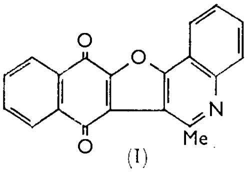
1138. *Oxygen Heterocycles. Part XII.*[1] *Synthesis of New Polycyclic Furans by Means of* 2,3-*Dichloro*-1,4-*naphthaquinone*

By N. P. BUU-HOÏ, J. P. HOEFFINGER, and P. JACQUIGNON

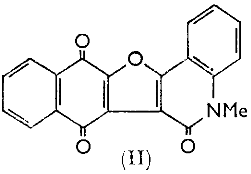
The synthesis of a number of quinonoid polycyclic furans, by condensation of 2,3-dichloro-1,4-naphthaquinone with phenols, is described.

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 keto-form,[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



(I)



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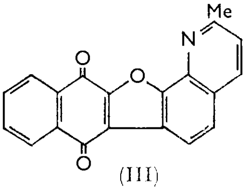

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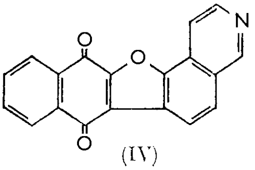

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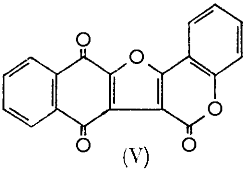
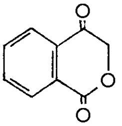
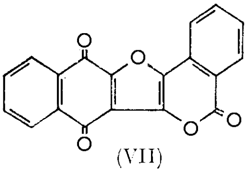


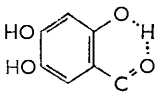
(V)



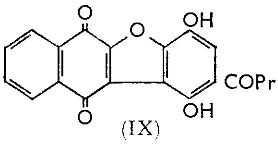
(VI)



(VII)



(VIII)



(IX)

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[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.

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 7,12-dihydro-6,7,12-trioxo-6*H*-naphtho[2′,3′:4,5]furo[3,2-*c*]chromen (V), and isochroman-1,4-dione (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 hydrogen-bonding,[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.