# HETEROCYCLIC COMPOUNDS. III\*. SYNTHESIS OF 9-ARYLAMINO-

### $\beta$ -QUININDANES<sup>†</sup>

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A method for the synthesis of 9-arylamino- $\beta$ -quinindanes from anilides of cyclopentylideneanthranilic acid has been devised. A number of previously undescribed compounds have been obtained, and their properties have been examined.

9-Alkylamino- $\beta$ -quinindanes are little-known, in consequence of the lack of convenient methods for their synthesis. The usual method of preparation is by reaction of 9-chloro- $\beta$ -quinindanes with amines in phenol solution [3]. The utility of this method, however, is diminished by the lack of reactivity of the halogen in 9-chloro- $\beta$ -quinindanes [3-5], and by the difficulty in obtaining the latter as a consequence of their inaccessibility from anthranilic acid and cyclopentanone [5]. 9-Arylamino- $\beta$ -quinindanes are completely unknown.

We have previously put forward a method for the synthesis of 9-arylamino-1, 2, 3,4-tetrahydroacridines and their halo-derivatives from anilides of cyclohexylideneanthranilic acid [1]. The present paper describes the synthesis of anilides of cyclopentylideneanthranilic acid, and the discovery of conditions for their conversion into 9-arylamino- $\beta$ -quinindanes.



It has been shown experimentally that anthranilic acid anilides (I) condense readily with cyclopentanone on heating in benzene to give the cyclopentylideneanthranilic acid anilides (II) (Table 1). On heating II with phosphoryl chloride in dry benzene, 9-arylamino- $\beta$ -quinindanes (III) are obtained in 95% yields (Table 2). The formation of III in this reaction is confirmed by comparison with an authentic sample of 9phenylamino- $\beta$ -quinindane, obtained by a method described in the literature [6].

The cyclization of some anilides of 2-arylaminocyclopentene-1-carboxylic acids (IV) to III by phosphoryl chloride was also attempted. Cyclization of 2-anilinocyclopentene-1-carboxanilide resulted in the formation of IIIa in 32% yield, but in all other cases, resinification of the reaction mixture occurred, and no III could be isolated.

The compounds III were colorless or slightly yellowish, crystalline compounds, which possessed basic properties.

The UV spectra of 9-arylamino- $\beta$ -quinindanes showed three absorption bands, with  $\lambda_{\text{max}}$  224-232, 248-254, and 330-344 nm. The IR spectra of III possessed bands  $\nu_{\text{NH}}$ , 3420 cm<sup>-1</sup>;  $\nu_{=\text{CH}}$ , 3068 cm<sup>-1</sup>;  $\nu_{\text{CH}}$ ,

† The name  $\beta$ -quinindanes has been suggested for 2, 3-trimethylenequinolines [2].

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<sup>\*</sup> For Parts I and II, see [1].

R		Molecular formula	N, %		$\lambda_{\text{max}}$ .		Yield.
	мр, С		found	calc.	nm	log E	%
H p-CH <sub>3</sub> o-CH <sub>3</sub> p-CH <sub>3</sub> O o-CH <sub>3</sub> O p-Cl	206-208 232-235 229-232 233-236 205-210 214-215	$\begin{array}{c} C_{18}H_{18}N_{2}O\\ C_{19}H_{20}N_{2}O\\ C_{19}H_{20}N_{2}O\\ C_{19}H_{20}N_{2}O_{2}\\ C_{19}H_{20}N_{2}O_{2}\\ C_{19}H_{20}N_{2}O_{2}\\ C_{18}H_{17}CIN_{2}O\end{array}$	10,15 9,85 9,78 9,07 8,80 9,00	10,05 9,58 9,58 9,09 9,09 8,97	342 342 338 346  348	3,49 3,56 3,61 3,68 	90 95 89 72 69 84,5
o-Cl p-Br	218-220 212-213	C <sub>18</sub> H <sub>17</sub> ClN <sub>2</sub> O C <sub>18</sub> H <sub>17</sub> BrN <sub>2</sub> O	9,03 8,14	8,97 7,85	348	3.80	71 72.5

TABLE 1. Anilides of Cyclopentylideneanthranilic Acid (II)

TABLE 2. 9-Arylamino- $\beta$ -quinindanes (III)

	Мр, ⁰С	Molecular formula	N, %				Yield
R			found	calc.	$\lambda_{max}$ , nm	log E	%
н	185	$C_{18}H_{16}N_2$ (IIIa)	10,82; 10,80	10,76	230; 250; 340	4,59; 4,50; 4,23	61,5
p-CH₃	160-162	C19H18N2	10,30; 10,20	10,20	228; 254; 340	4,49; 4,32; 4,25	63,5
o-CH₃	196-198	$C_{19}H_{18}N_2$	10,40; 10,00	10,20	224; 248; 330	4.57; 4,52; 4,23	63.5
p-CH₃O	144-146	$C_{19}H_{18}N_2O$	9,25; 9,40	9,65	226; 252; 344	4,45; 4,32; 4,03	48,0
o-CH <sub>3</sub> O	150	$C_{19}H_{18}N_2O$	9,38; 9,47	9,65	230; 252; 336	4,29; 3,97; 3,74	45.0
p-Cl	173-175	$C_{18}H_{15}CIN_{2}$	9,28; 9,41	9,52	230; 252; 340	4.40; 4.26; 4.15	50.0
p-Br	176-178	$C_{18}H_{15}BrN_2$	7,90; 7,90	8,27	232; 252; 342	4,50; 4,41; 4,20	95.3

\* Literature value [6], 173°.

2940 and 2855 cm<sup>-1</sup>. The UV spectra were taken on an SF-4 spectrophotometer, in alcoholic solution, and the IR spectra on an IKS-14 spectrograph in  $CCl_4$ , with LiF prisms.

### EXPERIMENTAL

Cyclopentylideneanthranilic Acid Anilides (II). Anthranilic acid arylamide (0.01 mole) and 0.01 mole of cyclopentanone were dissolved in 5 ml of benzene, and boiled on a sand bath for 4 h. The mixture was cooled, and the solid which separated was filtered off and recrystallized from alcohol.

Cyclization of Cyclopentylideneanthranilic Acid Anilides. The anilide (0.01 mole) was dissolved in 10 ml of dry benzene, and 3 ml of phosphoryl chloride was added. The mixture was heated on the water bath for 1 h, then the benzene and excess phosphoryl chloride were distilled off in vacuo at the water pump. The residue was dissolved in alcohol, and treated with ammonia. The precipitate of 9-arylamino- $\beta$ -quninin-dane (III) was filtered off and recrystallized from alcohol.

Cyclization of 2-anilinocyclopentene-1-carboxanilide. The anilide (5 g) was added to 5 ml of phosphoryl chloride, and the mixture was heated on the water bath for 2 h. The mixture was poured into icewater, and after the phosphoryl chloride had decomposed, the mixture was neutralized with ammonia. The precipitate was recrystallized from alcohol, giving 1.5 g (32.2%) of IIIa, mp 185-186°.

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