Influence on Counter Anion of Cyclic Thioamidium Salts by Introduction Oxygen Functional Substituent in Iodine-mediated Cyclization of *o*-Ethynylthiobenzamide

(*Graduate School of Engineering, Chiba University*) ○Takuto Nagamatsu, Motohiro Akazome, Shoji Matsumoto

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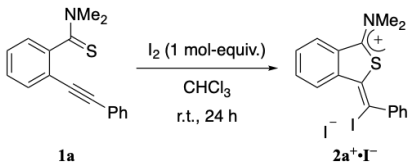
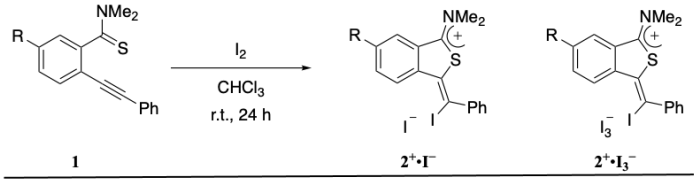
We have reported the formation of cyclic thioamidium salts using iodine-mediated cyclization reaction with *o*-ethynylthiobenzamides (Scheme 1) [1]. The cyclic compounds possess iodide (I^-) as a counter anion. But we also revealed the variation of counter anion (I^- and/or I_3^-) in the case of thiazole rings instead of thioamide moiety of **1** [2]. Herein we will report the reaction of the substrates with oxygen functional group on benzene ring of **1**.

Scheme 1



When **1b** bearing methoxy group was treated with 1 mol-equivalent of I_2, the cyclic thioamidium (**2b**$^+$) was obtained as the precipitated in 65% yield with ratio of I^- : I_3^- = 32 : 68 as anion parts (Table 1, Entry 2). The yield and the ratio of anion were increased by using 2 mol-equivalent of I_2 (Entry 3). However, the ratio of counter anion decreased in the case of the substrate bearing acetoxy group (**1c**) (Entry 4). Thus, the ration of counter anion would be affected by the electronic character of the substituent. And the electron-donating substituents enhance the formation of the product with I_3^- counter anion. It would be caused by the stabilization ability of the substituent against the cyclic cation part. The structures of **2b**$^+$**•I**$_3^-$ and **2c**$^+$**•I**$^-$ were clarified by single-crystal X-ray analysis (Figure 1).

Table 1. Reaction of **1** with Iodine



Entry	Substrate	Equiv of I_2	Yield (%)[a)]
1	**1a** (R = H)	1.0	77% (I^- : I_3^- = 100 : 0)
2	**1b** (R = OMe)	1.0	65% (I^- : I_3^- = 32 : 68)
3	**1b** (R = OMe)	2.0	92% (I^- : I_3^- = 7 : 93)
4	**1c** (R = OAc)	1.0	81% (I^- : I_3^- = 56 : 44)

a) Yield and ration were determined by the estimation with weight of the precipitate and the elemental analysis.

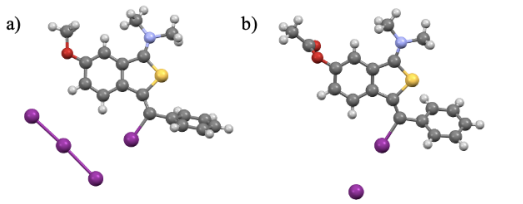


Figure 1. Single-crystal X-ray structures of a) **2b**$^+$**•I**$_3^-$ and b) **2c**$^+$**•I**$^-$

[1] S. Matsumoto, D. Takada, H. Kageyama, M. Akazome, *Tetrahedron Lett.*, **55**, 1082 (2014).
[2] S. Matsumoto, R. Sumida, S. E. Tan, M. Akazome, *Heterocycles*, **93**, 755 (2018).