Annulation Reactions Catalyzed by Amberlite-Bound Hexafluorophosphate

Significance: Amberlite resin-bound hexafluorophosphate (Amberlite-PF$_6$) was prepared by treatment of Amberlite 900 with aqueous NaPF$_6$ (eq. 1). In the presence of Amberlite-PF$_6$, the annulation of phenylenediamines 1 with aldehydes 2 took place to give the corresponding benzimidazoles 3 (25 examples, 72–96% yield).

Comment: The binding of hexafluorophosphate on Amberlite resin was confirmed by IR spectra (557 and 832 cm$^{-1}$), though other characterizations were not given. Phenylenediamines 1 also reacted with α-bromoketones 4 in the presence of Amberlite-PF$_6$ to give the corresponding quinoxalines 5 via an aromatization step.

**Selected examples:**

- **1** with **2** for benzimidazoles 3: 96% yield (r.t., 1 h), 88% yield (r.t., 2 h), 79% yield (r.t., 8 h), 82% yield (90 °C, 14 h), 84% yield (r.t., 4 h), 78% yield (r.t., 5 h), 68% yield (r.t., 8 h).

- **1** with **4** for quinoxalines 5: 94% yield (6 h), 86% yield (6 h), 84% yield (7 h), 98% yield (6.5 h), 58% yield (6 h).