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NIS-Assisted Aza-Friedel–Crafts Reaction with α-Carbamoysulfides as Precursors of *N*-Carbamoylimines

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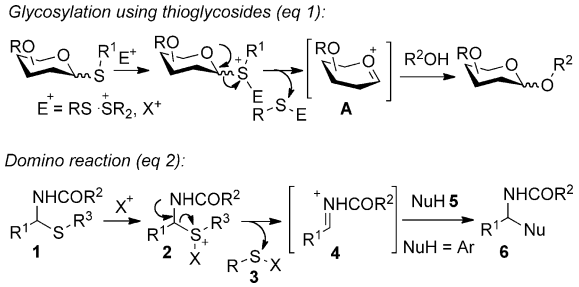
Abstract: A general and practical *N*-iodosuccinimide (NIS)-promoted aza-Friedel–Crafts reaction of various aromatic nucleophiles with *N*-acylimines generated in situ from α-amidosulfides to give a rapid access to highly functionalized amines is described. The newly developed methodology is very mild, fast, efficient, and complementary.

The *N*-acyl and *N*-carbamoylimines are one of the most important reactants for the preparation of nitrogen-containing building blocks.[1] However, their instability renders extremely laborious the handling of these activated imines. In this context, a number of researchers have reported the use of stable *N*-acyl and *N*-carbamoylimine precursors as efficient alternative strategy. Among them, α-amidoethers,[1e,2] α-amidosulfones,[3] α-amidoalkyl benzotriazoles,[4] bisamides,[5] and α-amidosufides[6,7] have been widely used to generate imines (or iminium ions) under basic or acidic conditions. Although above-mentioned elegant methods are effective, application of these protocols to sensitive, acid/base-labile or polyfunctional imines is limited. Therefore, the development of a mild method for the generation of imines from stable precursors is still required.

Recently, we have developed a novel one-pot three-component synthesis of α-aminosulfides (or *N*,*S*-acetals). We have demonstrated that phosphoric acids in catalytic amounts were able to promote the *N*-acyliminium formation as well as the Friedel–Crafts alkylation of 3-susbtituted indoles.[8] However, while the conditions used are quite mild, the presence of acid catalyst restricts its application. We therefore decided to explore the feasibility of a one-pot imine formation/Friedel–Crafts reaction under acid/base-free conditions.

Interestingly, thioglycosides (*S*,*O*-acetals) are currently one of the most commonly used glycosyl donors in glycosidation chemistry. Various promoter systems have been developed for efficient chemoselective activation of *S*,*O*-acetals to generate an oxocarbenium ion **A** that can react with various acceptors to form a glycosidic bond (Scheme 1a).[9] While early methods utilized metal salts as promoters,[10] recent work has allowed the development of milder and efficient strategies, using, for instance, sulfonium ($RS-S^+R_2$)[9,11] and halonium (X^+)[9,12] ion activators. Inspired by these seminal contributions, we envisioned that a soft electrophilic reagent, such as halonium activators X^+ could be efficient candidates to promote the formation of *N*-acyliminium **4** from α-aminosulfides **1** under neutral conditions (Scheme 1b). Indeed, the electrophilic ion might react with the sulfur atom of **1** forming an activated halosulfonium ion **2**. This reactive complex then could collapse into an *N*-acyliminium ion **4**, which can proceed with nucleophiles to form the addition product **6** and a sulfenyl halide compound **3**. For this study, arene nucleophile **5** was selected to allow a novel efficient access to monoalkylated aza-Friedel–Crafts product **6**, which is found in numerous biologically active molecules. Herein, we report a novel aza-Friedel–Crafts reaction protocol of α-aminosulfides under mild and neutral conditions, using *N*-iodosuccinimide (NIS) in stoichiometric or catalytic amounts.



Scheme 1. Proposed work hypothesis.

To validate our hypothesis, we initially examined the reaction of *tert*-butyl *N*-[(ethylthio)phenylmethyl]carbamate (**1a**) with 1,3,5-trimethoxybenzene (**5a**) in the presence of several *N*-halosuccinimides as halonium sources in dichloromethane (Table 1). Results (Table 1, entry 1) showed that the use of NIS at 0 °C promoted only a degradation of **1a** and partial iodination of **5a** was observed.[12f–h,13] However, to our delight, the reaction was complete in less than 5 min at −78 °C and furnished the desired product **6a** in 94% yield. Although CH_2Cl_2 is presently the preferred solvent, the reaction also gives good results when other solvents are used, such as THF and $CHCl_3$. In addition, *N*-chlorosuccinimide (NCS, entry 3) and *N*-bromo-

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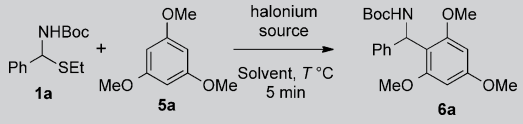
Table 1. Optimization of the activation/aminoalkylation reaction sequence.[a]



Entry	Halonium source	T [°C]	Solvent	Yield [%][b]
1	NIS	0	CH_2Cl_2	–[c]
2	NIS	−78	CH_2Cl_2	94
3	NIS	−50	$CHCl_3$	92
4	NIS	−78	THF	94
5	NCS	0	CH_2Cl_2	94
6	NBS	−35	CH_2Cl_2	90
7	–	25	CH_2Cl_2	trace

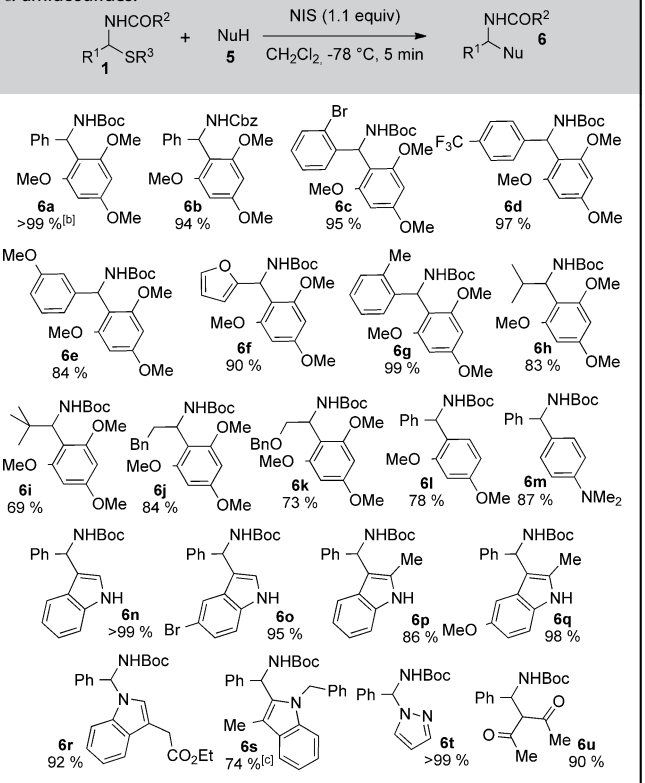
[a] Reaction conditions: amidosulfide **1a** (0.131 mmol), 1,3,5-trimethoxybenzene **5a** (0.157 mmol), and the halonium source (0.144 mmol) in 1 mL of solvent for 5 min. [b] Yields refer to chromatographically pure product. [c] Iodinated products of **5a** were formed. Boc = *tert*-butoxycarbonyl; NIS = *N*-iodosuccinimide; NBS = *N*-bromosuccinimide; NCS = *N*-chlorosuccinimide.

succinimide (NBS, entry 4) were also effective promoters at 0 and −35 °C, respectively, to conduct to **6a** with excellent isolated yields. In control reactions, in which *N*-halosuccinimide was omitted, a trace amount of product **6a** was observed (<5%), and the starting material was mainly recovered. It is noteworthy that the iodination of 1,3,5-trimethoxybenzene **5a** as well as the nucleophilic addition of succinimide were not observed, which demonstrates the high chemoselectivity of the reaction.

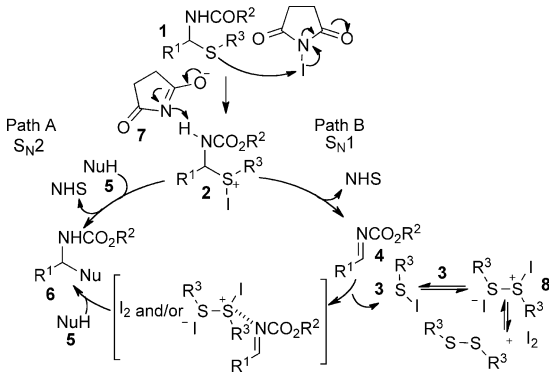
Encouraged by the excellent reactivity of α-amidosulfides as imine surrogates, we evaluated the scope of the Friedel–Crafts reaction to various nucleophilic aromatic partners. Under the optimum reaction conditions, aryls bearing electron-donating groups, such as 1,3-dimethoxybenzene (**6l**, 78% yield, Table 2) and *N,N*-dimethylaniline (**6m**, 87% yield) led to the formation of Fridel–Crafts products in excellent yields. Moreover, a range of heterocycles could be employed in the reaction system. Various indoles and pyrazole were examined with **1a**, and the results showed a good tolerance in this system (**6n–q**), although C_3-substituted indole and pyrazole led only to N-alkylated products **6r** and **6t**. Fortunately, the N-protected C_3-alkylated indole afforded the N-alkylated product **6s** in good yield. This reaction was not limited to aromatic nucleophile, acetylacetone was also tested, and it turned out that they could react with **1a** to give Mannich product **6u**, which demonstrated the broad scope of this transformation.

On the basis of the result that only a trace of product was obtained during the aza-Friedel–Crafts reaction of α-amidosulfides in the absence of NIS (Table 1, entry 7), we envisioned two plausible pathways for the formation of **6** (Scheme 2). Both are initiated by NIS activation of the α-amidosulfide to afford cationic amido-iodosulfonium intermediate **2**.[9,12] In one case, aryl might react with alkyl halides via an S_N2 mechanism. Alternatively, irreversible elimination of iodosulfonium ion and hydrogen abstraction by **7** might form the imine **4** which could then be activated by iodine and/or ethyl-iodo(alkylthio)-

Table 2. Substrate scope of the activation/aminoalkylation reaction of α-amidosufides.[a]

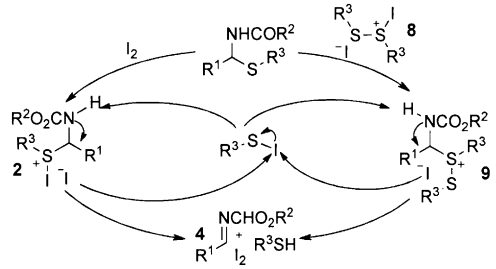


[a] Isolated yields. [b] From **1b** (R^3 = SPh). [c] Reaction conducted at −35 °C with only 0.67 equivalents of indole derivative.



Scheme 2. Putative mechanism.

sulfonium iodide **8** generated in situ from the decomposition of sulfenyl iodide compound **3**. Then, these species could act as Lewis acids to promote the Friedel–Craft reaction at this low temperature. In a control experiment, optically active α-amidosulfide afforded the Friedel–Craft product in a racemic form (see the Supporting Information). This experiment supports the S_N1 mechanism. A parallel experiment showed that no reaction takes place between the preformed imines and **5a** at −78 °C in the absence of NIS. Finally, the isolation of disulfides as well as purple coloration of the reaction medium provides

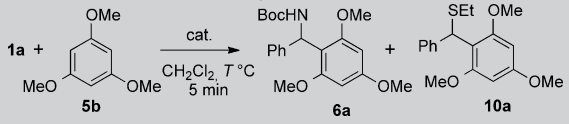


Scheme 3. Proposed catalytic mechanism.

support for the formation of iodine or sulfonium ion **8**. As these species are also highly electrophilic,[9,11] we hypothesized that they should also be able to promote the imine formation via reactive intermediates **2** and/or **9** (Scheme 3).[9,12j,l] In this case, the proton of **2** would be abstracted by sulfenyl iodide species **3** forming iodine and thiol as final products.

To verify the feasibility of these assumptions, an experiment with **1a** and 1,3,5-trimethoxybenzene (**5a**) in the presence of 10 mol% of NIS was performed (Table 3). While no reaction occurred at −78 °C (Table 3, entry 1), the reaction at 0 °C provided the desired product **6a** in 67% yield together with the sulfoalkylated product **10a** (29%). Much to our delight, when using only 0.1 mol% of NIS, the reaction was completed within 5 min to provide the desired product in 94% isolated yield (entry 5). We found that molecular iodine was also able to catalyze the reaction, although with slightly lower yields (entries 6–7). In addition, a very similar result was obtained when the reaction was performed in the presence of a catalytic amount of iodine and disulfide (entry 8). Moreover, contrary to our previous work (described above), unpleasant odor of thiol was observed at the end of the catalyzed reaction. These results seem to validate the catalytic cycle wherein the process is initiated by NIS and propagated by ethyl-iodo(alkylthio)sulfonium iodide **8** or I_2 (Scheme 3).[9,12j,l]

Table 3. Optimization of the catalytic process.[a]

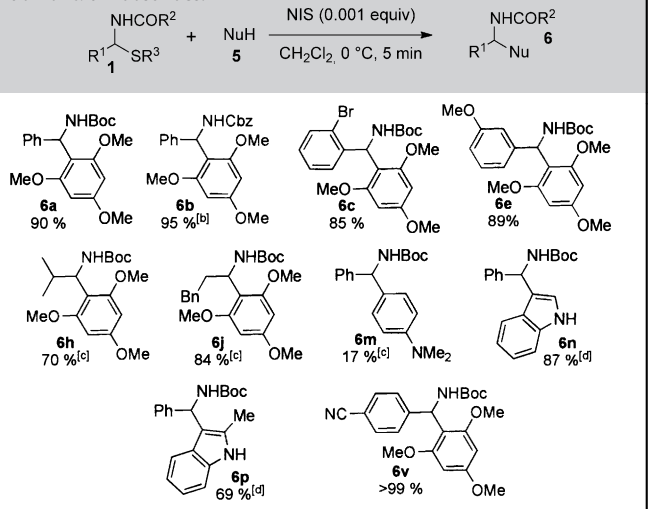


Entry	Halonium source	Loading [mol%]	T [°C]	Yield **6a** [%][b]	Yield **10a** [%][b]
1	NIS	10	−78	–	–
2	NIS	10	0	67	29
3	NIS	5	0	80	7
4	NIS	1	0	90	4
5	NIS	0.1	0	94	trace
6	I_2	1	0	82	6
7	I_2	0.1	0	84	5
8	I_2/PhSSPh[c]	0.5	0	89	trace

[a] Reaction conditions: α-amidosulfide **1a** (0.131 mmol), 1,3,5-trimethoxybenzene **5a** (0.157 mmol), and the halonium source in 1 mL of CH_2Cl_2 for 5 min. [b] Yields refer to chromatographically pure product. [c] Iodine and diphenyl disulfide were premixed together at 0 °C for 10 min before addition of **1a** and **5a**.

After having identified the optimal catalytic conditions of the process, the substrate scope was then investigated. As shown in Table 4, the process can be applied to aromatic α-amidosulfides in excellent yields (**6a**–**c**, **6e** and **6s**). We were pleased to find that various aliphatic α-amidosulfides were tolerated in the reaction. In this case, increases in catalyst loading were required to obtain full conversion (**6h** and **6j**). Next, the reactivity of other aromatic nucleophiles **5** was evaluated. To our satisfaction, indoles underwent nucleophilic addition to **1a** affording products **6n** and **6p** in good yield. With a less-electron-rich aryl, the corresponding Friedel–Craft product **6m** was isolated in a low yield even after prolonged reaction times. This can possibly be attributed to the interruption of the catalytic cycle because of the consumption of iodine, although at this time the exact reason is unclear.

Table 4. Substrate scope of the catalytic activation/aminoalkylation reaction of α-amidosufides.[a]



[a] Isolated yields. [b] From **1b** (R^3 = SPh). [c] 5 mol% of NIS. [d] Reaction with 3 equivalents of indole derivatives.

In summary, we have developed a novel NIS-promoted aza-Friedel–Crafts-type reaction, allowing a rapid access to highly functionalized amines from readily available α-amidosulfides. It is noteworthy that the present reaction proceeded in the absence of any strongly acidic or basic conditions. In this process, NIS initiates both the formation of *N*-carbamoylimine as well as the aza-Friedel–Crafts reaction. Furthermore, mechanism studies allow us to develop an efficient catalytic version, employing only 0.1 mol% of NIS. This simple system offers a powerful method for the utilization of various unstable *N*-carbamoylimines. Further investigations into an enantioselective version of the developed reaction, as well as application to the synthesis of biologically active compounds, are in progress.

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Keywords: Friedel–Crafts reaction · imines · *N*-iodosuccinimide · multicomponent reactions · tandem reactions

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