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An Improved Synthesis of the Strong Base $P(MeNCH_2CH_2)_3N$

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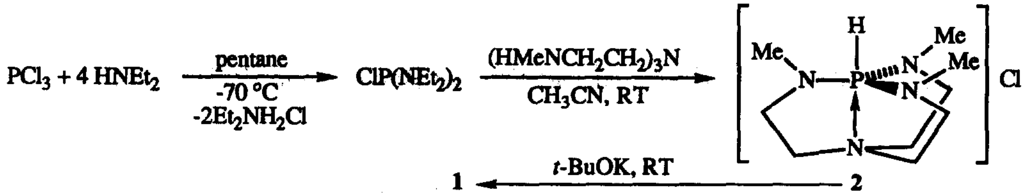
Abstract: The proazaphosphatrane $P(MeNCH_2CH_2)_3N$ is synthesized in high yield from $(HMeNCH_2CH_2)_3N$ and $ClP(NEt_2)_2$. The last compound is synthesized from inexpensive PCl_3 and $HNEt_2$.

Strong non-ionic bases play an important role in organic synthesis because of the milder reaction conditions they generally permit,[1] the enhanced reactivity of the more naked anions in the poorly associated ion pairs formed upon substrate deprotonation by such bases (in contrast to ionic bases),[2] and the better solubility of non-ionic bases in organic solvents at room temperature and below required for some reactions.[3] The title compound **1** is a very useful exceedingly strong non-ionic base[4] as well as a superior catalyst for the conversion of isocyanates to industrially relevant isocyanurates.[5] We earlier reported the synthesis of **1** from $ClP(NMe_2)_2$,[4] which was formed from PCl_3 and the relatively quite expensive reagent $P(NMe_2)_3$. It was therefore deemed important to design a more economical and efficient method to synthesize **1** in order to facilitate its wider utilization. Here we report that **1** can be synthesized in high yield from $(HMeNCH_2CH_2)_3N$ and $ClP(NEt_2)_2$.[6,7] The latter compound is about 800 times cheaper per mole than $P(NMe_2)_3$, thus rendering the synthesis of $ClP(NEt_2)_2$ over 130 times cheaper than $ClP(NMe_2)_2$ on a molar basis.

The reaction of one molar equivalent of $(HMeNCH_2CH_2)_3N$[4b] with $ClP(NEt_2)_2$ in Scheme 1 gave ^{31}P and ^{1}H NMR spectroscopically pure **1** in 81% yield in a one-pot reaction. Although $ClP(NEt_2)_2$ is more sterically hindered than $ClP(NMe_2)_2$, it is still sufficiently reactive to complete its condensation with $(HMeNCH_2CH_2)_3N$ in 1 h. New applications of **1** and its derivatives in organic synthesis as a potent proton abstractor or catalyst are currently being investigated in our laboratories.

Scheme 1



The one-pot synthesis of **1** is initiated by adding via a syringe to a stirred solution of $ClP(NEt_2)_2$ (5.5 g, 26 mmol) in 100 mL of dry CH_3CN 5.0 g of $(HNMeCH_2CH_2)_3N$ (26 mmol) over 5 min. After stirring the reaction mixture at RT for 1 h, the solution was transferred by syringe or cannula to a 500 mL flask containing *t*-BuOK (4.8 g, 42 mmol) in dry CH_3CN (20 mL). After stirring the reaction mixture for 1 h at room temperature, the solvent was removed under vacuum and the residue was extracted overnight while stirring with 480 mL of dry pentane which was transferred in by cannula. The extract was transferred by cannula to another flask and evaporated in vacuo to give a white solid which was purified by vacuum sublimation (50 °C/1 Torr) giving ^{31}P NMR and ^{1}H NMR spectroscopically pure proazaphosphatrane **1**[4a] (4.6 g, 81%).

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7. $ClP(NEt_2)_2$ was synthesized according to reference 6 with the modifications that dry benzene was used as the reaction solvent, and the salt formed was removed by filtration under vacuum using a medium frit in a closed system protected from moisture and was washed several times with dry pentane under nitrogen. As a result, the yield was raised from 71% to 85%.

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