SUBSTITUTED PYRIDINES

I. 4-n-Alkyl-2,5-Dimethylpyridines

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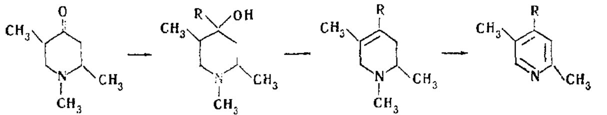
New 4-n-alkyl-1,2,5-trimethylpiperid-4-ols with pentyl, hexyl, heptyl, nonyl, and decyl radicals in the γ-position of the piperidine ring have been obtained. Similarly-substituted piperidines have been synthesized from them.

Cetylpyridinium chloride is an effective emulsifying agent in the polymerization of methyl methacrylate in the presence of benzoyl peroxide [1,2]. It appeared of interest to investigate how the emulsifying properties of a similar pyridinium system changes when the alkyl radical attached to the nitrogen is shifted into the γ-position of the pyridine ring.

With this object we have synthesized a number of new alkyl-substituted pyridines which, in the form of the ethyl bromide derivatives, have been studied as emulsifying agents in polymerization systems. The synthesis of the pyridines was preceded by the synthesis of new tertiary γ-piperidols—4-n-pentyl- (II), 4-n-hexyl- (III), 4-n-heptyl- (IV), 4-n-nonyl- (V), and 4-n-decyl-1,2,5-trimethylpiperid-4-ols (VI) (Table 1). These were obtained from the corresponding alkyllithiums or alkylmagnesium halides and 1,2,5-trimethylpiperid-4-one (I).



II, VIII, XIII R = n-C_5H_{11}; III, IX, XIV R = n-C_6H_{13}; IV, X, XV R = n-C_7H_{15}; V, XI, XVI R = n-C_9H_{19}; VI, XII, XVII R = n-$C_{10}H_{21}$

These alcohols were subjected to dehydration with the aid of hydrochloric acid. This gave satisfactory yields of the corresponding 4-n-alkyl-1,2,5-trimethyltetrahydropyridines (VIII–XII, respectively) (Table 2). Conversion into the corresponding pyridines XIII–XVII (Table 3) was performed catalytically. The dehydrogenation and the N-demethylation of the tetrahydropyridines were carried out on a type K-16 catalyst at 400–420° C.

N-Ethyl-2,5-dimethyl-4-n-nonylpyridinium bromide proved to be an effective emulsifying agent in polymerization systems. Detailed results of the investigation of the compounds obtained in this project will be published in the journal "Vysokomoledulyarine Soedineniya."

EXPERIMENTAL

4-n-Alkyl-1,2,5-trimethylpiperid-4-ols. Alkyllithiums were obtained in absolute ether (200 ml) from 0.5 mole of lithium and 0.25 mole of the alkyl bromide in each case; 0.2 mole of 1,2,5-trimethylpiperid-4-one (I) was added at 0° C, and the mixture was kept at room temperature and was treated with 50 ml of water and acidified (to Congo Red) with dil (1 : 1) HCl. The neutral substances were removed with the ethereal layer. The aqueous layer was treated with caustic potash. The organic bases were extracted with ether. Distillation of the ethereal extract yielded the initial piperidone (I) and the corresponding 4-n-alkyl-1,2,5-trimethylpiperid-4-ol.

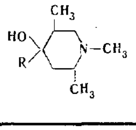
4-n-Pentyl-1,2,5-trimethylpiperid-4-ol (II) was obtained from n-pentylmagnesium bromide. Methiodide of the piperidol II—mp 105–108° C (from ethanol). Found, %: N 4.13, 3.79. Calculated for $C_{13}H_{27}NO \cdot CH_3I$, %: N 3.98. The characteristics of the piperidols II–VI synthesized are given in Table 1.

4-n-Pentyl-4-propionoxy-1,2,5-trimethylpiperidine hydrochloride (VII) (a white hygroscopic substance) was obtained by heating 1.3 g (6 mm) of the piperidol II and 1.2 g (13 mM) of propionyl chloride in 15 ml of benzene for 5 hr. Mp 135–140° C. Found, %: N 4.25, 4.18. Calculated for $C_{16}H_{31}NO_2 \cdot HCl$, %: N 4.58. Picrate of the base VII—mp 147–148° C (from ethanol). Found, %: N 11.24, 11.48. Calculated for $C_{16}H_{31}NO_2 \cdot C_6H_3N_3O_7$, %: N 11.23.

4-n-Alkyl-1,2,5-trimethyltetrahydropyridines. A 4-n-alkyl-1,2,5-trimethylpiperid-4-ol (0.05 mole) was boiled with a fivefold excess

Table 1

γ-Piperidols



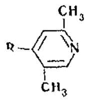
Compound	R	Bp, °C (pressure, mm)	Mp, °C	Empirical formula	N, %		Yield, % (on the piperidone I that reacted)
					found	calculated	
II	n-C_5H_{11}	122—124 (3,5)	—				28
III	n-C_6H_{13}	124—126 (2)	—	$C_{14}H_{29}NO$	6.08 6.31	6.16	28
IV	n-C_7H_{15}	139—141 (1,5)	—	$C_{15}H_{31}NO$	5.63 5.84	5.82	36.5
V	n-C_9H_{19}	159—161 (2)	49—53 (from gasoline)	$C_{17}H_{35}NO$	5.26 5.28	5.21	32
VI	n-$C_{10}H_{21}$	175—180 (2)	64—65 (from gasoline)	$C_{18}H_{37}NO$	4.94 5.24	4.95	53.9

Table 2

4-n-Alkyl-1, 2, 5-trimethyltetrahydropyridines

Compound	R	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	Empirical formula	Found		Calculated		Yield, %
						N, %	MR_D	N, %	MR_D	
VIII	n-C_5H_{11}	90—93 (3)	0.8594	1.4715	$C_{13}H_{25}N$	7.09 6.82	63.42	7.17	63,50	73,5
IX	n-C_6H_{13}	99—101 (1)	—	1.4745	$C_{14}H_{27}N$	6.47 6.34	—	6.69	—	69
X	n-C_7H_{15}	122—126 (2)	0.8612	1.4732	$C_{15}H_{29}N$	6.29 6.06	72.74	6.28	72.65	77
XI	n-C_9H_{19}	136—137 (1)	0.8646	1.4750	$C_{17}H_{33}N$	5.74 5.47	81.75	5.57	81.97	55
XII	n-$C_{10}H_{21}$	163—165 (2)	0.8648	1.4740	$C_{18}H_{35}N$	5.11 5.47	86.59	5.28	86.16	78

Table 3

Alkylpyridines 

Compound	R	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Yield, %	Picrate from ethanol				Mp of the ethyl bromide derivative, °C
					found	calculated		mp, °C	empirical formula	N, %		
										found	calculated	
XIII	n-C_5H_{11}	83—85 (2)		1.4959			54	106—107	$C_{12}H_{19}N \cdot C_6H_3(NO_2)_3OH$	13.73 13.67	13.79	170—171
XIV	n-C_6H_{13}	117—119 (2,5)	0.9007	1.4960	62.22	62.47	53.7	90—92	$C_{13}H_{21}N \cdot C_6H_3(NO_2)_3OH$	13.61 13.23	13.33	168—170
XV	n-C_7H_{15}	135—137 (2)	0.8930	1.4930	66.73	66.48	59.8	89.5—90	$C_{14}H_{23}N \cdot C_6H_3(NO_2)_3OH$	12.77 12.63	12.92	164.5—166
XVI	n-C_9H_{19}	151—152 (3)					50.1	80—82	$C_{16}H_{27}N \cdot C_6H_3(NO_2)_3OH$	11.80 12.10	12.12	160—162
XVII	n-$C_{10}H_{22}$	153—156 (2)	0.8973	1.5010	80.87	81.05	48.5	95—97	$C_{17}H_{29}N \cdot C_6H_3(NO_2)_3OH$	12.06 11.95	11.76	162—163.5

of conc HCl for 6 hr. The acid was distilled off in vacuum and the residue was dissolved in water, neutralized with sodium carbonate, and heated with an excess of sodium carbonate for 2 hr. The organic bases were extracted with ether and the extract was dried with magnesium sulfate and distilled (see Table 2).

4-n-Alkyl-2,5-dimethylpyridines. A solution of 0.1 mole of a 4-n-alkyl-1,2,5-trimethyltetrahydropyridine in 10 ml of benzene was passed over type K-16 catalyst (100 ml) during 3 hr. The temperature in the catalyst zone was 400–420° C. The condensate was dried with caustic potash, and the benzene was distilled off. Distillation of the residue yielded the corresponding 4-n-alkyl-2,5-dimethylpyridine.

To obtain the ethyl bromide derivatives, 25 mM of ethyl bromide was added gradually to a solution of 25 mM of a 4-n-alkyl-2,5-dimethylpyridine in 20 ml of nitromethane. The mixture was heated to the boil for 3 hr (with a calcium chloride tube). The nitromethane was distilled off and the residue was recrystallized from acetone. The compounds obtained are characterized in Table 3.

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