# UNUSUAL PATHWAY OF VICARIOUS NUCLEOPHILIC SUBSTITUTION FOR METHYL-CONTAINING 3-NITROPYRIDINES

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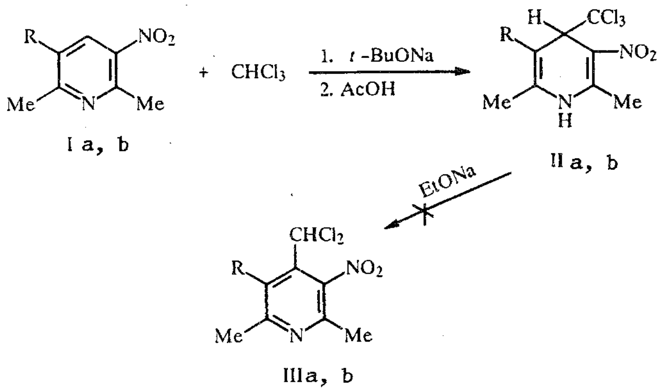
It is known that vicarious nucleophilic substitution under the influence of haloforms in basic media in the case of 3-nitropyridine or its 6-chloro and 6-methoxy derivatives proceeds in the usual way and leads to the corresponding 4-dihalomethyl-3-nitropyridines [1-3].

In an attempt to extend this reaction to 2,6-dimethyl-substituted 3-nitropyridines we unexpectedly observed that under the same conditions the process stops at the step involving the formation of 4-trichloromethyl-1,4-dihydro-3-nitropyridines — hypothetical intermediates of reactions involving vicarious nucleophilic substitution, which were found to be resistant to dehydrochlorination to the corresponding 4-dichloromethyl-3-nitropyridines even under the influence of a refluxing solution of sodium ethoxide in ethanol.



I-III a R=H, b R=Me

Thus a solution of 3 mmole of 3-nitropyridines Ia, b and 3.3 mmole of chloroform in dry DMF was added rapidly dropwise with constant stirring to a solution of sodium tert-butoxide (12 mmole) in a mixture of THF and DMF (−70°C, in a stream of argon) while maintaining the temperature at no higher than −68°C. Acetic acid (1-2 ml) was added, and the mixture was heated to room temperature and poured into water. the aqueous mixture was extracted with chloroform, and the extract was dried with $Na_2SO_4$ and evaporated in vacuo. The residue was recrystallized or purified by chromatography with a column packed with silica gel (40 by 100 $\mu$k) in benzene−ethyl acetate (10:1). This procedure gave IIa, b in 67% and 70% yields, respectively.

The presence, according to the mass-spectral data, of three chlorine atoms in the molecular ion and the existence of a process involving the elimination of a characteristic $CCl_3$ fragment serve to confirm the structure of IIa, b. In addition, the fact that they belong to the 1,4-dihydro-3-nitropyridine class is confirmed by a characteristic long-wave absorption maximum (375 and 372 nm for IIa and IIb, respectively) in the electronic absorption spectra [4]. Absorption bands of $NO_2$ groups [1480 (as), 1320-1350 (s) $cm^{-1}$] and a free imino (NH) group (3422 $cm^{-1}$) are observed in the IR spectra of IIa, b.

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**2,6-Dimethyl-3-nitro-4-trichloromethyl-1,4-dihydropyridine (IIa, $C_8H_9Cl_3N_2O_2$).** This compound had mp 160°C (benzene–hexane). PMR spectrum ($CDCl_3$, 400 MHz): 1.95 (3H, s, 6-$CH_3$), 2.50 (3H, s, 2-$CH_3$), 5.12 (1H, d, $J_{45}$ = 6.31 Hz, 4-H), 5.16 (1H, m, $J_{54}$ = 6.31 Hz, $J_{4\text{-H,NH}}$ = 1.91 Hz, $J_{4\text{-H,6-CH3}}$ = 1.24 Hz, 5-H), 6.14 ppm (1H, broad s, NH).

**2,5,6-Trimethyl-3-nitro-4-trichloromethyl-1,4-dihydropyridine (IIb, $C_9H_{11}Cl_3N_2O_2$).** This compound had mp 170-171°C (hexane–ethyl acetate). PMR spectrum ($CDCl_3$, 60 MHz): 1.87 (3H, s, 5-$CH_3$), 1.95 (3H, s, 6-$CH_3$), 2.29 (3H, s, 2-$CH_3$), 4.92 ppm (1H, s, 4-H).

The results of elementary analysis for C, H, and N were in agreement with the calculated values.

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