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SYNTHESIS OF SUBSTITUTED 3-BENZOYL-1,2,3,4-TETRAHYDROPYRIDINES BY THE ADDITION OF PRIMARY AMINES TO 1,3,5-TRIPHENYL-2-METHYLIDENE-1,5-PENTANEDIONE*

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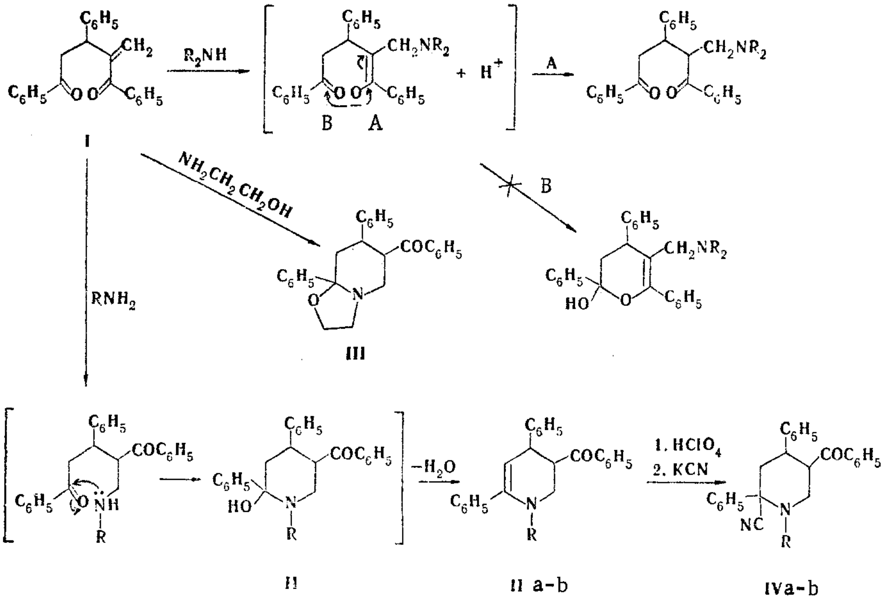
1,3,5-Triphenyl-2-methylidene-1,5-pentanedione adds methyl- and cyclohexylamines to give, respectively, 1-methyl- and 1-cyclohexyl-3-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydropyridines; 1-aza-3-benzoyl-4,6-diphenyl-7-oxabicyclo[4.3.0]nonane is obtained with ethanolamine.

Only secondary amines have been added to aryl-aliphatic α-methylidene-1,5-diketones [2]; in this case, of the two possible reaction pathways A and B, only pathway A was observed. The electrophilicity of the carbon atom of the aryl-aliphatic carbonyl group is evidently insufficient for the realization of pathway B. Thus reaction via pathway B proceeds successfully in the case of semicyclic α-methylidene-1,5-diketones, in which the more electrophilic alicyclic carbonyl group acts as a source of enolate ion [3]. The nucleophilicity of the nitrogen atom in the $-CH_2NR_2$ fragment is higher than that of the enol oxygen atom, but this cannot lead to a valence-saturated stable N,O-hemiacetal of the II form, as in the addition of a primary amine.

It therefore seemed of interest to test primary amines — methylamine, cyclohexaylamine, and ethanolamine — in the reaction with ketone I. As a result, we obtained 1-methyl- and 1-cyclohexyl-3-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydropyridines (IIa,b) and 1-aza-3-benzoyl-4,6-diphenyl-7-oxabicyclo[4.3.0]nonane (III) in good yields.



II, IV a $R=CH_3$; b $R=cyclo\text{-}C_6H_{11}$

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*Communication 33 from the series "Reactions of 1,5-Diketones." See [1] for communication 32.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C (crystallization solvent)	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IIa	136—138 (hexane)	84,9	6,7	4,3	$C_{25}H_{23}NO$	84,9	6,5	3,9	78
IIb	173—175 (hexane)	85,5	7,6	3,4	$C_{30}H_{31}NO$	85,5	7,3	3,3	55
III	132—134 (methanol)	81,7	6,5	3,4	$C_{26}H_{25}NO_2$	81,4	6,5	3,6	73
IVa	122—124 (alcohol)	82,3	6,6	7,5	$C_{26}H_{24}N_2O$	82,1	6,6	7,3	77
IVb	157—159 (alcohol)	83,3	7,2	9,1	$C_{31}H_{32}N_2O$	83,0	7,1	9,3	94
Perchlorate of IIa	119—120 (dioxane)	66,0	6,2	3,2	$C_{25}H_{23}NO \cdot HClO_4$	66,1	5,9	3,0	91
Perchlorate of IIb	122—124 (water)	69,0	6,1	3,0	$C_{30}H_{31}NO \cdot HClO_4$	69,0	6,1	2,6	73

Absorption at 1640 cm^{-1} (an enamine C-C bond) appears in the IR spectra of II in place of the band at 1620 cm^{-1} ($C=CH_2$) characteristic for diketone I; the carbonyl absorption is represented by one band at 1690 cm^{-1}. The structure of III is confirmed by the absence in its IR spectrum of absorption bands of a hydroxy group and an enamine double bond. In addition to other signals corresponding to the given structure, the PMR spectrum of IIa contains a doublet of doublets at 4.2 ppm from the proton in the 4 position and a doublet at 5.2 ppm from the vinyl proton attached to $C_{(3)}$.

The perchlorates of IIa,b readily undergo reaction with hydrocyanic acid to give 1-methyl-2-cyano-2,4-diphenyl-5-benzoylpiperidine IVa and its 1-cyclohexyl analog IVb. The absorption band of a carbonyl group at 1690 cm^{-1} is retained in the IR spectra of nitriles IVa,b, and a weak peak appears at 2240 cm^{-1} ($C \equiv N$).

EXPERIMENTAL

The IR spectra of solutions of the compounds in CH_2Cl_2 were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions of the compounds were recorded with a Brucker-90 spectrometer. Methylidene ketone I was obtained by the method in [2]. The perchlorates were obtained by mixing a solution of base II in dilute acetic acid with a saturated solution of ammonium perchlorate. The properties of the compounds obtained are presented in Table 1.

Addition of Primary Amines to Diketone I. A solution of 0.02 mole of the methylene diketone and 0.04 mole of the amine in dimethylformamide (DMF) (the methylamine was in the form of a 25% aqueous solution) was allowed to stand overnight. The solution was then diluted with water, and hydropyridines IIa,b and III were removed by filtration and purified by crystallization.

Addition of Hydrocyanic Acid to Enamines IIa,b. A 1-g sample of potassium cyanide was added in the course of 10 min to a solution of 1 g of the perchlorate of IIa or IIb in 50 ml of methanol, and the mixture was stirred for 1 h. The precipitated potassium perchlorate was then removed by filtration, and the filtrate was diluted with 50 ml of water. The precipitated nitriles IVa,b were removed by filtration, washed with water, and purified by crystallization.

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