

SYNTHESIS OF 1-(β -CYANOETHYL)-4-ETHYNYL-2, 5-DIMETHYL-4-PIPERIDINOLS AND THE CORRESPONDING 4-VINYL COMPOUNDS

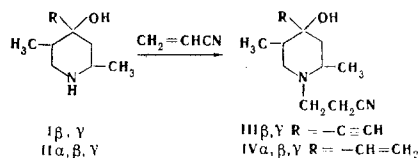
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Synthesis of 1-(β -cyanoethyl)-4e-ethynyl-2e, 5e-dimethylpiperidin-4a-ol and the corresponding 4e-vinyl compounds (β -isomers), 1-(β -cyanoethyl)-4a-ethynyl-2e, 5e-dimethylpiperidin-4e-ol (and the corresponding 4a-vinyl compound) (γ -isomers), and 1-(β -cyanoethyl)-2e, 5a-dimethyl-4a-vinylpiperidin-4e-ol (α -isomer) have been effected.

Previously, one of us together with I. N. Nazarov and others [1-3] synthesized 1-alkenyl-4-ethynyl-2, 5-dimethyl-4-piperidinols and the corresponding 4-vinyl compounds and various esters of them. Some of the latter possess a high anesthetic activity. Continuing our systematic studies on the synthesis of new physiologically active compounds based on the acetylene derivative of 2, 5-dimethyl-4-piperidinol [4], we have synthesized with high yields (70-92%) 1-(β -cyanoethyl)-4e-ethynyl-2e, 5e-dimethylpiperidin-4a-ol (III β) and the corresponding 4e-vinyl compound (IV β), 1-(β -cyanoethyl)-4a-ethynyl-2e, 5e-dimethylpiperidin-4e-ol (III γ) and the corresponding 4a-vinyl compound (IV γ), and 1-(β -cyanoethyl)-2e, 5a-dimethyl-4a-vinylpiperidin-4e-ol (IV α) by the cyanoethylation [5] of the individual isomers of 2, 5-dimethyl-4-ethynyl- (or -vinyl-) -4-piperidinol (I β , γ), (II α , β , γ) [6, 7] in anhydrous benzene.



EXPERIMENTAL

A flask fitted with a reflux condenser was charged with the starting materials (see table), and the reaction mixture was heated at 95-100° C for 20 hr. After the benzene and the excess of acrylonitrile had been distilled off in vacuum, the reaction product was purified by recrystallization from gasoline (60-80° C fraction) or by redistillation in vacuum.

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Alma-AtaStereoisomers of 1-(β -Cianoethyl)-4-ethynyl-2, 5-dimethyl-4-piperidinol and 1-(β -Cianoethyl)-2, 5-dimethyl-4-vinyl-4-piperidinol

Starting materials	piperidinol, g	acrylonitrile, g	benzene, ml	Reaction product	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
							C	H	N	C	H	N	
(I β)	3.30	1.40	5	III β	42-43	C ₁₂ H ₁₈ N ₂ O	69.60 69.98	8.96 9.10	13.48 13.46	69.90	8.70	13.59	84
(I γ)	7.65	3.10	10	III γ *	—	C ₁₂ H ₁₈ N ₂ O	69.87 70.04	8.92 8.83	13.80 13.90	69.90	8.70	13.59	77
(II β)	3.70	1.60	5	IV β	54-55	C ₁₂ H ₂₀ N ₂ O	69.34 69.50	9.83 9.87	13.60 13.71	69.23	9.61	13.46	92
(II γ)	7.75	2.90	30	IV γ	66-67	C ₁₂ H ₂₀ N ₂ O	69.05 69.21	9.70 9.88	13.30 13.49	69.23	9.61	13.46	70
(II α)	4.80	2.10	5	IV α **	—	C ₁₂ H ₂₀ N ₂ O	69.04 69.11	9.61 9.72	13.25 13.30	69.23	9.61	13.46	84

*Bp 153-155° C (1.5 mm).

**Bp 133-134° C (1.5 mm); d_4^{20} 1.0200; n_D^{20} 1.4980. Found MR_D 59.86. Calculated: MR_D 60.23.