-15** is plausible. The very weak acidity of species such as **3a, 3b, 14** and **15** is attested to by the necessity to use KO-t-Bu to deprotonate them.[18]

In acetonitrile, the chemical shift of 5.63 ppm assigned to **2b** lies between that for **2a** (109.3 ppm) and cation **3a** (-21.7 ppm) and further toward that of the latter suggesting that tautomer **2b** probably contains a five-coordinate phosphorus as shown. Five-coordination is indeed observed for cations analogous to **3a** as has been shown by crystallographic means.[18]If this were not the case, the $^{-}$N-P linkage would probably reveal considerable double bond character as shown in tautomer **2b'** in Scheme 5.

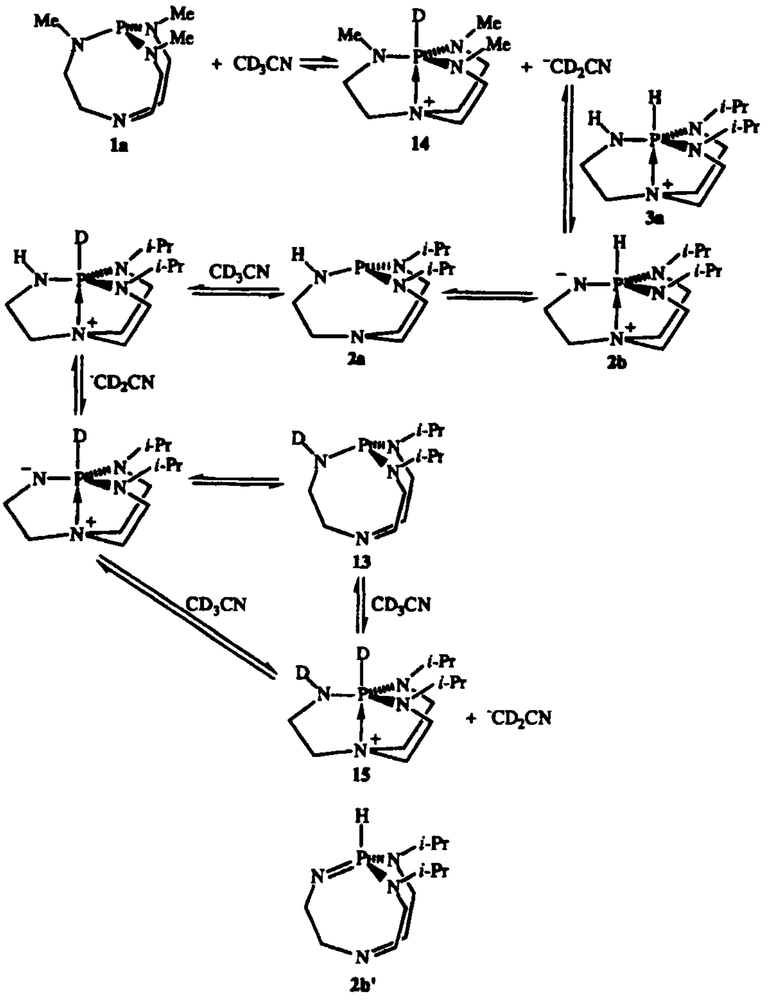
Experiments utilizing **2a** as an amide base equivalent in organic synthesis are underway.

CONCLUSIONS

The novel superbase **2a** was synthesized in 50-60% yield from **3b**. The conditions for the preparation and purification of **4a** starting from commercially available **6** were optimized. The existence of the novel tautomer **2b** was substantiated by NMR spectroscopy. The superbase **2a** crystallizes from its melt when cooled slowly to -4 °C, and remains as a solid for several days at room temperature. Hence it can be handled as a liquid or as solid.

EXPERIMENTAL SECTION

THF, pentane, C_6D_6 and ether were distilled from Na-benzophenone under nitrogen. Acetonitrile was distilled from calcium hydride and was stored over molecular seives. Potassium *t*-butoxide (95%), phosphorus trichloride, and triflic acid were purchased from Aldrich and were used as received. Acetone (99.7%), sodium acetate (anhyd.), glacial acetic acid, sodium borohydride, sodium iodide and hexanes was purchased from Fischer Scientific Co and were used as



SCHEME 5

received. Hexamethyl phosphorus triamide were purchased from Acros Chemical Co and was distilled before use. Preparations of **3a**, **3b** and **2a** were carried out under a nitrogen or argon atmosphere. Tren (**6**) was distilled before use. Only all-glass apparatus was used during deprotonation of **3a** and **3b** since the purity of **2a** is affected after contacting rubber septa.

Preparation of a mixture of 4a and 4b from 6

To a 1 L beaker containing 450 mL of stirred water, was added **6** (32 g, 0.22 mol) followed by the addition of anhydrous sodium acetate (81.0 g) and glacial acetic acid (225 mL). The clear solution was stored in a freezer for 2.5 h. The solution was then poured into a three-neck 2 L round bottom flask equipped with an efficient mechanical stirrer possessing an 11 cm stirring blade, and a thermometer. The solution was stirred at a speed of 500 rpm throughout the entire reaction while it was held at -8 °C using a salt-ice bath or an acetone-Dry Ice bath. To the reaction mixture was added reagent grade acetone (95 mL, 1.3 mol) dropwise over 14 min., during which time the temperature slowly increased to -2 °C. Finely powdered sodium borohydride (45 g, 1.2 mmol) was added in small portions over a period of 6.5 h while maintaining the reaction temperature at -2 °C. Stirring was continued for another 0.5 h and then 170 g of NaOH dissolved in 500 mL of water was added over 10 min. After stirring the reaction mixture for an additional 5 min., the pH of the solution was determined to be 11 by pH paper. An oily layer separated when the solution was allowed to stand for 10 min. This two-phase system was immediately extracted with 4 x 150 mL of ether. The combined organic layer and ether extracts were dried over anhyd. sodium sulfate, followed by concentration under vacuum giving 33 g of a crude yellow oil which was distilled to give 31 g of a mixture of **4a** and **4b** (Bp. 85-90 °C/200 mtorr) containing 60-70 mmol of **4a**.[19] ^{1}H NMR (C_6D_6) 1.05 (d, CH_3 of **4a**, J = 6 Hz), 1.07 (d, CH_3 of **4b**, J = 6 Hz), 1.45 (br, NH and NH_2), 2.26 (t, CH_2NH_2, J = 6 Hz), 2.39-2.44 (m, CH_2NH), 2.54-2.57 (m, NCH_2), 2.65-2.75 (m, CH).

Isolation of 4a from a mixture of 4a and 4b

A 1 L three-neck RB flask was fitted with a mechanical stirrer so that the 7.5 cm long stirring blade almost touched the bottom of the flask. To the flask was added 100 mL of hexanes which was stirred at 600 rpm while finely powdered sodium iodide (23 g, 0.15 mol) was added after the mixture had been stirred for 10 min at this speed. No solid was observed to settled down to the bottom of the flask during stirring. A solution prepared by mixing 31 g of a mixture of **4a** and **4b** containing ~ 70 mmol of **4a** in 85 mL hexanes was added via a dropping funnel to obtain a 0.32 M solution of **4a**.[19] The resulting mixture was stirred for 45 min. at 600 rpm. The speed was then reduced to 500 rpm and the suspension was stirred for another 5.5 h. The suspension was allowed to settle and the supernatant yellow solution was then decanted. The white solid was washed thoroughly with 3 x 50 mL of hexanes to remove any entrapped **4b**. Any lumps that formed were then dissolved in a minimum amount of water and extracted with 3 x 50 mL portions of ether. The aqueous layer was evaporated under vacuum to dryness to provide additional fine white solid which was washed with 20 mL of hexanes. This hexanes extract and the ether extracts were concentrated under vacuum to afford >95% pure **4a**. All of the white solids were dried under vacuum at 24 °C and then heated to 210 °C at 200 mtorr in a distillation apparatus, whereupon **5a** decomposed slowly to liberate 12 g of **4a** (Bp. 70 °C/200 mtorr) as a distillate, which was found to be >98% pure by ^{1}H NMR analysis. ^{1}H NMR (C_6D_6): 1.05 (d, CH_3, 12H, J = 6 Hz), 1.19 (br, NH and NH_2, 4H), 2.26 (t, CH_2NH_2, 2H, J = 6 Hz), 2.41 (t, CH_2NH, 4H, J = 6 Hz), 2.55 (t, NCH_2,6H,J = 6 Hz), 2.72 (sept, CH, 1H, J = 6 Hz); ^{13}C NMR ($CDCl_3$): 23.3 (s, CH_3), 40.3 (s, CH_2NH_2), 45.7 (s, CH_2NH), 49.2 (s, CH), 54.7 (s, NCH_2), 57.4 (s, NCH_2).

Preparation of 3a

Method A: To a 250 mL Schlenk flask containing an ice-cooled solution of $P(NMe_2)_3$ (8.4 mL, 46 mmol) in 40 mL of dry methylene chloride was added PCl_3 (2.0 mL, 23 mmol) via a syringe. After stirring the reaction mixture for 15 min. at 0 °C, a solution of **4a** (16 g, 70 mmol) in 10 mL of CH_2Cl_2 was added dropwise. The flask was equipped with an outlet for the dimethyl amine which is a by-product of the reaction. This reaction solution was then stirred at room temperature for another 30 min. after which the volatiles were removed under vacuum. The residue was then dissloved in a minimum amount of water and the resulting solution was extracted with 5 x 20 mL of CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give **3a** in 87% yield, which was found to be >98% pure by ^{1}H NMR analysis. ^{1}H NMR ($CDCl_3$): 1.09 (d, 6H, CH_3, J = 6 Hz), 1.13 (d, 6H, CH_3, J = 6 Hz), 2.91-3.00 (m, 4H, CH_2NP), 3.06-3.17 (m, 2H, CH_2NH), 3.25-3.36 (m, 6H, CH_2N), 3.47-3.60 (m, 2H, CH), 4.45 (d, 1H, NH, J = 33 Hz), 5.67 (d, 1H, PH, J = 488 Hz); ^{31}P NMR ($CDCl_3$): -21.7 (s); ^{13}C NMR ($CDCl_3$): 21.05 (d, CH_3, J = 4.9 Hz), 21.16 (d, CH_3, J = 5.3 Hz), 32.88 (s, CH_2N_{eq}), 32.96 (s, CH_2N_{eq}), 47.02 (d, CH_2N_{ax}, J = 3.9 Hz), 47.17 (d, CH_2N_{ax}, J = 3.9 Hz), 49.05 (d, CH_2NH, J = 11.3 Hz).

Method B: To a 250 mL Schlenk flask containing an ice-cooled solution of $P(NMe_2)_3$ (2x/3 mmol) in 10 mL of dry $CH_2Cl_2$was added PCl_3 (x/3 mmol) via a syringe.[19] After stirring the reaction mixture for 15 min. at 0 °C, a solution of a mixture of **4a** and **4b** containing x mmol (x = 60-70) of **4a** in 10 mL of CH_2Cl_2 was added dropwise. The flask was equipped with an outlet for effluent dimethyl amine. The reaction mixture was then stirred at room temperature for an additional 7 h. The volatiles were removed under vacuum and **3a** was precipitated by adding 150 mL of ethyl ether. The residue was dissolved in a minimum amount of water and the solution was extracted with 2 x 20 mL ethyl ether, followed by extraction with 5 x 20 mL CH_2Cl_2. The ether extracts were dried over Na_2SO_4 and concentrated under vacuum to give **4b**. The CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated under vacuum to give **3a** in 88% yield, which was found to be >98% pure by ^1H NMR analysis (see Method A above).

Preparation of 3b

To a 250 mL Schlenk flask containing an ice-cooled solution of **4a** (11 g, 46 mmol) and $P(NMe_2)_3$ (8.4 mL, 46 mmol) in 40 mL of dry CH_2Cl_2 was added dropwise a solution of triflic acid (3.8 mL, 46 mmol) dissolved in 20 mL of CH_2Cl_2. The flask was equipped with an outlet for the dimethyl amine that evolved. After addition, the solution was stirred at room temperature for an additional 30 min. The volatiles were removed under vacuum and the residue was dissolved in a minimum amount of THF. To this solution was added pentane with vigorous stirring to precipitate **3b** which was recrystallized from THF at -2 °C in 85% yield, and in 99% purity as revealed by ^1H and ^{31}PNMR analysis. ^1H NMR ($CDCl_3$): 1.08 (d, 6H, CH_3, J = 6Hz), 1.11 (d, 6H, CH_3, J = 6 Hz), 2.95-3.12 (m, 12H, CH_2CH_2N), 3.49 (m, 2H, NCH), 3.66 (d, 1H, NH, J = 33 Hz), 5.6 (d, 1H, PH, J = 488 Hz); ^{31}P NMR ($CDCl_3$): -21.8. ^{13}C NMR ($CDCl_3$): 20.83 (d, CH_3, J = 4.9 Hz), 21.05 (d, CH_3, J = 5.2 Hz), 32.62 (d, CH_2N_{eq}, J = 1.5 Hz), 32.77 (d, CH_2N_{eq}, J = 5.2 Hz), 46.96 (d, CH_2N_{ax}, J = 5.2 Hz), 47.12 (d, CH_2NH, J = 12.0 Hz), 48.85 (d, CH, J = 12.0 Hz). MS (FAB): m/z: 259.1 (100, cation of **3b**). Elemental analysis: Anal. Calcd: C, 38.19; H, 6.90; N, 13.72; S, 7.85. Found: C, 38.07; H, 6.87; N, 13.98; S, 7.83.

Preparation of 2a from 3a

To a suspension of *t*-BuOK (6.8 g, 60 mmol) in 55 mL of THF under nitrogen in a 250 mL Schlenk flask fitted with a filter flit was added **3a** (8.0 g, 30 mmol). After the suspension was stirred for 1.5 h, the volatiles were evaporated under vacuum and 100 mL of pentane was added to the residue. The resultant suspension was stirred for 6 h and then filtered through the flit under nitrogen. The solid was further washed with 50 mL of pentane. The pentane extracts were then evaporated to obtain crude **2a**, which was transferred under nitrogen into a 25 mL Schlenk flask by a pipet or a glass syringe. Crude **2a** was distilled (Bp. 90°C/200 mtorr) immediately to give **2a** in 28% yield. The product was found to be 95% pure by ^1H NMR analysis (see next preparation).

Preparation of 2a from 3b

To a suspension of *t*-BuOK (5.3 g, 47 mmol) in 55 mL THF under nitrogen in a 250 mL Schlenk flask fitted with a filter frit was added **3b** (16 g, 40 mmol) and the suspension was stirred for 1.5 h. The volatiles were evaporated under vacuum and 100 mL of pentane was added to the residue. The suspension was stirred for 6 h and then filtered through the frit under nitrogen. The solid was further washed with 50 mL of pentane and the pentane extracts were evaporated to obtain crude **2a**, which was transferred under nitrogen into a 25 mL Schlenk flask by a pipet or glass syringe. Crude **2a** was then distilled immediately to give >99% pure **2a** in 55% yield. The partially evacuated receiver flask was wrapped in cotton insulation and placed in a glass container which was placed in a freezer for 24 h whereupon **2a** crystallized out as a white solid. ^{1}H NMR (C_6D_6): 1.05 (d, 6H, CH_3, J = 3 Hz), 1.08 (d, 6H, CH_3, J = 3 Hz), 1.56 (d, 1H, NH, J = 38 Hz), 2.53-2.69 (m, 12H, CH_2CH_2N), 3.40 (septet, 2H, CH, J = 6 Hz); ^{31}P NMR (C_6D_6): 110.5 (s); ^{13}C NMR (C_6D_6): 22.46 (d, CH_3, J = 5 Hz), 22.55 (d, CH_3, J = 5 Hz), 38.60 (d, CH_2NH, J = 7 Hz), 39.17 (d, CH_2NP, J = 4.7 Hz), 51.90 (d, NCH, J = 53.1 Hz), 53.74 (d, CH_2N, J = 1.9 Hz), 54.63 (s, CH_2N). Elemental analysis: Anal. Calcd: C, 55.79; H, 10.53; N, 21.68. Found: C, 55.21; H, 10.82; N, 21.56. HRMS: Anal. Calcd: 258.19734. Measured: 258.19758.

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[19] The mol of **4a** in the mixture of **4a** and **4b** was determined as follows: The area under the multiplet at 2.70 ppm (assigned to CH of **4a** and **4b**) was set to unity and the area under the triplet at 2.26 ppm (assigned to the $C\underline{H}_2NH_2$ of **4a**) was found to be z as determined by the ^{1}H NMR integration of the distilled mixture of **4a** and **4b**. Hence the ratio mol **4a**/mol **4b** = 2z/3z(1-z) can be calculated. Letting x and y equal the weight in g of **4a** and the weight in g of **4b** in the mixture, respectively, we have that the mole ratio **4a**/**4b** is also 230y/272x where the molecular weights of **4a** and **4b** are 230 and 272 g/mol, respectively. Since the total weight of the mixture is known, the simultaneous equations provide the solution for x and y from which the total volume of hexanes in mL is {(mol of **4a** /0.32 M) - (g of **4b**)/ 0.92} where the density of **4b** = ~ 0.92 g/mL.