TABLE 2. Arylalkylsulfonamide Derivatives of Melatonin (VII-XII), 3,4-Dihydro-β-carboline (XIII-XVIII), and 1,2,3,4-Tetrahydro-β-carboline (XIX-XXIV)

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
VII	38—40	64,6	7,2	8,4	6,5	$C_{26}H_{35}N_3O_4S$	64,3	7,2	8,6	6,5	76
VIII	44—46	63,8	7,2	8,4	6,6	$C_{27}H_{37}N_3O_4S$	64,1	7,4	8,4	6,4	85
IX	53—56	65,4	7,6	8,1	5,8	$C_{28}H_{39}N_3O_4S$	65,5	7,6	8,2	6,2	74
X	56—58	65,8	7,6	7,8	6,4	$C_{28}H_{39}N_3O_4S$	65,5	7,6	8,2	6,2	77
XI	30—32	65,5	7,7	8,0	6,3	$C_{28}H_{39}N_3O_4S$	65,5	7,6	8,2	6,2	76
XII	32—35	65,3	7,6	8,1	6,2	$C_{28}H_{39}N_3O_4S$	65,5	7,6	8,2	6,2	80
XIII	78—80	66,8	7,3	8,9	6,5	$C_{26}H_{33}N_3O_3S$	66,8	7,1	9,0	6,8	72
XIV	97—99	67,5	7,4	8,6	6,4	$C_{27}H_{35}N_3O_3S$	67,8	7,3	8,4	6,6	75
XV	89—92	68,42	7,3	8,3	6,2	$C_{28}H_{37}N_3O_3S$	68,7	7,5	8,4	6,5	73
XVI	94—97	68,6	7,5	8,4	6,8	$C_{28}H_{37}N_3O_3S$	68,7	7,5	8,4	6,5	74
XVII	99—101	68,5	7,4	8,4	6,4	$C_{28}H_{37}N_3O_3S$	68,7	7,5	8,4	6,5	75
XVIII	98—100	68,6	7,5	8,2	6,1	$C_{28}H_{37}N_3O_3S$	68,7	7,5	8,4	6,5	74
XIX	100—101	66,4	7,4	8,7	6,5	$C_{26}H_{35}N_3O_3S$	66,5	7,5	8,9	6,8	70
XX	85—86	66,9	7,4	8,6	7,4	$C_{27}H_{37}N_3O_3S$	67,1	7,7	8,8	6,6	67
XXI	93—94	67,7	7,9	8,7	6,5	$C_{28}H_{39}N_3O_3S$	67,6	7,8	8,4	6,4	69
XXII	98—99	67,5	7,7	8,2	6,1	$C_{28}H_{39}N_3O_3S$	67,6	7,8	8,4	6,4	72
XXIII	102—103	67,6	7,9	8,2	6,6	$C_{28}H_{39}N_3O_3S$	67,6	7,8	8,4	6,4	71
XXIV	106—108	67,6	7,9	8,3	6,5	$C_{28}H_{39}N_3O_3S$	67,6	7,8	8,4	6,4	73

carbonate and evaporated to dryness to give 0.24 g (70%) of XIX with mp 100-101°C (from petroleum ether). UV spectrum (in alcohol), λ_{max} (log ε): 300 nm (3.6).

Compounds XX-XXIV were similarly obtained.

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CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS. IX.* DEHYDROGENATION OF THE HANTZSCH ESTER BY NITRO AND CARBOXY DERIVATIVES OF PYRIDINE N-OXIDE

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The dehydrogenating activity of 4-nitropyridine N-oxide and picolinic, nicotinic, isonicotinic, and quinolinic acid N-oxides was studied in the case of the reaction with the Hantzsch ester.

In a continuation of our study of the dehydrogenating capacity of N-oxides of pyridine bases it seemed of interest to study pyridine N-oxide derivatives with electronegative substituents, since the introduction of the latter into the N-oxide molecule sharply increases the redox potential [2]. In the present research in the case of the dehydrogenation of the Hantzsch ester (I) we studied the dehydrogenating activity of N-oxides of picolinic (II), nicotinic (III), isonicotinic (IV), and quinolinic (V) acids and 4-nitropyridine (VI).

Pyridinecarboxylic acid N-oxides dehydrogenate the Hantzsch ester at lower temperatures than the unsubstituted pyridine N-oxide, and better results are obtained when oxide II is used.

*See [1] for communication VIII.

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In this case the dehydrogenation product — lutidinedicarboxylic ester VII — is formed in highest yield (96%). The deoxidation of oxide II is accompanied by simultaneous decarboxylation to give pyridine, as evidenced by the results of a model experiment in which thermal decarboxylation took place over the same temperature range.

The dehydrogenation of the Hantzsch ester by acid oxides III-V gives the products in lower yields and is accompanied by resinification and decarboxylation. However, in this case decarboxylation cannot be regarded as a simultaneous process, since in model experiments the thermal decarboxylation of these acid N-oxides takes place at considerably higher temperatures. The decarboxylation of acid oxides III-V probably takes place during dehydrogenation with the participation of dehydrogenating agent—substrate intermediate complexes.

One should also note that dimerization products — dipyridyls — are formed in the thermal decarboxylation of pyridinecarboxylic acid N-oxides II-V, whereas this is not observed in the case of dehydrogenation of the Hantzsch ester by II-V. This can be explained by the fact that dihydropyridines are inhibitors of radical oxidation reactions [4].

The Hantzsch ester reacts explosively with 4-nitropyridine N-oxide (VI) when the compounds are fused at 130-140°C. When the dehydrogenation is carried out in a solvent (p-xylene), VII is formed in high yield. In this case nitrocompound VI is converted to a complex mixture of products of the reduction of the oxide and nitrogroups, among which 4-nitropyridine and 4-aminopyridine were identified by chromatography.

EXPERIMENTAL

The course of the reactions was monitored by paper chromatography in a butanol—hydrochloric acid—water (50:7:14) system (system A) and in a butanol—acetic acid—water (50:7:14) system (system B) with development by Dragendorf's reagent. The reaction products were identified by chromatography and from the absence of melting-point depressions in the case of mixtures of the reaction products with pure samples.

Dehydrogenation of the Hantzsch Ester (I). A) Picolinic acid N-oxide (II). A mixture of 1.27 g (5 mmole) of ester I and 0.7 g (5 mmole) of oxide II was heated at 150-160°C for 2 h, after which it was heated at 160-170° until it gave a negative test for ester I with picric acid. The carbon dioxide formed in the reaction was determined in the form of barium carbonate. The yield of CO_2 was 0.15 g (68%). The distillate contained 0.1 g (25%) of pyridine with R_f 0.3 (system A). The picrate had mp 159-160°C. The resinous residue was dissolved in chloroform, and the solution was washed with water. The aqueous solution was extracted with benzene, and the benzene extract was worked up to give traces of picolinic acid. The chloroform extract was evaporated, and the residue was mixed with aluminum oxide and extracted with petroleum ether in an apparatus for continuous extraction. Workup of the extract gave 1.22 g (96%) of ester VII with mp 68-69°C.

B) Nicotinic acid N-oxide (III). A mixture of 2.53 g (10 mmole) of ester I and 1.39 g (10 mmole) of oxide III was heated at 160-180°C for 10 min and at 190-210°C for 1 h until it gave a negative test for ester I. The yield of carbon dioxide was 0.2 g (45%). The distillate contained 0.2 g (25%) of pyridine. The reaction mixture was dissolved in chloroform, and the solution was washed with water. The aqueous solution was evaporated, and the residue was subjected to fractional extraction while heating with hexane, ether, and benzene. Workup of the hexane extract yielded an oily substance which was not identified. Workup of the ether and benzene extracts yielded 0.54 g (44%) of nicotinic acid with mp 230-232°C. The chloroform extract was evaporated, and the residue was mixed with aluminum oxide and extracted continuously with benzene. Workup of the extract gave 0.95 g (38%) of ester VII.

C) Isonicotinic acid N-oxide (IV). The experiment was carried out by dehydrogenation of ester I with oxide III at 180-200°C. The reaction gave 0.29 g (66%) of CO_2, 0.23 g (29%) of pyridine, traces of isonicotinic acid, and 1.05 g (42%) of ester VII.

D) Quinolinic acid N-oxide (V). A mixture of 0.63 g (2.5 mmole) of ester I and 0.47 g (2.5 mmole) of oxide V was heated at 160-165°C for 2 h and at 180-190°C until it gave a negative test for ester I. It was then worked up as described in the dehydrogenation of ester I with oxide III. The reaction gave 0.175 g (80%) of carbon dioxide, 0.1 g (50%) of pyridine, and 0.35 g (56%) of ester VII.

E) 4-Nitropyridine N-oxide (VI). A mixture of 3.81 g (15 mmole) of ester I, 2.1 g (15 mmole) of oxide VI, and 70 ml of dry p-xylene was heated at 120°C for 5 h until it gave a

negative test for starting ester I. It was then treated repeatedly with 5% HCl, and the acid extracts were made alkaline to pH 8 with K_2CO_3. The precipitated ester VII was removed by filtration and recrystallized from 50% alcohol to give 3.5 g (92%) of product with mp 68-70°C and R_f 0.9 (system A). The aqueous solution was extracted exhaustively with ether. The extract contained a total of 0.95 g of substances with R_f 0.06, 0.10, 0.15, 0.26, 0.60, 0.70, and 0.90 (system A). The substances with R_f 0.26 and 0.60 were identified as 4-nitropyridine and 4-aminopyridine, respectively.

Thermal Decarboxylation. A) Picolinic acid N-oxide (II). A 0.7-g (5 mmole) sample of picolinic acid N-oxide was heated at 140-145°C. The carbon dioxide was determined in the form of barium carbonate. The yield of CO_2 was 0.137 g (62%). The distillate contained 0.2 g (50%) of pyridine with R_f 0.3 (system A). Traces of pyridine N-oxide, with R_f 0.6 (system A), and of 2,2'-dipyridyl monoxide, with R_f 0.85 (system B), were detected in the residue.

B) Nicotinic acid N-oxide (III). The experiment was carried out by decarboxylation of N-oxide II at 270-280°C for 30 min. The yield of CO_2 was 0.12 g (54%), and the yield of pyridine was 0.11 g (27%); traces of 3,3'-dipyridyl and nicotinic acid were also detected.

C) Isonicotinic acid N-oxide (IV). A 0.7-g (5 mmole) sample of N-oxide IV was heated at 250-260° for 30 min. The reaction produced 0.12 g (54%) of carbon dioxide and 0.2 g (50%) of pyridine. The residue was dissolved in chloroform, the chloroform solution was washed with water, and the aqueous solution was evaporated to give 0.17 g (27%) of isonicotinic acid. Traces of 4,4'-dipyridyl with R_f 0.8 (system B) were detected in the chloroform solution.

D) Quinolinic acid N-oxide (V). A 0.47-g (2.5 mmole) sample of N-oxide V was heated at 255-260°C for 1 h. The reaction products were isolated as described in the decarboxylation of N-oxide II. The yield of CO_2 was 0.13 g (60%); traces of pyridine were also detected. Traces of nicotinic acid were detected in the sublimate.

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