Oxygen Heterocycles. Part XII.¹ Synthesis of New 1138. Polycyclic Furans by Means of 2,3-Dichloro-1,4-naphthaquinone

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The synthesis of a number of quinonoid polycyclic furans, by condensation of 2,3-dichloro-1,4-naphthaquinone with phenols, is described.

2,3-DICHLORO-1,4-NAPHTHAQUINONE is an intermediate of considerable value for the building up of condensed heterocycles derived from furan. It condenses with phenols having a reactive ortho position to give quinones of benzo[b]naphtho[2,3-d]furan, and with naphthols to give quinones of dinaphthofurans,² and more complex furan derivatives have been prepared for use as vat dyes.³ Recently this reaction was successfully extended to 5-, 6-, and 7-hydroxyquinoline.⁴ Hence it was interesting to investigate further the potentialities of 2,3-dichloro-1,4-naphthaquinone for building hitherto unknown polycyclic furan systems. Another interesting facet of the reaction is that it provides an evaluation of the reactivity of the position *ortho* to the hydroxyl group.

Although 4-hydroxyquinaldine is generally considered to exist predominantly in the ketoform,⁵ it nevertheless reacted with 2,3-dichloro-1,4-naphthaquinone to give 7,12-dihydro-6-methyl-7,12-dioxonaphtho[2',3':4,5]furo[3,2-c]quinoline (I), although in low yield; as expected, the increased reactivity of the ortho position as encountered in 4-hydroxy-1-



methylcarbostyril led in the same conditions to compound (II) in better yield. 8-Hydroxyquinaldine and 5-hydroxyisoquinoline reacted normally to give the quinones (III) and (IV), respectively. An interesting difference was noted in the halochromisms given in sulphuric acid: whereas with compounds (I) and (III) the coloration was respectively beetroot-red and violet, it was orange with (IV) and even lighter with (II); these variations

¹ Part XI, preceding Paper.

² Cf. B. Eistert, Chem. Ber., 1947, 80, 47; N. P. Buu-Hoï, J., 1952, 489; N. P. Buu-Hoï and P. Demerseman, J., 1952, 4699; N. P. Buu-Hoï and D. Lavit, J., 1955, 2776; 1956, 1743.
³ B. D. Tilak, in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields," Academic Press, New York and London, 1962, p. 537.

⁴ M. F. Sartori, *Gazzetta*, 1963, 93, 123.
⁵ See literature in G. M. Badger, "The Structures and Reactions of the Aromatic Compounds," Cambridge University Press, 1954, p. 66.

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are clearly due either to the different position occupied by the nitrogen atom in the molecule, and/or to the hypsochromic effect [compound (II)] of the amide carbonyl group.

Among the hydroxy-derivatives of α -pyrones, 4-hydroxycoumarin afforded 7,12dihydro-6,7,12-trioxo-6*H*-naphtho[2',3':4,5]furo[3,2-*c*]chromen (V), and isochroman-1,4dione (VI) reacted in its tautomeric 4-hydroxyisocoumarin form to give the isomer (VII).

Lastly, it is noteworthy that condensation of 2,3-dichloro-1,4-naphthaquinone with 2,4,5-trihydroxybutyrophenone (VIII) furnished a *single* product (instead of the expected two), to which we assigned structure (IX), in view of the deactivation, through hydrogenbonding,⁶ of the phenolic group situated *ortho* to the butyryl radical.

EXPERIMENTAL

7,12-Dihydro-6-methyl-7,12-dioxonaphtho[2',3':4,5]furo[3,2-c]quinoline—(I). A mixture of 4-hydroxyquinaldine (1.6 g.) and 2,3-dichloro-1,4-naphthaquinone (2.4 g.) in anhydrous pyridine (25 c.c.) was heated under reflux for 5 hr.; the precipitate which formed on cooling was filtered, washed with ethanol, dried, and recrystallised from nitrobenzene, to give microscopic, orange-yellow needles (2 g.), m. p. 314° (decomp. >265° on slow heating), whose solutions in sulphuric acid were beetroot-red (Found: C, 76.2; H, 3.7; N, 4.8. $C_{20}H_{11}NO_3$ requires C, 76.7; H, 3.5; N, 4.5%).

5,6,7,12-*Tetrahydro*-5-*methyl*-6,7,12-*trioxonaphtho*[2',3':4,5]*furo*[3,2-c]*quinoline* (II).—Prepared by refluxing for 2 hr. a solution of 4-hydroxy-1-methylcarbostyril (2 g.) and 2,3-dichloro-1,4-naphthaquinone (2.6 g.) in pyridine (20 c.c.), this *trione* crystallised as orange leaflets (3.2 g.), m. p. 315° (decomp. > 210°), from chlorobenzene, giving a deep yellow halochromism in sulphuric acid (Found: C, 72.5; H, 3.7; N, 4.2. $C_{20}H_{11}NO_4$ requires C, 73.0; H, 3.4; N, 4.3%).

7,12-Dihydro-2-methyl-7,12-dioxonaphtho[2',3':4,5]furo[3,2-h]quinoline (III). Prepared as for quinone (I), using 8-hydroxyquinaldine, this compound crystallised as red needles (2 g.), m. p. 315°, from o-dichlorobenzene, giving a violet halochromism in sulphuric acid (Found: C, 76.4; H, 3.5%).

7,12-Dihydro-7,12-dioxonaphtho[2',3':4,5]furo[2,3-f]isoquinoline (IV).—Prepared from 5-hydroxyisoquinoline (1.5 g.) and 2,3-dichloro-1,4-naphthaquinone (2.4 g.) in pyridine (25 c.c.), this quinone formed golden-yellow needles (2.2 g.), m. p. 277°, from nitrobenzene, giving an orange halochromism in sulphuric acid (Found: C, 76.2; H, 3.0; N, 4.7. $C_{19}H_9NO_3$ requires C, 76.3; H, 3.0; N, 4.7%).

7,12-Dihydro-6,7,12-trioxo-6H-naphtho[2',3':4,5]furo[3,2-c]chromen (V).—A suspension of 2,3-dichloro-1,4-naphthaquinone (0.5 g.) and 4-hydroxycoumarin (0.5 g.) in pyridine (5 c.c.) was refluxed for 3 hr., and the precipitate obtained was washed with methanol and recrystallised from ethanol, to give yellow prisms (0.5 g.), m. p. 269°, whose solutions in sulphuric acid were brown-violet (Found: C, 72.3; H, 2.6. $C_{19}H_8O_5$ requires C, 72.1; H, 2.5%).

7,12-Dihydro-5,7,12-trioxo-5H-naphtho[2',3':4,5]furo[3,2-c]isochromen (VII).—A solution of isochroman-1,4-dione ⁷ (1 g.) and the dichloronaphthaquinone (1 g.) in pyridine (10 c.c.) was refluxed for 24 hr., the solvent was distilled off *in vacuo*, and the residue washed with water; the remaining solid was crystallised from ethanol, giving reddish prisms (0.8 g.), m. p. 230°, whose solutions in sulphuric acid were violet (Found: C, 72.1; H, 2.8%).

2-Butyryl-6,11-dihydro-1,4-dihydroxy-6,11-dioxobenzo[b]naphtho[2,3-d]furan (IX).—A mixture of 2,4,5-trihydroxybutyrophenone (1.6 g.; commercial product used as an antioxidant) and the dichloronaphthaquinone (2.2 g.) in pyridine (25 c.c.) was refluxed for 4 hr.; after cooling, water (25 c.c.) was added, and the precipitate obtained was washed with water and recrystallised from ethanol-benzene, to give brick-red microprisms (2 g.), m. p. 225°, whose solutions in sulphuric acid were orange (Found: C, 68.5; H, 4.1. $C_{20}H_{14}O_6$ requires C, 68.6; H, 4.0%).

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⁶ Cf. W. Baker, J., 1934, 1684.

⁷ E. B. Knott, *J.*, 1963, 402; N. P. Buu-Hoï, P. Jacquignon, and M. Mangane, *Rec. Trav. chim.*, 1965, **84**, 334.