A Facile Approach to *N*-Unsubstituted Phosphinimines

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Phosphine oxides ($R_3P{=}O$) are conveniently converted into phosphinimines ($R_3P{=}NH$) by recycling several times through the sequence: triflic anhydride; ammonia; evaporation. Half of the triflic anhydride is used at each repeat.

While the common procedure for making *N*-substituted phosphinimines is the Staudinger reaction of azides and phosphines ($R_3P{:} + R'N_3 \rightarrow R_3P{=}NR'$),[2] the unsubstituted phosphinimines ($R_3P{=}NH$) are more difficult to prepare since their salts are often hygroscopic and easily hydrolyzed to the oxide. Trimethylsilyl azide[3] and hydroxylamine *O*-sulfonic acid[4] have been used, reacting with phosphines in modified Staudinger preparations. Instead of these reactions which oxidize the phosphine, we sought a simple replacement of NH for the oxygen of the phosphine oxide. This has previously been done using first phosgene on the oxide to prepare the hygroscopic chlorophosphonium chloride, followed by ammonia.[5] Our preparation of phosphonium anhydrides[6] by the reaction of 2 mol of phosphine oxide with 1 mol of triflic anhydride (Eq. 1) offered an easy alternative since the anhydrides react rapidly with ammonia (Eq. 2) to give the triflate salt of the phosphinimine.

$$2R_3PO + (CF_3SO_2)_2O \rightarrow (R_3P^+)_2O, 2CF_3SO_2O^- \qquad (1)$$

$$(R_3P^+)_2O + NH_3 \rightarrow R_3P{=}NH_2^+ + NH_4^+ + R_3PO \qquad (2)$$

$$\text{recycle:} \quad \nwarrow\!\!\text{———} + 1/2\ (CF_3SO_2)_2O \text{———}\!\!\nearrow$$

Because of the double nature of anhydrides this ammonolysis necessarily releases half the original phosphine oxide. However, both the formation of the phosphonium anhydride and its reaction with excess ammonia proceed quantitatively and require only 5–10 minutes each. Therefore, the phosphine oxide can be recycled by successive reactions to complete its conversion into the phosphinimine. After evaporation of the excess ammonia and solvent, half as much triflic anhydride in dichloromethane is added for each cycle. The phosphonium anhydride is selectively formed each time; no evidence of any phosphoranylidene $(R_3P^+)_2N^-$ was observed. Addition of excess ammonia then converts the anhydride into more phosphinimine and phosphine oxide, as indicated below Eq. 2.

Thus n repetitions yields $1 - (0.5)^n$ equivalents of imine and $(0.5)^n$ equivalents of phosphine oxide. For six cycles the yield of imine is theoretically 98.4%, for eight cycles, 99.6%. A further advantage of the procedure is that the triflate salts formed are not hygroscopic and they may be neutralized non-aqueously to avoid hydrolysis, simply distilling the product imine if desired. While the triphenylphosphinimine survived an aqueous workup, the tris(dimethylamino)phosphinimine was too sensitive and is also difficult to separate from its oxide by distillation.

Triphenylphosphinimine Cycle:

Ph_3PO (3.245 g, 11.5 mmol) was dissolved in CH_2Cl_2 (25 mL). Tf_2O (1.622 g, 0.96 mL, 5.75 mmol) was added dropwise via syringe, and a precipitate formed within 5 min. NH_3 was bubbled through the slurry for 10 min., and the solid dissolved. The solvent and NH_3 were removed in vacuo for 10 min to yield a semisolid. This represents one complete cycle. The cycle was repeated as follows: the semisolid was again dissolved in CH_2Cl_2 and Tf_2O (0.811 g, 0.48 mL, 2.88 mmol) was added dropwise via syringe, forming a precipitate within 5 min. NH_3 was bubbled through the slurry for 10 min and the solid dissolved. Removal of solvent in vacuo for 10 min again yielded a semisolid. The cycle was repeated 6 more times. Each time half as much Tf_2O was added as the time before. The semisolid triflate salt was dissolved in CH_2Cl_2 and neutralized by washing twice with 1 M aq NaOH, then twice with water, and once with brine, and dried (Na_2SO_4). The solvent was removed in vacuo to yield the known free base, triphenylphosphinimine[3] as a white solid, which was recrystallized from cyclohexane (2.36 g. 82%), mp 124–126 °C (Lit.[3] 126 °C).

The $P{=}N$ bond appeared in the IR spectrum at $\nu = 1190\ \mathrm{cm}^{-1}$ as in ref. 3.

^{31}P NMR (DMSO): $\delta = 21.9$.[7]

Tris(dimethylamino)phosphinimine Cycle:

The cycle above was repeated 6 times using hexamethylphosphoramide (HMPA) (4.46 g, 4.3 mL, 25 mmol) and triflic anhydride in comparable stoichiometric quantities, i.e., 12.5 mmol in the first pass, and half for each repeat, a total of 25 mmol. After the cycles were complete, the free base phosphinimine was purified directly just by distillation from 3 M methanolic KOH at 85 °C./1.5 Torr;[3] yield 4.0 g (90%).

The IR (neat) exhibited a $P{=}N$ band at $\nu = 1104\ \mathrm{cm}^{-1}$.

MS: $m/z = 178$, as in ref. 3.

^{31}P NMR (DMSO): $\delta = 42.3$.[8]

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