

355. *The Condensation of α -Formylphenylacetonitriles with Phenols. Part II.*

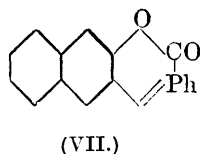
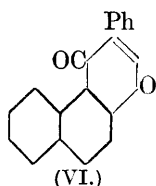
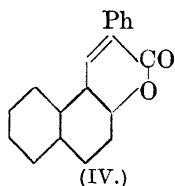
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THE Hoesch reaction between α -formylphenylacetonitrile, CHO·CHPh·CN (I), or its *O*-benzoyl derivative and resorcinol, phloroglucinol, or pyrogallol leads to 3-phenylcoumarins (Badhwar, Baker, Menon, and Venkataraman, J., 1931, 1541). In view, however, of the possible formation of isoflavones, it appeared desirable to study the condensation in the case of other phenols.

The nitrile (I) and hydroxyquinol triacetate (II) gave a small amount of 6:7-dihydroxy-3-phenylcoumarin, which was also prepared by condensing (II) with ethyl α -formylphenylacetate in presence of sulphuric acid. When a mixture of (II), benzoyloxymethylene-phenylacetonitrile (III), zinc chloride, and ether was saturated with hydrogen chloride, the main product obtained was 2:4:5-trihydroxyacetophenone, formed by (II) undergoing the Fries reaction; Bargellini and Avrutin obtained the same ketone by heating (II) with zinc chloride in acetic acid or chloroacetic acid solution (*Gazzetta*, 1911, 40, ii, 342, 347), and similar is the formation of 4:6-diacetylresorcinol from resorcinol diacetate in an attempted Hoesch reaction (Badhwar and others, *loc. cit.*). No trace of 6:7-dihydroxy-3-phenylcoumarin was isolated, the other products, of un-

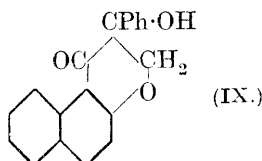
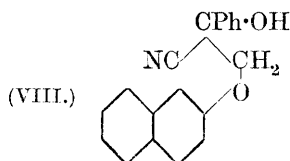
determined constitution, being probably formed by oxidation of hydroxyquinol.

The condensation of β -naphthol with (III) gave 2-phenyl-3:4- β -naphthapyrone (IV) (Bartsch, *Ber.*, 1903, 36, 1966) and a second substance (V), m. p. 242°, which was not the β -naphthaisoflavone (VI), synthesised by Baker, Pollard, and Robinson's method (J.,



1929, 1468). The substance (V) could not be the unknown coumarin (VII), as fusion with alkali and subsequent acidification led to (IV).

When α -2-naphthoxymethylmandelonitrile (VIII) in ether was saturated with hydrogen chloride, the precipitate obtained yielded



2-hydroxy-2-phenyl-1:4-3-naphthapyranone (IX), and hydrolysis of the ethereal portion led to the coumarin (IV) (compare the production of 7-methoxy-3-phenylcoumarin from methyl α -*m*-methoxyphenoxyethylmandelate; Baker, Pollard, and Robinson, *loc. cit.*).

EXPERIMENTAL.

6:7-Dihydroxy-3-phenylcoumarin.—A paste of hydroxyquinol triacetate (6.5 g.) and ethyl hydroxymethylenephanylacetate (5.0 g.) was treated with 80% H_2SO_4 (40 c.c.) in small portions, and the deep orange solution finally obtained was heated for 30 mins. at 80°, cooled, and poured into H_2O (200 c.c.). Two crystns. of the ppt. from EtOH gave long, pale yellow needles, m. p. 242° (Found: C, 70.8; H, 4.1. $C_{15}H_{10}O_4$ requires C, 70.8; H, 3.9%). The pale yellow solution in H_2SO_4 had a brilliant green fluorescence. The green-fluorescent alc. solution gave with $FeCl_3$ a brownish-green colour, turned dark brown by NH_3 . The substance dyed wool different shades of yellow with Al, Cr, and Sn mordants and greenish-grey with Fe. The diacetate crystallised from EtOH in colourless needles, m. p. 190—191° (Found: C, 67.7; H, 4.3. $C_{19}H_{14}O_6$ requires C, 67.5; H, 4.1%).

Condensation of hydroxyquinol triacetate (II) with α -formylphenylacetonitrile (I). A mixture of (II) (10 g.), (I) (5.7 g.), $ZnCl_2$ (3 g.), and anhyd. Et_2O (50 c.c.) was saturated with HCl during several hrs. and left at 0° for 3 days, finally becoming deep red. The Et_2O was decanted, and the semi-solid mass washed with dry Et_2O and boiled with H_2O (100 c.c.) in a current of CO_2 for

2 hrs. The residue, repeatedly cryst. from EtOH, gave long yellow needles (0.2 g.), m. p. 242°, of 6 : 7-dihydroxy-3-phenylcoumarin. Needles of the unchanged nitrile (I) separated from the aq. filtrate on cooling.

Condensation of Hydroxyquinol Triacetate (II) with Benzoyloxymethylenephylacetone (III).—The reaction was carried out as in the preceding case, with (II) (15 g.), (III) (14.7 g.), $ZnCl_2$ (4 g.), and dry Et_2O (100 c.c.), the mixture being finally treated under reflux at 45° with HCl for 8 hrs. The orange-red solid was boiled with H_2O (150 c.c.) for 3 hrs.; the yellow residue was (III). The filtrate deposited a brick-red substance (3.5 g.), which, cryst. several times from abs. EtOH- C_6H_6 in an evacuated desiccator, gave long, golden-yellow, prismatic needles, m. p. 202° (Found : C, 56.7; H, 4.9. Calc. for $C_8H_8O_4$: C, 57.1; H, 4.8%); acetyl derivative, m. p. 110° (Found : C, 57.2; H, 4.8. Calc. : C, 57.1; H, 4.8%). Bargellini (*Gazzetta*, 1913, 43, i, 164) describes 2 : 4 : 5-trihydroxyacetophenone as garnet-red needles, m. p. 200—202°; acetyl derivative, m. p. 110—111°.

Condensation of Benzoyloxymethylenephylacetone (III) with β -Naphthol.—HCl was passed for 8 hrs. into a mixture of (III) (17 g.), β -naphthol (10 g.), $ZnCl_2$ (4 g.), and dry Et_2O (100 c.c.) at -10°. After 3 days at 0°, the solid was collected, washed with dry Et_2O , boiled with H_2O (100 c.c.) for 2 hrs., and crystallised twice from EtOH; long, pale yellow needles (2.5 g.), m. p. 143—144°, were obtained (Found : C, 83.6; H, 4.6. Calc. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.5%). 2-Phenyl-3 : 4- β -naphthapyrone (IV) (Bartsch, *loc. cit.*) melts at 142°. An alc. solution has a bright bluish-violet, and an H_2SO_4 solution an intense green, fluorescence.

The ethereal filtrate and washings were evaporated and the residue was boiled with H_2O (100 c.c.) for 2 hrs. and crystallised 7—8 times from AcOH, colourless irregular plates (2.7 g.), m. p. 242°, being obtained (Found : C, 83.5; H, 4.9. $C_{19}H_{12}O_2$ requires C, 83.8; H, 4.5%), which displayed a bluish-green fluorescence in H_2SO_4 but none in EtOH. A mixture of the substance (1.2 g.) and Na (2.4 g.) was dissolved in the minimum amount of abs. EtOH and heated for 16 hrs. on the water-bath. The EtOH was removed, and the product dissolved in H_2O (200 c.c.) and acidified; pale yellow needles (from EtOH), m. p. 143—144°, identical with (IV), were obtained.

β -Naphthoxyacetophenone.—Solutions of ω -bromoacetophenone (25 g.) in acetone (25 c.c.) and of β -naphthol (26 g.) in 20% NaOH aq. (110 c.c.) were mixed slowly and heated for 30 mins. on the water-bath, the acetone distilled off, and the residue poured into H_2O . The ppt. crystallised from EtOH in stout colourless needles (17 g.), m. p. 108° (Found : C, 82.3; H, 5.6. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.4%). The orange solution in H_2SO_4 has a green fluorescence.

α -2-Naphthoxymethylmandelonitrile (VIII).—30% H_2SO_4 was added during 24 hrs. to a mixture of β -naphthoxyacetophenone (12 g.), Et_2O (125 c.c.), KCN (14 g.), and H_2O (60 c.c.), and after 24 hrs.' stirring the ethereal layer was separated, washed with H_2O , dried over $MgSO_4$, and evaporated; the residue crystallised from $CHCl_3$ -ligroin in stout colourless prisms (9 g.), m. p. 115—116° (Found : N, 5.0. $C_{19}H_{15}O_2N$ requires N, 4.8%).

2-Hydroxy-2-phenyl-1 : 4- β -naphthapyranone (IX).—HCl was led for 12 hrs. into a mixture of (VIII) (7.5 g.), $ZnCl_2$ (2 g.), and dry Et_2O (50 c.c.) at 0° and after 3 days the liquid was decanted and the solid was washed with Et_2O , boiled with H_2O (150 c.c.) for 2 hrs., and crystallised from EtOH; cream-coloured, stout, prismatic needles (5.5 g.), m. p. 124°, were obtained (Found :

C, 78.6; H, 5.0. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.8%). The yellow solution in H_2SO_4 has a green fluorescence, which becomes intense on standing. The alc. solution turns deep orange on addition of $FeCl_3$. The behaviour with $Na-Hg$ is exactly similar to that of 3-hydroxy-7-methoxyisoflavanone. Treatment with boiling Ac_2O and pyridine gave the *acetyl* derivative, colourless needles, m. p. 125—126°, from aq. EtOH (Found : C, 75.9; H, 5.0. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.8%).

The ethereal solution was evaporated : the residue, boiled with H_2O and twice cryst. from EtOH, gave yellow needles (0.03 g.), m. p. 141—142°, of (IV).

2-Phenyl-1 : 4- β -naphthapyrone (VI).—The naphthapyranone (IX) (3 g.) was dissolved in cold conc. H_2SO_4 (20 c.c.) and, after 1 hr., poured on ice. The ppt. crystallised from dil. EtOH in colourless needles (2.9 g.), m. p. 129—130° (Found : C, 81.1; H, 4.7; loss at 150° after 6 hrs., 3.3. $C_{19}H_{12}O_2, \frac{1}{2}H_2O$ requires C, 81.1; H, 4.6; H_2O , 3.2%). The colourless solution in H_2SO_4 has a sky-blue fluorescence, much less intense than that exhibited by the naphthapyranone (IX).

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