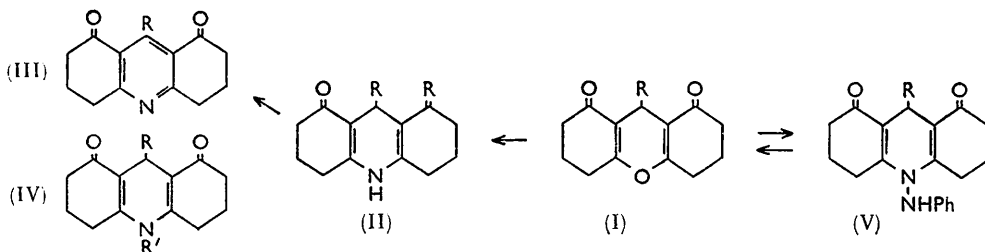


405. *Some Derivatives of Decahydro-1,8-dioxoacridine*

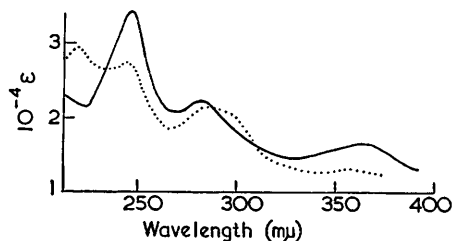
By H. ANTAKI

AFTER synthesis<sup>1</sup> of 9-aryldecahydro-1,8-dioxoacridines by condensing aromatic aldehydes with cyclohexane-1,3-dione in presence of ammonium acetate we have extended the reaction to aromatic amines, obtaining 9,10-diaryl-1,8-dioxodecahydroacridines (IV) by this reaction in glacial acetic acid. With 2-aminopyridine and its 4-methyl derivative as the amine, only the 9-arylocta-hydro-1,8-dioxoxanthen (I) was isolated. The latter is recovered unchanged after treatment with aromatic amines, indicating that the reaction does not proceed through the xanthen.



The xanthen (I) passed smoothly into the acridines (II) on treatment with ammonium acetate in glacial acetic acid, and 2,2'-arylidene-biscyclohexa-1,3-diene with aromatic amines gave the 9,10-diaryl derivatives (IV); oxidation with chromium trioxide gave the octahydroacridine (III). The 10-anilinoacridines (V) obtained by treatment with phenylhydrazine of the xanthen (I) readily reverted to the latter on reflux with ethanolic hydrochloric acid: 9-arylocta-hydro- and 9-aryldecahydro-1,8-dioxoacridines and 9,10-diaryldecahydro-1,8-dioxoacridines were stable to acid treatment. Reduction of the 1,8-dioxo-group in the compounds (I), (II), and (IV) with thioglycolic acid<sup>2</sup> gave the corresponding 1,8-diols. Whereas the dihydroxy xanthen is rapidly oxidised in hot ethanol, acetic acid, or acetic

Ultraviolet absorption of deca- (—) and octa-hydro-9-*p*-nitrophenyl-1,8-dioxoacridine (---) in absolute alcohol



anhydride solution to the 1,8-diketone, the diol from the acridine (IV) is only oxidised in boiling acetic anhydride. Octahydroacridines have been prepared from 1,5-diketones<sup>3</sup> by the Stobbe-Volland synthesis.<sup>4</sup> The ultraviolet absorption spectra of the deca- and octa-hydroacridine (II and III; R = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>) are shown in the Figure.

*Experimental.*—1,2,3,4,5,6,7,8,9,10-Decahydro-9-*p*-nitrophenyl-1,8-dioxo-10-phenylacridine. *p*-Nitrobenzaldehyde (3 g., 1 mol.), cyclohexane-1,3-dione (2.2 g., 1 mol.), and aniline (1.8 g., 1 mol.) in glacial acetic acid (100 c.c.) were refluxed for 1 hr. The solution was concentrated and diluted with water. The product crystallised, on cooling, in yellow prisms, m. p. 282°

<sup>1</sup> Antaki, *J.*, 1963, 4877.

<sup>2</sup> Bongartz, *Ber.*, 1888, **21**, 483.

<sup>3</sup> Colange, Dreux, and Delplace, *Bull. Soc. chim. France*, 1957, 447.

<sup>4</sup> Stobbe and Volland, *Ber.*, 1902, **35**, 3973.

(decomp.) (38%) (Found: C, 71.8; H, 5.6; O, 15.0; N, 6.2.  $C_{25}H_{22}N_2O_4$  requires C, 72.4; H, 5.3; O, 15.4; N, 6.7%). The 10- $\beta$ -*naphthyl derivative* formed yellow prisms, m. p. 297° (decomp.) (70%) (Found: C, 74.6; H, 5.2; O, 13.7; N, 6.1.  $C_{29}H_{24}N_2O_4$  requires C, 75.0; H, 5.1; O, 13.8; N, 6.0%), and the 10-*p-chlorophenyl derivative* in yellow plates m. p. 300° (decomp.) (56%) (Found: C, 67.1; H, 4.9; O, 14.5; N, 6.3; Cl, 7.8.  $C_{25}H_{21}ClN_2O_4$  requires C, 66.8; H, 4.6; O, 14.2; N, 6.2; Cl, 7.9%). The 10-*o-hydroxyphenyl derivative* crystallised in brown plates, m. p. >300° (47%) (Found: C, 68.9; H, 5.2; O, 18.4; N, 5.9.  $C_{25}H_{22}N_2O_5$  requires C, 69.3; H, 5.1; O, 18.5; N, 6.2%).

1,2,3,4,5,6,7,8,9,10-*Decahydro-9-p-methoxyphenyl-1,8-dioxo-10-phenylacridine*. 2,2'-*p*-Methoxybenzylidenebiscyclohexa-1,3-dione (1 g., 1 mol.) and aniline (0.3 g., 1 mol.) in acetic acid (100 c.c.) were heated under reflux for 1 hr. The *product* separated, on cooling, from the concentrated solution in yellow prisms m. p. 267° (decomp.) (42%) (Found: C, 78.0; H, 6.1; O, 11.4; N, 3.2.  $C_{26}H_{25}NO_3$  requires C, 78.1; H, 6.2; O, 12.0; N, 3.5%). The 10-*p-chlorophenyl derivative* formed yellow plates, m. p. 285° (decomp.) (Found: C, 71.7; H, 5.5; O, 10.9; N, 3.2; Cl, 7.6.  $C_{26}H_{24}ClNO_3$  requires C, 71.9; H, 5.5; O, 11.0; N, 3.2; Cl, 8.1%) as did the *o-hydroxyphenyl derivative* (68%), m. p. 300° (Found: C, 75.1; H, 5.4; O, 15.3; N, 3.1.  $C_{26}H_{25}NO_4$  requires C, 75.3; H, 5.7; O, 15.4; N, 3.4%).

1,2,3,4,5,6,7,8-*Octahydro-1,8-dihydroxy-9-p-nitrophenylxanthen*. 10-Anilinodecahydro-9-*p*-nitrophenyl-1,8-dioxoacridine<sup>1</sup> (0.5 g.) in ethanol (150 c.c.) was saturated with hydrogen chloride and then heated under reflux for 30 min. with intermittent passage of a stream of hydrogen chloride. The solution, when concentrated and cooled, deposited the xanthen in white needles, m. p. 269° (decomp.). The xanthen (0.3 g., 1 mol.) and sodium thioglycollate (0.4 g., 4 mol.) in acetic acid (30 c.c.) were refluxed for 30 min. The 1,8-*diol* separated from the concentrated solution on dilution and cooling in white needles m. p. 210° (Found: C, 66.2; H, 5.5; O, 24.5; N, 3.7.  $C_{19}H_{21}NO_5$  requires C, 66.4; H, 6.1; O, 23.3; N, 4.0%).

1,2,3,4,5,6,7,8,9,10-*Decahydro-1,8-dihydroxy-10- $\beta$ -naphthyl-9-p-nitrophenylacridine*. The acridine (IV; R = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, R' =  $\beta$ -C<sub>10</sub>H<sub>7</sub>) (0.5 g., 1 mol.) and sodium thioglycollate (0.4 g., 4 mol.) were refluxed for 0.5 hr. The solution was concentrated, diluted, and cooled; the *product* separated in yellow prisms, m. p. 270° (decomp.) (Found: C, 74.0; H, 4.8; O, 13.3; N, 5.8.  $C_{29}H_{28}N_2O_4$  requires C, 74.3; H, 5.1; O, 13.6; N, 5.9%).

1,2,3,4,5,6,7,8-*Octahydro-9-p-nitrophenyl-1,8-dioxoacridine*. To the decahydroacridine (II; R = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>) (1 g., 1 mol.) in acetic acid (140 c.c.) and water (60 c.c.) at 70° chromium trioxide (0.7 g., 1 mol.) in 70% acetic acid (20 c.c.) was added. When the solution became pale brown it was diluted with water and cooled. The *product* separated in yellow prisms, m. p. >300° (64%) (Found: C, 67.5; H, 4.7; O, 18.6; N, 8.1.  $C_{19}H_{16}N_2O_4$  requires C, 67.8; H, 4.7; O, 19.0; N, 8.3%). The 9-*p-methoxyphenyl derivative* formed yellow prisms, m. p. >300° (Found: C, 74.6; H, 5.7; O, 14.6; N, 4.2.  $C_{20}H_{19}NO_3$  requires C, 74.7; H, 5.9; O, 14.9; N, 4.3%).