CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS

IV.* DEHYDROGENATION OF THE HANTZSCH ESTER WITH 2,3'-, 3,3'-, and 4,4'-DIPYRIDYL N-TOSYLIMIDES

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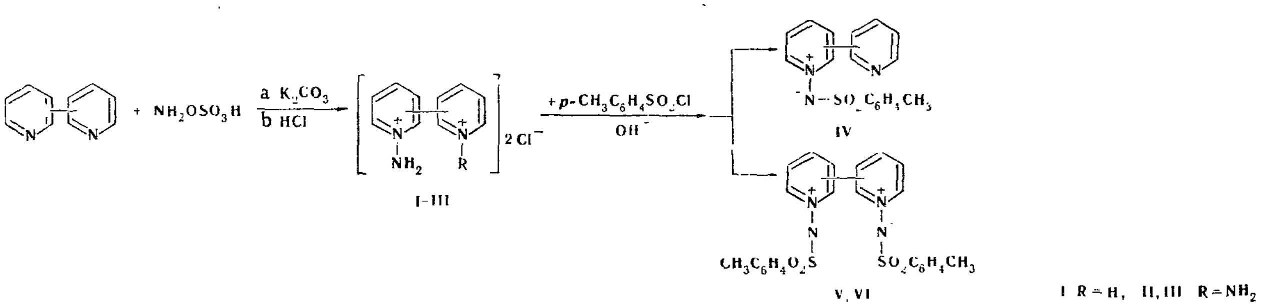
The synthesis of 2,3'-, 3,3'-, and 4,4'-dipyridyl N-tosylimides, for which the dehydrogenating activity was investigated in the case of reaction with the Hantzsch ester, was accomplished.

The possibility of the use of N-imines of pyridine bases – nitrogen analogs of N-oxides – as homogeneous dehydrogenating agents has been demonstrated by us in the case of the dehydrogenation of anabasine and the Hantzsch ester, respectively, by the hydrochloride and N-tosyl derivative of pyridine N-imine [1]. Inasmuch as the most active dehydrogenating agents among the N-oxides of pyridine bases are dipyridyl N-oxides [2], it was necessary to investigate the reactivities of N-tosylimidodipyridyls as hydrogen acceptors. In the present research we studied the homogeneous dehydrogenation of diethyl 1,4-dihydro-2,6-lutidine-3,5-dicarboxylate (the Hantzsch ester) with 2,3'-, 3,3'-, and 4,4'-dipyridyl N-tosylimides.

The starting materials – 2,3'-, 3,3'-, and 4,4'-dipyridyl N-imine hydrochlorides (I-III) and their N-tosyl derivatives (IV-VI) – were obtained by the method used to prepare the corresponding pyridine [1] derivatives via the scheme



Data on the properties and structures of the compounds obtained are presented in Table 1. The UV spectra of I-VI contain absorption bands in the region of $\pi\rightarrow\pi^*$-transitions that attest to the presence of the skeleton of the corresponding dipyridyl [3]. The structure of N-tosyl derivatives IV-VI was also confirmed by hydrolysis, as a result of which dipyridyl N-imines I-III were obtained.

The dehydrogenation of the Hantzsch ester (VII) with dipyridyl N-tosylimides (IV-VI) proceeds rapidly, is accompanied by slight resinification, and gives an aromatic compound – diethyl 2,6-lutidine-3,5-dicarboxylate – and products of reductive deimidation – dipyridyl and p-toluenesulfonamide – in rather high yields (Table 2).

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*See [1] for communication III.

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TABLE 1. Properties of Derivatives of Dipyridyl N-Imines

Compound	mp, °C*	Empirical formula	Found, %		Calc. %		R_f	UV spectra			Yield, %
			Cl	N	Cl	N		λ_{max}, nm	lg ε	solvent	
I	175—176	$C_{10}H_9N_8 \cdot 2HCl$	28,7	—	28,97	—	0,52 (A)	243 271	4,22 4,15	95% alcohol	14
Dipicrate of I	176—177	$C_{10}H_9N_3 \cdot 2C_6H_3N_3O_7$	—	20,3	—	20,0	—	—	—	—	
IV	176—177	$C_{17}H_{15}N_3O_2S$	—	12,9	—	12,9	0,62 (C)	243 263	4,34 4,15	95% alcohol	83
II	264 (dec)	$C_{10}H_{10}N_4 \cdot 2HCl$	27,6	—	27,5	—	0,05 (A)	240	4,38	95% alcohol	28
Dipicrate of II	245	$C_{10}H_{10}N_4 \cdot 2C_6H_3N_3O_7$	—	22,5	—	21,7	—	—	—	—	
V†	268 (dec)	$C_{24}H_{22}N_4O_4S_2$	—	11,4	—	11,3	—	—	—	—	88
III‡	288	—	—	—	—	—	0,25 (B)	290 305	4,17 4,29	5% HCl glacial CH_3COOH	91
Dipicrate of III	239 (dec)	$C_{10}H_{10}N_4 \cdot 2C_6H_3N_3O_7$	—	21,2	—	21,7	—	—	—	—	
VI	271 (dec)	$C_{24}H_{22}N_4O_4S_2$	—	11,5	—	11,3	—	233 280 282 270	4,39 4,30 4,33 3,98	5% HCl 5% HCl glacial CH_3COOH glacial CH_3COOH	100

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*Crystallization solvents: absolute alcohol for I, 95 % alcohol for the dipicrate of I and IV, 80 % alcohol for II and the dipicrate of II, dimethylformamide for V and VI, and 50 % alcohol for III and the dipicrate of III.

†The UV spectrum was not recorded in view of the limited solubility of this compound.

‡The melting point and UV spectrum are in agreement with the literature data [5].

TABLE 2. Dehydrogenation of the Hantzsch Ester

Dehydrogenating agent	Reaction temp., °C	Reaction time, min	Yield, %		
			VIII	Dipyridyl	IX
IV	150—160	10	92	76	77
V	210—220	5	88	50	78
VI	210—220	30	70	77	80

A comparison of the results obtained in this study with the results of the dehydrogenation of the Hantzsch ester with N-oxides of pyridine bases [4], including dipyridyl N-oxides [2], makes it possible to note that dipyridyl N-tosylimides are similar to N-oxides as hydrogen acceptors, and if one takes into account the short-term character of the reactions, they somewhat surpass them.

EXPERIMENTAL

The separation of the reaction mixtures was monitored by chromatography on paper ("fast" brand) in n-butanol–acetic acid–water (50 : 7 : 14) (system A) and n-propanol–hydrochloric acid–water (50 : 7 : 14) (system B) with development with Dragendorff's reagent and by means of TLC on activity II aluminum oxide in chloroform–benzene–alcohol (22 : 8 : 2) (system C) with development by iodine vapors. The UV spectra of the synthesized compounds (concentration $1 \cdot 10^{-4}$ M) were recorded with an SF-4A spectrophotometer.

Dipyridyl N-Imine Hydrochlorides (I-III). A 7-g (60 mmole) sample of O-hydroxylaminosulfonic acid previously neutralized at 0° with 5 N KOH was added slowly with vigorous stirring to a solution of 3.5 g (20 mmole) of the dipyridyl in 4 ml of water heated to 70°, after which the mixture was allowed to stand with the periodic addition of potassium acetate until it gave a negative test for O-hydroxylamino sulfonic acid (with the aid of starch-iodide paper) at pH 7-8. The solution was then cooled, acidified with HCl (1 : 1), and the sulfates were precipitated by the addition of an equivalent amount of barium chloride. The precipitate was removed by filtration and washed with water, the filtrate was vacuum evaporated to dryness, and the residue was extracted in a Soxhlet apparatus with absolute alcohol to give I-III.

Dipyridyl N-Tosylimides (IV-VI). A 0.74-g (3 mmole) sample of dipyridyl N-imine hydrochloride (I-III) was dissolved in 10 ml of water, and the solution was made alkaline to pH 8 with potassium acetate. A solution of 1.2 g (60 mmole) of p-toluenesulfonyl chloride in 10 ml of acetone was then added with vigorous stirring, after which the mixture was stirred for 1 h and allowed to stand overnight. The precipitated crystals were removed by filtration and washed successively with water and acetone.

Hydrolysis of Dipyridyl N-Tosylimides. A 0.2-g (0.6 mmole of IV or 0.4 mmole of V and VI) sample of dipyridyl N-tosylimide was refluxed in 20 ml of 20% HCl for 15 h, after which the mixture was vacuum evaporated to dryness, and the residue was extracted with ether in an apparatus for continuous extraction to give p-toluenesulfonic acid in yields, respectively, of 90, 89, and 97% for IV-VI. Compounds I-III were obtained in yields of 94, 94, and 96%, respectively, from the residues.

Dehydrogenation of the Hantzsch Ester (VII) with Dipyridyl N-Tosylimides (IV-VI). An equivalent mixture of VII and dipyridyl N-tosylimide was heated at 150-220° for 5-30 min until it gave a negative test for the presence of VII on treatment with picric acid. The melt was treated with HCl (1 : 1) and extracted with chloroform. The chloroform solution contained a mixture of diethyl 2,6-lutidine-3,5-dicarboxylate (VIII) and p-toluenesulfonamide (IX), which were separated by treatment with ether. The solvent was removed by distillation to give VIII. The residue contained IX. The mother liquid was made alkaline to pH 5 with potassium carbonate and extracted with chloroform to give the dipyridyl. The reaction products were identified by mixed-melting-point determinations with genuine samples; no melting-point depressions were observed.

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