CCCLXVI.—*ω-Cyano-ω-arylideneacetanilides and the Conversion of their* o-*Nitro-derivatives into Quinoline Derivatives.*

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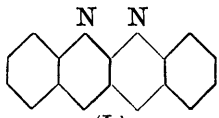
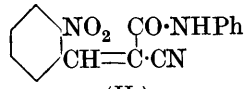
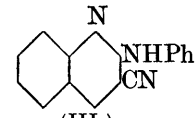
It seemed to the authors that naphthinoline (I), a tetrahydro-derivative of which was prepared by Reissert by the reduction of di-*o*-nitrobenzylacetic acid (*Ber.*, 1894, **27**, 2244), might be obtained from ω-*cyano*-ω-*o*-*nitrobenzylideneacetanilide* (II). This substance, however, gave 2-*anilino*-3-*cyanoquinoline*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

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


(I.)



(II.)



(III.)

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

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

EXPERIMENTAL.

ω-Cyanoacetanilide.—ω-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.), ω-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.

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

A solution of ω-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 1¼ hours. After 12 hours, the *ω-cyano-ω-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%).

ω-Cyano-ω-m-methoxybenzylideneacetanilide, m. p. 141° (Found: N, 10·2. $C_{17}H_{14}O_2N_2$ requires N, 10·1%), *ω-cyano-ω-3 : 4-dimethoxybenzylideneacetanilide*, m. p. 168° (Found: N, 9·1. $C_{18}H_{16}O_3N_2$ requires N, 9·1%), *ω-cyano-ω-o-nitrobenzylideneacetanilide*, yellow silky needles, m. p. 206° (Found: N, 14·3. $C_{16}H_{11}O_3N_3$ requires N, 14·3%), *ω-cyano-ω-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 *ω-cyano-ω-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 ω-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: *ω-cyano-ω-3 : 4-dimethoxybenzylideneaceto*-p-*toluidide*, m. p. 198° (Found: N, 8·7. $C_{19}H_{18}O_3N_2$ requires N, 8·7%), ω-cyano-ω-piperonylideneaceto-*p*-toluidide, m. p. 183°, *ω-cyano-ω-m-methoxybenzylideneaceto*-p-*toluidide*, m. p. 144°

(Found : N, 9·9. $C_{18}H_{16}O_2N_2$ requires N, 9·6%), *ω-cyano-ω-o-nitrobenzylideneaceto-p-toluidide*, m. p. 182° (Found : N, 13·7. $C_{17}H_{13}O_3N_3$ requires N, 13·7%), *ω-cyano-ω-6-nitro-3 : 4-methylenedioxybenzylideneaceto-p-toluidide*, m. p. 216° (Found : N, 12·3. $C_{18}H_{13}O_5N_3$ requires N, 12·0%), and *ω-cyano-ω-6-nitro-3 : 4-dimethoxybenzylideneaceto-p-toluidide*, m. p. 174° (Found : N, 11·5. $C_{19}H_{17}O_5N_3$ requires N, 11·4%).

Preparation of 2-Arylamino-3-cyanoquinolines.—ω-Cyano-ω-*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° (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° (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° (Found : N, 13·9. $C_{18}H_{15}O_2N_3$ requires N, 13·8%), *2-p-toluidino-3-cyanoquinoline*, m. p. 221—222° (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° (Found : N, 13·2. $C_{19}H_{17}O_2N_3$ requires N, 13·2%).

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