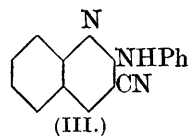
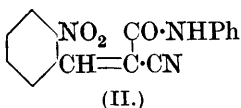
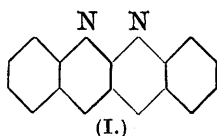


CCCLXVI.— $\omega$ -Cyano- $\omega$ -arylidenacetanilides and the  
Conversion of their o-Nitro-derivatives into Quinol-  
ine Derivatives.

By MOHAMMAD ISHAQ and JÑANENDRA NATH RÂY.

IT seemed to the authors that naphthinoine (I), a tetrahydro-derivative of which was prepared by Reissert by the reduction of di-o-nitrobenzylacetic acid (*Ber.*, 1894, **27**, 2244), might be obtained from  $\omega$ -cyano- $\omega$ -o-nitrobenzylidenacetanilide (II). This substance, however, gave 2-anilino-3-cyanoquinoline (III) on reduction and could

not be converted into a naphtholine derivative under any of the conditions tried.



A number of 2-arylamino-3-cyanoquinolines are described below.

Attempts to convert  $\omega$ -cyanoacetanilide into 2:4-diketo-1:2:3:4-tetrahydroquinoline failed (compare Clemo and Perkin, J., 1924, 125, 1608).

### EXPERIMENTAL.

$\omega$ -Cyanoacetanilide.— $\omega$ -Chloroacetanilide (5.6 g.), dissolved in alcohol (25 c.c.), was treated at 70–80° with an aqueous solution of potassium cyanide (3 g. in 5 c.c.) for 2 hours. When the product was poured into water (100 c.c.),  $\omega$ -cyanoacetanilide was precipitated in quantitative yield; m. p. 195° after crystallisation from alcohol. It could not be hydrolysed to give either an ester or an acid.

$\omega$ -Cyano- $\omega$ -arylideneacetanilides.—These substances are produced in quantitative yield under the conditions exemplified below.

A solution of  $\omega$ -cyanoacetanilide (1.6 g.) and piperonal (1.5 g.) in the minimum quantity of pyridine was treated with a drop or two of piperidine and heated at 60–70° for 1½ hours. After 12 hours, the  $\omega$ -cyano- $\omega$ -piperonylideneacetanilide, which either crystallised from the mixture or was precipitated by addition of water, was collected and recrystallised from alcohol; m. p. 182° (Found: N, 9.6.  $C_{27}H_{12}O_3N_2$  requires N, 9.6%).

$\omega$ -Cyano- $\omega$ -m-methoxybenzylideneacetanilide, m. p. 141° (Found: N, 10.2.  $C_{17}H_{14}O_2N_2$  requires N, 10.1%),  $\omega$ -cyano- $\omega$ -3:4-dimethoxybenzylideneacetanilide, m. p. 168° (Found: N, 9.1.  $C_{18}H_{16}O_3N_2$  requires N, 9.1%),  $\omega$ -cyano- $\omega$ -o-nitrobenzylideneacetanilide, yellow silky needles, m. p. 206° (Found: N, 14.3.  $C_{16}H_{11}O_3N_3$  requires N, 14.3%),  $\omega$ -cyano- $\omega$ -6-nitro-3:4-methylenedioxybenzylideneacetanilide (from 6-nitropiperonal), m. p. 227° (Found: N, 12.6.  $C_{17}H_{11}O_5N_3$  requires N, 12.5%), and  $\omega$ -cyano- $\omega$ -6-nitro-3:4-dimethoxybenzylideneacetanilide, m. p. 169° (Found: N, 12.0.  $C_{18}H_{15}O_5N_3$  requires N, 11.9%), were prepared.

From  $\omega$ -cyanoaceto-*p*-toluidide (obtained in the same way as the anilide and having m. p. 180° after crystallisation from alcohol), the following derivatives were prepared:  $\omega$ -cyano- $\omega$ -3:4-dimethoxybenzylideneaceto-*p*-toluidide, m. p. 198° (Found: N, 8.7.  $C_{19}H_{18}O_3N_2$  requires N, 8.7%),  $\omega$ -cyano- $\omega$ -piperonylideneaceto-*p*-toluidide, m. p. 183°,  $\omega$ -cyano- $\omega$ -m-methoxybenzylideneaceto-*p*-toluidide, m. p. 144°

(Found : N, 9.9.  $C_{18}H_{16}O_2N_2$  requires N, 9.6%),  $\omega$ -cyano- $\omega$ -o-nitrobenzylideneaceto-p-toluidide, m. p.  $182^\circ$  (Found : N, 13.7.  $C_{17}H_{13}O_3N_3$  requires N, 13.7%),  $\omega$ -cyano- $\omega$ -6-nitro-3 : 4-methylenedioxybenzylideneaceto-p-toluidide, m. p.  $216^\circ$  (Found : N, 12.3.  $C_{18}H_{13}O_5N_3$  requires N, 12.0%), and  $\omega$ -cyano- $\omega$ -6-nitro-3 : 4-dimethoxybenzylideneaceto-p-toluidide, m. p.  $174^\circ$  (Found : N, 11.5.  $C_{19}H_{17}O_5N_3$  requires N, 11.4%).

*Preparation of 2-Arylamino-3-cyanoquinolines.*— $\omega$ -Cyano- $\omega$ -o-nitrobenzylideneacetanilide (2 g.) was added to hot glacial acetic acid containing zinc dust (5 g.). The liquid was boiled vigorously for 5 minutes, filtered, and diluted with water to twice its volume; it was then made strongly alkaline, care being taken that it did not get too warm. The voluminous precipitate of 2-anilino-3-cyanoquinoline (III) crystallised from dilute alcohol in pale yellow needles, m. p.  $208^\circ$  (Found : N, 17.1.  $C_{16}H_{11}N_3$  requires N, 17.1%). The substance easily forms a picrate.

The following compounds were prepared by a similar procedure : 2-anilino-3-cyano-6 : 7-methylenedioxyquinoline, pale yellow scales, m. p.  $287^\circ$  (Found : N, 14.5.  $C_{17}H_{11}O_2N_3$  requires N, 14.5%), 2-anilino-3-cyano-6 : 7-dimethoxyquinoline, m. p.  $237^\circ$  (Found : N, 13.9.  $C_{18}H_{15}O_2N_3$  requires N, 13.8%), 2-p-toluidino-3-cyanoquinoline, m. p.  $221$ — $222^\circ$  (Found : N, 16.3.  $C_{17}H_{13}N_3$  requires N, 16.2%), and 2-p-toluidino-3-cyano-6 : 7-dimethoxyquinoline, m. p.  $253^\circ$  (Found : N, 13.2.  $C_{19}H_{17}O_2N_3$  requires N, 13.2%).

UNIVERSITY OF THE PUNJAB,  
LAHORE, INDIA.

[Received, November 13th, 1930.]