

Photoinduced Molecular Transformations. Part 146.¹ Photoacylation and Photoalkylation of 2-Arylamino- and 2-Alkylamino-1,4-naphthoquinones

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The photoacylation of 2-arylamino- or 2-alkylamino-1,4-naphthoquinones with aromatic or aliphatic aldehydes can be achieved in high yields when a solution of *N*-substituted 2-amino-1,4-naphthoquinones and an aldehyde in benzene is irradiated in the presence of benzophenone. Irradiation of 2-anilino-1,4-naphthoquinones and cyclic ethers, such as tetrahydrofuran or dioxane, in the presence of benzophenone led to analogous photoalkylation products, 3-alkyl-2-anilino-1,4-naphthoquinones, in high yield. 1,4-Dihydroxy-2-diphenylamino-3-propionynaphthalene, characterized as the diacetate, could be isolated from the photoacylation of 2-diphenylamino-1,4-naphthoquinones with propanal. The photoacylation thus involves hydroquinone derivatives as intermediates. Radical processes involving the formation of acyl or alkyl radicals from aldehydes or cyclic ethers by hydrogen abstraction with excited benzophenone for these photoacylations and photoalkylations are proposed.

The direct irradiation of benzoquinone and 1,4-naphthoquinone with aliphatic and aromatic aldehydes in acetonitrile has been reported to give the corresponding 2-acylquinones in low yields (9.8% from propanal and 1,4-naphthoquinone with 425 nm light).² Direct irradiation of 1,4-naphthoquinone with some α,β -unsaturated aldehydes in benzene has also been reported to give the corresponding 2-acylnaphthalene-1,4-diol in 48–53% yield.³ More recently, it was reported that the direct irradiation of 2- or 3-halogeno-8-methoxy-1,4-naphthoquinone with aliphatic aldehydes in benzene or acetonitrile with a high-pressure mercury arc results in a displacement of the 2- or 3-halogeno substituent to give a mixture of 2- or 3-acyl-1,4-naphthoquinone and 2- or 3-acylnaphthalene-1,4-diols, respectively.⁴

In this paper, we report that the photoacylation of 2-arylamino- or 2-alkylamino-1,4-naphthoquinone with aromatic or aliphatic aldehydes can be achieved in high yields when a solution of *N*-substituted 2-amino-1,4-naphthoquinone and an excess of aldehyde in benzene is irradiated in the presence of benzophenone. We also report a similar high-yield photoalkylation, by irradiating a solution of a 2-arylamino-1,4-naphthoquinone and a cyclic ether in the presence of benzophenone.

3-Acyl-2-arylamino-1,4-naphthoquinones, the products of the photoacylation, have been used as intermediates for the synthesis of such heterocyclic molecules as benzo[*b*]acridine-5,12-diones;⁵ many of these have potential for further transformations.

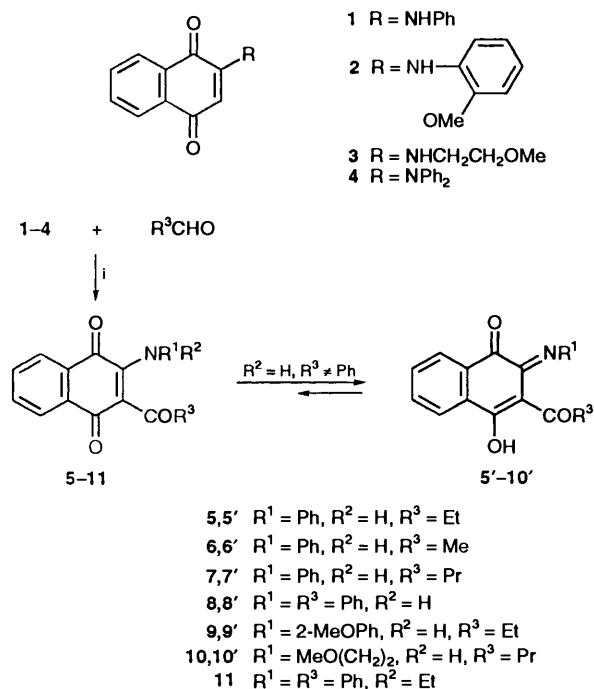
Results and Discussion

Preparation of the Substrates 1–4 for Photoacylation and Photoalkylation.—Four 2-substituted-1,4-naphthoquinones were used as substrates for the photoacylation. 2-Anilino-1,4-naphthoquinone **1**⁶ was commercially available. 2-(2-Methoxyanilino)-1,4-naphthoquinone **2** was prepared according to a published procedure.⁷ 2-[(2-Methoxyethyl)amino]-1,4-naphthoquinone **3** was prepared by the reaction of 1,4-naphthoquinone with 2-methoxyethylamine in ethanol at room temperature. 2-Diphenylamino-1,4-naphthoquinone **4** was prepared by the reaction of 1,4-naphthoquinone with diphenylamine in the presence of a catalytic amount of boron trifluoride–diethyl ether complex in ethanol at room temperature.

Electronic Spectra of 2-Arylamino- and 2-Alkylamino-1,4-Naphthoquinones.—1,4-Naphthoquinones, unsubstituted in their benzene ring, show an intense benzenoid and quinoid electron-transfer $\pi \rightarrow \pi^*$ band in the 240–290 nm region (ϵ 13 000–25 000), a benzenoid electron transfer $\pi \rightarrow \pi^*$ band at about 335 nm (ϵ 2600–3200), and a broad local excitation band of low intensity ($\epsilon < 100$) in the 400–500 nm region attributable to the $n \rightarrow \pi^*$ transition of the quinone carbonyls.⁸

The electronic spectrum of 2-amino-1,4-naphthoquinone was recently reported by us⁹ while Ogata and Kano reported the spectrum of 2-(*N*-methylanilino)-1,4-naphthoquinone which exhibited intense bands around 270 and 460 nm.¹⁰ While the 1,4-naphthoquinones **1** and **2** used in the present photoreaction exhibited absorption bands at 270–280 (ϵ ca. 30 000) and 465–475 nm (ϵ 5500) in methanol assignable to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, the absorptions of the 1,4-naphthoquinone **3** showed hypsochromic shifts of both absorption maxima. The electronic spectrum of the 1,4-naphthoquinone **4** exhibited absorption maxima at 311 (ϵ ca. 30 000) and 516 nm (ϵ 8000), thus displaying appreciable bathochromic shifts of the absorption maxima and a hyperchromic effect in the absorption at the longer wavelength.

Photochemical Acylation of 2-Arylamino and 2-Alkylamino-1,4-naphthoquinones with an Aromatic or Aliphatic Aldehyde (Scheme 1).—Typically, the irradiation of a solution (3.3×10^{-2} mol dm⁻³) of the 1,4-naphthoquinones **1** and an excess of propanal in benzene containing benzophenone (2 equiv.) with a 500 W high-pressure mercury arc through a Pyrex filter under nitrogen gave a crystalline product in 89% yield. Combustion analysis and mass spectrometry indicated the molecular formula of the product to be C₁₉H₁₅NO₃. The ¹H NMR and IR spectra indicated that it was 4-hydroxy-2-phenylimino-3-propionyl-2*H*-naphthalene-1-one **5'**, the imino form of 2-anilino-3-propionyl-1,4-naphthoquinone **5**. Its ¹H NMR spectrum exhibited not only a 3 H triplet at δ 1.05 and a 2 H quartet at δ 3.06, both assignable to the ethyl group of the propionyl group, but the absence of any vinylic proton signal present in the 2-anilino-1,4-naphthoquinone. ¹H NMR spectroscopy also indicated that (a) while signals due to 5-H and 8-H of **1–4** appear as overlapped doublets of doublets at δ 8.0–8.2, the signals due to 5-H and 8-H of **5'** appear as two separate doublets of doublets at δ 7.94 and 8.17, and (b) while the NH



Scheme 1 Reagents and conditions: i, Ph₂CO, benzene, hv

signals of the aminoquinones 1-3 appear as broad singlets at δ 6.1-7.9, product 5a' lacked the corresponding signal and exhibited a singlet at δ 11.8 ascribable to the hydrogen-bonded hydroxy proton.

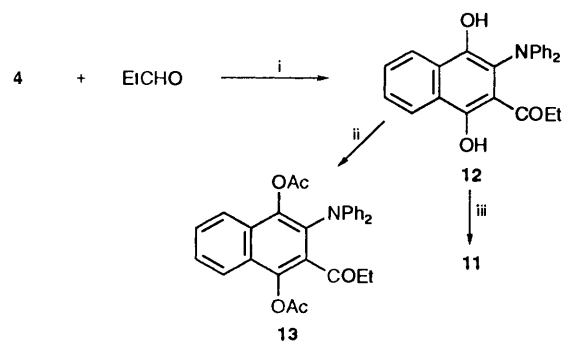
The IR spectrum of product 5' in Nujol exhibited a broad band at 2500-3600 cm⁻¹ assignable to an enolic hydroxy group stabilized by an intramolecular hydrogen bond and lacked a band assignable to an NH group, while the 2-aminoquinones 1-3 exhibited sharp bands at 3200-3300 cm⁻¹. Product 5' also exhibited intense bands at 1685 cm⁻¹ assignable to a carbonyl group conjugated to phenyl and imino groups, 1638 cm⁻¹ assignable to an enolized β -diketone group, and 1598 and 1586 cm⁻¹ assignable to the aryl and conjugated double bonds. All of these spectral results, in conjunction with the formation mechanism discussed below, accommodate the assigned structure. There have been previous reports concerning the tautomerism of 2-anilino-1,4-naphthoquinones by several workers.¹¹ The imino form 5' is apparently more stable than the corresponding quinone form 5 in these 2-amino-3-acyl-1,4-naphthoquinones, presumably as a result of the formation of an intramolecular hydrogen bond between the 3-acyl and 4-hydroxy groups. We found that the presence of benzophenone, which was recovered from the photoreaction in 85% yield, was essential in the photoacylation and that photoacylation was slower when only 1 equiv. of benzophenone was used, giving a lower yield of 5'. We also confirmed the absence of any significant formation of benzopinacol (1,1,2,2-tetraphenylethane-1,2-diol) and benzhydrol in the product mixture by means of TLC, ¹H NMR and mass spectrometry.

The photoacylation of the 1,4-naphthoquinone 1 with acetaldehyde and butanal employing the above-mentioned conditions similarly gave imino forms of the corresponding 3-acyl-1,4-naphthoquinones 6' and 7' in 79 and 82% yields, respectively. Analogously, the photoacylation of naphthoquinone 2 with propanal and naphthoquinone 3 with butanal afforded the imino forms of the corresponding 3-acyl-1,4-naphthoquinones 9' and 10' in 76 and 54% yields, respectively. The imino-enol structures of all these products 6', 7', 9', 10' were confirmed by their ¹H NMR and IR spectra in a manner analogous to the case of the imino-enol 5'; the ¹H NMR spectra exhibited the two doublet of doublet signals at δ 7.89-7.98 and

8.17-8.18; they lacked signals due to NH but they exhibited singlets at δ 11.8-12.7 assignable to hydrogen-bonded OH. Their IR spectra in Nujol showed broad bands assignable to the enolized hydroxy groups and an absence of any bands due to NH.

In contrast to the photoacylation of 1,4-naphthoquinones 1 and 2 with aliphatic aldehydes, in which the imino forms of the corresponding 3-acyl derivatives are always the products, the photoacylation of 1,4-naphthoquinone 1 with benzaldehyde under similar conditions afforded the corresponding 3-acyl derivative 8 in 68% yield. The molecular formula of product 8 was established to be C₂₃H₁₅NO₃ by combustion analysis and mass spectrometry. The ¹H NMR spectrum indicated the absence of vinylic and hydroxy protons. It also showed the presence of an NH proton. Moreover, in contrast to the imino-enols 6', 7', 9', 10', the signals due to 5- and 8-H appeared at δ 8.05-8.25 as overlapped, rather than separate, doublets. The IR spectrum exhibited bands at 3292 cm⁻¹ ascribable to the NH group and a series of bands attributable to the 1,4-naphthoquinone system. It also exhibited a band at 1670 cm⁻¹ ascribable to the benzoyl group.

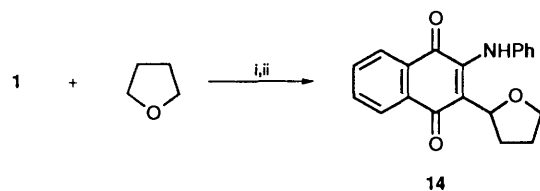
The photoacylation of diphenylamino-1,4-naphthoquinone 4 with propanal, however, resulted in the formation of product 12 which was neither the 3-acyl-1,4-naphthoquinone 11 nor its imino form (Scheme 2). Oxidation of the product by air in the



Scheme 2 Reagents and conditions: i, Ph₂CO, hv; ii, Ac₂O, pyridine; iii, FeCl₃, O₂

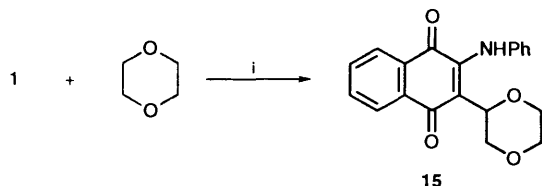
presence of FeCl₃ gave 3-acyl-1,4-naphthoquinone 11 in 84% yield. The product was thus 1,4-dihydroxy-2-diphenylamino-3-propionyl-naphthalene 12. 1,4-Diacetoxy-2-diphenylamino-3-propionyl-naphthalene 4 can be isolated in 88% yield when a solution of 2-diphenylamino-1,4-naphthoquinone 8 and an excess of propanal in benzene containing benzophenone is irradiated and the resulting product 12 is then treated with acetic anhydride in pyridine at room temperature (Scheme 2). These results indicate that the initial products in the present photoacylation are hydroquinones which are oxidized to the corresponding quinones by air during work-up.

Photochemical Alkylation of 2-Anilino-1,4-naphthoquinones 1 (Schemes 3 and 4).—We have found that irradiation of a solution of 2-anilino-1,4-naphthoquinone 1 with cyclic ethers in the presence of benzophenone (2 equiv.) gave 3-alkylated 2-arylamino-1,4-naphthoquinones in high yields. Thus, irradiation of a solution of the 1,4-naphthoquinone 1 and an excess of tetrahydrofuran containing benzophenone (2 equiv.) gave a product mixture which upon examination by TLC, showed the formation of a major yellow product and a more polar, colourless minor product. These products, when treated with FeCl₃ gave 2-anilino-3-(tetrahydro-2-furyl)-1,4-naphthoquinone 14 in 78% yield (Scheme 3). The colourless minor product detected by TLC was most likely ascribable to the corresponding hydroquinone. The photoalkylation of 2-anilino-1,4-naphthoquinone 1 with dioxane as solvent containing



Scheme 3 Reagents and conditions: i, Ph₂CO, hv; ii, FeCl₃·6H₂O

benzophenone (2 equiv.) similarly gave 2-anilino-3-(1,4-dioxan-1-yl)-1,4-naphthoquinone **15** in 82% yield without need for treatment with FeCl₃ (Scheme 4).



Scheme 4 Reagents and conditions: i, Ph₂CO, hv

Pathways for the Formation of 3-Acyl- or 3-Alkyl-1,4-naphthoquinones in the Photoacylation and Photoalkylation.—The experiments described in the foregoing section disclosed that the 2-acyl or 3-alkyl derivatives can be formed in high yields when 2-arylamino- or 2-alkylamino-1,4-naphthoquinone and an excess of aromatic or aliphatic aldehyde in benzene containing benzophenone (2 equiv.) are irradiated with a Pyrex-filtered light.

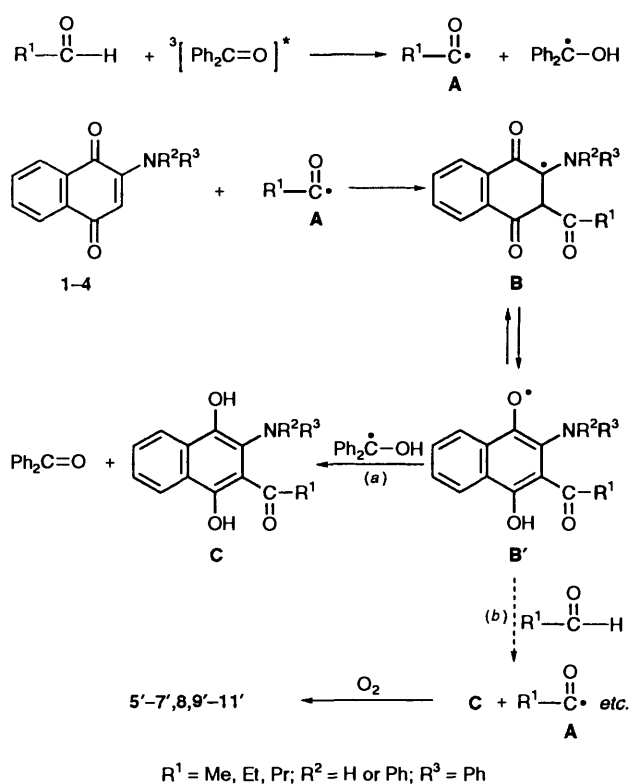
We found that in the absence of benzophenone neither photoacylation nor photoalkylation takes place in these reactions and, furthermore, that the yields of the acylated or alkylated products are significantly reduced when only 1 equiv. of benzophenone is used. The role of benzophenone is thus either to abstract a hydrogen atom from the aldehyde/ether component or to act as a triplet sensitizer of the quinone component.

The most probable reaction path for the photoacylation is outlined in Scheme 5; hydrogen abstraction from the formyl group of the aldehyde by a triplet-excited benzophenone^{12,13} generates the acyl radical **A**.¹² The addition of **A** to the double bond of quinones **1-4** then gives the stabilized semiquinone radicals **B** and **B'** to which Ph₂COH donates a hydrogen atom to give the hydroquinone **C** [pathway (a)]. The hydroquinone formed is then oxidized by air during work-up to give the observed acylated products **5'-7', 8, 9', 10'** and **11**. The alternative radical chain process outlined in Scheme 5 [hydrogen abstraction from the aldehydes by a semiquinone radical, pathway (b)] can be discounted on the grounds that no benzopinacol was isolated from the reaction products and that the yields of the acylated products were significantly lower when only 1 equiv. of benzophenone was used.

The triplet energy of benzophenone (69 kcal)* may well be greater than that of the quinones (58 kcal for 1,4-naphthoquinone¹⁴) and, therefore, the formation of triplet benzophenone in this system seems to be unfavourable.† The alternative possibility for the generation of triplet benzophenone would be by energy transfer from excited high energy quinone; in view of the rather high concentration of the substrates in the present photolysis, T-T annihilation of two

* 1 cal = 4.18 J.

† One of the referees suggested that direct light absorption by benzophenone seems improbable since in the 300–400 nm region, benzophenone has ϵ ca. 100 whereas the quinones have ϵ ca. 3000, and absorb beyond 400 nm as well; the only alternative source of triplet benzophenone would be by energy transfer from the quinone, an endothermic process which thus cannot be significant.

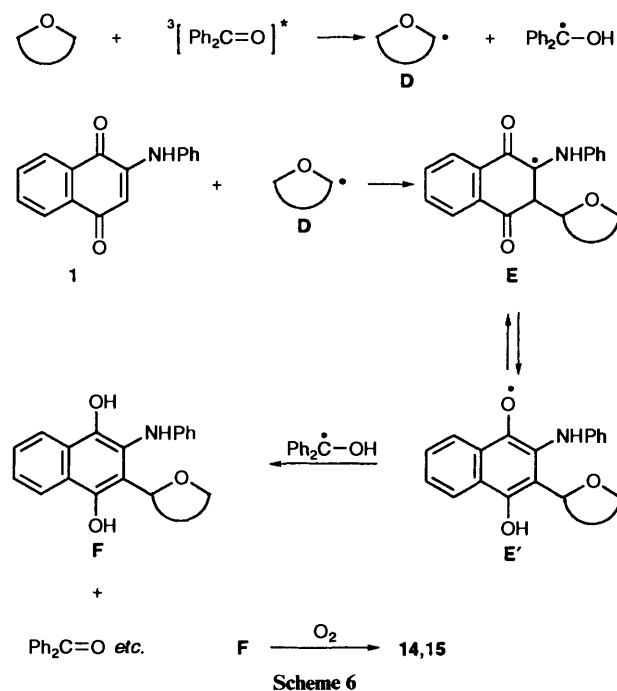


Scheme 5

triplet quinones may well produce an excited singlet quinone capable of generating singlet benzophenone (and then the triplet) by energy transfer.

An alternative path for the formation of the acylated products may be by hydrogen abstraction from the aldehyde or ether component by triplet quinones, since S₁→T₁ intersystem crossing in excited quinones generally occurs with high efficiency (0.8–1.0)^{15,16} and thus triplet excited quinones should be present in the reaction system. This possibility is, however, excluded since no acylation took place in the absence of benzophenone.

Scheme 6 outlines a similar reaction path for alkylation. A



Scheme 6

triplet excited benzophenone abstracts an α -hydrogen from an ether to give the stabilized alkyl radical **D**. The addition of radical **D** to the double bond of the ground state quinones then gives stabilized radicals **E** and **E'** which accept a hydrogen atom from a ketyl radical to afford the hydroquinone **F**. The hydroquinone **F** is then oxidized by air to the observed 3-substituted quinones.

The high-yield formation of 3-acyl- and 3-alkyl-1,4-naphthoquinones in these benzophenone-initiated photoadditions of acyl and alkyl radicals to the quinone system, compared with an ordinary α,β -unsaturated double bond,^{12,13} may, perhaps, be due to the formation of highly stabilized radicals such as **B** and **B'** or **E** and **E'**.

Experimental

For descriptions of the instruments and general experimental procedure, see ref. 17. UV spectra were measured with a JASCO U best-30 instrument. *J* Values are given in Hz.

2-Anilino-1,4-naphthoquinone 1.⁶—Commercially available quinone **1** was used in the photoreaction. See text for electronic spectral data.

2-(2-Methoxyanilino)-1,4-naphthoquinone 2.—This naphthoquinone was prepared according to the procedure by Grossmann.⁷ $\nu_{\max}/\text{cm}^{-1}$ 3304, 1616, 1596 and 1574; $\lambda_{\max}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 23 000) 277 (27 900) and 475 (5500); $\delta(90 \text{ MHz})$ 3.92 (3 H, s, OMe), 6.48 (1 H, s, 3-H), 6.9–7.5 (4 H, m), 7.5–7.8 (2 H, m, 6- and 7-H), 7.97 (1 H, br s, NH) and 8.0–8.25 (2 H, m, 5- and 8-H).

2-[(2-Methoxyethyl)amino]-1,4-naphthoquinone 3.—A solution of 1,4-naphthoquinone (0.79 g, 5 mmol) and (2-methoxyethyl)amine (0.20 g, 2.5 mmol) in ethanol (40 cm³) was stirred for 65 h at room temperature and then filtered. The filtrate was evaporated and the residue was subjected to PLC on SiO₂ to give the pure quinone **3** (0.58 g, 99% based on amine); *R*_F 0.10 (1 : 3 EtOAc–hexane); m.p. 101–103 °C (from hexane); $\nu_{\max}/\text{cm}^{-1}$ 3230, 1684, 1636, 1606 and 1577; $\lambda_{\max}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 17 800), 269 (23 800), 328 (2800) and 449 (3800); $\delta(90 \text{ MHz})$ 3.31 (2 H, t, *J* 4.84, NHCH₂), 3.41 (3 H, s, OMe), 3.64 (2 H, t, *J* 4.84, CH₂O), 5.74 (1 H, s, 3-H), 6.1 (1 H, br s, NH), 7.5–7.85 (2 H, m, 6- and 7-H) and 8.0–8.15 (2 H, m, 5- and 8-H); *m/z* 231 (*M*⁺, 39%) and 186 [(*M* – CH₂OMe)⁺, 100] (Found: C, 67.6; H, 5.6; N, 5.9. C₁₃H₁₃NO₃ requires C, 67.52; H, 5.67; N, 6.06%).

2-Diphenylamino-1,4-naphthoquinone 4.—A solution of 1,4-naphthoquinone (1.0 g, 6.33 mmol), diphenylamine (0.53 g, 3.16 mmol) and a few drops of BF₃·OEt₂ in ethanol (20 cm³) was stirred for 24 h at room temperature. Evaporation of the mixture afforded a residue, which crystallized upon addition of hexane (10 cm³) and Et₂O (10 cm³). After filtration, the crystals were recrystallized from ethanol to give **4** (343 mg, 34% based on amine); m.p. 162–164 °C; $\nu_{\max}/\text{cm}^{-1}$ 1667, 1641 and 1591; $\lambda_{\max}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 15 700), 311 (26 200) and 516 (8000); $\delta(270 \text{ MHz})$ 7.0–7.15 (5 H, m), 7.18 (2 H, d, *J* 8.26), 7.34 (2 H, *J* 8.26), 7.57 (2 H, t, *J* 8.26), 7.7–7.8 (2 H, m, 6- and 7-H) and 8.05–8.2 (2 H, m, 5- and 8-H); *m/z* 325 (*M*⁺, 100%) (Found: C, 81.5; H, 4.6; N, 4.2. C₂₂H₁₅NO₂ requires C, 81.21; H, 4.65; N, 4.31%).

4-Hydroxy-2-phenylimino-3-propionyl-2H-naphthalen-1-one 5' (*R*¹ = Ph, *R*² = H, *R*³ = Et); *a General Procedure for the Photoacylation of the N-Substituted Amino-1,4-naphthoquinone 1.*—A solution of the 1,4-naphthoquinone **1** (125 mg, 0.50 mmol), propanal (2.90 g, 50 mmol) and benzophenone (182 mg,

1.0 mmol) in benzene (15 cm³) was irradiated with a 500 W high-pressure mercury arc through a Pyrex filter under nitrogen for 8 h. After evaporation of the solvent, the resulting residue was examined by mass spectrometry. No peaks due to the fragmentation of benzopinacol and benzhydrol were found in the mass spectrum. The ¹H NMR spectrum of the product exhibited no peak due to benzopinacol. The product mixture was then subjected to PLC on SiO₂ to recover benzophenone (155 mg, 85%) and give **5'** (136 mg, 89%); *R*_F 0.37 (chloroform); m.p. 125–127 °C (from hexane); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500 (enolic OH), 1685 (C₆H₅CO), 1638, 1598 and 1586 (enolized β -diketone); $\lambda_{\max}(\text{MeOH})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 23 300) and 458 (3940). $\delta(90 \text{ MHz})$ 1.05 (3 H, t, *J* 7.25, CH₂CH₃), 3.06 (2 H, q, *J* 7.25, CH₂CH₃), 7.05–7.45 (1 H, m), 7.6–7.85 (2 H, m, 6- and 7-H), 7.94 (1 H, dd, *J* 7.03 and 1.32, 5-H), 8.17 (1 H, dd, *J* 7.37 and 1.47 Hz, 8-H) and 11.8 (1 H, br s, OH); *m/z* 305 (*M*⁺, 100%) (Found: C, 74.9; H, 5.2; N, 4.3. C₁₉H₁₅NO₃ requires C, 74.74; H, 4.95; N, 4.59%).

3-Acetyl-4-hydroxy-2-phenylimino-2H-naphthalen-1-one 6' (*R*¹ = Ph, *R*² = H, *R*³ = Me).—Irradiation of a solution of the 1,4-naphthoquinone **1**, acetaldehyde and benzophenone in benzene according to the procedure described for **5'** gave the imino form **6'** of the 3-substituted quinone **6** (see Table 1 for more details); m.p. 136–137 °C (hexane); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500, 1685, 1646, 1617, 1597 and 1573; $\delta(90 \text{ MHz})$ 2.71 (3 H, s), 7.0–7.45 (5 H, m), 7.65–7.8 (2 H, m, 6- and 7-H), 7.91 (1 H, dd, *J* 7.03 and 1.98, 5-H), 7.0–7.9 (8 H, m), 8.19 (1 H, dd, *J* 7.69 and 1.47 Hz, 8-H) and 12.7 (1 H, br s, OH); *m/z* 291 (*M*⁺, 100%) (Found: C, 74.4; H, 4.5; N, 5.0. C₁₈H₁₃NO₃ requires C, 74.20; H, 4.50; N, 4.81%).

3-Butyryl-4-hydroxy-2-phenylimino-2H-naphthalen-1-one 7' (*R*¹ = Ph, *R*² = H, *R*³ = Pr).—Irradiation of a solution of the 1,4-naphthoquinone **1**, butanal and benzophenone in benzene for 9 h according to the procedure described for **5'** gave the imino form **7'** of the 3-substituted quinone **7** (see Table 1 for more details); m.p. 141–142 °C (hexane); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500, 1688, 1643, 1595 and 1561; $\delta(90 \text{ MHz})$ 0.96 (3 H, t, *J* 7.25, CH₂CH₃), 1.4–1.8 (2 H, m), 3.04 (2 H, t, *J* 7.25, COCH₂), 7.05–7.45 (5 H, m), 7.6–7.8 (2 H, m, 6- and 7-H), 7.93 (1 H, dd, *J* 7.03 and 1.98, 5-H), 8.17 (1 H, dd, *J* 7.67 and 1.47, 8-H) and 12.1 (1 H, br s, OH); *m/z* 319 (*M*⁺, 100%) (Found: C, 75.2; H, 5.3; N, 4.3. C₂₀H₁₇NO₃ requires C, 75.22; H, 5.37; N, 4.39%).

4-Hydroxy-2-(2-methoxyphenyl)imino-3-propionyl-naphthalen-1(2H)-one 9' (*R*¹ = 2-MeOPh, *R*² = H, *R*³ = Et).—Irradiation of a solution of the 1,4-naphthoquinone **2**, propanal and benzophenone in benzene for 5 h according to the procedure described for **5'** gave the imino form **9'** of the 3-substituted quinone **9** (see Table 1 for further details); m.p. 114–115 °C (hexane); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500, 1684, 1641, 1619, 1596 and 1561; $\delta(90 \text{ MHz})$ 1.11 (3 H, t, *J* 7.25, CH₂CH₃), 3.14 (2 H, q, *J* 7.25, CH₂CH₃), 6.8–7.3 (4 H, m), 7.55–7.8 (2 H, m, 6- and 7-H), 7.89 (1 H, dd, *J* 7.25 and 1.75, 5-H), 8.18 (1 H, dd, *J* 7.48 and 1.48, 8-H) and 12.3 (1 H, br s, OH); *m/z* 335 (*M*⁺, 100%) (Found: C, 71.6; H, 5.1; N, 4.4. C₂₀H₁₇NO₄ requires C, 71.63; H, 5.11; N, 4.18%).

3-Butyryl-4-hydroxy-2-(methoxyethyl)iminonaphthalen-1(2-H)-one 10' [*R*¹ = MeO(CH₂)₂, *R*² = H, *R*³ = Pr].—Irradiation of a solution of the 1,4-naphthoquinone **3**, butanal and benzophenone in benzene for 15 h according to the procedure described for **5'** gave the imino form **10'** of the 3-substituted quinone **10** (see Table 1 for further details); m.p. 60–64 °C (hexane); $\nu_{\max}/\text{cm}^{-1}$ 3600–2500, 1687, 1626, 1597 and 1575; $\delta(90 \text{ MHz})$ 1.01 (3 H, t, *J* 7.47, CH₂CH₃), 1.55–1.85 (2 H, m), 3.12 (2 H, t, *J* 7.47, COCH₂), 3.44 (3 H, s, OMe), 3.65 (2 H, t,

Table 1

	Quinone R ¹	R ²	Aldehyde R ³ CHO (equiv.)	Equiv. of PhCOPh	Irradiation time (t/h)	Product	Yield (%) ^a
1	Ph	H	Et (100)	1	15	5'	41
1	Ph	H	Et (100)	2	7	5'	89
1	Ph	H	Me (100)	2	20	6'	82
1	Ph	H	Pr (50)	2	9	7'	79
1	Ph	H	Ph (20)	2	4	8	68
2	2MeOPh	H	Et (100)	2	5	9'	76
3	MeO(CH ₂) ₂	H	Pr (20)	2	15	10'	84
4	Ph	Ph	Et (100)	2	8	11	54 ^b

^a Isolated yields after purification by PLC. ^b The reaction mixture was treated with FeCl₃·6H₂O prior to purification.

J 5.05), 3.95–4.05 (2 H, m), 7.5–7.8 (2 H, m, 6- and 7-H), 7.98 (1 H, dd, *J* 7.25 and 1.54, 5-H), 8.18 (1 H, dd, *J* 7.33 and 1.47, 8-H) and 11.9 (1 H, br s, OH); *m/z* 301 (M⁺, 38%) and [(M – CH₂OCH₃)⁺, 100] (Found: C, 69.2, H, 5.9; N, 4.3. C₁₉H₁₉NO₄ requires C, 68.99; H, 6.11; N, 4.47%).

2-Anilino-3-benzoyl-1,4-naphthoquinone 8 (R¹ = R³ = Ph, R² = H).—A solution of the 1,4-naphthoquinone **1** (125 mg, 0.50 mmol), benzaldehyde (1.06 g, 10 mmol) and benzophenone (182 mg, 1.0 mmol) in benzene (15 cm³) was irradiated for 4 h according to the procedure for **5'**. Separation by PLC on SiO₂ gave **8** (101 mg, 68%); *R_F* 0.39 (2:10:5 EtOAc–hexane–CH₂Cl₂); m.p. 229–230 °C (Et₂O–hexane); *v*_{max}/cm^{–1} 3292 (NH), 1681, 1670, 1605, 1595 and 1562; δ (90 MHz) 6.8–7.05 (5 H, m), 7.2–7.6 (5 H, m), 7.65–7.9 (3 H, m, 6-, 7-H and NH) and 8.05–8.25 (2 H, m, 5- and 8-H); *m/z* 353 (M⁺, 50%) and 352 [(M – 1)⁺, 100] (Found: C, 78.2; H, 4.2; N, 3.8. C₂₃H₁₅NO₃ requires C, 78.18; H, 4.28; N, 3.96%).

2-Diphenylamino-3-propionyl-1,4-naphthoquinone 11 (R¹ = R² = Ph, R³ = Et).—After irradiation of a solution of the 1,4-naphthoquinone **4** (163 mg, 0.50 mmol), propanal (2.90 g, 50 mmol) and benzophenone (182 mg, 1.0 mmol) in benzene (15 cm³) for 8 h, the solvent and excess of aldehyde were evaporated. FeCl₃·6H₂O (135 mg) in 60% aqueous MeOH (0.50 cm³) was added to the residue and the mixture was stirred for 20 h at room temperature; it was then evaporated. The product was extracted with diethyl ether and the extract was washed with brine, dried (MgSO₄) and evaporated. The residue was subject to PLC on SiO₂ to give the title compound **11** (160 mg, 84%); *R_F* 0.28 (CH₂Cl₂); m.p. 179–181 °C (Et₂O–hexane); *v*_{max}/cm^{–1} 1705, 1670, 1648, and 1592; λ _{max}(MeOH)/nm 248 (ϵ /dm³ mol^{–1} cm^{–1} 17 220), 252 (16 970), 306 (25 100) and 527 (6120); δ (90 MHz) 0.99 (3 H, t, *J* 7.04, CH₂CH₃), 2.37 (2 H, q, *J* 7.04, CH₂CH₃) 6.95–7.35 (10 H, m), 7.7–7.85 (2 H, m, 6- and 7-H) and 8.05–8.2 (2 H, m, 5- and 8-H); *m/z* 381 (M⁺, 100%) (Found: C, 79.0; H, 4.8; N, 3.9. C₂₅H₁₉NO₃ requires C, 78.72; H, 5.02; N, 3.67%).

1,4-Diacetoxy-2-diphenylamino-3-propionyl-naphthalene 13.—After photolysis of a solution of the 1,4-naphthoquinone **4**, propanal, and benzophenone in benzene as described for **11**, the resulting product **12** was immediately treated with acetic anhydride (153 mg, 1.5 mmol) in pyridine (1.5 cm³) for 2 d at room temperature. Excess of reagents were removed under reduced pressure and the residue was recrystallized from Et₂O–hexane to give the hydroquinone diacetate **13** (205 mg, 88%); m.p. 159–161 °C; *v*_{max}/cm^{–1} 1765, 1695 and 1592; δ (270 MHz) 0.84 (3 H, t, *J* 7.26, CH₂CH₃), 2.19 (3 H, s), 2.25 (2 H, q, *J* 7.26, CH₂CH₃), 2.41 (3 H, s), 6.99 (1 H, dd, *J* 7.59 and 7.26), 7.05–7.35 (9 H, m), 7.55–7.65 (2 H, m, 6- and 7-H) and 7.75–7.9 (2 H, m, 5- and 8-H); *m/z* 467 (M⁺, 30%) and 383 [(M – 2CH₂CO)⁺, 100] (Found: C, 74.4; H, 5.5; N, 3.3. C₂₉H₂₅NO₅ requires C, 74.50; H, 5.39; N, 3.00%).

2-Anilino-3-(tetrahydro-2-furyl)-1,4-naphthoquinone 14.—The 1,4-naphthoquinone **1** (100 mg, 0.40 mmol) and tetrahydrofuran (3 cm³) in the presence of benzophenone (140 mg, 0.80 mmol) in benzene (7 cm³) was irradiated for 8 h. Work-up of the reaction mixture and examination of the products by TLC showed the presence of yellow and colourless spots (in descending order of mobility) assignable to the quinone **14** and the corresponding hydroquinone. The products were then treated with FeCl₃·6H₂O (96 mg, 0.4 mmol) and worked up in a same manner as described for the preparation of acylated quinone **11**; this gave the quinone **14** (100 mg, 78%); *R_F* 0.10 (CHCl₃); m.p. 126–128 °C (Et₂O–hexane); *v*_{max}/cm^{–1} 3240, 1685, 1624, 1609, 1596 and 1575; λ _{max}(MeOH)/nm 276 (ϵ /dm³ mol^{–1} cm^{–1} 25 700) and 484 (3700); δ (270 MHz) 1.85–2.3 (4 H, m), 3.80 (1 H, ddd, *J* 8.25, 5.84 and 5.61), 4.09 (1 H, ddd, *J* 8.25, 7.59 and 6.27), 5.12 (1 H, dd, *J* 9.24 and 6.59), 7.31 (2 H, dd, *J* 7.59 and 1.32), 7.62 (1 H, td, 7.59 and 1.32), 7.71 (1 H, td, *J* 1.59 and 1.32), 7.97 (1 H, dd, *J* 7.59 and 1.32, 5-H) 8.08 (1 H, dd, *J* 7.59 and 1.32, 8-H) and 8.29 (1 H, s, NH); *m/z* 319 (M⁺, 100%) (Found: C, 74.9; H, 5.4; N, 4.4. C₂₀H₁₇NO₃ requires C, 75.22; H, 5.37; N, 4.39%).

2-Anilino-3-(1,4-dioxan-2-yl)-1,4-naphthoquinone 15.—Irradiation of a solution of the 1,4-naphthoquinone **1** (81 mg, 0.33 mmol) and benzophenone (120 mg, 0.66 mmol) in dioxane (30 cm³) for 10 h gave the title compound **15** (91 mg, 82%); m.p. 185–187 °C (hexane–Et₂O–CH₂Cl₂); *v*_{max}/cm^{–1} 3284, 1679, 1628, 1606, 1595 and 1575; δ (90 MHz), 3.5–4.0 (6 H, m), 5.06 (1 H, dd, *J* 8.13 and 4.61), 6.9–8.1 (9 H, m) and 8.37 (1 H, br s, NH); *m/z* 335 (M⁺, 80%) and 276 (100) (Found: C, 71.4; H, 5.3; N, 4.15. C₂₀H₁₇NO₄ requires C, 71.63; H, 5.11; N, 4.18%).

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Paper 3/05260E

Received 2nd September 1993

Accepted 22nd December 1993