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# One-pot Synthesis of 2'-Aminobenzothiazolomethylnaphtols In water catalyzed by Wells-Dawson heteropolyacid

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## Abstract

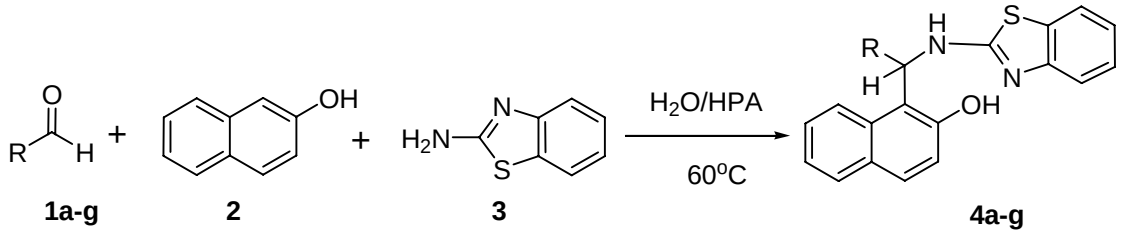
A one- pot three-component reaction of 2-aminobenzothiazole, 2-naphthol, and aldehydes has efficiently been carried out in the presence of Wells-Dawson heteropolyacid ($H_6P_2W_{18}O_{62}$ _ $24H_2O$) in water at 60 °C to form the corresponding 2'-aminobenzothiazolomethylnaphthols in high yields.

*Keywords:* Multi-component reaction, Wells-Dawson Heteropolyacid (HPA), water, 2'-aminobenzothiazolomethylnaphthols

## Introduction

2-aminobenzothiazole and its derivatives have gained interest in both synthetic organic chemistry and biological fields, since they are highly reactive compounds and reaction intermediates, through the $NH_2$ and endocyclic *N* functions suitably situated to enable reaction with *bis*-electrophilic reagents to form a variety of fused biologically active heterocyclic compounds [1]. On other hand, multi-component reactions (MCRs) have become an efficient and powerful tool for the construction of complex molecules because of the fact that the products are formed in a one-pot reaction without isolating the intermediates or modification of the reaction condition [2-4]. MCRs are particularly useful to generate diverse chemical libraries of ‘‘drug- like molecules" for biological screening. Furthermore, during the recent years water has been explored as an environmentally-friendly solvent. Many biological processes and organic compound synthesis in nature occur very efficiently in water. The diversity of reactant seen *in vivo* should promote chemists to discover the potential of water as a green solvent. Also, heteropolyacids (HPAs) are known to eco-friendly applicable, industrial and green catalyst since they are strong, highly stable toward humidity, air stable, having low toxicity. They have been widely used as solid acid catalysts for organic synthesis and transformations [5 - 10]. Recently the interest in the Wells–Dawson type HPAs with $[X2M18O62]n^-$ anions (where X= P, As and M= Mo, W) is growing [11-13].

As a part of our research to develop a green catalyst for one-pot multi-component reactions and synthesis of the target molecules in water as a green reaction media, here we wish to report one-pot three component condensation reaction of 2-aminobenzothiazle, 2-naphthole and aldehyde to prepare 2'-aminobenzothiazolomethylnaphtholes catalyzed by HPA in water at 60 °C in high yields (**Scheme 1**).




Scheme-1

## Results and discussions

To achieve a suitable condition for the above condensation reaction a set of experiments was carried out. First, we investigate the reaction of 2-aminobenzothiazole, 2-naphthol, and benzaldehyde in the presence of different amount of Wells–Dawson type HPA in water at 45°C and the results are summarized in (**Table 1**). The effects of temperature on the yield of product, and reaction time were also studied (**Table 2**).

**Table 1.** Catalyst effect on the reaction of 2-aminobenzothiazole, 2-naphthol, and benzaldehyde on the synthesis of 2-aminobenzothiazolomethyl-2-naphthols in water

| Entry | Amount of (HPA) g | Time (h) | Temperature (˚C) | Isolated yield, % |
|---|---|---|---|---|
| 1 | 0.05 | 8 | 45 | 50 |
| 2 | 0.09 | 8 | 45 | 78 |

**Table2.** Temperature effect on the reaction of 2-aminobenzothiazole, 2-naphthol and benzaldehyde on the synthesis of 2'-aminobenzothiazolomethylnaphthols in water in the presence of 0.09g HPA

| Entry | Temperature (˚C) | Time (h) | Isolated yield, % |
|---|---|---|---|
| 1 | 45 | 8 | 78 |
| 2 | 60 | 5 | 90 |

After optimizing the suitable reaction conditions a series of aromatic aldehydes, heterocyclic aldehydes, and also aliphatic aldehydes were involved in the above conditions and the results are shown in (Table 3). The reaction proceeds well between the aromatic aldehydes containing both electron-donating and electron-withdrawing groups. Heterocyclic aldehydes react smoothly in the same conditions but in a lower yield. In the case of aliphatic

aldehydes, the desired product was obtained only at trace amounts and in the case of cinamaldehyde a mixture of compound was obtained and the desired product could not be isolated.

**Table3.** The reaction of 2-aminobenzothiazole, 2-naphthol and aldehydes in the presence of Wells–Dawson in water

| Product | R | isolated yield (%) | Time (min) | Mp(˚C) |
|---|---|---|---|---|
| 6a | 4-$CH_3$- $C_6H_4$- | 91% | 100 | 183-184 |
| 6b | $C_6H_5$- | 90% | 120 | 200-201 |
| 6c | 4-$CH_3O$-$C_6H_4$- | 92% | 105 | 172-173 |
| 6d | Furyl- | 64% | 80 | 176-177 |
| 6e | 4-CN-$C_6H_4$- | 91% | 80 | 214-215 |
| 6f | 4-Cl-$C_6H_4$- | 90% | 110 | 208-209 |
| 6g | 3-$NO_2$-$C_6H_4$- | 86% | 105 | 198-199 |

Next, we extended this reaction to 2-aminobenzimidazole, and 3-amino 1,2,4-triazole. As our experiment shows, the reaction didn't proceed in the case of 3-amino 1,2,4-triazole and in the case of 2-aminobenzimidazole the reaction proceeded in a very low yield after heating the reaction mixture at 90°C for 24 h.

## Conclusion

We have reported a rapid and efficient environmentally-friendly method for the preparation of 2'-aminobenzothiazolomethylnaphtholes via a three component condensation of 2- aminobenzothiazole, 2-naphthol, and aldehydes in the presence of Wells-Dawson heteropolyacid in water at in a high yields. The reaction conditions are mild and green and also safe from environmental point of view.

## Acknowledgment

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*General procedure for the preparation of 2'aminobenzothiazolomethylnaphthols*:

To a mixture of 2-aminobenzohiazole (1 mmol), 2-naphthol (1 mmol), and aldehyde (1 mmol) in water (3 mL) was add (0.09g) HPA. The reaction mixture was stirred at 60°C for the time shown in Table 3. The reaction was followed by TLC and after completion of the

reaction, the precipitate was washed with water and recrystalized from acetone/water to afford the desired pure product. All the products obtained products were fully characterized by IR, $^{1}H$, $^{13}C$ NMR spectroscopy, and also by comparison of their spectra data with those reported [14].

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