

[1956] 1 : 2-Dihydro-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)isoquinoline. 2477

480. The Synthesis of 1 : 2-Dihydro-1-oxo-5'-phenylfurano-(2' : 3'-3 : 4)isoquinoline.

By A. S. BAILEY and D. L. SWALLOW.

A general method for the preparation of 4-phenacylhomophthalimides is described; their cyclisation leads to derivatives of furano(2' : 3'-3 : 4)isoquinoline.

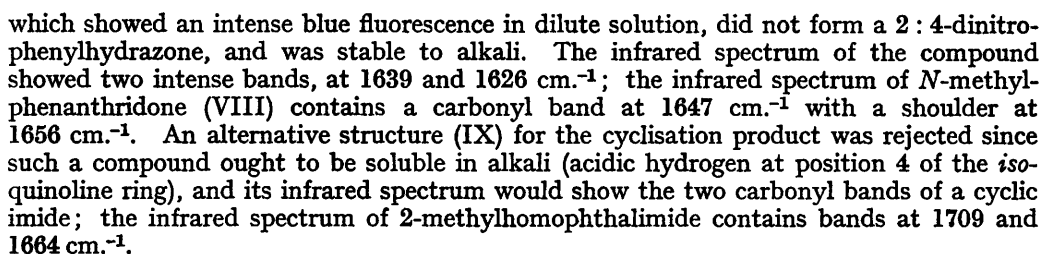
HEATING β -benzoyl- α -(2-carboxy-3 : 4-dimethoxyphenyl)propionitrile (I; R = OMe) with mineral acid causes loss of water and formation of a compound which was thought to be 1 : 2-dihydro-7 : 8-dimethoxy-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)isoquinoline (II; R = OMe, R' = H).¹ The reaction was shown² to be general for compounds of type (I), and the alternative structure, 7 : 8-dimethoxy-5'-phenylpyrrolo(2' : 3'-3 : 4)isocoumarin (III; R = OMe), was put forward by analogy with the cyclisation of α -aryl- β -benzoyl-propionitriles to form pyrrole derivatives.³ It was, therefore, decided to attempt the synthesis of the furano-compound (II; R = R' = H) to distinguish between these alternatives.

It is reported¹ that 4-acylhomophthalimides are readily alkylated with sodium ethoxide and an alkyl halide, but attempts to prepare the phenacylimide (IV; R = CH₂COPh) by treating 4-acetyl-2-methylhomophthalimide (IV; R = H) with phenacyl bromide failed, although phenacyl halides readily react with sodioacetoacetic ester and sodiomalonic ester.⁴ Alkylation of *N*-substituted homophthalimides gives mainly 4 : 4-dialkyl derivatives,⁵ and treatment of 2-methylhomophthalimide with phenacyl bromide was said to give 2-methyl-4 : 4-diphenacylhomophthalimide.¹ We have repeated this preparation and observed that the monosubstitution product, 2-methyl-4-phenacylhomophthalimide (V; R = Me), is also formed; the two compounds are easily separated by crystallisation from acetic acid. Structure (V; R = Me) is supported by the fact that the compound is soluble in sodium hydroxide solution, forms a 2 : 4-dinitrophenylhydrazone, and on alkaline hydrolysis affords the acid² (VI). The overall yield of the phenacyl compound (V; R = Me) is too small for the method to be of preparative value and a more general method was sought.

Homophthalimide and its *N*-alkyl derivatives condense with aldehydes,⁶ and treatment

¹ Haworth, *J.*, 1937, 1312.² Bailey and Robinson, *J.*, 1950, 1375; Bailey and Staunton, *J.*, 1952, 2153.³ Rogers, *J.*, 1943, 590; Davies and Rogers, *J.*, 1944, 126; Knott, *J.*, 1947, 1196.⁴ Paal, *Ber.*, 1883, 16, 2865; Dalglish, *J.*, 1952, 137.⁵ Harriman, Shelton, Van Campen, and Warren, *J. Amer. Chem. Soc.*, 1945, 67, 1481.⁶ Haworth and Pink, *J.*, 1927, 2345; Buu-Hoi, *Bull. Soc. chim. France*, 1945, 12, 313; Forrest, Haworth, Pinder, and Stevens, *J.*, 1949, 1311.

Cyclisation of 1:4-diketones to furans is readily accomplished by heating them with polyphosphoric acid⁷ and by this method the compound (V; R = Me) yielded 1:2-dihydro-2-methyl-1-oxo-5'-phenylfurano(2':3'-3:4)*isoquinoline* (II; R = H, R' = Me)



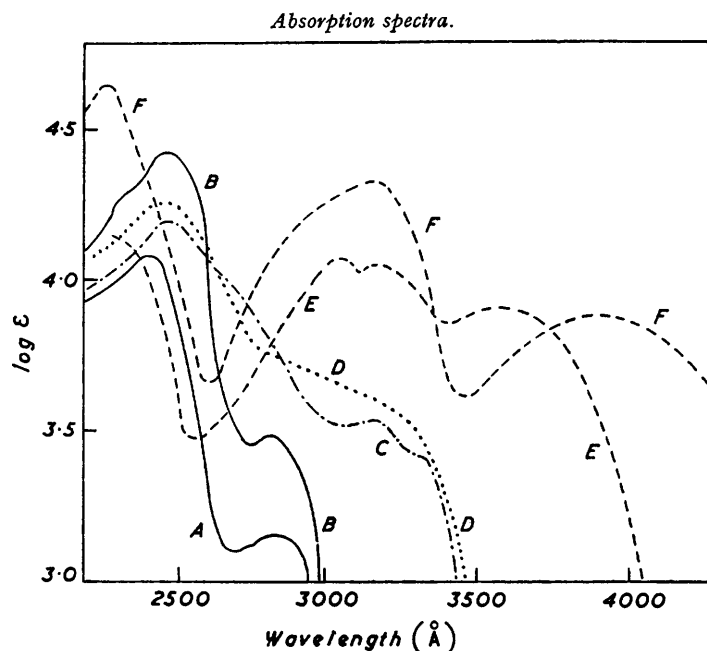
Treatment of the homophthalimide (V; R = Me) with concentrated sulphuric acid gave a furanoisquinolone containing a sulphonic acid group; the same compound was obtained by similar treatment of the furano-compound (II; R = H, R' = Me); the position of the sulphonic acid group is not known.

Since homophthalimide is only sparingly soluble in ethanol it was condensed with phenylglyoxal in pyridine at room temperature, affording 4-phenacylidenehomophthalimide (VII; R = H) which was then reduced to 4-phenacylhomophthalimide (V; R = H), and the last-named cyclised with polyphosphoric acid to 1:2-dihydro-1-oxo-5'-phenyl-furano(2':3'-3:4)isoquinoline (II; R = R' = H). This compound (m. p. 280—282°) was different (colour, mixed m. p., and infrared spectrum) from the pyrrole (III; R = H) (m. p. 278—280°) obtained² by the action of acid on the starting material (I; R = H), confirming the correctness of the suggestion made by Bailey and Robinson² regarding the structure of the cyclisation products of compounds of type (I). The infrared spectrum of the furano-compound (II; R = R' = H) contains bands at 1634 and 1603 cm.⁻¹ consistent with a CO·NH structure, whilst the infrared spectrum of the pyrrolo-compound (III;

⁷ Nowlin, *J. Amer. Chem. Soc.*, 1950, **72**, 5754.

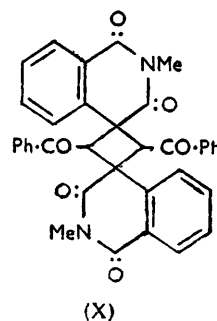
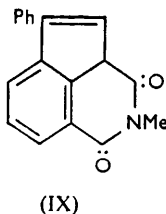
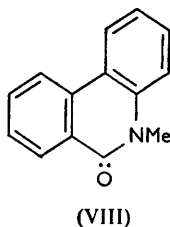
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R = H) shows bands at 1718 and 1707 cm^{-1} typical of a lactone; the latter compound absorbs at distinctly longer wavelengths in the ultraviolet region than the former (see Figure).



2-Methylhomophthalimide, — (A); 2-methyl-4-phenacylhomophthalimide (V; R = Me), — (B); 2-methyl-4-phenacylidenehomophthalimide (VII; R = Me), — · — · (C); 4-phenacylidenehomophthalimide (VII; R = H), · · · · (D); 1 : 2-dihydro-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)isoquinoline (II; R = R' = H), ---- (E); 5'-phenylpyrrolo(2' : 3'-3 : 4)isocoumarin (III; R = H), ---- (F).

During the purification of the phenacylidene derivative (VII; R = Me), it was observed that the m. p. (200°) varied with the solvent used for crystallisation, and refluxing the compound with acetic acid gave a product of m. p. 285° . It was originally thought to be a



geometrical isomer due to the presence of the exocyclic ethylenic bond.⁸ The compound did not react with 2 : 4-dinitrophenylhydrazine and could not be reduced to the phenacyl analogue (V; R = Me). Bromination was then found to give a product $\text{C}_{36}\text{H}_{25}\text{O}_6\text{N}_2\text{Br}$, indicating that the compound, m. p. 285° , is in fact a dimer of (VII; R = Me) and a molecular-weight determination in benzene confirmed this. $\alpha\beta$ -Unsaturated ketones are known⁹ to form cyclobutane derivatives, but a structure such as (X) ought to be rather

⁸ (a) Conant and Cutter, *J. Amer. Chem. Soc.*, 1922, **44**, 2651; (b) Conant and Lutz, *ibid.*, 1923, **45**, 1303; (c) Lutz and Bailey, *ibid.*, 1945, **67**, 2229.

unstable and would be expected to form a dibromo-compound and possibly a 2 : 4-dinitrophenylhydrazone. It is hoped to report later on the structure of this dimeric product.

EXPERIMENTAL

Ultraviolet absorption spectra were determined in EtOH unless otherwise stated; infrared spectra were measured on Nujol mulls.

Homophthalic acid was prepared as described by Fieser and Pechet,¹⁰ except that the sulphuric acid was diluted with half its volume of water before being added to the chromic acid-indene mixture; this markedly reduced the formation of tar and gave a much cleaner product.

*Homophthalimide.*¹¹—Homophthalic acid (10 g.) was dissolved in aqueous ammonia (15 c.c.; d 0.88), and the solution evaporated to dryness *in vacuo*; more ammonia (5 c.c.) was added and the evaporation repeated. *o*-Dichlorobenzene (20 c.c.) was then added and the mixture heated at 200° (oil-bath), the dichlorobenzene being allowed to distil away. The liquid was cooled and methanol (20 c.c.) added. Next day the solid was collected and washed with methanol, giving the imide (7.4 g.), m. p. 234—236° (decomp.), unchanged by crystallisation from aqueous pyridine. This method gave a cleaner product than direct heating⁵ of the ammonium salt. Light absorption: λ_{\max} , 2400 (ϵ 12,460) and 2800 Å (ϵ 1465); infrared bands at 3155, 3058, 1704, 1678, and 1610 cm^{-1} .

N-Methylhomophthalimide¹² formed needles (from aqueous acetic acid), m. p. 123°, and had λ_{\max} , 2450 (ϵ 12,100) and 2800 Å (ϵ 1334), and infrared bands at 1709, 1664, and 1608 cm^{-1} .

4-Acetyl-2-methylhomophthalimide.—(a) (cf. Haworth.¹) After one crystallisation from methanol the product had m. p. 85—113° (52%); two more crystallisations gave a product of m. p. 115° in very small yield. Haworth reported a 70% yield and m. p. 113°. (b) (cf. Voaden, B.Sc. Thesis, Oxford, 1953.) 2-Methylhomophthalimide (2.25 g.) was dissolved in dry pyridine (14 c.c.), and acetic anhydride (1.2 c.c.) added dropwise with shaking. After 4 hr. the solution was acidified with a mixture of acetic acid (8 c.c.) and water (12 c.c.). The solid was collected, and crystallised from methanol; it had m. p. and mixed m. p. 115° (2.10 g.), λ_{\max} , 2350 (ϵ 24,300), 2850 (ϵ 5700), and 3400 Å (ϵ 11,500).

2-Methyl-4-phenacylhomophthalimide.—Sodium (0.46 g.) was dissolved in dry methanol (10 c.c.), and a solution of 2-methylhomophthalimide (3.5 g.) in warm methanol (40 c.c.) added, followed by phenacyl bromide¹³ (4 g.). The mixture was refluxed for 0.5 hr.; a precipitate of sodium bromide rapidly separated. The mixture was then poured into water, and the flocculent precipitate collected, washed, dried, and crystallised from glacial acetic acid, giving 2-methyl-4 : 4-diphenacylhomophthalimide (1.53 g.), m. p. 247—248° (Found: C, 75.5; H, 4.9; N, 3.2. Calc. for $\text{C}_{26}\text{H}_{21}\text{O}_4\text{N}$: C, 75.9; H, 5.1; N, 3.4%). Haworth¹ reports m. p. 247—248°. Light absorption: λ_{\max} , 2500 (ϵ 37,000) and 2800 Å (ϵ 3800). The acetic acid mother-liquors were poured into water, and the white precipitate collected and dried (1.72 g.) (m. p. 134—135°). Crystallisation from ethanol gave 2-methyl-4-phenacylhomophthalimide as needles, m. p. 138° [Found: C, 73.3; H, 5.1; N, 4.6%; M (cryoscopic in camphor), 226. $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$ requires C, 73.7; H, 5.1; N, 4.8%; M , 293]. Light absorption: λ_{\max} , 2450 (ϵ 27,000) and 2800 Å (ϵ 3100). The infrared spectrum had bands at 1712, 1661, 1605, and 1592 cm^{-1} . Attempts to increase the proportion of monophenacyl derivative by varying the quantities of reagents were unsuccessful. The 2 : 4-dinitrophenylhydrazone crystallised from acetic acid as orange prisms, m. p. 180—182° (Found: C, 60.4; H, 4.2; N, 14.8. $\text{C}_{24}\text{H}_{15}\text{O}_8\text{N}_5$ requires C, 60.8; H, 4.0; N, 14.8%).

Hydrolysis of 2-Methyl-4-phenacylhomophthalimide.—A solution of the imide (0.5 g.) in *n*-potassium hydroxide (10 c.c.) was refluxed for 6 hr. in an atmosphere of nitrogen. The solution was cooled and acidified with hydrochloric acid; an oil separated which slowly solidified. The solid was collected and dissolved in *n*-potassium hydroxide, and the solution carefully acidified until a small quantity of brown solid separated; this was removed and the solution made strongly acid, yielding a pale yellow solid. Two crystallisations from 50% acetic acid gave β -benzoyl- α -*o*-carboxyphenylpropionic acid, m. p. 180—181° (decomp.), identical with a specimen prepared by Bailey and Staunton² (mixed m. p. and infrared spectrum).

⁹ Raphael in "Chemistry of Carbon Compounds," ed. Rodd, Elsevier, Amsterdam, 1953, Vol. IIA, p. 48.

¹⁰ Fieser and Pechet, *J. Amer. Chem. Soc.*, 1946, **68**, 2578; cf. *Org. Synth.*, 1949, **29**, 49.

¹¹ U.S.P. 2,351,391; *Chem. Abs.*, 1944, **38**, 5228.

¹² Gabriel, *Ber.*, 1886, **19**, 1654, 2363.

¹³ *Org. Synth.*, Coll. Vol. II, p. 480.

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2-Methyl-4-phenacylidenehomophthalimide.—2-Methylhomophthalimide (1 g.) was dissolved in boiling ethanol (10 c.c.) containing pyridine (5 drops), the solution poured on solid phenylglyoxal hydrate (2 g.),¹⁴ and the mixture refluxed on a water-bath for 10 min. The solution became green and after 2–3 min. a solid started to separate. After 2 hr. at 0° the solid was collected (1.54 g.; m. p. 185–186°). Two crystallisations from benzene gave 2-methyl-4-phenacylidenehomophthalimide as colourless, hexagonal prisms, m. p. 199–200° [Found: C, 74.1; H, 4.5; N, 4.8%; *M* (ebullioscopic in benzene), 280. $C_{18}H_{13}O_3N$ requires C, 74.2; H, 4.5; N, 4.8%; *M*, 291]. Light absorption: λ_{\max} , 2450 (ϵ 16,180), 3150 (ϵ 3568), and 3300 Å (ϵ 2755). The infrared spectrum contained bands at 1701, 1656, 1603, 1592, and 1577 cm^{-1} . Warming the compound gently with 2*N*-alkali gave a deep green solution; the compound gave a deep orange solution in concentrated sulphuric acid. The 2 : 4-dinitrophenylhydrazine (prepared in propanol) crystallised from acetic acid as orange needles, m. p. 262–264° (decomp.) (Found: C, 60.9; H, 3.7; N, 14.3. $C_{24}H_{17}O_6N_5$ requires C, 61.2; H, 3.6; N, 14.9%).

A sample of 2-methyl-4-phenacylidenehomophthalimide which had been crystallised 3 times from butan-1-ol had m. p. ca. 270°. A solution of 2-methyl-4-phenacylidenehomophthalimide (5 g.) in glacial acetic acid (25 c.c.) was refluxed for 4 hr.; next day the solid (4.0–4.4 g.) was collected (m. p. 280–285°). Two crystallisations from benzene–light petroleum (b. p. 60–80°) gave the dimer as colourless prisms, m. p. 284–285° (decomp., m. p. very sensitive to rate of heating) [Found: C, 74.5, 74.5; H, 4.6, 4.7; N, 4.8, 5.0%; *M* (ebullioscopic in benzene), 609, 555. $C_{36}H_{26}O_6N_2$ requires C, 74.2; H, 4.5; N, 4.8%; *M*, 582]. Light absorption: λ_{\max} , 2500 (ϵ 30,620) and 3250 Å (ϵ 5390). The infrared spectrum contained bands at 1715, 1667, and 1600 cm^{-1} .

The dimer (1.0 g.) was dissolved in chloroform (15 c.c.) and bromine (0.18 c.c.) in chloroform (5 c.c.) added. After 7 days at room temperature the solution was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. The residual oil was crystallised from benzene–light petroleum (b. p. 60–80°) [yield 0.9 g.; m. p. 226–228° (decomp.)]. Recrystallisation from benzene–light petroleum and then from toluene gave a bromo-derivative as white needles, darkening at 210°, m. p. 227–229° (decomp.), unchanged by further crystallisation from acetic acid (Found: C, 65.2, 65.2; H, 3.9, 3.75; N, 4.2, 4.0; Br, 12.3, 13.0. $C_{36}H_{26}O_6N_2Br$ requires C, 65.4; H, 3.8; N, 4.2; Br, 12.1%).

The compound, m. p. 285° (1.0 g.), was suspended in water (5 c.c.), 2*N*-potassium hydroxide (1.75 c.c.) added, and the mixture heated to the b. p. An orange solid separated. Alcohol was added dropwise until the solid dissolved and the solution was then cooled. An amorphous, orange precipitate separated which was collected on a centrifuge; it contained potassium (flame test), did not appear to melt, and did not crystallise. Treatment of this solid with acetic acid yielded the starting material (m. p. and mixed m. p. 285°).

Reduction of 2-Methyl-4-phenacylidenehomophthalimide.^{8a, b}—2-Methyl-4-phenacylidenehomophthalimide (1.0 g.) was dissolved in boiling dioxan (10 c.c.), and a solution of sodium dithionite (1 g.) in water (5 c.c.) added. The mixture was heated on a water-bath for 2.5 min., cooled, and diluted with water. A gum separated which rapidly solidified. It was collected, washed with water, and dried (m. p. 135–137°). Crystallisation from ethanol gave 2-methyl-4-phenacylhomophthalimide (0.72 g.), m. p. and mixed m. p. 136° (the infrared spectra of the two specimens were identical). Reduction was also effected by zinc and acetic acid,¹⁵ stannous chloride,¹⁶ and catalytically in benzene with palladium black.

Reduction of the dimer, m. p. 285°, could not be accomplished by any of the above routes.

1 : 2-Dihydro-2-methyl-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)isoquinoline.—A mixture of syrupy phosphoric acid (2 c.c.) and phosphoric oxide (1.0 g.) was heated at 100° for 1 hr., 2-methyl-4-phenacylhomophthalimide (0.5 g.) added, and the mixture kept at 120° for 1 hr., then cooled, and poured on ice. The solid which separated was collected, washed with water, and dried (0.48 g.; m. p. 190–195°). Crystallisation from ethanol gave the furan as pale cream needles, m. p. 199° (Found: C, 78.2; H, 4.8; N, 5.0. $C_{18}H_{13}O_2N$ requires C, 78.6; H, 4.7; N, 5.1%). Light absorption: λ_{\max} , 3100 (ϵ 19,100), 3550 (ϵ 12,000), and 3650 Å (ϵ 10,900). The infrared spectrum contained bands at 1639, 1626, 1603, 1582, 1567, and 1527 cm^{-1} . The compound is insoluble in hot, dilute hydrochloric acid and 2*N*-sodium hydroxide and does not react with 2 : 4-dinitrophenylhydrazine. Dilute alcoholic solutions of the furan have a strong blue fluorescence; the solution in concentrated sulphuric acid is green. The product was recovered

¹⁴ *Org. Synth.*, Coll. Vol. II, p. 509.

¹⁵ Lutz and Taylor, *J. Amer. Chem. Soc.*, 1933, **55**, 1177; Bailey, Waggoner, Nowlin, and Rushton, *ibid.*, 1954, **76**, 2249.

¹⁶ Lutz and McGinn, *ibid.*, 1942, **64**, 2585.

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unchanged after refluxing with 5% alcoholic potassium hydroxide (6 hr.) and formed a crystalline adduct, m. p. ca. 150° (decomp.), with 1 : 3 : 5-trinitrobenzene. Attempts to crystallise the complex resulted in its decomposition (Found, in crude material : C, 61.8; H, 3.4; N, 10.6. Calc. for $C_{24}H_{16}O_8N_4$: C, 59.0; H, 3.3; N, 11.5%).

2-Methyl-4-phenacylhomophthalimide (0.5 g.) was dissolved in concentrated sulphuric acid (6 c.c.), kept at room temperature for 30 min., and then poured on ice. The solid was collected and crystallised from ethanol-ethyl acetate. The *sulphonic acid* formed pale yellow prisms, m. p. 293—295° (decomp.) (Found : C, 58.3; H, 4.0; N, 3.8; S, 8.6. $C_{18}H_{13}O_6NS.H_2O$ requires C, 58.0; H, 4.0; N, 3.8; S, 8.6. Found, after drying at 130° for 5 hr. : C, 59.0; H, 3.8; N, 3.6. $C_{18}H_{13}O_6NS.\frac{1}{2}H_2O$ requires C, 59.4; H, 3.8; N, 3.8%). Light absorption : λ_{max} 3300 (ϵ 23,050) and 3600 Å (ϵ 22,530). The infrared spectrum contained bands at 1637 and 1600 cm^{-1} . 1 : 2-Dihydro-2-methyl-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)-isoquinoline (0.1 g.) was dissolved in concentrated sulphuric acid (2 c.c.). After 30 min. at room temperature the blue-green solution was poured on ice. The oil which separated rapidly solidified. Crystallisation gave the sulphonic acid, m. p. and mixed m. p. 293° (decomp.). Dilute alcoholic solutions of the sulphonic acid showed an intense blue fluorescence.

4-Phenacylidenehomophthalimide.—Homophthalimide (5 g.) was dissolved in warm pyridine (75 c.c.), the solution cooled to room temperature, and phenylglyoxal hydrate (10 g.) in pyridine (25 c.c.) added. After 1 hr. the green solution was poured into water, and the solid collected, washed well with water and dried at 100°. The *product* was dissolved in boiling dioxan, and an equal volume of ethanol added to the filtered solution, giving a pale pink solid (6.1 g.), softening at 205—210°, m. p. 220—225°. Two further crystallisations from dioxan-ethanol gave colourless needles, softening at 210°, m. p. 220—225°, resolidifying and melting at 294—296° (decomp.) (m. p. 227—230° from a bath at 200°) (Found : C, 72.0; H, 4.5; N, 4.3. $C_{17}H_{11}O_3N.\frac{1}{2}H_2O$ requires C, 71.4; H, 4.2; N, 4.9. Found, after drying at 110° for 24 hr. : C, 73.8; H, 4.3; N, 5.0. $C_{17}H_{11}O_3N$ requires C, 73.6; H, 4.0; N, 5.0%). Light absorption : λ_{max} 2450 (ϵ 18,500), λ_{inf} 3050 Å (ϵ 4677). The infrared spectrum contained bands at 3165, 3058, 1709 (shoulder), 1689, 1658, 1616, 1600, and 1580 cm^{-1} . The compound dissolved in 2N-sodium hydroxide to form a deep green solution. The 2 : 4-dinitrophenylhydrazones formed orange prisms, m. p. 244—246° (from 2-methoxyethanol) (Found : C, 60.3; H, 3.4; N, 15.1. $C_{23}H_{15}O_6N_5$ requires C, 60.4; H, 3.3; N, 15.3%).

4-Phenacylhomophthalimide.—A solution of 4-phenacylidenehomophthalimide (1.5 g.) in 2-methoxyethanol (75 c.c.) was hydrogenated in the presence of palladium black (0.2 g.) at room temperature (uptake 120 c.c. in 30 min.). Solid then started to separate from the solution. When absorption ceased the mixture was boiled and filtered, half the solvent was removed *in vacuo* on a water-bath, and water (35 c.c.) added to the residue. The resulting solid *product* formed colourless prisms, sintering at 230°, m. p. 248—250° (Found : C, 72.6; H, 4.6; N, 4.9. $C_{17}H_{13}O_3N$ requires C, 73.1; H, 4.7; N, 5.0%). Light absorption : λ_{max} 2800 Å (ϵ 3960) in $CHCl_3$. The infrared spectrum had bands at 3165, 3058, 1715, 1684, 1605, and 1595 cm^{-1} .

1 : 2-Dihydro-1-oxo-5'-phenylfurano(2' : 3'-3 : 4)isoquinoline.—4-Phenacylhomophthalimide was cyclised with polyphosphoric acid (110—120°; 1 hr.) as described for the 2-methyl derivative, giving the *uran* (74%), crystallising from acetic acid as very pale cream plates, m. p. 280—282° (decomp.) (Found : C, 77.7; H, 4.2; N, 5.5. $C_{17}H_{11}O_3N$ requires C, 78.2; H, 4.2; N, 5.4%). Light absorption : λ_{max} 3050 (ϵ 11,900), 3150 (ϵ 11,800), and 3550 Å (ϵ 8370). The infrared spectrum contained bands at 2941—2632 (broad band), 1634, 1603, 1550, and 1481 cm^{-1} . The m. p. was lowered 20° by admixture with the compound (III; R = H). A dilute alcoholic solution had an intense blue fluorescence; the solution in concentrated sulphuric acid was emerald-green. The substance was soluble in warm, dilute sodium hydroxide solution and did not react with 2 : 4-dinitrophenylhydrazine.

A solution of 4-phenacylhomophthalimide (0.2 g.) in concentrated sulphuric acid (5 c.c.) was kept at room temperature for 30 min. and then poured on ice. The *sulphonic acid* formed pale cream prisms (from ethanol-ethyl acetate), m. p. 318—320° (decomp.) (Found : C, 56.9, 57.0; H, 3.3, 3.9; N, 3.7. $C_{17}H_{11}O_6NS.H_2O$ requires C, 56.9; H, 3.6; N, 3.9%). The acid showed an intense blue fluorescence in dilute alcoholic solution.

5'-Phenylpyrrolo(2' : 3'-3 : 4)isocoumarin,^a m. p. 278—280°, had λ_{max} 2270 (ϵ 45,100), 3150 (ϵ 21,750), and 3900 Å (ϵ 7492), and infrared bands at 3215, 1718, 1701, 1626, 1600, 1360, 1543, and 1529 cm^{-1} .

One of us (D. L. S.) thanks the Derbyshire Education Committee for financial assistance.

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[Received, February 9th, 1956.]