



Annulation reaction of methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene) acetate with β -nitrostyrenes and 3-nitrochromenes

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ABSTRACT

The acid catalyzed domino reaction of β -nitrostyrenes with methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene) acetate, which were previously prepared from the cyclization of 2-aminobenzenethiol and methyl 4-chloroacetoacetate, resulted in 2-arylbenzo[*b*]pyrrolo[1,2-*d*][1,4]thiazine-3-carboxylates in high yields. Under same reaction conditions, the similar reaction with 3-nitrochromenes afforded corresponding benzo[*b*]chromeno[4',3':4,5]pyrrolo[1,2-*d*][1,4]thiazine derivatives in good yields.

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1. Introduction

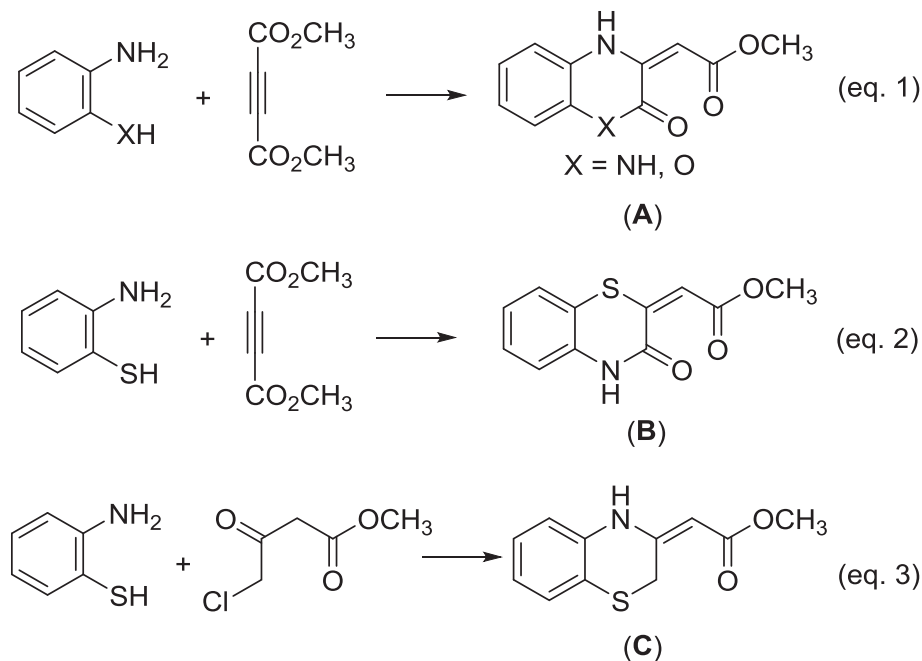
β -enaminones and the corresponding β -enamino esters combined the nucleophilic enamine and the electrophilic enone (ester, amide) moieties into one molecule and showed highly attractive multi-reactivity.¹ In recent years, they have been extensively employed as important synthetic building blocks for construction of widely various nitrogen-containing heterocycles.^{2,3} In this respect, the reaction of 2-aminophenol⁴ or *o*-phenylenediamine⁵ with dimethyl but-2-ynedioate in mild reaction conditions quickly resulted in methyl 2-(2-oxo-2H-benzo[*b*][1,4]oxazin-3-ylidene)acetate or 2-(3-oxo-3,4-dihydroquinoxalin-2-ylidene)acetate (**A**) (eq. (1) in Scheme 1), which retain the structural character of the common β -enamino esters and have been employed as valuable synthons to construct various polycyclic skeletons.^{6–9} As examples, Rostami and coworkers developed sulfamic acid catalyzed three-component reaction of 2-aminophenol (*o*-phenylenediamine), acetylenic esters and β -nitrostyrenes for the synthesis of pyrrole-fused benzoxazines (quinoxalines).¹⁰ Vovk also reported the reaction of ethyl 2-(3-oxopiperazin-2-ylidene)acetate derived from addition of 1,2-diaminoethane and dimethyl but-2-ynedioate

with α -chlorobenzylisocyanates for the synthesis of pyrazino[1,2-*c*]pyrimidine derivatives.¹¹ Recently, Peddinti developed a highly regioselective iodine-mediated cascade reaction of the intermediate (**A**) with 3-phenacylideneoxindoles for the synthesis of multi-functional polyheterocyclic systems.¹² However, the similar reaction of 2-aminobenzenethiol with dimethyl but-2-ynedioate at room temperature afforded methyl 2-(3-oxo-3,4-dihydrobenzo[*b*][1,4]thiazin-2-ylidene)acetate (**B**)¹³ (eq. (2) in Scheme 1), which does not contain the scaffold of β -enamino ester and cannot be used further as a useful synthetic block. On the other hand, the cyclization of 2-aminobenzenethiol with methyl 4-chloroacetoacetate resulted in methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene)acetate (**C**)¹⁴ (eq. (3) in Scheme 1), which would behave as one special kind of cyclic β -enamino ester and have potential synthetic applications in heterocyclic chemistry. The synthetic application of it for the functionalized or fused [1,4]thiazines have been occasionally described in the literature.¹⁵ For further developing the reactivity of this kind of cyclic β -enamino ester and providing efficient synthetic methodology for N,S-containing heterocyclic compounds, herein, we wish to report the annulation reaction of methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene)acetate with β -nitrostyrenes and 3-nitrochromenes for the convenient synthesis of functionalized benzo[*b*]pyrrolo[1,2-*d*][1,4]thiazine and benzo[*b*]chromeno[4',3':4,5]pyrrolo[1,2-*d*][1,4]thiazine derivatives.

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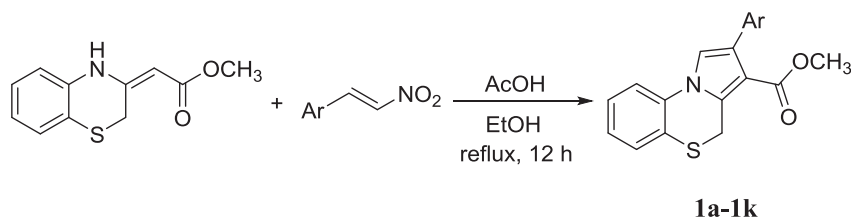
Scheme 1. The generation methods of the cyclic β -enamino ester.

2. Results and discussions

At first, the reaction conditions were examined by using methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene)acetate and (*E*)-1-methyl-4-(2-nitrovinyl)benzene as standard. When stronger acids such as TsOH, TFA and TfOH were used as catalyst, the decomposition of methyl 2-(benzo[*b*][1,4]thiazin-3-ylidene)acetate was obviously observed and the reaction gave much more complicate mixtures. Thus, the relative weaker acid were tested in the reaction. In the presence of acetic acid (20–50 mol %), the reaction in refluxing ethanol readily furnished the expected product **1b** in moderate yields. If the reaction was carried out in pure acetic acid, in which

acetic acid acted both as catalyst and as solvent, the product **1b** was obtained in 51% yields. After careful examination, we successfully found that the product **1b** could be obtained in 78% yield when the reaction was conducted in refluxing mixture of acetic acid and ethanol (V/V = 1/2) for 12 h. Under this simple reaction conditions, various substituted β -nitrostyrenes were successfully employed in the reaction. The corresponding substituted benzo[*b*]pyrrolo[1,2-*d*][1,4]thiazines **1a–1k** were obtained in good to high yields (Table 1). The substituents on the phenyl group showed marginal effect on the reaction. The nitro group was eliminated out and a pyrrole ring was formed in the reaction. The structure of the compounds **1a–1k** were fully characterized by IR, HRMS, ^1H and ^{13}C NMR spectra. In

Table 1
Synthesis of benzo[*b*]pyrrolo[1,2-*d*][1,4]thiazines.^a



Entry	Compd	Ar	Yield (%) ^b
1	1a	C ₆ H ₅	78
2	1b	<i>p</i> -CH ₃ C ₆ H ₄	89
3	1c	<i>p</i> -C(CH ₃) ₃ C ₆ H ₄	82
4	1d	<i>m</i> -CH ₃ OC ₆ H ₄	87
5	1e	<i>p</i> -CH ₃ OC ₆ H ₄	76
6	1f	<i>m</i> -ClC ₆ H ₄	87
7	1g	<i>p</i> -ClC ₆ H ₄	81
8	1h	<i>p</i> -BrC ₆ H ₄	73
9	1i	<i>o</i> -NO ₂ C ₆ H ₄	71
10	1j	<i>m</i> -NO ₂ C ₆ H ₄	69
11	1k	<i>p</i> -NO ₂ C ₆ H ₄	85

^a Reaction conditions: cyclic β -enamino ester (0.5 mmol), β -nitrostyrene (0.5 mmol), AcOH (5.0 mL), EtOH (10.0 mL), reflux, 12 h.

^b Isolated yields.

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