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2-Halogenoimidazolium Salt Catalyzed Aza-Diels–Alder Reaction through Halogen-Bond Formation

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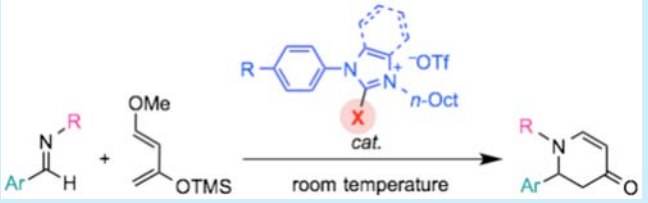
Supporting Information

ABSTRACT: 2-Halogenoimidazolium salts are found to catalyze aza-Diels–Alder reaction of aldimines with Danishefsky diene in an efficient manner. Comparative studies and titration experiments support the formation of halogen bonding between imines and catalysts.



Halogen bonding (XB), which refers to any noncovalent interactions operating between an electrophilic region developed on a halogen atom (X) of R–X (R = any atoms or a group of atoms) and Lewis bases (LBs),[1,2] dates back to the discovery of $NH_3\cdots I_2$ complex by Guthrie in 1863.[3] Despite the pioneering crystallographic works of Hassel in the 1960s,[4] XB had been almost forgotten until Resnati and Metrangolo demonstrated the high capability of perfluorohalocarbons to function as XB donors in the crystal engineering field.[5] Since then, XB has been recognized as a powerful tool in supramolecular chemistry, albeit mostly in the solid state.[5] Compared to the studies on XB *in the solid state*, the application studies of XB *in the solution phase* have sluggishly progressed over the last two decades,[6] encompassing the construction of XB-induced molecular recognition systems such as anion receptors,[7] self-assembling architectures,[8] and anion transporters.[9] Additionally, in terms of medicinal chemistry, it should be noted that XB plays an important role in the recognition of halogenated substrates by biopolymers such as proteins and DNAs.[10]

Nevertheless, application studies of XB in the field of organic synthesis and catalysis have been less explored.[11−18] In light of the linearity and the strength of XB comparable to hydrogen bonding (HB), XB donors should serve as unique organocatalysts in organic reactions. The milestone in this field was set by Bolm and co-workers in 2008 by demonstrating the catalytic capability of highly fluorinated alkyl halides (bromides or iodides) in the reduction of 2-substituted quinolines by a Hantzsch ester,[11a] although the involvement of hidden Brønsted acid catalysis[19] was not completely ruled out. Since then, several examples, in which XB donors activate organic substrates through the formation of XB, have been reported: bis(2-iododihydroimidazolium) salt catalyzed hydrogen transfer to C=N bonds;[11b] ICl_3-catalyzed ring-opening polymerization (ROP) of L-lactide;[12] neutral multidentate XB donor catalyzed nucleophilic substitution reaction of 1-chloroisochroman.[13,14] Herein, we disclose the XB catalysis of 2-halogenoimidazolium salts in the aza-Diels–Alder reaction of aldimines with Danishefsky diene. As a closely related work, more recently, the Huber group has reported bis(2-iodoimidazolium) salt catalyzed classical Diels–Alder reaction of an enone with cyclopentadiene.[20]

Over the past few years, we have developed oxidative homo- and cross-dimerization of aromatic amines leading to aromatic azo compounds,[21] in which we proposed the XB formation between aromatic amines with an electrophilic iodinating reagent (*t*-BuOI) plays an important role in the selective recognition of amine substrates. During continuous studies in the utilization of XB in organic synthesis, we became interested in the catalysis of monovalent iodine organic compounds. Keeping in mind that aza-Diels–Alder (DA) reactions allow for atom-economical access to biologically valuable saturated aza-heterocyclic compounds in a single step from readily available imines with diene components,[22] we chose the aza-DA reaction as a probe to explore XB donor-catalyzed reactions.

Our preliminary research began with identifying appropriate XB donors that are able to serve as a catalyst in aza-DA reaction, applying *N*-phenylbenzaldimine (**1a**) and Danishefsky diene (**2**) as the model reactants (Table 1). A blank experiment showed that no reaction took place in the absence of the third component at room temperature (entry 1). The addition of a catalytic amount of perfluoroalkyl iodide and perfluoroiodobenzene, which are representative XB donors in the crystal engineering field,[5] resulted in no reactions (entries 2 and 3). Hence, we then turned our attention to the use of more powerful XB donors as a catalyst. Recently, Huber and co-workers have reported that 2,2′-diiodoimidazolium salts function as a bidentate XB donor to strongly bind to halides (K_a 10^4–10^5 mol^{-1} order).[14,23] Impressed by their elegant works, we designed and synthesized XB donors **A**–**C** (Table 1) as a catalyst based on the blueprint as follows:[24] (1) a highly electron-deficient imidazolium core would facilitate the formation of a strong XB through largely developed "σ hole";[2d] (2) monodentate XB-donor structure would offer a

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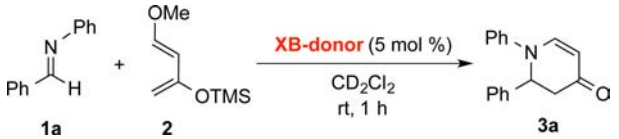
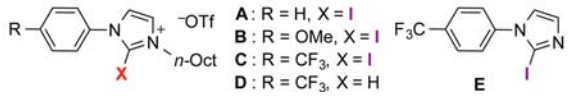
Table 1. Screening of XB-Donor Catalysts[a]

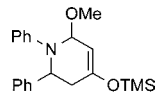


entry	XB-donor	additive	**3a** (%)[b]
1	–	–	0
2	$CF_3(CF_2)_7$–I	–	0
3	C_6F_5–I	–	0
4	**A**	–	57[c]
5	**B**	–	41[c]
6	**C**	–	85[c]
7	**D**	–	0
8	**E**	–	0
9	**C**	K_2CO_3 (10 mol %)	80[c]
10	–	*n*-Bu_4NOTf (5 mol %)	0
11	**C**	*n*-Bu_4NCl (5 mol %)[d]	0

structure of XB-donors



[a]Reaction conditions: **1a** (0.125 mmol), **2a** (0.15 mmol), and XB donor (6.25 μmol) were mixed in CD_2Cl_2 (0.50 mL) at room temperature, stirred for 1 h, and analyzed with ^{1}H NMR. [b]Mole fraction of **3a** × 100 (%) determined by ^{1}H NMR integration. [c]Trace amounts of adduct **4a** were observed. [d]*n*-Bu_4NCl was premixed with **C** before **1a** and **2** were added.



4a

geometrically suitable binding site for bent-type molecules like imines to fit in; (3) a long alkyl attachment to an imidazolium nitrogen would allow the ionic entity for solubilization in various organic solvents.[23] To our delight, in the presence of catalyst **A**, the desired DA reaction proceeded moderately even at room temperature within 1 h, producing **3a** in 57% yield with 43% recovery of imine **1a** (entry 4). As the σ_p value of the substituent on the benzene unit of 2-iodoimidazolium salt increased (σ_p (OMe) −0.27, σ_p (H) 0, σ_p (CF_3) 0.54),[25] the yield of **3a** was enhanced (entries 4−6), showing good agreement with the general tendency in the strength of XB: XB becomes stronger as the organic part of R−X becomes more electron-deficient.[2] As a proof of the catalyst design, the reaction using an iodine-free imidazolium salt **D** did not give **3a** at all (entry 7). The cationic structure was also found to be indispensable for the catalytic reaction (entry 8). The possibility of hidden Brønsted acid (TfOH) catalysis,[19] which might be generated by the hydrolysis of imidazolium salts by moisture or the E2 elimination from octyl moiety, was excluded by the experiment of adventitious addition of K_2CO_3 (entry 9). Furthermore, the involvement of Lewis base catalysis of the counteranion (TfO^-) to activate Danishefsky diene was also excluded by the experiment of *n*-Bu_4NOTf addition (entry 10). Furthermore, the catalysis through XB formation was supported by the fact that the reaction was completely inhibited by the addition of Cl^- (entry 11).[13] The formation of XB between **C** and Cl^- was also confirmed by the upfield shift of ^{1}H NMR resonances of aromatic C−H of the imidazolium ring.[26]

To investigate the effect of halogen on the 2-position of imidazolium salts and the core structure of catalyst, the reaction profiles in the presence of a catalytic amount of imidazolium salts **C**, **F**, and **G** and benzimidazolium salt **H** were monitored by ^{1}H NMR (Figure 1). The variation in halogen element at the C-2

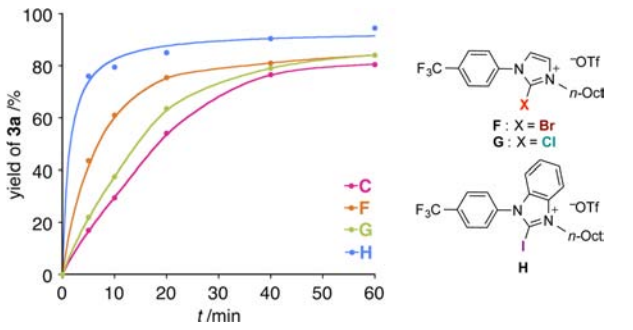


Figure 1. Reaction profiles.

position (**C**, **F**, and **G**) gave a slightly complex result in terms of the initial reaction rates [**F** (Br) > **G** (Cl) >**C** (I)], which does not follow the general strength of XB (I > Br > Cl).[2] Although this unusual discrepancy should await further investigation, the possibility of the cooperative involvement of some other noncovalent interactions along with XB such as cation−π[27] and van der Waals interactions in these catalytic systems cannot completely ruled out at this moment. Regarding the effect of structural variation, a significant acceleration effect was observed when 2-iodobenzimidazolium salt **H** was applied as a catalyst (blue line in Figure 1). This acceleration effect can be reasonably interpreted in terms of the carbon acidity of related imidazolium salts (pK_a of *N*,*N*′-dimethylimidazolium: 22.3 in H_2O, pK_a of *N*,*N*′-dimethylbenzimidazolium: 21.6 in H_2O).[28]

For deeper understanding of the interactions operating in the unique organocatalytic systems, we then performed titration experiments of imidazolium salts with imines in CD_2Cl_2 using the ^{1}H NMR technique.[26] Figure 2a illustrates plot and fitting isotherm curve for the titration of **C** as a representative result. As imine **1a** was added to the CD_2Cl_2 solution of **C** (50 mM), the resonances corresponding to the methylene (H^a) as well as imidazolium hydrogens (H^b and H^c) were shifted to the upper

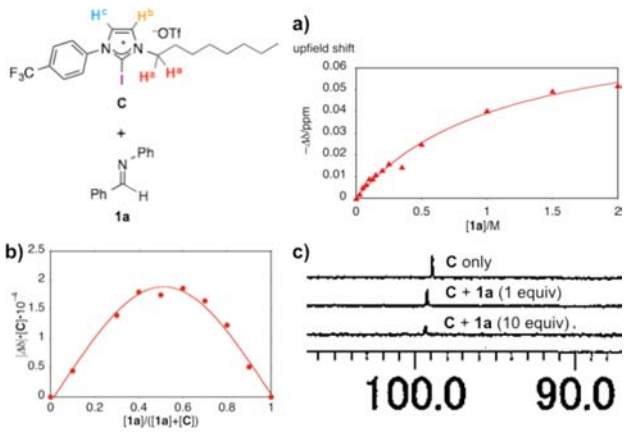


Figure 2. (a) Titration plot (H^a of **C**); (b) Job's plot (H^a of **C**); (c) ^{13}C NMR titration of **1a** with **C** (the 2-position carbon of **C**).

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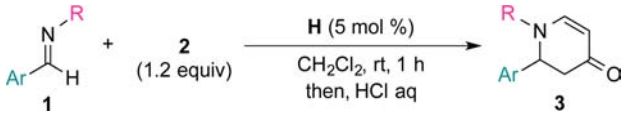
field regime (Figure 2a), suggesting the increased electron density of the imidazolium ring through XB formation. Furthermore, Job's plot indicated that the complex is composed of 1:1 stoichiometry (Figure 2b). Therefore, the binding constant for the 1:1 complexation [**C**·**1a**] was determined to be K_a 0.93 M^{-1} by fitting the data to the 1:1 binding model. On one hand, the titration of iodine-free imidazolium salt **D** with **1a** exhibited a downfield shift of the 2-H resonance of the imidazolium ring, suggesting the operation of hydrogen bonding between 2-H and **1a** (K_a 0.45 M^{-1}). Likewise, the other 2-halogenoimidazolium salts were titrated with imine **1a** to provide the binding constants (K_a for [**F**·**1a**]: 1.19 M^{-1}, K_a for [**G**·**1a**]: 0.97 M^{-1}, K_a for [**H**·**1a**]: 1.59 M^{-1}). The order of binding constants follows the order of initial reaction rates (**H** > **F** > **G** > **C**). Furthermore, the XB formation between 2-iodoimidazolium salt **C** and imine **1a** was strongly supported by the ^{13}C NMR titration (Figure 2c):[26] as imine **1a** was added to a CD_2Cl_2 solution of **C**, the resonance corresponding to the iodine-connected carbon (*C*–I: δ 98.92 ppm) of **C** was shifted to the downfield regime (e.g., when 1 equiv of **1a** was added, $\Delta\delta$ = +0.33 ppm; when 10 equiv of **1a** was added, $\Delta\delta$ = +0.63 ppm) while other resonances did not move.[29]

The synthetic versatility of XB donor-catalyzed aza-DA reaction was demonstrated by applying various aromatic imines to the reaction conditions (Table 2). Despite the electronic

Table 2. Scope of Aldimines[a]

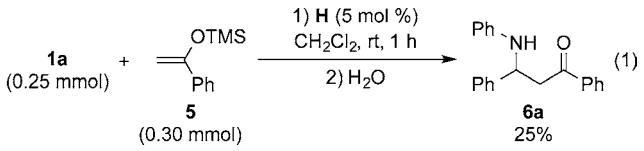


entry	1	Ar	R	3[b] (%)
1	**1b**	*p*-$MeOC_6H_4$	Ph	**3b** (74)
2	**1c**	*p*-MeC_6H_4	Ph	**3c** (68)
3	**1d**	*p*-$O_2NC_6H_4$	Ph	**3d** (67)
4	**1e**	*p*-BrC_6H_4	Ph	**3e** (70)
5	**1f**	2-pyridyl	Ph	**3f** (47)
6	**1g**	Ph	*p*-$MeOC_6H_4$	**3g** (68)
7	**1h**	Ph	*p*-ClC_6H_4	**3h** (65)
8[c]	**1i**	Ph	Me	**3i** (36)
9[c]	**1j**	Ph	Bn	**3j** (34)

[a]Reaction conditions: **1** (0.25 mmol), **2a** (0.3 mmol), and cat. **H** (12.5 μmol) in CH_2Cl_2 (0.1 mL) at room temperature for 1 h. [b]Isolated yields. [c]**C** (5 mol %) was used as a catalyst, and MeCN (0.1 mL) was used as a solvent.

structures of Ar and R moieties of **1**, the reaction proceeded smoothly to produce the corresponding 2,3-dihydropyridinones **3** in good to high yields (entries 1–7). In addition to *N*-arylimines, *N*-alkylimines **1i** and **1j** were also applicable to the DA reaction to give **3i** and **3j**, albeit in modest yields (entries 8 and 9). In terms of diene substrates, however, no product was formed with other dienes like cyclohexadiene, 2,3-dimethyl-1,3-butadiene, and furan. Furthermore, the catalytic system was found applicable to the Mannich-type reaction of **1a** with **5** in the presence of 2-iodobenzimidazolium salt **H** as a catalyst to give **6a** in 25% yield (eq 1), although conditions are not fully optimized.[30]

In conclusion, we have revealed that 2-halogenoimidazolium salts efficiently catalyze aza-Diels–Alder reaction of aldimines with Danishefsky diene. Comparative studies supported the halogen bonding formation in the catalytic systems. Further



investigation of reaction mechanism and the development of reactions catalyzed by XB donor systems are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data of all new compounds, NMR charts, Job's plot, and titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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