

## DERIVATIVES IN THE sym-OCTAHYDROACRIDINE SERIES

## IV. Synthesis and Some Properties of 4, 5-Diarylideneoctahydroacridines\*

V. I. Vysotskii and M. N. Tilichenko

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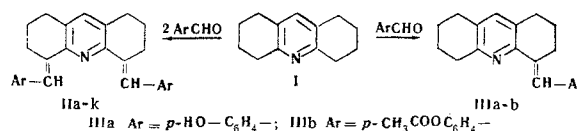
A number of previously unknown 4,5-diarylideneoctahydroacridines have been synthesized by the condensation of sym-octahydroacridine with aromatic aldehydes, and their fluorescence has been described.

We have previously reported [2] the condensation of sym-octahydroacridine (I) with benzaldehyde. Continuing our investigation, we have applied the reaction to hydroxy- and nitrobenzaldehydes, piperonal, and cinnamaldehyde. With a two-molar excess of aldehyde, the expected diarylideneoctahydroacridines II are readily obtained (see table). The condensation of p-hydroxybenzaldehyde with an excess of octahydroacridine yields 4-p-hydroxybenzylideneoctahydroacridine (IIIa). The reaction of 1 mole of 9-phenyloctahydroacridine with 2 moles of benzaldehyde gave 4,5-dibenzylidene-9-phenyloctahydroacridine (IV).

Compounds with one arylidene group in the molecule (IIIa, IIIb) were not detected on visual observation of the fluorescence in solutions, while the diarylideneoctahydroacridines II possess a blue-violet fluores-

cence\*. Of them only compounds IIa-IIIc do not fluoresce and IIIh has a pale blue fluorescence.

Stable salts with HCl are formed only by the monoarylidene compounds III, and not the diarylidene compounds II. In addition, both the former and the latter form picrates among which the picrate of IIIh is distinguished by a red color, the other picrates being yellow. No methiodide could be obtained from any of the condensation products, although octahydroacridine itself forms a methiodide [3].

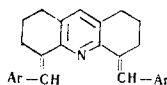


## EXPERIMENTAL

G. A. Klimov, T. F. Solov'eva, V. P. Marinin, V. A. Stonik, and T. V. Bogdanova participated in the experimentation.

\* For part III, see [1].

\* The fluorescence was determined visually for 0.1% solutions of the substances in benzene or chloroform.



Compound	Ar	Mp., °C	Empirical formula	Found, %				Calc., %				Picrate		Yield %	
				C	H	N	mol. wt.	C	H	N	M	Mp., °C	N, % found    calc.		
II a	<i>o</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	221	C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub>	71.81 71.61	5.30 5.41	9.44	487	71.50	5.08	9.27	457	178	12.77	12.31	24
II b	<i>m</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	201-202	C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub>	71.35 71.14	4.96 4.88	9.16 9.38	421	71.50	5.08	9.27	457	200	12.50	12.31	66
II c	<i>p</i> -O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	253	C <sub>27</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub>	71.36 71.12	5.18 5.41	9.43 9.33		71.50	5.08	9.27					85
II d	<i>o</i> -HO-C <sub>6</sub> H <sub>4</sub>	223-224	C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub>	82.29 82.15	6.22 6.19	3.65 3.81	410 418	82.01	6.32	3.55	395	216	9.05	8.97	64
II e	<i>m</i> -HO-C <sub>6</sub> H <sub>4</sub>	212-213	C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub>	82.04 82.04	6.49 6.27		391 376	82.01	6.32		395	199.5	9.24 9.21	8.97	66
II f	<i>p</i> -HO-C <sub>6</sub> H <sub>4</sub>	243	C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub>			3.55 3.40				3.55					22
II g		187	C <sub>29</sub> H <sub>25</sub> NO <sub>4</sub>	77.78 77.84	5.71 5.25	3.35 3.36	461 445	77.14	5.58	3.10	452	227	7.85 7.77	8.23	51
II h	C <sub>6</sub> H <sub>5</sub> CH=CH	227	C <sub>31</sub> H <sub>29</sub> N	89.00 89.51	7.22 6.95		413	89.64	6.98		415	235	8.98	8.72	78
II i	<i>o</i> -CH <sub>3</sub> COO-C <sub>6</sub> H <sub>4</sub>	155-155.5	C <sub>31</sub> H <sub>29</sub> NO <sub>4</sub> *	77.13 77.00	6.13 6.15			77.66	6.05						64
II j	<i>m</i> -CH <sub>3</sub> COO-C <sub>6</sub> H <sub>4</sub>	197-198	C <sub>31</sub> H <sub>29</sub> NO <sub>4</sub>	77.77 77.70	6.04 6.26			77.66	6.05						66
II k	<i>p</i> -CH <sub>3</sub> COO-C <sub>6</sub> H <sub>4</sub>	180-180.5	C <sub>31</sub> H <sub>29</sub> NO <sub>4</sub> **	77.31 77.13	6.10 6.09			77.66	6.05						22

\* Found, %: CH<sub>3</sub>CO 18.23, 18.31. Calculated, %: CH<sub>3</sub>CO 17.95.

\*\* Found, %: CH<sub>3</sub>CO 18.66, 18.62. Calculated, %: CH<sub>3</sub>CO 17.95.

**General procedure for the synthesis of the diarylideneoctahydroacridines.** A mixture of 0.01 mole of I, 0.02 mole of an aldehyde, and 5 ml of acetic anhydride was boiled for 6 hr. The reaction product crystallized out when the reaction mixture was cooled. In some cases, when the mother liquors were diluted with ethanol it was possible to isolate a further small amount of the product. The hydroxy compounds **II d-II f** were obtained in the form of the acetyl derivatives **III i-III k**. Hydrolysis of the latter was carried out with 0.5 N ethanolic KOH, and then it was necessary to acidify the mixture with 0.5 N aqueous HCl. Under these conditions the hydroxy compounds were obtained in quantitative yields.

**4, 5-Dibenzylidene-9-phenyloctahydroacridine (IV)** was obtained similarly from 9-phenyloctahydroacridine and its aldehyde. Yield 59%, mp 169-170° C (from dioxane). Solutions of the substance possess a blue-violet fluorescence. Found, %: C 90.16, 89.93; H 6.90, 6.82. Calculated for  $C_{33}H_{29}N$ , %: C 90.13; H 6.65.

**4-p-Hydroxybenzylideneoctahydroacridine (III a).** A mixture of 0.04 mole of I, 0.01 mole of p-hydroxybenzaldehyde, and 5 ml of acetic anhydride was heated at 160-165° C for 6 hr. After a day, crystals of the acetyl derivative of **III b** crystallized out. Yield 1.98 g (59%). The filtrate after the separation of the **III b** was diluted with an equal volume of conc. HCl; after 2 days, crystals of the hydrochloride of **III a** deposited. Yield 0.7 g (19%). Compound **III a** was isolated from the acetyl derivative in a manner similar to that de-

scribed above. The substance consisted of white crystals with mp 241.5-242° C (from ethanol). Found, %: C 81.75; H 7.60; N 4.71; 4.91. Calculated for  $C_{20}H_{21}NO$ , %: C 82.42; H 7.27; N 4.81. Acetyl derivative, mp 128° C. Found, %: C 78.83, 78.86; H 6.98, 7.11; N 4.43, 4.32; mol. wt. 320. Calculated for  $C_{22}H_{23}NO_2$ , %: C 79.23; H 6.96; N 4.20; mol. wt. 333. Hydrochloride, bright yellow needles with mp 253° C. Found, %: Cl 11.35, 11.21. Calculated for  $C_{20}H_{21}NO \cdot HCl$ , %: Cl 11.00. Picrate, mp 171° C. Found, %: N 11.12, 11.20. Calculated for  $C_{26}H_{24}N_4O_8$ , %: N 10.76.

#### REFERENCES

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2. M. N. Tilichenko and V. I. Vysotskii, ZhOKh, 32, 84, 1962.
3. J. V. Braun, A. Petzold, and A. Schultheiss, Ber., 56, 1349, 1923.

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Far Eastern State University,  
Vladivostok