

SHORT  
COMMUNICATIONS

## Behavior of Dimethylaminonaphthalenes in the Vilsmeier–Haak Reaction

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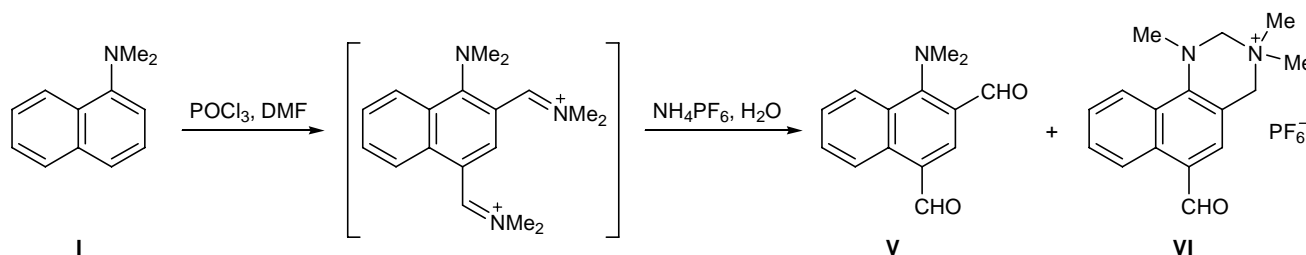
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4-Substituted *N,N*-dimethylanilines [1, 2], derivatives of 4-dimethylaminonaphthoic acid [3], and dimethylamino-substituted 2,5-diaryl-1,3-oxazoles and 2,5-diaryl-1,3,4-oxadiazoles [4] react with the POCl<sub>3</sub>–DMF complex (Vilsmeier–Haak reaction) to afford tetrahydroquinazolinium salts instead of the corresponding aldehydes or together with the latter. The mechanism of this reaction was proposed for the first time in a brief communication by Meth-Cohn and Taylor [1] and was studied by quantum-chemical methods by Patsenker [5]. In continuation of these studies, we examined Vilsmeier–Haak reactions of mono- and bis(dimethylamino)naphthalenes I–IV.

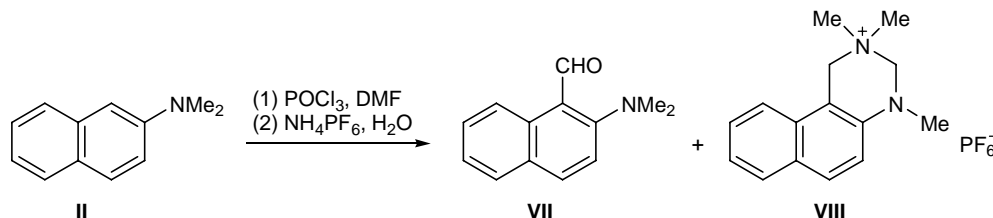
1-Dimethylaminonaphthalene (I) reacted with POCl<sub>3</sub> and DMF in 15 min at 80°C to give a mixture of aldehyde V and tetrahydroquinazolinium salt VI at a ratio of 12:88 (Scheme 1). The product ratio did not

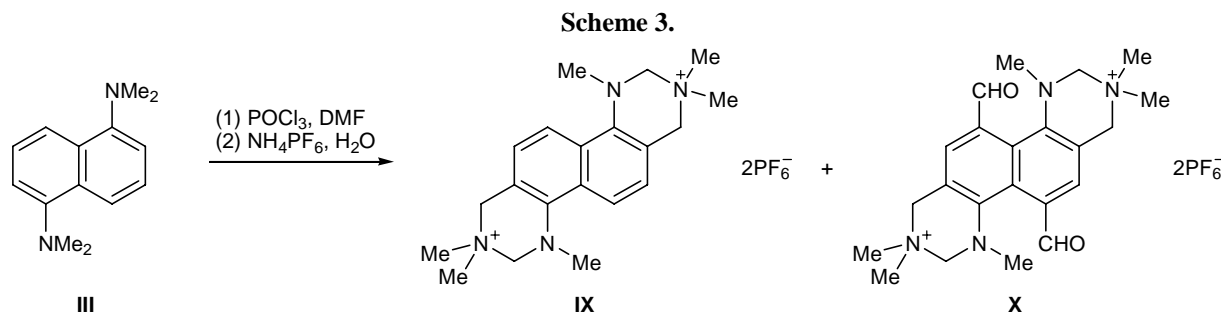
change on further heating of the reaction mixture. Under analogous conditions, 2-dimethylaminonaphthalene (II) gave rise to a mixture of products containing 60% of aldehyde VII and 40% of salt VIII (Scheme 2). In this case, prolonged heating favored heterocyclization. After 1 h, salt VIII was isolated from the reaction mixture in 90% yield. The reaction of 1,5-bis(dimethylamino)naphthalene (III) with POCl<sub>3</sub>–DMF resulted in formation of an intractable mixture of products. On the basis of the <sup>1</sup>H NMR data, the products were assigned structures IX and X (Scheme 3). 1,8-Bis(dimethylamino)naphthalene (IV) failed to react with the POCl<sub>3</sub>–DMF complex. According to quantum-chemical calculations, two dimethylamino groups in the *peri* positions create steric hindrances to each other; as a result, their conjugation with the naphthalene π-system is disrupted, and elec-

Scheme 1.



Scheme 2.





trophilic substitution becomes impossible. This conclusion is consistent with the data of [6] on acid-catalyzed deuterium exchange in compound **IV**.

Initial dimethylaminonaphthalenes **I–IV** were synthesized by the procedures described in [7–9].

**Vilsmeier–Haak reactions of dimethylaminonaphthalenes I–IV.** Phosphoryl chloride, 3.7 ml (40 mmol), was added dropwise at 40°C to a solution of 1.7 g (10 mmol) of dimethylamino-substituted naphthalene **I–IV** in 4.2 ml of DMF. The mixture was heated for 15 min at 80°C and poured onto ice, sodium acetate was added, and the corresponding aldehyde was filtered off. Ammonium hexafluorophosphate(V), 10 mmol, was added to the filtrate, and the precipitate of salt **VI** or **VIII** was filtered off.

**4-Dimethylaminonaphthalene-1,3-dicarbaldehyde (V).** Yield 7.5%, mp 158–160°C.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.55 s [6H,  $\text{N}(\text{CH}_3)_2$ ], 7.74–7.97 m (2H, 6-H, 7-H), 8.47 s (1H, 3-H), 8.62 d (1H, 8-H,  $J = 8.3$  Hz), 9.39 d (1H, 5-H,  $J = 8.4$  Hz), 10.38 s (1H, CHO), 10.77 s (1H, CHO). Found, %: C 74.16; H 5.59; N 6.32.  $\text{C}_{14}\text{H}_{13}\text{NO}_2$ . Calculated, %: C 74.01; H 5.72; N 6.17.

**6-Formyl-1,3,3-trimethyl-1,2,3,4-tetrahydrobenzo[h]quinazolin-3-ium hexafluorophosphate(VI)** (**VI**). Yield 82%, mp 223–225°C.  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.20 s [6H,  $\text{N}(\text{CH}_3)_2$ ], 3.56 s (3H,  $\text{NCH}_3$ ), 4.84 s (2H,  $\text{CH}_2$ ), 4.99 s (2H,  $\text{CH}_2$ ), 7.63–7.84 m (2H, 6-H, 7-H), 7.90 s (1H, 3-H), 8.21 d (1H, 8-H,  $J = 8.3$  Hz), 9.23 d (1H, 5-H,  $J = 8.3$  Hz), 10.25 s (1H, CHO). Found, %: C 48.23; H 4.60; N 7.01.  $\text{C}_{16}\text{H}_{19}\text{F}_6\text{N}_2\text{OP}$ . Calculated, %: C 48.00; H 4.75; N 7.00.

**2-Dimethylaminonaphthalene-1-carbaldehyde (VII).** Yield 45%,  $n_D^{20} = 1.665$ .  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.10 s [6H,  $\text{N}(\text{CH}_3)_2$ ], 7.36 t (1H, 6-H,  $J = 7.4$  Hz), 7.46 d (1H, 3-H,  $J = 9.1$  Hz), 7.56 t (1H, 7-H,  $J = 7.4$  Hz), 7.84 (1H, 5-H,  $J = 8.3$  Hz), 8.03 d (1H, 4-H,  $J = 9.2$  Hz), 8.97 d (1H, 8-H,  $J =$

8.3 Hz), 10.24 s (1H, CHO). Found, %: C 78.49; H 6.50; N 6.31.  $\text{C}_{13}\text{H}_{13}\text{NO}$ . Calculated, %: C 78.39; H 6.53; N 7.04.

**2,2,4-Trimethyl-1,2,3,4-tetrahydrobenzo[f]quinazolin-2-ium hexafluorophosphate (VIII).** Yield 32%, mp 167–169°C.  $^1\text{H}$  NMR spectrum ( $\text{DMSO}-d_6$ ),  $\delta$ , ppm: 3.15 s [6H,  $\text{N}(\text{CH}_3)_2$ ], 3.29 s (3H,  $\text{NCH}_3$ ), 4.75 s (2H,  $\text{CH}_2$ ), 4.97 s (2H,  $\text{CH}_2$ ), 7.33–7.63 m (4H,  $\text{H}_{\text{arom}}$ ), 7.90 d (1H, 8-H,  $J = 8.1$  Hz), 7.92 d (1H, 4-H,  $J = 9.2$  Hz). Found, %: C 48.53; H 5.01; N 7.34.  $\text{C}_{15}\text{H}_{19}\text{F}_6\text{N}_2\text{P}$ . Calculated, %: C 48.39; H 5.11; N 7.53.

The  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury-VX-200 spectrometer (200 MHz) using tetramethylsilane as internal reference.

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