

## A New Synthesis of the Pyrrole Ring

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**Abstract:** Treatment of a quaternary 3-amino-5-nitrocollidinium salt with aqueous methylamine at room temperature leads to the formation of a nitroacetylpyrrole.

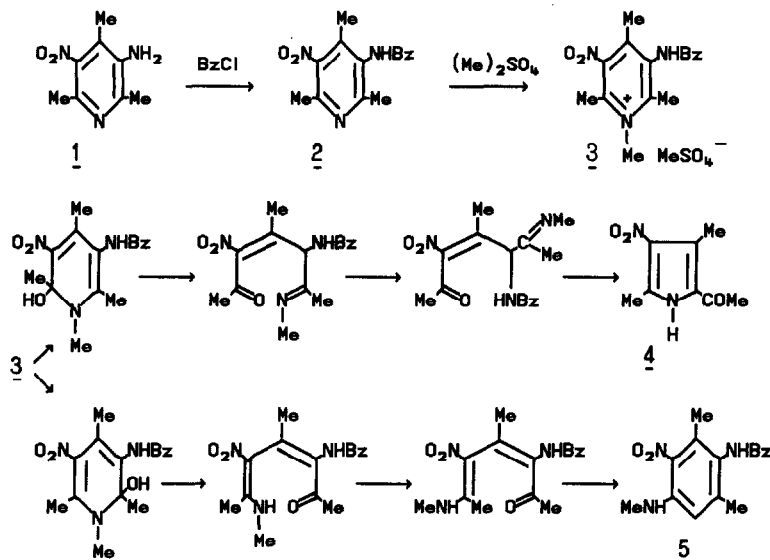
It has been established that on treatment with bases pyridinium salts containing cyano,alkoxycarbonyl,acetyl and amide groups undergo scission of the pyridinium ring C-N bond followed by recyclization, resulting the formation of a new hetero- or carbocycle with participation of the functional group in position 3<sup>1</sup>.

It therefore seemed reasonable to suppose that recyclization of a 3-aminopyridinium salt would lead to pyrrole formation due to participation of the exocyclic amino-group in the ring closure.

We find formation of the expected 2-acetyl-4-nitropyrrole 4 in 69% yield as a result of the recyclization of the quaternary 3-benzoylamino-5-nitrocollidinium salt<sup>3</sup>. The reaction probably proceeds by attack at position 6 of the pyridine by hydroxide anion followed by ring-opening of the pseudobase and further intramolecular interaction of the acetyl and amino groups with elimination of methylamine and benzoic acid. The earlier described<sup>2</sup> reaction route leading to the nitroaniline 5 in this case occurs in only 19% yield.

3-Amino-5-nitrocollidine 1 was obtained according to the procedure<sup>3</sup> described earlier. Benzoyl chloride reacts with 1 in pyridine forming 3-benzoylamino-5-nitrocollidine 2, mp. 196-197°C. IR (CHCl<sub>3</sub>): 3420 cm<sup>-1</sup> (NH), 1480 and 1275 (NO<sub>2</sub>), 1680 (CO). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm): 10.04 s (1H, NH), 7.96-7.41 m (5H, Ph), 2.35 s (3H, Me), 2.32 s (3H, Me), 2.03 s (3H, Me). MS (m/z): 285 M.

Salt 3 was obtained by alkylation of 2 with dimethyl sulfate, mp. 207-208 °C / H<sub>2</sub>O. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm): 10.46 s (1H, NH), 7.45-7.25 m (5H, Ph), 3.84 s (3H, Me), 3.02 s (3H, Me), 2.43 s (6H, 2Me).



Orange needles of 4-benzoylamino-N,3,5-trimethyl-2-nitroaniline **5** separated from an aqueous methylamine solution of the salt **3** over 48 hr. Mp. 213–214 °C /EtOH. IR (CHCl<sub>3</sub>): 3420 cm<sup>-1</sup>(NH), 1480 and 1275 (NO<sub>2</sub>), 1680 (CO). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm): 9.34 s (1H, NHCO), 7.90–7.43 m (5H, Ph), 6.60 s (1H, 6-H), 6.26 q (1H, NHMe), 2.74 d (3H, MeNH), 2.12 s (3H, 3-Me), 2.05 s (3H, 5Me). MS (m/z): 299 [M].

2-Acetyl-3,5-dimethyl-4-nitropyrrole **4** was obtained after evaporation of the filtrate in 69% yield. Mp. 192–193 °C /EtOH. IR (CHCl<sub>3</sub>): 3415 cm<sup>-1</sup>(NH), 1650 (CO), 1500 and 1350 (NO<sub>2</sub>). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm): 12.30 s (1H, NH), 2.50 s (3H, MeCO), 2.47 s (3H, Me), 2.38 s (3H, Me). MS (m/z): 182 [M].

All elemental analyses consistent with the structures assigned.

#### References:

1. H.C. van der Plas, *Tetrahedron* 1985, **41**, 237.
2. R.S. Sagitullin and A.N. Kost, *Zh. Org. Khim.* 1980, **16**, 658.
3. P. Tomasik and W. Drzeniek, *Roczniki Chem.* 1969, **43**, 569.

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