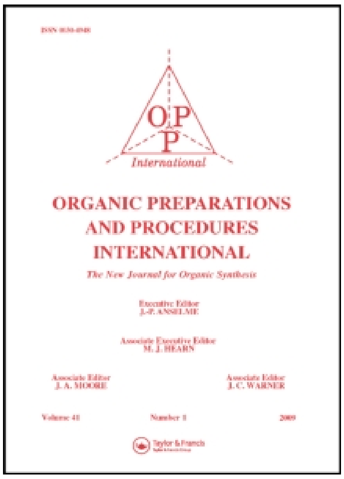

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OXIDATIVE NITROMETHYLENATION (S_NH SUBSTITUTION) IN PYRIDINIUM SALTS

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OPPI BRIEFS

OXIDATIVE NITROMETHYLENATION (S_NH SUBSTITUTION) IN PYRIDINIUM SALTS

Submitted by (02/19/88)
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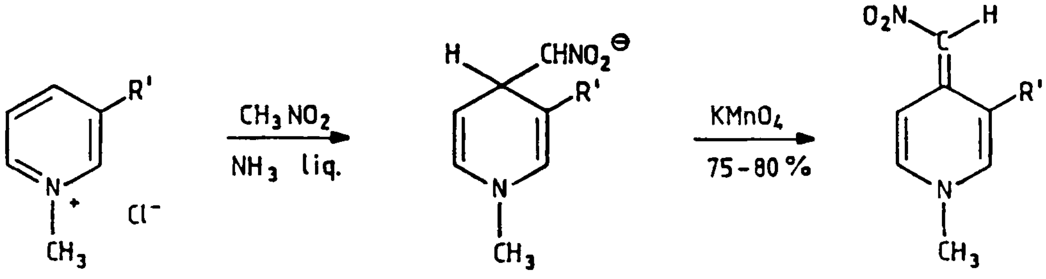
In an extension of our work on S_NH substitution reactions,[1,2] it was of interest to determine whether pyridinium salts are also able to undergo oxidative nitromethylenation (Eq. 1). Therefore, we studied the reaction of 1,3-dimethylpyridinium chloride (1a) with nitromethide in the presence of potassium permanganate. It has been reported[3] that nitromethide is readily formed from nitromethane and liquid ammonia at -10° or lower temperatures. We now report that when 1a or 1b was dissolved in liquid ammonia (-40°) containing nitromethane, and the resulting suspension was treated with potassium permanganate, 3a, or 3b was isolated.



1a. R' = CH_3
1b. R' = C_6H_5

2

3a. R' = CH_3
3b. R' = C_6H_5

It has been established[4] that nitromethide in liquid ammonia adds easily at position 4 of pyridinium salts and thus it seems reasonable to assume that 2 is the intermediate of the nitromethylenation reaction of 1a and 1b.

EXPERIMENTAL SECTION

Mps are uncorrected. Mass spectra were determined on an AEI MS 902 mass spectrometer equipped with a VG ZAB console. The ^1H NMR spectra were recorded on a Varian EM-390 spectrometer. Compounds 1a and 1b were prepared from the corresponding iodides[5,6] by passage over a Dowex 1-X 2 column.

General Procedure.- To a suspension of 4 mmol of starting material and 8 mmol of nitromethane in 25-30 ml of liquid ammonia were added 4 mmol of potassium permanganate. After stirring this suspension at -40° to -50° for 4 hrs, ammonia was evaporated and the residue extracted with chloroform. The extract was evaporated *in vacuo* and the residue obtained was purified by column chromatography, using silica gel and chloroform-methanol (4:1). Crystallization from benzene gave pure products.

1,4-Dihydro-1,3-dimethyl-4-nitromethylenepyridine (*3a*), mp. 229-230°. ^{1}H NMR ($CDCl_3$): d 7.17 (d, 2 H), 8.65 (d, 5H), 7.32 (dd, 6H), 3.75 (s, $N\text{-}CH_3$), 2.04 (s, CH_3), 6.87 (s, $H\text{-}CNO_2$), $J_{5,6}$ = 7.3 Hz, $J_{2,6}$ = 1.6 Hz. MS: Calcd. m/e 166.0742, found: m/e 166.0743.

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86

Found: C, 57.64; H, 6.06; N, 17.03

1,4-Dihydro-1-methyl-4-nitromethylene-3-phenylpyridine (*3b*), mp. 207-208°. ^{1}H NMR ($CDCl_3$): d 7.16 (d, 2H), 8.73 (d, 5H), 7.36 (dd, 6H), 3.80(s, NCH_3), 6.76 (s, $\underline{H}CNO_2$), 7.25 and 7.40 (m, C_6H_5), $J_{5,6}$ = 7.3 Hz, $J_{2,6}$ = 1.8 Hz. MS: Calcd. m/e 228.0899. Found, m/e 228.0899.

Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.40; H, 5.29; N, 12.27

Found : C, 68.66; H, 5.28; N, 12.19

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