SYNTHESIS OF 1,2-DIHYDROACRIDINE

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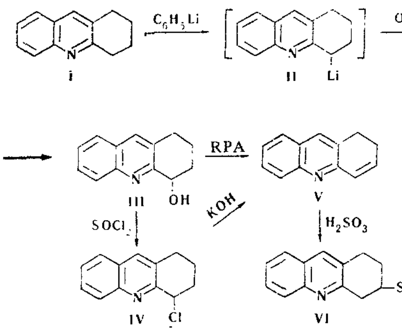
In the dihydroacridine series only 9,10-dihydroacridine (acridane) is known. We have now obtained 1,2-dihydroacridine (**V**), a cyclic analog of 2-vinylquinoline in the following way:



When ethereal solutions of phenyllithium and 1,2,3,4-tetrahydroacridine (**I**) were mixed in an atmosphere of argon, a red precipitate of 4-lithio-1,2,3,4-tetrahydroacridine (**II**) deposited; the passage of oxygen through the reaction mixture led to 1,2,3,4-tetrahydroacridin-4-ol (**III**). The dehydration of **III** with polyphosphoric acid gave **V** in good yield. The reaction of **III** with thionyl chloride formed 4-chloro-1,2,3,4-tetrahydroacridine (**IV**), the boiling of which with alcoholic alkali gave **V** in low yield.

Compound **V**, like its analogs [1, 2] adds a molecule of sulfurous acid and forms 1,2,3,4-tetrahydroacridine-3-sulfonic acid (**IV**) when an aqueous ethanolic solution of **V** is saturated with sulfur dioxide.

1,2,3,4-Tetrahydroacridin-4-ol (III), mp 115–116° C (ethanol); a mixture with a sample obtained by a published method [3], mp 114–115° C, melted without depression.

4-Chloro-1,2,3,4-tetrahydroacridine (IV), mp 81–83° C (petroleum ether). Found, %: C 72.11; H 5.75. Calculated for $C_{13}H_{12}NCl$, %: C 71.69; H 5.56. **Picrate,** mp 158.5–159° C (ethanol). Found, %: N 12.45. Calculated for $C_{13}H_{12}NCl \cdot C_6H_3N_3O_7$, %: N 12.54.

1,2-Dihydroacridine (V), colorless needles, mp 47–48° C (sublimed at 0.1 mm). Found, %: C 86.62; H 6.47. Calculated for $C_{13}H_{11}N$, %: C 86.15; H 6.13. IR spectrum (UR-20, CCl_4): absorption in the 2840–2940 cm^{-1} region ($-CH_2-$) weaker, and that in the 3000–3100 cm^{-1} region ($=C-H$) stronger, than in the IR spectrum of **I**. **Picrate,** mp 246–248° C (decomp.). Found, %: N 13.65. Calculated for $C_{13}H_{11}N \cdot C_6H_3N_3O_7$, %: N 13.65.

1,2,3,4-Tetrahydroacridine-3-sulfonic acid (VI), colorless rods, mp 242–244° C (ethanol). Found, %: C 59.13; H 51.2; equiv. 260. Calculated for $C_{13}H_{13}NSO_3$, %: C 59.30; H 4.98; equiv. 263.

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SYNTHESIS OF SYM-OCTAHYDROPYRIDO[2,3-g]QUINOLINE-4,9-DIONE

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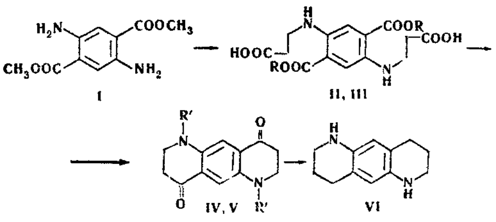
The single attempt at the cyclization of N,N,N',N'-tetra(β-cyanoethyl)-p-phenylenediamine to form the N^1,N^6-di(β-cyanoethyl) analog of **V** did not lead to a satisfactory result. We have effected the synthesis of **V** in the following way:



II R=CH_3, III R=H; IV R'=$COCH_3$, V R'=H

2,5-Di(β-carboxyethylamino)terephthalic acid (III). By heating **I** with propiolactone in acetone we obtained a quantitative yield of **II**, mp 215–216° C (decomp., from aqueous ethanol). Found, %: N 7.55. Calculated for $C_{16}H_{20}N_2O_8$, %: N 7.61. By alkaline hydrolysis, **II** was converted quantitatively into **III**, mp 344–346° C (decomp., from water). Found, %: N 8.46. Calculated for $C_{14}H_{16}N_2O_8$, %: N 8.23.

N^1,N^6-Diacetyl-sym-octahydropyrido[2,3-g]quinoline-4,9-dione (IV). This was obtained by the cyclization of **III** in acetic anhydride in the presence of potassium acetate [2] by heating the mixture to 100° C until the evolution of CO_2 ceased. The yield of **IV** was 16%, mp 244–246° C (from ethyl acetate–ethanol). Found, %: N 8.34. Calculated for $C_{16}H_{16}N_2O_4 \cdot 2H_2O$, %: N 8.33. IR spectrum: ν_{CO} 1762 cm^{-1}.

sym-Octahydropyrido[2,3-g]quinoline-4,9-dione (V). This was obtained by the acid hydrolysis of **IV** in 92.5% yield in the form of lustrous dark cherry-red crystals, mp 280° C (decomp., from benzene), readily soluble in ethanol and acetone, moderately in benzene, and sparingly in water. Found, %: C 66.58; H 5.52; N 13.05. Calculated for $C_{12}H_{12}N_2O_2$, %: C 66.65; H 5.59; N 12.95. IR spectrum: ν_{NH} 3365 cm^{-1}, ν_{CO} 1673 cm^{-1}.

sym-Octahydropyrido[2,3-g]quinoline (VI). This was obtained by the Kizhner-Wolff [Wolff-Kishner] reduction of **V**. The yield of **VI** was 80.5%, mp 161–162° C (from ethyl acetate). According to the literature [3], mp 161–162° C. Found, %: N 15.05. Calculated for $C_{12}H_{16}N_2$, %: N 14.9. IR spectrum: ν_{NH} 3362 cm^{-1}.

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ARYLAMINATION OF QUATERNARY ACRIDINIUM SALTS

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In studying the reactivity of quaternary acridinium salts, we have found that at 110–130° C in the presence of sulfur they react with arylamines. In this way, for example, high yields of 10-alkyl-9-(p-aminophenyl)- and 10-alkyl-9-(p-dimethylaminophenyl)acridinium halides (**I** and **II**) are formed.

The presence of a free amino group in **I** is shown by IR spectroscopy and by diazotization followed by azo-coupling.

The structure of the substances of type **II** was shown by independent synthesis, namely by the quaternization with methyl iodide of 9-(p-dimethylaminophenyl)acridine, which we obtained by Ullman's method [1].

The reaction described also extends to acridine base, but in contrast to the reaction with acridinium salts, it takes place with low yields (12–13%). The reaction of acridine with aniline and dimethylaniline in the presence of sulfur yielded 9-(p-aminophenyl)- and 9-(p-dimethylaminophenyl)acridines (**III** and **IV**), respectively.

The structure of **III** was confirmed by its IR spectrum and by deamination via the diazonium compound to 9-phenylacridine, which gave no depression in admixture with the substance obtained by Berntsen's method [2].

The quaternization of **III** and **IV** with equimolecular amounts of methyl iodide gave their quaternary salts with yields of 65–80%.

When ethanolic solutions of these salts were passed through Al_2O_3, compounds **III** and **IV** were re-formed quantitatively.

Some characteristics of the compounds synthesized are given in the table.

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Characteristics of the Compounds Obtained

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
10-Methyl-9-(p-aminophenyl) acridinium iodide	234 (ethanol)	$C_{20}H_{17}N_2I$	58.20	4.13	6.93	58.26	4.15	6.79	90
10-Methyl-9-(p-dimethylaminophenyl)acridinium iodide	216 (ethanol)	$C_{22}H_{21}N_2I$	59.77	4.77	6.30	60.00	4.80	6.36	91
9-(p-Aminophenyl)acridine	269 (ethanol)	$C_{19}H_{14}N_2$	84.66	5.23	10.14	84.41	5.22	10.37	12
9-(p-Dimethylaminophenyl) acridine	279 (xylene)	$C_{21}H_{18}N_2$	85.06	6.13	9.25	84.88	6.08	9.39	13
10-Ethyl-9-(p-aminophenyl) acridinium iodide	220 (ethanol)	$C_{21}H_{19}N_2I$	59.51	4.61	6.69	59.16	4.49	6.57	90
10-Ethyl-9-(p-methylaminophenyl)acridinium iodide	214 (ethanol)	$C_{22}H_{21}N_2I$	59.73	5.01	6.55	60.01	4.81	6.36	96
10-Ethyl-9-(p-dimethylaminophenyl)acridinium iodide	224 (ethanol)	$C_{23}H_{23}N_2I$	60.42	4.90	6.06	60.80	5.10	6.16	94
10-Benzyl-9-(p-dimethylaminophenyl)acridinium iodide dihydrate	**melts diffusely**	$C_{28}H_{25}N_2I \cdot 2H_2O$	60.99	5.41	5.66	60.87	5.29	5.07	91