

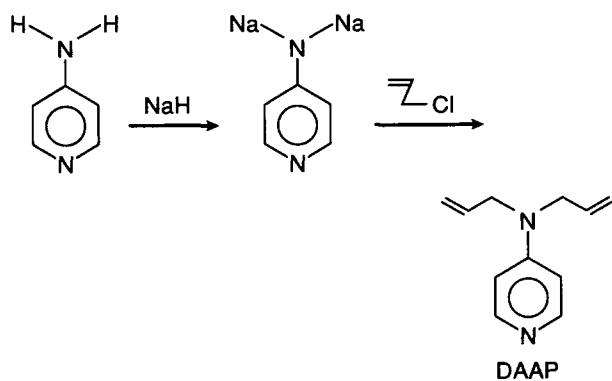
# NOTE

## An Efficient Synthesis of 4-(*N,N*-Diallylamino)pyridines

### INTRODUCTION

4-(*N,N*-Dialkylamino)pyridines can all serve as excellent supernucleophilic catalysts in bringing about catalysis in a wide range of organic reactions including acylation, silylation, and other related reactions.<sup>1-3</sup> Of all the alkylaminopyridines known so far, the homopolymer of 4-(*N,N*-diallylamino)pyridine (DAAP) should be counted as the highest in terms of catalytic activity.<sup>4,5</sup> Mathias succeeded in preparing DAAP by starting from 4-chloropyridine and diallylamine. Such a reaction process, however, usually takes 72 h and needs a temperature of 111–112°C.<sup>6</sup>

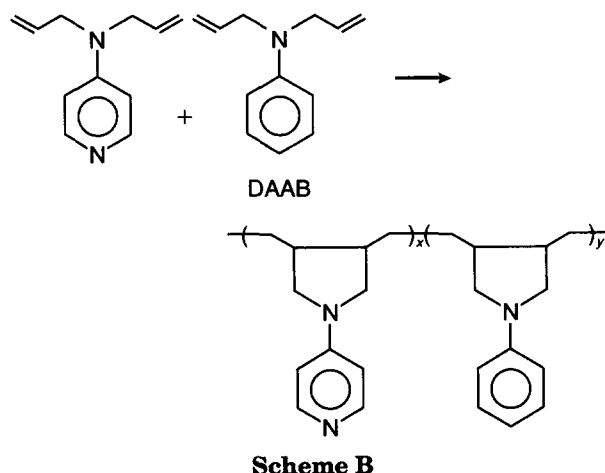
Recently, we explored the possibility of a novel approach to synthesizing the same compound and obtained DAAP (in a good yield) in the *N*-allylation reaction of sodium salt of 4-aminopyridine with allyl chloride for 6 h at 67°C (Scheme A):



Scheme A

The structure of DAAP thus produced has been confirmed by IR spectral data and has proved to be identical with an authentic sample provided by Mathias.<sup>7</sup> With the *N*-allylation reaction, we also became interested in the synthesis of *N,N*-diallylaminobenzene (DAAB) for the following reason: The copolymer of DAAP and DAAB is a new polymer supernucleophilic catalyst containing a al-

kyaminopyridines and a potential ion-exchange resin structure (Scheme B):



Scheme B

### EXPERIMENTAL

Tetrahydrofuran (THF) was dried and distilled on sodium/benzophenone before use. IR spectra were recorded on a Nicolet 205 infrared spectrometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker AC-P 200 spectrometer.

#### 4-(*N,N*-Diallylamino)pyridine (DAAP)

In a 250 mL four-necked flask, 8.0 g (0.2 mol) of sodium hydride (60 wt % in mineral oil) was placed and washed with hexane twice to remove the mineral oil. Then, 9.4 g (0.1 mol) of 4-aminopyridine and 60 mL of THF were added into the flask. The mixture was stirred under an atmosphere of nitrogen at room temperature until the evolution of hydrogen was complete. A solution formed of 15.4 g (0.2 mol) of allyl chloride in 20 mL of THF was added dropwise to the mixture at 0°C. The mixture was refluxed under a nitrogen atmosphere for 5 h.

Sodium chloride was separated from the mixture by filtration. THF was evaporated from the filtrate. The product was purified by fractional distillation under reduced pressure. DAAP, 11.3 g (in a 65% yield), was isolated as a yellowish or bright-red liquid.

ANAL: Calcd for  $C_{11}H_{14}N_2$ : C, 75.82%; H, 8.10%; N, 16.08%. Found: C, 75.81%; H, 8.13%; N, 16.10%.

IR: 1600, 1360, 1000, 805  $cm^{-1}$ . NMR ( $CDCl_3$ , 200 MHz):  $\delta$  3.87 (d, 4H); 5.23 (q, 4H); 6.06 (m, 2H); 7.90 (m, 2H); 8.18 (m, 3H).

#### *N,N*-Diallylaminobenzene (DAAB)

*N,N*-Diallylaminobenzene (DAAB) was prepared by a similar procedure to that used for DAAP using 9.3 g (0.1 mol) of aniline, 15.4 g (0.2 mol) of allyl chloride, and 8.0 g (0.2 mol) of sodium hydride in 80 mL of THF. The mixture was refluxed to yield 5.5 g of DAAB as a dull red liquid (in a 32% yield).

ANAL Calcd for  $C_{12}H_{15}N$ : C, 83.19%; H, 8.73%; N, 8.08%. Found: C, 83.17%; H, 8.73%; N, 8.07%.

IR: 1645, 1601, 1540, 1317  $cm^{-1}$ . NMR ( $CDCl_3$ , 200 MHz):  $\delta$  3.79 (d, 4H); 5.18 (m, 4H); 5.95 (m, 2H); 6.74 (m, 3H); 7.20 (m, 2H).

#### Poly(DAAP-co-DAAB)

DAAP, 17.4 g (0.1 mol), and DAAB, 17.3 g (0.1 mol), were dissolved in excess concentrated HCl (22.0 mL of 36.5% HCl) at 0°C under a nitrogen blanket. The initiator, 0.8 g 2,2-azo-bis(2-amidinopropane)hydrochloride (V-50), in 20 mL of water was added and mixed and the solution was stirred at 60°C under nitrogen for 48 h until a highly viscous solution was obtained.

The product was precipitated by aqueous sodium hydroxide and water to remove monomers and oligomers. The dark-red solid was dried under vacuum. IR: 3000, 1590, 1500, 1240, 985, 800, 745  $cm^{-1}$ .

ANAL Calcd for  $C_{23}H_{29}N_3$ : C, 79.50%; H, 8.41%; N, 12.09%. Found: C, 79.53%; H, 8.42%; N, 12.11%.

#### REFERENCES

1. G. Hofle, W. Steglich, and H. Vorbruggen, *Angew. Chem. Int. Ed. Engl.*, **17**, 569 (1978).
2. A. Hassner, L. R. Krepski, and V. Alexanian, *Tetrahedron*, **34**, 2069 (1978).
3. E. F. V. Scriven, *Chem. Soc. Rev.*, **12**, 129 (1983).
4. R. A. Vaidya, and L. J. Mathias, *J. Am. Chem. Soc.*, **108**, 5514 (1986).
5. L. J. Mathias and G. Cei, *Macromolecules*, **20**(11) 2645 (1987).
6. L. J. Mathias, Hattiesburg, MI, U.S. Pat. 4,591,625 (1986).
7. L. J. Mathias, R. A. Vaidya, and R. H. Bloodworth, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 289 (1985).

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Received November 28, 1994

Accepted January 6, 1995

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