PREPARATION OF ARYLAMINES USING DIPHENYL PHOSPHORAZIDATE (DPPA)

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We have already reported[1] that diphenyl phosphorazidate (DPPA, $(PhO)_2P(O)N_3$) reacts with the Grignard reagent prepared from chloromethyltrimethylsilane to give trimethylsilyldiazomethane ($TMSCHN_2$, $(CH_3)_3SiCHN_2$), a stable and safe substitute for hazardous diazomethane, by a diazo-transfer reaction.

$$(CH_3)_3SiCH_2Cl \xrightarrow{Mg} [(CH_3)_3SiCH_2MgCl] \xrightarrow{(PhO)_2P(O)N_3} (CH_3)_3SiCHN_2$$

We now discovered that DPPA reacted with Grignard reagents prepared from aromatic halides to yield labile triazene intermediates, which were conveniently transformed to aromatic primary amines by the reduction with sodium bis(2-methoxyethoxy)aluminum hydride or lithium aluminum hydride. Aromatic lithium compounds were also converted to aromatic primary amines by the treatment with DPPA followed by the hydride reduction.

$$\left.\begin{matrix} Ar\text{-}MgBr \\ or \\ Ar\text{-}Li \end{matrix}\right\} \xrightarrow{(PhO)_2P(O)N_3} [Ar\text{-}N{=}N\text{-}\underset{M}{N}\text{-}P(O)(OPh)_2] \xrightarrow{NaAlH_2(OCH_2CH_2OCH_3)_2} ArNH_2$$

M= MgBr or Li

Application of the method to the preparation of heteroaromatic primary amines will be presented.

1) S. Mori, I. Sakai, T. Aoyama, and T. Shioiri, Chem. Pharm. Bull., 30, 3380 (1982).