HETEROCYCLIC COMPOUNDS

IV.* 4-ARYLAMINO-2,3-PENTAMETHYLENEQUINOLINES

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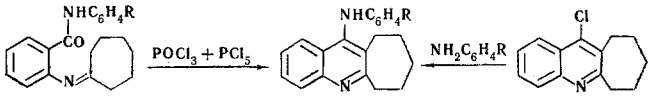
Two methods for obtaining 4-arylamino-2,3-pentamethylenequinolines are proposed: cyclization of arylamides of cycloheptylidineanthranilic acid and reaction of 4-chloro-2,3-pentamethylenequinoline with aromatic amines.

This paper is devoted to the synthesis of previously unknown 4-arylamino-2,3-pentamethylenequinolines (II). Arylamides of cycloheptylidineanthranilic acid (I) (method A) or 4-chloro-2,3-pentamethylenequinolines (III) and aromatic amines (method B) were used as the starting materials:



I II III

4-Arylamino-2,3-pentamethylenequinolines (II) (Table 1) are formed in good yields by heating I with a mixture of phosphorus pentachloride and phosphorus oxychloride (1:3). The reaction of III with aromatic amines in phenol (20 h at 140-145 deg C) gives somewhat lower yields of II.

The 4-arylamino-2,3-pentamethylenequinolines are colorless, crystalline substances with basic propties. Their IR spectra† have the following bands ν_{NH} 3409-3443 cm^{-1}; $\nu_{=CH}$ 3040-3083 cm^{-1}; ν_{CH_2} 2911-2937; 2849-2869 cm^{-1}; δ_{NH} 1575-1582, 1492-1507 cm^{-1}; ν_{ring} 1612, 1595-1597, 1556-1566, and 1476-1488 cm^{-1} (compare with the assignment of the bands in the IR spectra of quinoline and its derivatives [2,-3]).

Compounds I (Table 2) were obtained by the reaction of arylamides of anthranilic acid with cycloheptanone in benzene. Cycloheptanone condenses with much more difficulty than cyclohexanone with arylamides of anthranilic acid [4].

EXPERIMENTAL

Arylamides of Cycloheptylideneantharanilic Acid (I). A solution of equimolecular amounts of the appropriate arylamide of anthranilic acid and cycloheptanones in benzene was heated on a sand bath for 14-16 h. The precipitate resulting on cooling was filtered and crystallized from alcohol.

4-Arylamino-2,3-pentamethylenequinolines (II). A. Phosphorus pentachloride (1 g) was added to a solution of 0.01 mole of I in 3 ml of phosphorus oxychloride. The reaction mass was heated on a water bath for 1 h. It was then poured into ice water, and the mixture wasneutralized with ammonium hydroxide

*See [1] for Communication III.

† The IR spectra in mineral oil were measured with an IKS-14 spectrometer with an NaCl prism and in CCl_4 with an LiF prism.

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TABLE 1. 4-Arylamino-2,3-pentamethylenequinolines (II)

R	Mp	Empirical formula	N, %		λ_{max}, nm (lg ε) (in alcohol)	Yield, %		Hydrochloride mp
			found	calc.		A	B	
C_6H_5	195—196	$C_{20}H_{20}N_2$	9,97	9,72	232 (4,7); 250 (4,25); 320 (3,67); 344 (3,67)	63	52	228—229
p-$CH_3C_6H_4$	164—165	$C_{21}H_{22}N_2$	9,58	9,64	230 (4,68); 252 (4,28); 294 (3,75); 320 (3,73); 346 (3,86)	66	55	243—245
o-$CH_3C_6H_4$	152—153	$C_{21}H_{22}N_2$	9,85	9,64	232 (4,91); 320 (3,80)	47	42	223—225
m-$CH_3C_6H_4$	140—141	$C_{21}H_{22}N_2$	9,37	9,64	232 (4,66); 250 (4,3); 292 (3,82); 320 (3,78); 344 (3,84)	41	—	237—240
p-ClC_6H_4	149—150	$C_{20}H_{19}ClN_2$	8,60	8,34	234 (4,76); 254 (4,57); 306 (3,91); 320 (3,92); 342 (3,94)	49	41	215—216
o-ClC_6H_4	167—168	$C_{20}H_{19}ClN_2$	8,63	8,34		38	—	—
m-ClC_6H_4	179—181	$C_{20}H_{19}ClN_2$	8,66	8,34	232 (4,75); 250 (4,40); 298 (3,94); 320 (3,96); 338 (3,90)	47	—	233—235
p-BrC_6H_4	157—158	$C_{20}H_{19}BrN_2$	8,11	7,88	232 (4,38); 254 (3,99); 306 (3,74); 320 (3,51); 342 (3,50)	51	40	241—242
o-BrC_6H_4	114—116	$C_{20}H_{19}BrN_2$	8,15	7,88	232 (4,82); 320 (3,76)	38	—	228—231
m-BrC_6H_4	172—173	$C_{20}H_{19}BrN_2$	7,93	7,88		33	—	—
p-$CH_3OC_6H_4$	120—121	$C_{21}H_{22}N_2O$	8,99	8,76	230 (4,67); 254 (4,25); 320 (3,86); 348 (3,93)	29	21	219—222
o-$CH_3OC_6H_4$	110—111	$C_{21}H_{22}N_2O$	8,94	8,76	234 (4,62); 308 (3,37); 320 (3,46); 348 (3,41)	33	31	214—217

TABLE 2. Arylamides of Cycloheptylideneanthranilic Acid (I)

R	Mp	Empirical formula	N, % found	N, % calc.	λ_{max}, nm (lg ε) (in alcohol)	Yield, %
C_6H_5	172—174	$C_{20}H_{22}N_2O$	9,20	9,15	226 (4,58); 334 (3,57)	50
p-$CH_3C_6H_4$	198	$C_{21}H_{24}N_2O$	8,65	8,74	226 (4,5); 334 (3,45)	61
o-$CH_3C_6H_4$	163—165	$C_{21}H_{24}N_2O$	9,07	8,74	226 (4,62); 336 (3,54)	50
m-$CH_3C_6H_4$	183—185	$C_{21}H_{24}N_2O$	9,1	8,74	224 (4,58); 336 (3,77)	48
p-ClC_6H_4	179—180	$C_{20}H_{21}ClN_2O$	7,97	8,21	226 (4,92); 344 (3,97)	50
o-ClC_6H_4	192—195	$C_{20}H_{21}ClN_2O$	8,10	8,21	226 (4,45); 346 (3,7)	40
m-ClC_6H_4	186—188	$C_{20}H_{21}ClN_2O$	8,11	8,21	224 (4,6); 336 (3,5)	50
p-BrC_6H_4	186—189	$C_{20}H_{21}BrN_2O$	7,55	7,30	226 (4,62); 346 (3,58)	50
o-BrC_6H_4	178—180	$C_{20}H_{21}BrN_2O$	7,53	7,30	224 (4,49); 346 (3,7)	47
m-BrC_6H_4	189—192	$C_{20}H_{21}BrN_2O$	7,6	7,30	226 (4,56); 346 (3,5)	43
p-$CH_3OC_6H_4$	205—207	$C_{21}H_{24}N_2O_2$	8,50	8,33	224 (4,66); 336 (3,92)	39
o-$CH_3OC_6H_4$	190—191	$C_{21}H_{24}N_2O_2$	8,62	8,33	224 (4,6); 338 (3,92)	34

after decomposition of the phosphorus oxychloride. The resulting precipitate was filtered and crystallized.

B. III (0.01 mole) was dissolved by heating in 5 g of phenol, 0.02 mole of aromatic amine was added to the solution, and the mixture was heated on a metal bath at 140-145 deg for 20 h. At the end of the heating period, the mixture was treated with 10% alkali to remove the phenol. The residue was crystallized.

LITERATURE CITED

1. M. E. Konshin, Khim. Geterotsikl Soedin., 1242 (1970).
2. H. Luther, D. Mootz, and F. Radwitz, J. Pr. Chem., 5, 242 (1958).
3. A. R. Katritzky and R. A. Jones, J. Chem. Soc., 2942 (1960).
4. P. A. Petyunin, M. E. Konshin, and Yu. V. Kozhevnikov, Zh. VKhO, 12, 238 (1967).