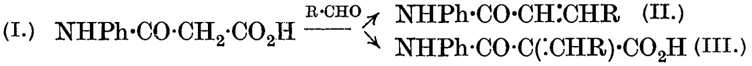
CCLXXX.—*The Condensation of Aromatic Aldehydes with Malonanilic Acid and its Derivatives.*

By Gurcharan Singh Ahluwalia, Muhammad Abdul Haq, and Jñanendra Nath Rây.

Clemo and Johnson (J., 1930, 2133) have indicated that the replacement of the nitrogen atom in trimethoxytetrahydro*iso*indenoquinolines by oxygen by the method of von Braun (*Ber.*, 1905, **38**, 850) offers possibilities for the synthesis of trimethylbrazilin. The starting point in the synthesis of their *iso*indenoquinolines was 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline (J., 1924, **125**, 2608).

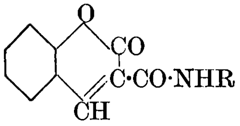
Malonanilic acid (I) has now been condensed with certain aromatic aldehydes in pyridine solution at 40—50°, and the corresponding arylidene derivatives (III) and also cinnamanilides (II) have been isolated. The acids (III) are easily reduced to the corresponding dihydro-derivatives by sodium amalgam. These substances cannot

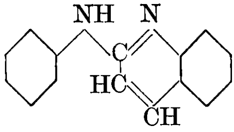


$$\text{(I.)}\ \mathrm{NHPh{\cdot}CO{\cdot}CH_2{\cdot}CO_2H} \xrightarrow{\mathrm{R{\cdot}CHO}} \begin{cases} \mathrm{NHPh{\cdot}CO{\cdot}CH{:}CHR} & \text{(II.)} \\ \mathrm{NHPh{\cdot}CO{\cdot}C({:}CHR){\cdot}CO_2H} & \text{(III.)} \end{cases}$$

be dehydrated to give a quinolone, indenoquinolone, *iso*indenoquinolone, or an anilide of a hydrindonecarboxylic acid.

(IV.)





(V.)

The interaction of malonanilic acid or its derivatives with salicylaldehyde gives anilides of coumarin-3-carboxylic acid (IV), and its condensation with *o*-nitrated aromatic aldehydes gives *o*-nitroarylidene derivatives analogous to (III). The latter substances on reduction are decarboxylated and converted by ring closure into 2-arylaminoquinolines (V), the 3-cyano-derivatives of which have been prepared by Ishaq and Rây (J., 1930, 2740) and are very resistant to hydrolysis.

EXPERIMENTAL.

Malonanilic acid can be prepared in a greater yield than that obtained by Chattaway and Olmsted (J., 1910, **97**, 940) if more ethyl malonate is taken (0·25 mol. in excess of that recorded) and the mixture heated for 40 minutes. The hydrolysis of ethyl malonanilate is facilitated by the use of a more concentrated solution of sodium carbonate (8 g. in 70 c.c.). Malon-*o*- and -*m*-toluidic acids were prepared by similar modifications of the method.

Condensation of Malonanilic Acid and Piperonal.—Malonanilic acid (1·8 g.), piperonal (1·5 g.), pyridine (4 c.c.), and piperidine (4 drops) were heated at 50—60° for 1 hour, and the product was poured into cold water (20 c.c.). 3 : 4-*Methylenedioxycinnamanilide* (II), deposited as an oil which soon solidified, crystallised from alcohol in plates (1·3 g.), m. p. 158°, insoluble in water and sodium carbonate solution, soluble in chloroform, and sparingly soluble in hot water (Found : N, 5·5. $C_{16}H_{13}O_3N$ requires N, 5·3%). The anilide, when kept or exposed to light, undergoes a change, possibly partial transformation into the geometrical isomeride or an *allo*-form, which affects its m. p.

The aqueous filtrate on acidification gave *piperonylidenemalonanilic acid*, which was recrystallised from 50% alcohol; yield, 0·5 g.; m. p. 202° (decomp.) (Found : N, 4·5. $C_{17}H_{13}O_5N$ requires N, 4·5%).

3 : 4-*Dimethoxycinnamanilide*, similarly formed from veratraldehyde at 30°, had m. p. 111° (varying with the rate of heating) (Found : N, 5·1. $C_{17}H_{17}O_3N$ requires N, 5·0%); 3 : 4-*dimethoxybenzylidenemalonanilic acid*, isolated from the filtrate, had m. p. 222° (decomp.) (Found : N, 4·6. $C_{18}H_{17}O_5N$ requires N, 4·3%. Found in the *silver* salt : Ag, 24·3. $C_{18}H_{16}O_5NAg$ requires Ag, 24·8%).

p-*Methoxycinnamanilide*, m. p. 140° (Found : N, 5·7. $C_{16}H_{15}O_2N$ requires N, 5·5%), 3 : 4-*methylenedioxycinnam*-o-*toluidide*, m. p. 181° (Found : N, 5·1. $C_{17}H_{15}O_3N$ requires N, 5·0%), p-*methoxybenzylidenemalonanilic acid*, m. p. 213° (decomp.) (Found : N, 4·8. $C_{17}H_{15}O_4N$ requires N, 4·7%), *piperonylidenemalon*-o-*toluidic acid*, m. p. 213° (Found : N, 4·3. $C_{18}H_{15}O_5N$ requires N, 4·15%), *veratrylidenemalon*-o-*toluidic acid*, m. p. 219° (Found : N, 4·2. $C_{19}H_{19}O_5N$ requires N, 4·1%), p-*methoxybenzylidenemalon*-o-*toluidic acid*, m. p. 217° (Found : N, 4·6. $C_{18}H_{17}O_4N$ requires N, 4·5%), and p-*methoxycinnam*-o-*toluidide*, m. p. 177° (Found : N, 5·1. $C_{17}H_{17}O_2N$ requires N, 5·2%), were prepared.

α-*Homopiperonylmalonanilic acid* was prepared by reduction of sodium piperonylidenemalonanilate by 2% sodium amalgam, care being taken to keep the temperature low and the solution nearly neutral with acetic acid. The product, isolated after acidification, crystallised from dilute alcohol in colourless needles, m. p. 172° (decomp.) (Found : N, 4·6. $C_{17}H_{15}O_5N$ requires N, 4·5%).

α-Homoveratrylmalonanilic acid, similarly prepared, crystallised from dilute alcohol in silvery needles, m. p. 173°, rather easily soluble in hot water (Found : N, 4·5. $C_{18}H_{19}O_5N$ requires N, 4·25%). *α-Homopiperonylmalon-*o*-toluidic acid*, m. p. 163° (decomp.) (Found : N, 4·5. $C_{18}H_{17}O_5N$ requires N, 4·3%), and *α-homoveratrylmalon-*o*-toluidic acid*, m. p. 128° (Found : N, 4·2. $C_{19}H_{21}O_5N$ requires N, 4·1%), were similarly prepared by reduction of the appropriate acids.

The foregoing acids were treated with phosphoric oxide in benzene, toluene, or xylene, with hot 80% sulphuric acid, zinc chloride, sulphuric acid in acetic acid, and with phosphoryl chloride, but no ring closure took place; either the acids were recovered unchanged or profound decomposition took place. α-Homopiperonylmalonanilic acid gave with phosphoryl chloride a chlorine-free product, m. p. 203°, which was not obtained in sufficient amount for further investigation.

Condensation of Malonanilic Acid and Salicylaldehyde.—A mixture of malonanilic acid (1·8 g.), salicylaldehyde (1·3 g.), pyridine (3 c.c.), and piperidine (2 drops) was heated on the steam-bath for 1 hour, a pale yellow substance separating. The product, poured into water (20 c.c.), deposited an oil mixed with crystals; the whole solidified when stirred with a few drops of alcohol. *Coumarin-3-carboxyanilide* (IV) crystallised from hot alcohol, in which it was sparingly soluble, in small yellow needles, m. p. 247° (Found : N, 5·3. $C_{16}H_{11}O_3N$ requires N, 5·3%). The o-*toluidide*, m. p. 226° (Found : N, 5·2. $C_{17}H_{13}O_3N$ requires N, 5·0%), and m-*toluidide*, m. p. 200° (Found : N, 5·2%), of coumarin-3-carboxylic acid were similarly prepared from salicylaldehyde and malon-*o*-toluidic and malon-*m*-toluidic acid respectively.

o-*Nitrobenzylidenemalonanilic acid* was prepared in good yield from *o*-nitrobenzaldehyde and malonanilic acid, very little of the decarboxylated product being formed in the reaction at 100°. The substance, purified by dissolution in sodium carbonate solution and precipitation with acid, crystallised from dilute alcohol in almost colourless needles, m. p. 172° (decomp.) (Found: N, 9·1. $C_{16}H_{12}O_5N_2$ requires N, 9·0%).

o-*Nitrobenzylidenemalon-*o*-toluidic acid*, m. p. 221° (decomp.) (Found: N, 8·6. $C_{17}H_{14}O_5N_2$ requires N, 8·6%), was similarly prepared from malon-*o*-toluidic acid.

o-*Nitropiperonylidenemalonanilic acid* had m. p. 230° (Found : N, 7·9. $C_{17}H_{12}O_7N_2$ requires N, 7·8%).

2-Anilinoquinoline (V).—Into a mixture of zinc dust and boiling acetic acid, *o*-nitrobenzylidenemalonanilic acid was introduced in small portions, and after ½ hour's boiling the liquid was filtered hot and diluted with water. The orange-coloured precipitate was collected and treated with potassium hydroxide solution. The dirty white precipitate thus obtained was crystallised several times from alcohol; m. p. above 320° (decomp.). The substance was soluble in acetic acid and could be crystallised from hot pyridine, but it was not obtained analytically pure. Probably it was a ketonaphthiolin (compare Ishaq and Rây, *loc. cit.*). Basification of the acid filtrate furnished 2-anilinoquinoline, m. p. 98° (Friedländer and Weinberg, *Ber.*, 1885, **18**, 1532, give m. p. 98°). This substance can also be obtained by reduction in hot acetic acid with stannous chloride, whereby the high-melting substance is formed in very small yield.

UNIVERSITY OF THE PUNJAB,
LAHORE, INDIA.

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