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Visible-Light-Promoted Reactions of Organoborates with Imines
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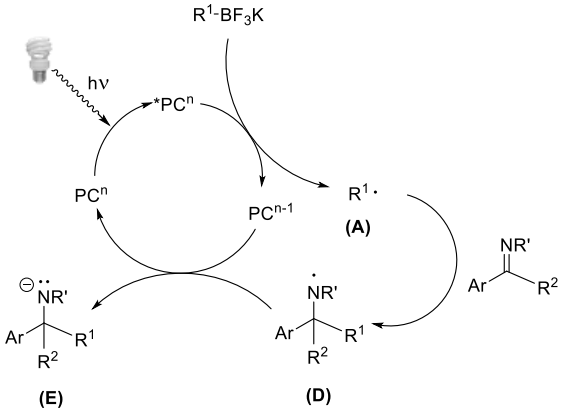
Overview

The goal of this work is to develop the visible light-promoted reaction of potassium organoborates (R-BX_3K, X = F or OR′) with imines (R_2C=NR′). If successful, this would extend the applicability of visible light photoredox catalysis and represent a novel approach to the formal addition of potassium organoborates to imines, a desirable goal given the properties of organoborates, such as their stability, availability, ease of preparation, and functional group tolerance. The mechanistic hypothesis is shown in Figure 1 (PC = photocatalyst).

Figure 1. Mechanistic Hypothesis for the Addition of RBF_3K to Imines using Visible Light Photoredox Catalysis.

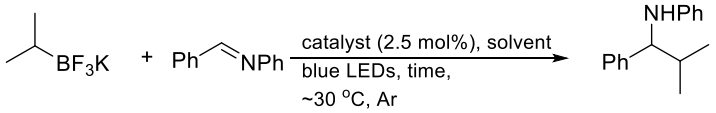


Year 2 Results

Evaluation of Alternative Catalysts and Solvents

Because of the much lower cost of organic photocatalysts (~$50/mmol for acridinium-based catalysts vs ~$1000/mmol for Ir-based catalysts), we desired to explore the use of organic photocatalysts in our previously developed protocol. Using the reaction of potassium isopropyltrifluoroborate (**1a**) with benzalaniline (**2a**), we evaluated several alternative catalysts (organic and inorganic) and solvents (CH_2Cl_2, dioxane, THF, CH_3CN, DMF, DMSO). Our results indicate that, in CH_2Cl_2 solvent, the organic photocatalysts 9-mesityl-10-methylacridinium tetrafluoroborate (***Mes-Acr-Me***) and 9-mesityl-10-phenylacridinium tetrafluoroborate (***Mes-Acr-Ph***) performed equally well in this protocol, giving ~95% conversion of starting material and resulting in an 88% yield (by NMR) of product **3aa** after 46 h. (Table 1). Since ***Mes-Acr-Me*** is much easier for us to obtain commercially, we chose to use it for further scope and limitations work.

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3aa**

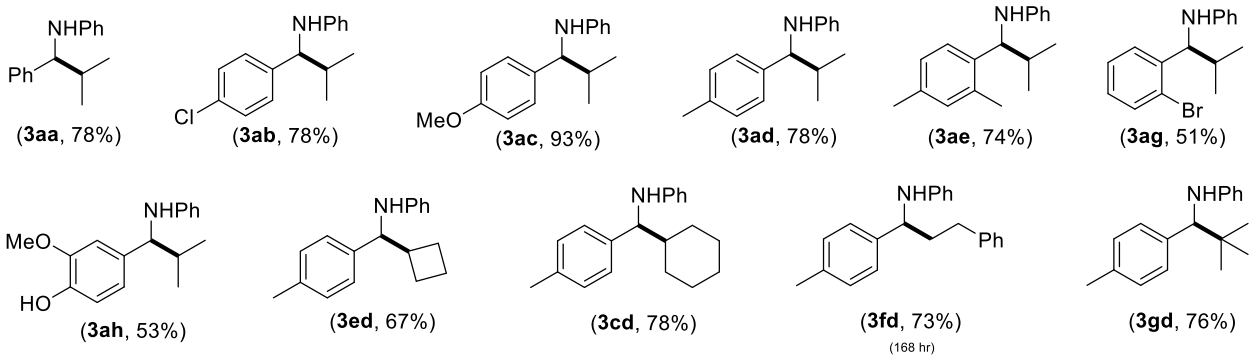
Entry	Catalyst	Solvent	Time (h)	Yield 3aa (%)[b]	Recovered 2a (%)[b]
1	***Ir-dF(CF3)-dtb***	CH_2Cl_2	20	49	31
2	***Ir-dF(CF3)-dtb***	Dioxane	20	47	13
3	***Ir-dF(CF3)-dtb***	DMF	20	8	47
4	***Ir-dF(CF3)-dtb***	DMSO	20	9	31
5	***Ir-dF(CF3)-dtb***	MeCN	20	4	76
6	***Ir-dF(CF3)-dtb***	THF	20	40	0
7	***Ir-dF(CF3)-dtb***	CH_2Cl_2	46	77	13
8	***Ir-dF(CF3)***	CH_2Cl_2	46	72	0
9	***Mes-Acr-Ph***	CH_2Cl_2	46	88	6
10	***Mes-Acr-Me***	CH_2Cl_2	46	88	4
11	***Mes-Acr-Me***	CH_2Cl_2	20	0	72
12	***4-CzIPN***	CH_2Cl_2	46	78	15
13	***DCA***	CH_2Cl_2	46	20	49

[a]Reaction conditions: **1a** (0.38 mmol), **2a** (0.25 mmol), catalyst 0.0063 mmol), solvent (5 mL), blue LEDs, rt, Ar. [b] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]No light.

Scope and Limitations

Several imines and potassium organotrifluoroborates were evaluated for competency in the protocol using the optimized conditions determined above. Preliminary results are shown in Table 2.

Table 2. Scope and Limitations



The protocol appears to be applicable to broad range of substituted aldimines. As observed in our previous work with the Ir-based photocatalyst ***Ir-dF(CF$_3$)-dtb***, a range of potassium alkyltrifluoroborates were also shown to be competent reaction partners, and extended reaction time was necessary to complete the reaction with potassium phenethyltrifluoroborate, presumably because it required formation of the less stable primary radical.

Competition Studies

We are currently attempting to understand the substituent effects on the reaction using competition experiments. Preliminary results indicate poor correlation with σ, or σ^+, but there seems to be good correlation with σ_α· (Dust and Arnold *JACS* **1983**, *105*, 1221).

Career Impact

During this grant year, ACS-PRF travel funds were used to support my attendance at the National Organic Symposium in Bloomington, IN. Undergraduate student stipends were used to support three undergraduate students during the 2018-19 academic year and the summer of 2019. Two students presented their results at SERMACS 2018 in Augusta, GA in November, 2018. One will present his latest results at SERMACS 2019 in Savannah, GA; and again at NC Photochem at Appalachian State University. One graduated in May 2019 with a BS in Chemistry, and one was able to secure a summer 2019 REU position at UNC Charlotte.