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α-Oxo Ketene Dithioacetals Chemistry-A Facile Route to the Synthesis of Fused Heterocyclic Compounds

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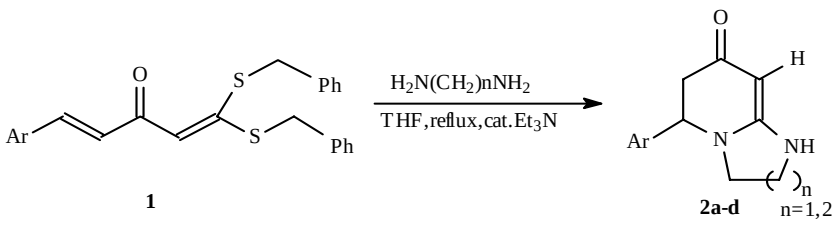
Abstract: The fused heterocyclic compounds **2** : imidazo [1,2-a] pyridine **2a-c** and pyrido [1,2-a] pyrimidine **2d** were obtained from the reaction of α-cinnamoyl ketene dibenzylthio acetals **1** with diamine. When α-cinnamoyl -α'-benzoyl ketene N, N-acetals **3a-b** were treated by t-BuONa/t-BuOH solution, 8- benzoyl-pyrido[1,2-a] pyrimidine **4** was produced.

Keywords: α-Cinnamoyl ketene dibenzylthio acetals, diamine, α-cinnamoyl-α'-benzoyl ketene N, N-acetals, fused heterocyclic compounds

α-Oxo ketene dithioacetals and related compounds are versatile synthons in organic synthesis[1-3]. The substitution reaction of α-oxo ketene dimethylthio acetals with diamine is one of the important applications for the synthesis of corresponding α-oxo ketene cyclic N, N-acetals. Junjappa and co-workers described this reaction in a review[2]. However, since some kinds of ketene dimethylthio acetals are not easy to prepare, the method mentioned above is limited. Zhu and co-workers had successfully synthesized some simple α,α'-dioxo (ester) ketene cyclic N, N-acetals by the substitution reaction of α,α'-dioxo (ester) ketene cyclic S,S-acetals with ethylenediamine[4], and we also reported the synthesis of α,α'-dicinnamoyl ketene cyclic N,N-acetals by the similar reaction in a previous paper[5].The process provided a new method for the synthesis of this special kind of N,N-acetals which can not be easily obtained by other methods.

Recently, in order to compare the activity of various alkylthio groups to the substitution reaction, α-cinnamoyl ketene dibenzylthio acetals **1** were chosen as substrates to react with diamine in our work. However, instead of α-cinnamoyl ketene cyclic N, N-acetals, fused heterocyclic compounds **2** imidazo [1,2-a] pyridine(n=1) and pyrido [1,2-a] pyrimidine (n=2) were resulted. **(Scheme 1)**

Scheme 1



1 **2a-d** n=1,2

From the experimental results, it should be assumed that the process involves the substitution reaction of α-cinnamoyl ketene dibenzylthio acetals with diamine and a consecutive intramolecular Michael addition. According to this consideration, when α-cinnamoyl- α'-benzoyl ketene cyclic N, N- acetals **3** were treated with t-BuONa/t-BuOH solution, **3b** (n=2) was converted into the expected fused heterocyclic compounds **4**, 8-benzoyl-pyrido[1,2-]pyrimidine, **3a** (n=1) did not react at all **(Scheme 2)**. Due to the substrates can be obtained easily [6,7], the method mentioned above provide a facile route to the synthesis of fused heterocyclic compounds **2** and **4**. The studies on the intra-molecular Michael addition of the other kinds α-cinnamoyl ketene cyclic N, N- acetals to obtain the fused heterocyclic compounds are in progress. The structures of all the compounds were characterized by their IR, ^{1}H NMR. Compounds **2a** was taken as example: IR: 3432 (N-H), 2360, 1610, 1455, 699 ^{1}H NMR: 2.70 (2H, d, J=8.0, CH_2), 3.48(4H, s, 2 ×NCH_2), 4.31(1H, t, J=8.0, CH), 4.56 (1H ,broad, NH), 7.18 (1H,s, =CH) 7.01~7.06 (5H ,m, ArH)

Scheme 2

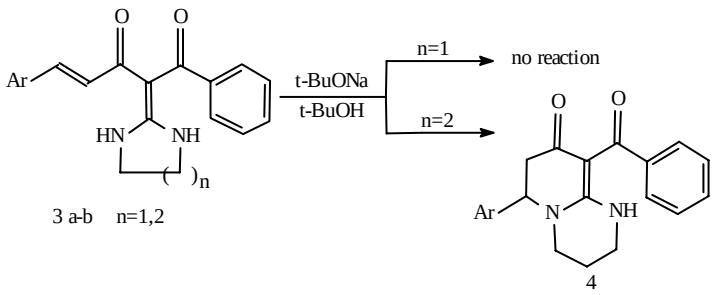


Table 1 Melting points and yields of the title compounds

Entry	Substrate	n	Ar	Product	Yield (%)
1	1a	1	C_6H_5	2a	23.4
2	1b	1	3,4-$OCH_2OC_6H_3$	2b	24.8
3	1c	1	4-$CH_3C_6H_4$	2c	20.1
4	1d	2	C_6H_5	2d	74.9
5	3b	2	C_6H_5	4	24.8

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