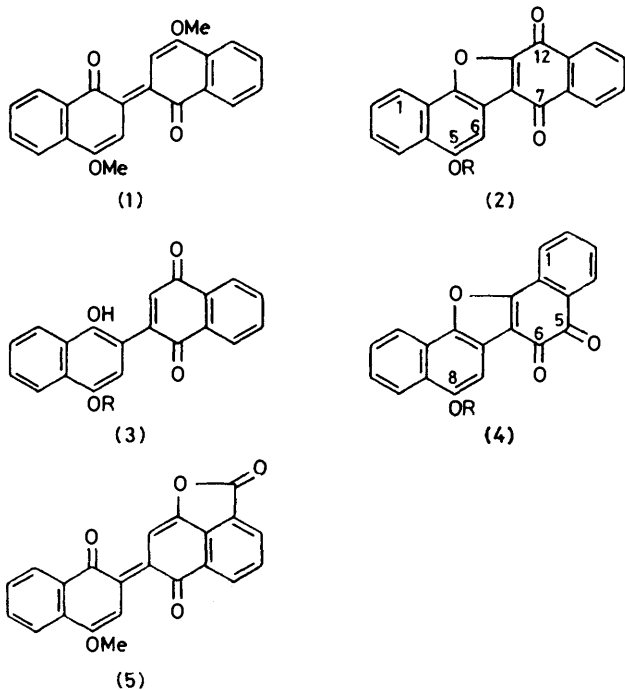


Photoproducts from 4,4'-Dimethoxy-2,2'-binaphthyl-1,1'-quinone

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Exposure of its solutions to visible light causes the title quinone (1) to undergo cyclisations and to react with water, ethanol, and carbon tetrachloride. The products include the furo-1,4-quinones (2; R = Me and Et) and the related 1,2-quinone (4; R = Me), the hydroxy-quinones (3; R = Me and Et), the lactone (5), and the quinone dichloromethide (7).

SOLUTIONS of the naturally occurring blue quinones, diosindigos A and B,^{1,2} which are derivatives of 4,4'-dimethoxy-2,2'-binaphthyl-1,1'-quinone (1), rapidly become orange-yellow on exposure to sunlight. As little is known^{3,4} about the photochemistry of compounds of this type we have examined the products obtained by the action of light on the parent quinone (1).



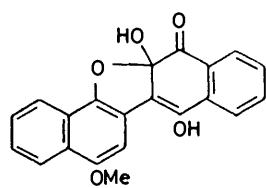
Illumination of a solution of the quinone in carbon tetrachloride-methanol using a tungsten lamp produced a red quinone, $C_{21}H_{12}O_4$, and a blue quinone, $C_{21}H_{14}O_4$, each of which contained one methoxy group. The former and its leucoacetate show u.v. absorptions which resemble those⁵ of the hydroxy-quinone (2; R = H) and the corresponding leucotriacetate, respectively, and accordingly the red quinone is the dinaphthofuran derivative (2; R = Me). The blue quinone forms a monoacetate and shows n.m.r. signals resembling those of 4-methoxy-1-naphthol and 1,4-naphthoquinone,⁶ and we formulate it as the hydroxy-quinone (3; R = Me). More prolonged illumination of the quinone (1) in carbon tetrachloride-methanol again gave the dinaphthofuran-quinone (2; R = Me) as the major product, together

with small amounts of an isomeric purple quinone and a blue quinone, $C_{22}H_{12}O_5$, each of which contained one methoxy group. The i.r. absorption of the purple compound in the carbonyl region is typical⁷ of a 1,2-naphthoquinone, and its u.v. absorption resembles closely that of the hydroxy-quinone (4; R = H)⁸ and we consider it to be the corresponding methyl ether (4; R = Me). The mass spectrum of the compound is consistent with this structure, the dominant initial fragmentation of the molecular ion involving loss of carbon monoxide as happens with other 1,2-quinones.^{9,10} The compound does not afford an $[M + 2]^+$ ion of significant intensity presumably because of the effect of the fused furan ring on the quinone system.⁹ The light absorption of the blue quinone indicates that it is the lactone (5). The u.v. absorption shows a marked resemblance to that of the parent quinone (1), and the i.r. bands at 1757, and at 1664 and 1590 cm^{-1} are characteristic of the carbonyl groups of an $\alpha\beta$ -unsaturated γ -lactone and an unsymmetrical quinone, respectively.

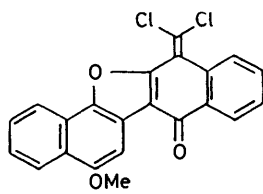
The following reaction sequences account for the formation of the above-mentioned products. Absorption of visible light by the quinone (1) leads to $n \rightarrow \pi^*$ excitation with the production of an excited molecule which is hydrolysed by the water present in the solvent with the loss of a methyl group and the formation of the hydroxy-quinone (3; R = Me). The latter undergoes photocyclisation and aerial oxidation to give the furo-quinone (2; R = Me) and water. Prolonged illumination results in the addition of water to the furo-quinone (2; R = Me) and the product (6) then isomerises and undergoes dehydration forming the 1,2-quinone (4; R = Me). Although acids can effect the conversion of related 1,4-quinones into 1,2-quinones,¹¹ such isomerisations have not been encountered previously during photochemical reactions. Finally, abstraction of a hydrogen atom or a hydride ion from a methoxy group of the quinone (1) by the excited molecule and reaction of the resulting species with the adjacent aromatic ring gives a cyclic ether which undergoes autoxidation to form the γ -lactone (5).

The prolonged exposure of a chloroform solution of the quinone (1) to sunlight led to the formation of the ethoxy-quinones (2; R = Et) and (3; R = Et). Presumably the starting quinone first reacts with the ethanol, present as stabiliser in the chloroform, before the normal photoreactions occur. Finally, while the furo-

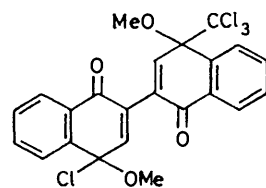
quinone (2; R = Me) was the main product from the illumination of the quinone (1) in carbon tetrachloride alone, the reaction also afforded a yellow, chlorine-containing product, $C_{22}H_{12}Cl_2O_3$. Because its u.v. and n.m.r. spectra resemble those of the furo-quinone (2; R = Me), we formulate this as the quinone dichloromethide (7). We think that it results from the reaction of carbon tetrachloride with the excited quinone which gives an adduct¹² such as (8). Partial reduction of the trichloromethyl group of the latter by the quinol corresponding to the furo-quinone (2; R = Me) and expulsion of the adjoining methoxy group as methanol leads to the formation of the quinone dichloromethide system. Subsequent cyclisation, with attendant loss of hydrogen chloride gives the dichloro-furanone (7).



(6)



(7)



(8)

EXPERIMENTAL

General instructions are given elsewhere.¹ The photochemical experiments were conducted in AnalaR grade solvents at 30–40 °C; no attempt was made to exclude air from the solutions. No reactions occurred when solutions of the quinone (1) were kept in the dark. The products were crystallised from light petroleum (b.p. 80–100 °C).

4,4'-Dimethoxy-2,2'-binaphthyl-1,1'-quinone (1).—This¹³ had m.p. 256–258° (lit.,¹³ 258°), ν_{\max} 1 606 and 1 586 cm^{-1} (quinone C=O), λ_{\max} (CHCl₃) 282 (log ϵ 4.41), 319 (4.15), and 638 nm (4.28), λ_{infl} 608 nm (log ϵ 4.23), δ 4.08 (6 H, s, CH₃OR), 7.20–8.25 (8 H, m, ArH), and 8.40 [2 H, s, -CH=C(OR)-], *m/e* 346 [30%, (M + 2 H)⁺], 344 [70%, (M)⁺], 329 [50%, (M - Me)⁺], and 313 [100%, (M - MeO)⁺].

Photolysis of 4,4'-Dimethoxy-2,2'-binaphthyl-1,1'-quinone in Carbon Tetrachloride-Methanol.—(a) A solution of the quinone (150 mg) in carbon tetrachloride (150 ml) and methanol (100 ml) was illuminated using a 150 W tungsten lamp for 4 h and then evaporated. The residue was separated by t.l.c. on silica gel (dichloromethane) into (i) 5-methoxydinaphtho[1,2-b:2',3'-d]furan-7,12-quinone (2; R = Me), red needles (104 mg), m.p. 293–295° (lit.,¹⁴ 290–291°) (Found: C, 76.5; H, 3.8%; M, 328.072 6). Calc. for C₂₁H₁₂O₄: C, 76.8; H, 3.7%; M, 328.073 6), ν_{\max} 1 669 cm^{-1} (quinone C=O), λ_{\max} (CHCl₃) 267 (log ϵ 4.85) and 475 nm (3.86), λ_{infl} 291 (log ϵ 4.10), 313 (3.91), 325 (3.72), and 342 nm (3.42), δ (CDCl₃) 4.11 (3 H, s, CH₃OAr), 7.46 (1 H, s, H-6), 7.5–7.9 (4 H, m, H-2, H-3, H-9, and

H-10), and 8.1–8.5 (4 H, m, H-1, H-4, H-8, and H-11), *m/e* 328 [100%, (M)⁺], 313 [66%, (M - Me)⁺], and 285 (33%, 313 - CO), the leucoacetate of which formed needles, m.p. 266–267° (lit.,¹⁴ 271–272°) (Found: M, 414.110 3). C₂₅H₁₈O₆ requires M, 414.110 3), ν_{\max} 1 761 cm^{-1} (aryl acetate C=O), λ_{\max} 269 (log ϵ 5.07), 326 (4.01), 339 (4.07), 358 (4.09), and 375 nm (4.23), λ_{infl} 262 (log ϵ 4.82), 285 (4.21), and 298 nm (3.83), δ (CDCl₃-CF₃CO₂D) 2.74 and 2.76 (each 3 H, s, CH₃CO₂Ar), 4.14 (3 H, s, CH₃OAr), 7.20 (1 H, s, H-6), and 7.5–8.5 (8 H, m, ArH), and (ii) 1'-hydroxy-4'-methoxy-2,2'-binaphthyl-1,4-quinone (3; R = Me), blue needles (28 mg), m.p. 196–198° (lit.,¹⁴ 185–186°) (Found: M, 330.088 0). Calc. for C₂₁H₁₄O₄: M, 330.089 2), ν_{\max} 3 340 (HO) and 1 660 cm^{-1} (quinone C=O), λ_{\max} 247 (log ϵ 4.48), 316 (4.11), and 510 nm (3.07), λ_{infl} 348 nm (log ϵ 3.64), δ (CDCl₃-(CD₃)₂SO) 3.94 (3 H, s, CH₃OAr), 6.66 (1 H, s, H-3), 7.09 (1 H, s, H-3'), 7.4–8.3 (8 H, m, ArH), *m/e* 330 [100%, (M)⁺], 315 (48%, (M - Me)⁺], and 299 [34%, (M - MeO)⁺], which gave the corresponding acetate as red crystals, m.p. 184–186.5° (Found: M, 372.100 4). C₂₃-H₁₆O₅ requires M, 372.099 8), ν_{\max} 1 748 (ester C=O) and 1 657 cm^{-1} (quinone C=O), λ_{\max} 243 (log ϵ 4.46), 299 (4.08), and 436 nm (2.99), λ_{infl} 336 nm (log ϵ 3.63).

4-Methoxy-1-naphthol¹⁵ had δ (CDCl₃) 3.93 (3 H, s, CH₃OAr), *ca.* 4.9 (1 H, br, ArOH), 6.66 (2 H, s, H-2 and H-3), 7.35–7.65 (2 H, m, H-6 and H-7), and 8.0–8.35 (2 H, m, H-4 and H-8).

(b) A similar reaction in which illumination was continued for 24 h gave (i) 5-methoxydinaphtho[1,2-b:2',3'-d]furan-7,12-quinone (61 mg), (ii) 8-methoxydinaphtho[1,2-b:2',1'-d]furan-5,6-quinone (4; R = Me), purple needles (8 mg), m.p. 291–293° (Found: M, 328.074 8). C₂₁H₁₂O₄ requires M, 328.073 6), ν_{\max} 1 699w and 1 671 cm^{-1} (ortho-quinone C=O), λ_{\max} 279 (log ϵ 4.55), 327 (3.82), 345 (3.74), and 530 nm (3.34), λ_{infl} 259 (log ϵ 4.41), 273 (4.54), 299 (4.00), 307 (3.95), 311 (3.93), and 580 nm (3.27), *m/e* 328 [100%, (M)⁺], 300 [28%, (M - CO)⁺], and 285 (44%, 300 - Me), and (iii) the lactone of 5-carboxy-4-hydroxy-4'-methoxy-2,2'-binaphthyl-1,1'-quinone (5), deep blue needles (4 mg), m.p. 318–320° (Found: M, 356.068 3). C₂₂H₁₂O₅ requires M, 356.068 5), ν_{\max} 1 757 (γ -lactone C=O), 1 664 and 1 590 cm^{-1} (quinone C=O), λ_{\max} (CHCl₃) 268 (log ϵ 4.47), 301 (4.18), and 560 nm (3.76), λ_{infl} 264 (log ϵ 4.45), 326 (4.03), and 380 nm (3.65), δ (CCl₄-CF₃CO₂D) 4.19 (3 H, s, CH₃OR), 7.68–8.60 [9 H, m, ArH and -CH=C(OR)-], *m/e* 356 [100%, (M)⁺], 313 [14%, (M - Me - CO)⁺], and 285 (43%, 313 - CO).

Photolysis in Chloroform.—A solution of 4,4'-dimethoxy-2,2'-binaphthyl-1,1'-quinone (50 mg) in chloroform (20 ml) in a Pyrex vessel was exposed to sunlight for 6 weeks and then evaporated. Separation of the residue by t.l.c. (dichloromethane) gave (i) 5-ethoxydinaphtho[1,2-b:2',3'-d]furan-7,12-quinone (2; R = Et) as red needles (12 mg), m.p. 280–281° (Found: M, 342.089 4). C₂₂H₁₄O₄ requires M, 342.089 2), ν_{\max} 1 668 cm^{-1} (quinone C=O), λ_{\max} 268 (log ϵ 4.71) and 475 nm (3.81), λ_{infl} 262 (log ϵ 4.69), 292 (4.11), 326 (3.73), and 342 nm (3.52), δ (CDCl₃-CF₃CO₂D) 1.56 (3 H, t, J 7 Hz, CH₃CH₂OAr), 4.23 (2 H, q, J 7 Hz, CH₃CH₂OAr), 7.20 (1 H, s, H-6), 7.50–7.85 (4 H, m, H-2, H-3, H-9, H-10), and 8.06–8.30 (4 H, m, H-1, H-4, H-8, H-11), *m/e* 342 [71%, (M)⁺], 314 [100%, (M - C₂H₅)⁺], 313 [42%, (M - C₂H₅)⁺], and 285 (22%, 313 - CO), and (ii) 4'-ethoxy-1'-hydroxy-2,2'-binaphthyl-1,4-quinone (3; R = Et) as blue needles (9 mg), m.p. 178–180° (Found: M, 344.105 5). C₂₂H₁₆O₄ requires M, 344.104 9),

ν_{\max} . 3 340 (OH) and 1 663 cm^{-1} (quinone C=O), λ_{\max} . 249 (log ϵ 4.72), 321 (4.21), and 536 nm (3.19), δ [CDCl_3 - $(\text{CD}_3)_2\text{SO}$], 1.50 (3 H, t, J 7 Hz, $\text{CH}_3\text{CH}_2\text{OAr}$), 4.15 (2 H, q, J 7 Hz, $\text{CH}_2\text{CH}_2\text{OAr}$), 6.64 (1 H, s, H-3), 7.07 (1 H, s, H-3'), 7.40—7.90 (4 H, m, H-6', H-7', H-6, and H-7), 8.00—8.40 (4 H, m, H-5', H-8', H-5, and H-8), and 8.94 (1 H, s, HOAr), m/e 344 [98%, (M)⁺] and 315 [100%, ($M - \text{C}_2\text{H}_5$)⁺].

Photolysis in Carbon Tetrachloride.—A solution of 4,4'-dimethoxy-2,2'-binaphthyl-1,1'-quinone (150 mg) in carbon tetrachloride (250 ml) was illuminated for 24 h using a 150 W tungsten lamp and then evaporated. Separation of the residue by t.l.c. (dichloromethane) gave (i) 5-methoxydinaphtho[1,2-*b*:2',3'-*d'*]furan-7,12-quinone (108 mg) and (ii) 12-dichloromethylene-5-methoxydinaphtho[1,2-*b*:2',3'-*d'*]furan-7(12H)-one (7) as yellow needles (24 mg), m.p. 252—254° (Found: M , 394.017 4. $\text{C}_{22}\text{H}_{12}^{35}\text{Cl}_2\text{O}_3$ requires M , 394.016 3), ν_{\max} . 1 658 cm^{-1} (quinone methide C=O), λ_{\max} . 257 (log ϵ 4.67) and 433 nm (3.64), λ_{infl} . 276 (log ϵ 4.42), 300 (4.22), and 332 nm (4.08), δ (CDCl_3 - $\text{CF}_3\text{CO}_2\text{D}$) 4.12 (3 H, s, CH_3OAr), 7.26 (1 H, s, H-6), 7.45—7.85 (4 H, m, H-2, H-3, H-9, and H-10), and 8.10—8.74 (4 H, m, H-1, H-4, H-8, and H-11), m/e 394 [100%, (M)⁺] and 379 [35%, ($M - \text{Me}$)⁺].

We thank the S.R.C. for a Research Studentship.

[8/1163 Received, 23rd June, 1978]

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