CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS

II.* NITRATION OF 2,3'-DIPYRIDYL MONO-N-OXIDES

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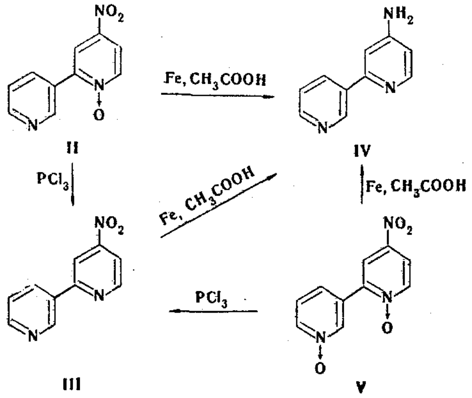
2,3'-Dipyridyl N-oxide is nitrated with a nitrating mixture to give 4-nitro-2,3'-dipyridyl N-oxide. The isomeric 2,3'-dipyridyl N'-oxide is deoxidized under these conditions, probably with the participation of the nitrosyl cation.

The present paper is a further study of the reactivities and orientation in a series of isomeric dipyridyl N-oxides in electrophilic substitution reactions [2-5].

4-Nitro-2,3'-dipyridyl N-oxide (II) is formed in the nitration of 2,3'-dipyridyl N-oxide (I) under the conditions of the nitration of 2,3'-dipyridyl N,N'-dioxide [2]. The close yields of the nitro derivatives of these compounds indicate the relatively small differences in reactivity. The structure of nitro compound II was proved by reduction to 4-nitro-2,3'-dipyridyl (III)and 4-amino-2,3'-dipyridyl (IV) and by comparison with the corresponding derivatives obtained from 4-nitro-2,3'-dipyridyl N,N'-dioxide (V):



In contrast to I, 2,3'-dipyridyl N'-oxide (VI) is not nitrated under similar conditions, and the N-oxide oxygen is eliminated to give 2,3'-dipyridyl (VII). On the basis of [6, 7], it can be assumed that the deoxidation of VI occurs with the participation of either nitric oxide or the nitrosyl cation. In order to substantiate the probable course of the reductive deoxidation, we studied model reactions of VI with nitric oxide and nitrosylsulfuric acid under the nitration conditions. The higher yields indicate the most probable participation of the nitrosyl cation [8] during the deoxidation of VI:

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* See [1] for communication I.

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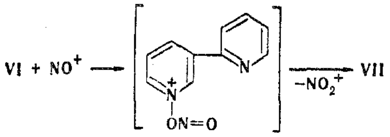
$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO^+ + H_3O^+ + 3HSO_4^-$$



The results of the present investigation are in good agreement with the data obtained for other isomeric dipyridyl N-oxides [2-5, 9-12] and reduce to the following: The α-substituted ring is subjected to nitration, and the substituent in this case is directed to the γ position; the β-substituted ring does not enter into the reaction, and the N-oxide oxygen is partially eliminated, probably with the participation of the nitrosyl cation.

EXPERIMENTAL

The UV spectra were recorded with an SF-4A spectrometer. The course of the reactions was monitored by paper chromatography with butanol–acetic acid–water (50 : 7 : 14) (system A) and by means of thin-layer chromatography on activity-II aluminum oxide with benzene–acetone (3 : 2) (system B).

4-Nitro-2,3'-dipyridyl N-oxide (II). A mixture of 0.1 g (0.6 mmole) of 2,3'-dipyridyl N-Oxide [2], 0.3 ml (5.6 mmole) of concentrated sulfuric acid (sp. gr. 1.84), and 0.26 ml (6.3 mmole) of fuming nitric acid (sp. gr. 1.53) was heated on a boiling-water bath for 10 h. The mixture was then cooled, treated with ice, and made weakly alkaline with potassium carbonate. The resulting precipitate was separated, washed with water, and recrystallized from water to give 0.05 g (40%) of yellow needles of II with mp 196-198° (from water) and R_f 0.82 (system A) and 0.45 (system B). The product was only slightly soluble in the usual organic solvents and relatively soluble in hot alcohol and water. UV spectra: λ_{max}, nm (log ε): 276 (4.24), 332 (4.18). Found: C 55.4; H 3.3; N 18.8%. $C_{10}H_7N_3O_3$. Calculated: C 55.3; H 3.2; N 19.3%.

4-Nitro-2,3'-dipyridyl (III). A mixture of 0.05 g (0.2 mmole) of N-oxide II and 1.5 ml of phosphorus trichloride was heated at 60° for 24 h, after which the excess reagents were removed by distillation, and the residue was dissolved in water. The aqueous solution was made alkaline with potassium carbonate, and the precipitate was removed by filtration and recrystallized from water to give 0.01 g (21%) of a product with mp 119-121° (from petroleum ether) and R_f 0.92 (system A) and 0.78 (system B). A mixture of this product with 4-nitro-2,3'-dipyridyl [3] melted at 120-121°.

4-Amino-2,3'-dipyridyl (IV). A. A 2.2-g sample of iron powder was added to 1 g (4.3 mmole) of V in 30 ml of glacial acetic acid, and the mixture was refluxed for 3 h. The excess acetic acid was removed by distillation, and the residue was diluted with water. The aqueous solution was made weakly alkaline with potassium carbonate, evaporated to dryness, and extracted with hot ether to give 0.25 g (30%) of a product with mp 114-115° (from benzene) and R_f 0.64 (system A) and 0.2 (system B). The product was quite soluble in alcohols, acetone, hot benzene, toluene, and ether, and insoluble in water. UV spectrum: λ_{max}, nm (log ε): 238 (4.55). Found: C 70.3; H 5.4; N 23.8%. $C_{10}H_9N_3$. Calculated: C 70.2; H 5.3; N 24.2%.

B. Method A was used to obtain 0.04 g (50%) of amine IV with mp 114-115° from 0.1 g of 4-nitro-2,3'-dipyridyl.

C. Method A was used to obtain ~ 0.02 g (50%) of amine IV with mp 114-115° from 0.05 g of N-oxide II.

Nitration of 2,3'-Dipyridyl N'-Oxide (VI). A. An 0.86-g (5 mmole) sample of N'-oxide VI was dissolved with stirring in 3 ml (56 mmole) of concentrated sulfuric acid (sp. gr. 1.84), and 0.86 ml (21 mmole) of fuming nitric acid (sp. gr. 1.53) was added. The mixture was then heated on a water bath for 24 h, cooled, and poured over ice. The aqueous mixture was made alkaline with 20% sodium hydroxide and extracted with ether to give 0.62 g (79%) of 2,3'-dipyridyl (VII) R_f 0.88 (system A) and 0.8 (system B). The picrate had mp 153-154° (from water). A mixture of this picrate with the picrate of VII melted at 153-154°. The aqueous mother liquor was evaporated to dryness, and the residue was extracted with hot ether to give 0.12 g (14%) of starting VI.

B. A mixture of 0.67 g (3.8 mmole) of VI, 2.4 ml (50 mmole) of concentrated sulfuric acid (sp. gr. 1.84), and 0.68 ml of fuming nitric acid (sp. gr. 1.53) was heated at 128-130° for 10 h. Workup gave 0.26 g (43%) of VII and 0.24 g (34%) of starting VI.

Reduction of 2,3'-Dipyridyl N'-Oxide (VI) with Nitrosylsulfuric Acid. A solution of 0.1 g (58 mmole) of VI and 0.2 g (1.5 mmole) of nitrosylsulfuric acid in 0.4 ml (8 mmole) of concentrated sulfuric acid was heated on a boiling-water bath for 10 h, after which the mixture was made alkaline and extracted with ether to give ~ 0.01 g (10%) of 2,3'-dipyridyl (VII). The picrate had mp 153-154°. A mixture of this picrate with the picrate of VII melted at 153-154°. The mother liquor was evaporated to dryness, and the residue was extracted with ether to give 0.08 g (80%) of starting oxide VI.

The yields of VII and VI at 128-130° were 37% and 53%, respectively.

Reduction of 2,3'-Dipyridyl N'-Oxide (VI) with Nitric Oxide. A stream of nitric oxide was passed through a solution of 0.14 g (8 mmole) of VI in 0.3 ml of concentrated sulfuric acid (sp. gr. 1.84) at 130° for 10 h. The usual workup of the reaction mixture gave 0.014 g (11%) of 2,3'-dipyridyl (VII) and 0.09 g (64%) of starting oxide VI.

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