LETTERS TO THE EDITOR

NEW METHOD OF SYNTHESIZING ALKYL ESTERS OF FUROXANDICARBOXYLIC ACID

I. V. Vigalok, I. E. Moisak, and N. V. Svetlakov

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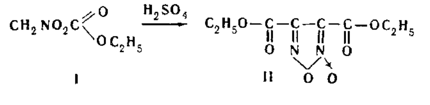
By the action of sulfuric acid on ethyl nitroacetate (I) we have isolated diethyl furoxandicarboxylate (II):



The structure of **II** was confirmed by the analogy of the IR spectrum with that of an authentic sample [1] and by its conversion into furoxandicarboxyamide by treatment with an aqueous solution of ammonia.

Diethyl furoxandicarboxylate (II). 13.3 g (0.1 mole) of **I** was added to 49 g (0.5 mole) of sulfuric acid (d_4^{20} 1.84) in such a way that the temperature did not exceed −5° C. After the reaction mixture had been kept at the same temperature for 12 hours, it was poured into water, and the oil that separated was extracted with ether. The ethereal extract was washed with water and dried with sodium sulfate. Distillation yielded **II**.

Esters of furoxandicarboxylic acid have been obtained from other alkyl nitroacetates under similar conditions.

The substances synthesized and their yields and constants are given in the table.

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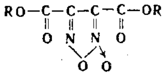
Kirov Kazan Chemical and
Technological Institute



R	Bp, °C (pressure, mm)	d_4^{20}	n_d^{20}	MR_D		Empirical formula	Found, %			Calculated, %			Yield, %
				found	Calculated		C	H	N	C	H	N	
CH_3	112/2	1.410	1.486	41.14	40.90	$C_6H_6O_6N_2$	35.63	3.05	13.72	35.15	2.97	13.86	67
C_2H_5	113/2	1.2783	1.475	50.67	50.20	$C_8H_{10}O_6N_2$	42.03	4.02	12.33	41.78	4.35	12.17	65
C_3H_7	130/2	1.2051	1.472	59.95	59.50	$C_{10}H_{14}O_6N_2$	46.17	5.42	10.68	46.51	5.42	10.85	61
C_4H_9	143/2	1.1542	1.470	69.14	68.79	$C_{12}H_{18}O_6N_2$	49.73	6.23	10.06	50.00	6.25	9.73	73

REACTION OF sym-OCTAHYDROACRIDINE N-OXIDE WITH ACETIC ANHYDRIDE IN THE PRESENCE OF AN AROMATIC ALDEHYDE

G. A. Klimov and M. N. Tilichenko

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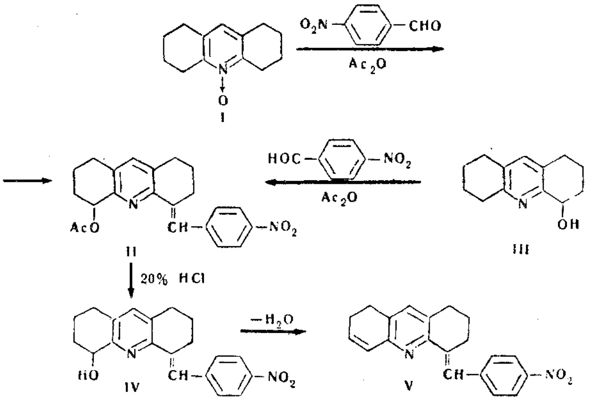
It is known that when sym-octahydroacridine N-oxide (I) is boiled with acetic anhydride, the acetate of sym-octahydroacridin-4-ol is formed [1]. We have found that if equimolecular amounts of I and p-nitrobenzaldehyde (PNBA) are boiled in acetic anhydride, C-acetoxylation takes place at one methylene group and condensation at another. No such reaction has previously been performed in the cycloalkylpyridine N-oxide series. The structure of the acetate of 4-(p-nitrobenzylidene)-sym-octahydroacridin-5-ol (II) formed was confirmed by independent synthesis. When equimolecular amounts of the previously-described [1] sym-octahydroacridin-4-ol (**III**) and PNBA are boiled in acetic anhydride, **II** is formed. On being heated with 20% HCl, the latter is hydrolyzed to 4-(p-nitrobenzylidene)-sym-octahydroacridin-5-ol (**IV**). The dehydration of **IV** with polyphosphoric acid leads to 4-(p-nitrobenzylidene)-1, 2, 3, 4, 7, 8-hexahydroacridine (**V**).



II. Pale yellow rods, mp 202–203° C (ethanol–acetone, 4 : 3), yield 50% by direct synthesis and 60% by indirect. Found, %: N 7.41. Calculated for $C_{22}H_{22}N_2O_4$, %: N 7.40. IR spectrum (in KBr): 1260 and 1760 cm^{-1} (ester bond); 1360 and 1540 cm^{-1} (nitro group).

IV. Yellow rhombs, mp 174–175° C (ethanol), yield 73%. Found, %: N 8.17. Calculated for $C_{20}H_{20}N_2O_3$, %: N 8.33. IR spectrum (in KBr): 3530 cm^{-1} (hydroxy group); 1360 and 1540 cm^{-1} (nitro group). **Picrate**, mp 182.5–183° C (decomp., methanol–benzene, 1:1). Found, %: N 13.01. Calculated for $C_{20}H_{20}N_2O_3 \cdot C_6H_3N_3O_7$, %: N 12.39. **Hydrochloride**, mp 189.5–190.5° C (ethyl acetate–dioxane, 1:1). Found, %: N 7.51. Calculated for $C_{20}H_{20}N_2O_3 \cdot HCl$, %: N 7.52.

V. Sirupy oil (purified chromatographically), yield 68%. Found, %: N 8.89. Calculated for $C_{20}H_{18}N_2O_2$, %: N 8.80. **Picrate**, mp 176–177° C (methanol–benzene, 1:1). Found, %: N 13.17. Calculated for $C_{20}H_{18}N_2O_2 \cdot C_6H_3N_3O_7$, %: N 12.79. **Hydrochloride**, mp 118–120° C (ethyl acetate). Found, %: N 7.92. Calculated for $C_{20}H_{18}N_2O_2 \cdot HCl$, %: N 7.89.

The chromatography was carried out on alumina of activity II and the IR spectra were recorded on a UR-10 spectrometer.

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Far Eastern State University,
Vladivostok

SYNTHESIS OF DERIVATIVES OF IMIDAZO[1,2-a]IMIDAZOLE

P. M. Kochergin and B. A. Priimenko

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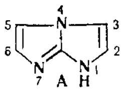
The preparation of derivatives of imidazo[1,2-a]imidazole (**A**) from α-amino aldehydes is known [1]. In analogy with the synthesis of derivatives of imidazo[1,2-a]benzimidazole [2] and imidazo[1,2-f]-purine [3], by the reaction of 1-alkyl-2-aminoimidazoles with α-halo ketones we have obtained 3-acylmethyl-1-alkyl-2-iminoimidazolines, which, on being heated with mineral acids, cyclize to the derivatives **A**. With secondary α-halo ketones, the reaction takes place in one stage with the formation of the derivatives **A**.



A

2-Imino-1-methyl-3-phenacylimidazoline hydrobromide (I). Mp 234–236° C (decomp.) (methanol). Found, %: C 48.70; H 4.50; Br 27.00; N 14.35. Calculated for $C_{12}H_{13}N_3O \cdot HBr$, %: C 48.67; H 4.76; Br 26.98; N 14.19. **3-(p-Bromophenacyl)-2-imino-1-methylimidazoline hydrobromide (II).** Mp 233–234° C (decomp., ethanol). Found, %: C 40.58; H 3.36; Br (total) 45.27; Br (ion) 22.48; N 11.71. Calculated for $C_{12}H_{12}BrN_3O \cdot HBr$, %: C 40.36; H 3.10; Br (total) 44.76; Br (ion) 22.38; N 11.77. **1-Methyl-6-phenylimidazo[1,2-a]imidazole hydro bromide (III).** Mp 207–208° C (decomp., methanol). Found, %: C 48.56; H 4.84; Br 27.46; N 13.99. Calculated for $C_{12}H_{11}N_3 \cdot HBr \cdot H_2O$, %: C 48.67; H 4.76; Br 26.98; N 14.19. **6-(p-Bromophenyl)-1-methylimidazo[1,2-a]imidazole hydrobromide (IV).** Mp 224–225° C (decomp., methanol). Found, %: C 39.98; H 3.31; Br 45.24; N 11.73. Calculated for $C_{12}H_{10}Br$, %: C 40.36; H 3.10; Br 44.76; N 11.77. **1,5-Dimethyl-6-phenylimidazo[1,2-a]imidazole, picrate** (V). Mp 162–163° C (methanol). Found, %: C 51.57; H 3.72; N 19.17. Calculated for $C_{13}H_{13}N_3 \cdot C_6H_3N_3O_7$ %: C 51.82; H 3.66; N 19.09. **1,6-Dimethylimidazo[1,2-a]imidazole, picrate** (VI). Mp 209–210° C (decomp., methanol). Found, %: C 52.16; H 3.86; N 19.30. Calculated for $C_{13}H_{13}N_3O_7$, %: C 51.82; H 3.66; N 19.09.

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Ordzhonikidze All-Union Chemical
and Pharmaceutical Scientific-
Research Institute, Moscow

Zaporozh'e Medical Institute