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Abstract

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CATALYTIC CONDENSATIONS OF SCHIFF BASES FROM 4-AMINODIPHENYL AND AROMATIC ALDEHYDES WITH FATTY-AROMATIC KETONES

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In the work ([1]) of one of us, a method was described for the synthesis of β-arylaminoketones by catalytic condensation of Schiff bases with ketones. The present work is its continuation. For the investigation, Schiff bases obtained from 4-aminodiphenyl and aromatic aldehydes were taken and introduced into condensation with a series of fatty-aromatic ketones. The aim of our work was to obtain new organic compounds with potential physiological activity, since it is known that 4-aminodiphenyl and a number of its derivatives possess considerable and varied physiological activity. Thus, for example, it is known that 4-aminodiphenyl exhibits tuberculostatic action already at a concentration of $1.25 \cdot 10^{-7}$ mole/l ([2]), which is approximately 20 times greater than the activity of such a well-known drug as PASK ([3]).

L. F. Trefilova and I. Ya. Postovskii ([4]) synthesized a series of new derivatives of 4-aminodiphenyl and, in particular, azomethines and N, N^1-substituted thioureas. Of these, some azomethines proved to be very active and suppressed the growth of the tubercle bacillus at a concentration of the preparation from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-7}$ mole/l.

Ch. P. Ivanov and I. M. Panaiotov ([5]), for physiological tests, synthesized a series of alkyl ethers of 4-hydroxy-4-aminodiphenyl and its aminoacetyl derivative. Since 4-aminodiphenyl has high toxicity and is readily oxidized, D. Sh. Rozina and R. P. Lastovskii ([6]) synthesized the glucoside of 4-aminodiphenyl and 4-aminodiphenyl-4-acetylaminosalicylic acid. In recent years it has been established that 4-aminodiphenyl has a noticeable carcinogenic action ([7,8]).

In the present work, in the condensation of benzal-4-aminodiphenyl with acetophenone, β-(4-phenylanilino)-β-phenylpropiophenone (I) was synthesized. In the condensation of benzal-4-aminodiphenyl with 4-methylacetophenone, 4-tolyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (II) was obtained. In the condensation of benzal-4-aminodiphenyl with 4-methoxyacetophenone, 4-anisyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (III) was obtained. In the condensation of benzal-4-aminodiphenyl with 4-chloroacetophenone, 4-chlorophenyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (IV) was obtained.

In the condensation of benzal-4-aminodiphenyl with 4-bromoacetophenone, 4-bromophenyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (V) was obtained. In the condensation of benzal-4-aminodiphenyl with methyl diphenyl ketone, 4-diphenyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (VI) was obtained. In the condensation of benzal-4-aminodiphenyl with methyl-α-naphthyl ketone, α-naphthyl-[β-(4-phenylanilino)-β-phenylethyl]-ketone (VII) was obtained. In the condensation of 4-tolyl-4-aminodiphenyl with acetophenone, β-(4-phenylanilino)-β-4-tolylpropiophenone (VIII) was obtained. In the condensation of 4-tolyl-4-aminodiphenyl with 4-methylacetophenone, 4-tolyl-[β-(4-phenylanilino)-β-4-tolylethyl]-ketone (IX) was obtained. In the condensation of 4-tolyl-4-aminodiphenyl with 4-methoxyaceto-

Table 1

No.	Compounds	m.p., °C	Yield, %	N, % found	N, % calc.
I	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—C_6H_5	183–184	77.0	3.91	3.71
II	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—$C_6H_4OCH_3$	136–137	80.0	3.78	3.58
III	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—$C_6H_4OCH_3$	186–187	75.0	3.60	3.44
IV	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—C_6H_4Cl	166–168	85.0	3.46	3.40
V	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—C_6H_4Br	174–175	63.0	3.25	3.06
VI	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—C_6H_5	217–218	85.0	3.32	3.09
VII	p-$C_6H_5C_6H_4$—NH—CH(C_6H_5)—CH_2—CO—$C_{10}H_7$	214–215	72.0	3.13	3.17
VIII	p-$C_6H_5C_6H_4$—NH—CH(C_6H_4—CH_3)—CH_2—CO—C_6H_5	171–172	70.0	3.22	3.54
IX	p-$C_6H_5C_6H_4$—NH—CH(C_6H_4—CH_3)—CH_2—CO—C_6H_4—CH_3	153–154	78.0	3.70	3.45
X	p-$C_6H_5C_6H_4$—NH—CH(C_6H_4—CH_3)—CH_2—CO—C_6H_4—OCH_3	176–177	73.0	3.42	3.32
XI	p-$C_6H_5C_6H_4$—NH—CH(C_6H_4—CH_3)—CH_2—CO—C_6H_4—Cl	145–147	77.0	3.07	3.29
XII	p-$C_6H_5C_6H_4$—NH—CH(C_6H_4—CH_3)—CH_2—CO—C_6H_4—Br	145–146	77.0	2.78	2.97

with phenone, 4-anisyl-[β-(4-phenylanilino)-β-4-tolylethyl]-ketone (X) was obtained. In the condensation of 4-tolyl-4-aminodiphenyl with 4-chloroacetophenone, 4-chlorophenyl-[β-(4-phenylanilino)-β-4-tolylethyl]-ketone (XI) was obtained. In the condensation of 4-tolyl-4-aminodiphenyl with 4-bromoacetophenone, 4-bromophenyl-[β-(4-phenylanilino)-β-4-tolylethyl]-ketone (XII) was obtained.

All the compounds synthesized by us were obtained for the first time. The hydrochloride salt of 4-aminodiphenyl was used as the catalyst. The mechanism of the reaction we studied may be represented by the equation

$$\langle \mathrm{Ph{-}Ph} \rangle{-}\mathrm{N{=}CH{-}Ar} \xrightarrow{\mathrm{CH_3{-}CO{-}Ar'}} \langle \mathrm{Ph{-}Ph} \rangle{-}\mathrm{NH{-}CH{-}Ar} \Big| \mathrm{CH_2{-}CO{-}Ar'}$$

Description of the procedure. The method for synthesizing β-arylaminoketones is as follows: a reaction mixture consisting of 0.05 g-mol

of the Schiff base, 0.05 g-mol of the aliphatic-aromatic ketone, 10–15 ml of alcohol, and 0.5–1.0 g of hydrochloride 4-aminodiphenyl was heated on a water bath for 15–30 min. After cooling, the precipitate that separated was filtered off, treated with aqueous ammonia, and crystallized from a mixture of alcohol with benzene. The results obtained by us and the constants of the synthesized compounds are given in Table 1.

Thus, in the present work it proved possible to develop a new convenient method for the synthesis of β-arylaminoketones containing a diphenyl ring.

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Note: Figure translations are in progress. See original paper for figures.