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1, 3-Dipolar Cycloaddition Reaction between Vinyl Acetate and N-Alkyl Hydroxypyridinium Halide

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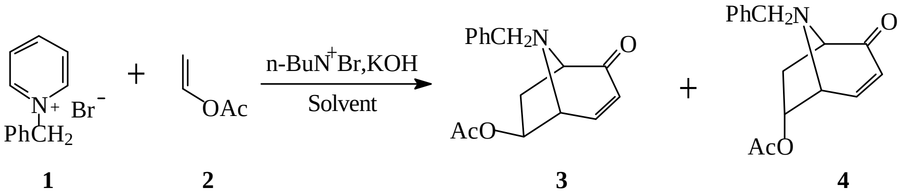
Abstract: 1, 3 Dipolar cycloaddition reaction between vinyl acetate and 3-hydroxypyridiniun betaine was performed under solid-liquid phase transfer catalytic condition. This reaction has been successfully used on the synthesis of an analogue of Bao-Gong-Teng A.

Keywords: 1, 3-Dipolar cycloaddition, 3-hydroxypyridiniun betaines, dipolarphiles.

The 1, 3-dipolar cycloaddition reaction between 3-hydroxypyridiniun betaines and a great variety of dipolarphiles, such as CH_2=CH-CN, CH_2=CH-$COCH_3$, CH_2=CH-$COOCH_3$, CH_2=CH(CH_3)-$COOCH_3$ were first investigated by Alan R. Katritzky *et al.*[1-3]. Generally, the olefinic dipolarphiles containing a strongly electron-withdrawing group are more active. Vinyl acetate **2** is an electron-rich dipolarphile, it is very difficult to carry out 1, 3-dipolar cycloaddition reaction with 3-hydropyridinium betaines. For shortening the reaction steps of the synthesis of Bao-Gong-Teng A **5**[4] and its analogue **6**, the 1, 3 cycloaddition reaction between **2** and betaine **1** have been studied (**Scheme 1)**. Herein, we report an improved procedure to perform this reaction.

Scheme 1 1, 3-Dipolar cycloaddition reaction between N-benzyl-3-hydroxypyridinium bromide and vinyl acetate



Et_3N was first chosen for generating ylide. There was no cycloadduct could be found. When Lewis acid was used, vinyl acetate polymerized quickly. However, when **1** and vinyl acetate **2** (10 equiv) with solid KOH (1.5 equiv) were stirred in EtOAc at r.t. in the presence of Bu_4NBr (0.3~0.5 equiv.) for 8 days, the cycloadducts **3** and **4** were afforded in 40% combined yield. Raising temperature would decrease the yield and increase the stereoselectivity of the reaction (**Table 1**). The stereochemistry of adducts were determined by NMR method according to the ratio of the proton signals at C-4 (δ 6.93)

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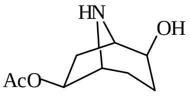
in **3** and C-4 (δ 6.76) in **4**.

Table 1 The results of 1.3-dipolar cycloaddition reactions of the vinyl acetate and N-benzyl-3-hydroxypyridinium bromide[a]

entry	solvent	Temp.	Reaction time/(d)	Products (exo/endo)[b]	Combined yield[c] (%)
1	THF	rt	8	7/ 93	33
2	THF	reflux	2	3/97	24
3	CH_3CN	rt	8	8/92	31
4	CH_3CN	Reflux	2	3/97	12
5	EtOAc	rt	8	7/93	40
6	EtOAc	Reflux	2	1/99	20
7	C_2H_3OAc	rt	8	7/93	35
8	C_2H_3OAc	reflux	2	3/97	16

a) In the presence of KOH and under PTC condition. b) determined by ^{1}H-NMR c) isolated yield.

The major product was in endo form as shown in **Table 1**. Bao-Gong-Teng A analogue **6**, can be synthesized using **4** as intermediate in shout rout[5].



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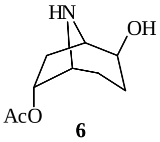

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